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The disintegration of Portland cement concrete structures when subjected to the action of certain chemical agents has long since been a recognized fact. As early as 1843, only two decades after the original development of Portland cement, the French Engineer, L.J. Vicat published a study upon the disintegration brought about by the action of sea water upon concrete in the "Bulletin de la Societe de L'Encouragement" Volume 42, Pages 483-484.

Since then, and especially in the last few years, an extensive series of investigations has brought much light upon the action of chemical agents on Portland cement concrete. Searching for the underlying cause of the disintegration, leading engineers and chemists have brought about various modifications of Portland cements, all aiming at the production of a hydraulic cement which will offer the physical characteristics of Portland, with in addition a high degree of resistance to disintegration under adverse weather conditions. One group of these modified Portland cements can be classed under the general title of "Blended Cements", which include in their category all artificial pozzolanas.

Whether or not any blended cement will entirely answer the purpose, that is, will furnish a product capable of withstanding indefinitely the disintegrating action of sulfate, alkali and sea water, etc., is still an exceedingly debatable question.

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Division of Highways
MATERIALS AND RESEARCH DEPARTMENT

A STUDY OF

POZZOLANAS

and

POZZOLANIC OR BLENDED CEMENTS

Conducted under the direction

of

Thos. E. Stanton, Jr.
M. Am. Soc. C. E.
Materials and Research Engineer

34-01
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Sacramento, California

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F O R E W O R D

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The development of the high silica type of hydraulic cement resulting from recent determinations relative to the probable cause of disintegration of Standard Portland Cement Concretes under adverse weathering conditions, places the added burden upon the Engineer of developing specifications which will insure a sound durable product, superior to Standard Portland Cements insofar as durability is concerned.

The theory behind the high silica or blended type of cement is primarily based on the demonstrated service of the Italian pozzolanas throughout the ages, and claims are made that certain domestic products will present equal resistance to weathering.

An intelligent consideration of such claims requires that the student of the problem be in the possession of information as to the attributes, both chemical and physical, of a true pozzolana.

C O R R E C T E D

The disintegration of Portland cement concrete structures when subjected to the action of certain chemical agents has long since been a recognized fact. As early as 1842, only two decades after the original development of Portland cement, the French Engineer, L. J. Vicat published a study upon the disintegration brought about by the action of sea water upon concrete in the "Bulletin de la Societe de l'Encouragement", Volume 42, Pages 182-204.

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The theory behind the high silica or blended type of cement is primarily based on the demonstrated service of the Roman pozzolanas throughout the ages, and claims are made that certain domestic products will present equal resistance to weathering.

An intelligent consideration of such claims requires that the student of the problem be in the possession of information as to the activities, both chemical and physical, of pozzolanic materials.

A search of English literature failed to produce the information as completely as desired and it was therefore determined that a thorough study should be made of Italian and other foreign technical literature for the purpose of bringing out clearly, if possible, the distinction, if any, between the Italian pozzolanas and pozzolanic cements, and the domestic high silica or blended cements.

The study herewith presented, is confined to a general statement of the problem and a definition of a pozzolana as presented by Italian and other foreign authorities together with a Bibliography on the subject which includes much material not previously available in English.

Much of the research and all of the translation of foreign material has been carried on by Mr. Mario Palmieri of this Department, an Associate Member American Society of Civil Engineers, and a graduate of the Royal University of Naples, Italy. Without his assistance in translating Italian and French publications it would have been impossible to have carried on the study.

Much valuable data was secured from Professor O. Rebuffat, Professor of Chemistry of the Royal University of Naples, Italy, who likewise furnished invaluable assistance in arranging for shipment of samples of pozzolana and pozzolana cement from Italy.

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C H A P T E R 1

The Resistance of Cementitious Materials to Physical and Chemical Agents

Following the history of the development of cementitious materials we find that the almost universal and constant aim behind their manufacture has been that of producing a material of high physical resistance. We pass thus from the old lime-sand mortars with a compressive strength of 500# per square inch to the modern super-cements which exceed 10,000# per square inch in compression, and 750# in tension. The main contributing agent to such high physical resistance has been the development of Portland cement. No other known cementitious material has undergone such a wonderful progress in less than a century.

Vicat concluded that even though Portland cement satisfied physical requirements better than any other cementitious material it has definite deficiencies in so far as durability is concerned. If Vicat is correct we must reckon with the two characteristics of cementitious materials, physical and chemical resistance. With our present knowledge of the subject it is debatable if with standard commercial Portland cements, we can obtain an optimum of the first without sacrificing the second and vice versa.

To place a cement of very high physical resistance, but offering little or no chemical resistance in a chemically active surrounding medium, inevitably results in the disintegration of the cement. That such disintegration is inevitable with all Portland cement mortars and concrete, regardless of quality, when exposed to the action of chemically aggressive waters is contested by many who point to the fact that some structures seem to be still in a perfect state of preservation after many years of exposure to sea water.

There is reason to believe however that the preservation of Portland cement structures built in sea water is frequently if not always due to high quality and density of the concrete combined with protective natural coatings rather than as a result of the inherent resistance of the cement itself.

Professor A. M. Mononilov, Director of the Mechanical Laboratory of the Moscow Institute of Transport Engineers in commenting upon the report on concrete in sea water at the International Congress of Navigation held in London in 1923 said:

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"All these numerous scientific labors in investigating the decay of Portland cement in sea water have definitely shown that the cause of this decay is not to be assigned to faulty work in building concrete structures, nor to faulty Portland cement used in the cases in question but is inherent in the very nature of Portland cement."

Professor A. H. White, Professor of Chemical Engineering, University of Michigan, in his article on "The Fundamental Cause of the Disintegration of Concrete", in "Concrete", May 1925, states:

"Portland cement has many valuable properties and is one of our most important structural materials, but it has latent possibilities of harm which no other major building material possesses. The faults are, so far as we know, necessarily inherent in the material."

Dr. W. Michaelis, Jr., says in "Engineering News", Volume 60, Page 342:

"The reason why all harbor work does not go to destruction as rapidly as sample blocks submerged in sea water in quiet places, generally in reservoirs where the water is renewed from time to time (for which blocks their disintegration can be observed after a very few years, no matter how good a brand of Portland cement may have been used or how well the concreting may have been done) is the fact that in the open sea, the concrete is soon covered with moss, algae, or other forms of vegetation in the same way as wooden piles kept under water are covered with vegetable matter. Moreover, the rise and fall of the tides or of the river feeding into the harbor and carrying mineral matter of various origin in suspension, contribute to the formation of a shiney film on the surface of the concrete. This film of vegetable and clayey substance protects the concrete for some time and retards the injurious action of sea water but does not prevent it. Ultimate destruction is merely delayed."

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To these accidental causes of increased sea resistance listed by Dr. Michaelis, another can be added as due to the formation of a superficial coating of carbonate of lime which increases the impermeability of the superficial stratum, whenever the lime liberated from the interior of the mass has combined with carbonic acid.

Dr. F. Ferrari contends that even when an impermeable superficial stratum initially protects the concrete, the tensions to which the hydration of silicates and aluminates gives origin in the interior of the mass, in time destroy the continuity of this superficial stratum, thus allowing the first infiltration of sea water and the first depositing of disruptive crystalline formations.

Henry Le Chatelier in his work "La Decomposition des Ciments a la Mer", states:

> "The question of the decomposition of cements in sea water is nowadays one of those questions of which the study becomes absolutely necessary. None of the hydraulic products employed in current use can resist in a sufficient manner the chemical disintegrating action of sea water." (Paris 1904).

and E. Maynard in "Le Genie Civil", August, 1927 says:

> "There is no hydraulic product capable of indefinitely resisting the action of sea water, when deposited in the sea at the time of mixing. Its decomposition is only a question of time, although the disintegrating actions often require a period (30 years or more) to complete their cycle."

Owing to the fact that lime is the largest component of Portland cement, there is a close relationship between the lime content and the chemical as well as the physical resistance of a cement. Because, however, in addition to calcium oxide, a Portland cement contains silica, alumina, iron, etc., it becomes necessary to delve deeper into the nature of the chemical reactions between these components of the cement and various chemical agents, and inasmuch as these elements, calcium, silica, aluminum, etc., are not found in the final product in their original state of oxides but in complex states of binary and ternary compounds, any study of the chemical reactions which may take place must be preceded by a study of the chemical nature of the cement itself.

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Without going into possibly superfluous details and controversial issues we may recall for the time being, that Portland cement is not an individual chemical compound, but a mixture of various (and not as yet exactly defined) chemical compounds. Among them, and playing a prominent part in the hydraulic process, are the binary compounds of calcium silicates and aluminates. These compounds of highly basic nature confer to Portland cement its most characteristic property: that of being an eminently basic product.

To say, "most characteristic", means to express a property which will serve very usefully to distinguish it from other cementitious products as, for instance, high-alumina cements, high-silica cements, pozzolanic cements, etc.

We are also warranted in calling this characteristic "most important", on account of the fact that the resistance of Portland cement to physical and chemical agents is dependent upon it. While high basicity spells high resistance to physical agents, many authorities contend that it involves, at the same time, low resistance to chemical agents.

This dual role of the basicity of Portland was put forth as early as 1859 by the famous French engineer, L. J. Vicat, who, in the "Annales of the Ponts and Chaussees" of that year, wrote (page 232):

> ....."Whenever it is a question of physical resistance Portland cement predominates on account of its high basicity, but whenever it is a question of chemical resistance, this characteristic is essentially dependent upon the ratio of the percentages in weight of the acid to the basic elements; and increases directly with the increase of the index: $\frac{\text{Silica + Alumina}}{\text{Lime}}$ "

In establishing as the lower limit of this index the value of one (1) for cements chemically resistant, he automatically ruled out standard Portland from the category of this class of cements. In standard Portland, the ratio of the percentages in weight of the acid to the basic elements is seldom larger than 0.50, and, frequently, is lower than 0.25.

Vicat in 1859, writing in the "Annales des Ponts et Chaussees" about "Quelques Reflexions sur L'Opportunite de Certain Materiaux pour les Travaux a la Mer", said:

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> "Whenever it is a question of hydraulic lime intended for the high piers of bridges, or on account of the high humidity, but when over it is a question of chemical resistance, time characteristics is essentially dependent upon the ratio of the percentages in weight of the acid to the basic elements and increases objectively with the increase of the index." Editor's Italics

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Vicat in 1859, writing in the "Annales des Ponts et Chaussees" about "Quelques Reflexions sur L'Opportunite de Certain Materiaux Pour les Travaux a la Mer", said:

"If the characteristic of strength were a sure guarantee against the destruction of cements by sea water, it may be pointed out that the cements known nowadays as Portland cements are undoubtedly superior in this respect to natural cements. But long experience, both in the open sea and in the laboratory has shown that, among these natural cements, there are some which are indestructible, while one could not show analogous examples of Portland cement. Portland cement is always more or less attacked in the laboratory, and its use in the open sea dates from too short a time to inspire absolute confidence.

"Now Portland cements owe their great strength to the clinkering through high temperature of an intimate mixture of 20 to 23 parts of clay to 80 parts of lime. This excess of heat, giving to the product greater strength than could be obtained through heating at ordinary temperatures, may help to retard its destruction in the sea. But it cannot guarantee the same duration as cements having three times as much clay for the same quantity of lime, having stability indexes of as high as 0.90 to 0.97, and of which the clinkering temperature rests within ordinary limits.

"For maritime construction, it is less a question of opposing excessive and superfluous strength to the destructive action of this element which in the end exacts a high penalty, than of assuring a strong chemical cohesion, by virtue of which the lime of the cements employed cannot be attacked by the acids of some salts well recognized today as causing all the ill effects. Now it is a fact that -- if the laws of chemical statics have any value whatsoever --in a cement in which there is less lime in combination, the affinities of the various acids for this lime will have less facility to bring about its destruction; and this is exactly what experience has thoroughly proved, in the open sea as well as in the diluted solutions of sulphate magnesia, in which the Portland cements have ended by disintegrating.

"It is characteristic of strength were a sure guarantee against the destruction of cements by sea water, it may be pointed out that the cements known nowadays as Portland cements are undoubtedly superior in this respect to natural cements, but long experience, both in the open sea and in the laboratory has shown that, among these natural cements, there are some which are indestructible, while one could not show analogous examples of Portland cement. Portland cement is always more or less attacked in the laboratory, and its use in the open sea dates from too short a time to inspire absolute confidence.

"How Portland cements owe their great strength to the clinkering through high temperature of an intimate mixture of 20 to 25 parts of clay to 80 parts of lime. This excess of heat, giving to the product greater strength than could be obtained through heating at ordinary temperatures, may help to retard its destruction in the sea, but it cannot guarantee the same curation as cements having three times as much clay for the same quantity of lime, bearing stability indexes of as high as 0.80 to 0.90, and of which the clinkering temperature reaches a high ordinary limits.

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"If then, one is compelled to choose for maritime works, between a Portland cement capable of showing an ultimate strength in tension of from 25 to 30 Kilograms per square centimeter (355 to 427 pounds per square inch) and a cement of which the ultimate strength in tension is seldom above 10 Kilograms (142 pounds per square inch) the last one has more probability of indefinite stability than the first."

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C H A P T E R 2.

Resume of the Chemistry of Portland Cement

Portland cement is not a single chemical compound; it is instead a mixture of chemical compounds. A knowledge of the percentage of oxide components of a Portland cement is not enough for a complete determination of the physical and chemical properties which are only in a general way dependent upon the oxide percentages. Although the type and the percentage of oxides can be readily determined, the compounds themselves are not so exactly known and can be determined only with some difficulty. The main constituents of Portland cement are calcium oxide (CaO); Silica (SiO_2); Alumina (Al_2O_3); Ferric Oxide (Fe_2O_3); Magnesia (MgO); and Sulphuric Anhydride (SO_3). Their proportions can be slightly variable within certain limits, but they must satisfy certain indexes called hydraulic modulus, calcareous modulus, siliceous modulus, and sesquioxide modulus.

The hydraulic modulus is expressed by the ratio:

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3 + Fe_2O_3}$$

The siliceous modulus by the ratio:

$$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

The sesquioxide modulus by the ratio:

$$\frac{Al_2O_3}{Fe_2O_3}$$

The calcareous modulus is expressed by the ratio between the lime combined with the silica and the silica itself.

For Portland cement the hydraulic modulus should never be smaller than 1.7 nor larger than 2.25; the siliceous modulus variable between the values of 2.0 and 3.0 and the sesquioxide modulus should be the highest possible for a high physical strength Portland cement and the lowest possible for a high chemically resistant Portland cement.

CHAPTER 3

Phases of the Chemistry of Portland Cement

Portland cement is not a single chemical compound; it is instead a mixture of chemical compounds. A knowledge of the properties of oxide components of a Portland cement is not enough for a complete determination of the physical and chemical properties which are only in a general way dependent upon the oxide percentages. Although the type and percentage of oxides can be readily determined, the compounds themselves are not so exactly known and can be determined only with some difficulty. The main constituents of Portland cement are calcium oxide (CaO); silica (SiO_2); alumina (Al_2O_3); Ferric Oxide (Fe_2O_3); Magnesia (MgO); and Sulphuric Anhydride (SO_3). Their proportions can be slightly variable within certain limits, but they must satisfy certain indexes called hydraulic modulus, calcareous modulus, siliceous modulus, and aequioxide modulus.

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The aequioxide modulus by the ratio:

$$\frac{Al_2O_3}{Fe_2O_3}$$

The calcareous modulus is expressed by the ratio between the lime combined with the silica and the silica itself.

For Portland cement the hydraulic modulus should never be smaller than 1.9 nor larger than 2.35; the siliceous modulus variable between the values of 2.0 and 3.0 and the aequioxide modulus should be the highest possible for a high physical strength Portland cement and the lowest possible for a high chemically resistant Portland cement.

Given these elements, their proportions and the temperature of clinkering, it should apparently be a simple matter to determine the compounds in the final clinker. It is only of late however that an apparently satisfactory conception of the compound composition of Portland cements has been reached. This conception was developed through the detailed study of the binary systems, calcium silica, silica alumina, calcium alumina, and of the ternary systems calcium silica alumina, calcium silica iron, calcium alumina iron.

The study of the binary system, calcium silica indicates that all the components that can be formed in sets of equilibrium in such a system are three: monocalcium silicate ($CaO.SiO_2$), also called meta-calcium silicate; di-calcium silicate ($2\ CaO.SiO_2$) also called ortho-calcium silicate; and tri-calcium silicate ($3\ CaO.SiO_2$).

The mono-calcium silicate exists in two forms, alfa and beta - the latter transforming itself into the first at 1200°C. and the first being brought to fusion at 1540°C.

Apparently mono-calcium silicate has no hydraulic properties, is easily dissolved by acids and reacts only slightly with water. It can exist only at temperatures lower than 800°C.

Di-calcium silicate presents itself in three modifications. The first, alfa, which is stable at high temperatures, changes to the form of beta at 1420°C. which in turn changes to the form gamma at 675°C. This compound has good hydraulic qualities, is not easily attacked by acids and reacts readily with water.

Tri-calcium silicate has only one stable form at high temperatures (1300°C to 1900°C). Below 1300°C. it dissociates into di-calcium silicate and free lime.

Of these three compounds only the last two are found in Portland cement, because owing to the high temperatures of clinkering there is no possibility of the formation of mono-calcium silicate. The study of the binary systems, silica-alumina is not of great importance in the chemistry of Portland because there is apparently no possibility of the formation of any silicate of alumina owing to the fact that these compounds are formed at temperatures higher than those at which Portland cement clinkers are commonly burned.

The study of the binary system - calcium alumina, is however rather interesting because it shows the possibility of formation of four different compounds, tri-calcium aluminate ($3\ CaO.Al_2O_3$); mono-calcium aluminate ($CaO.Al_2O_3$); and the calcium aluminates ($5\ CaO.3\ Al_2O_3$) and ($5\ CaO.5\ Al_2O_3$).

of these compounds, the first is always part of Portland, the second is a major constituent of high alumina cement and the third and fourth are found occasionally as additional constituents of Portland.

The tri-calcium aluminate at 1535°C. is decomposed into free lime and a liquid calcium aluminate purer in lime.

The mono-calcium aluminate fuses at 1600°C.

The other two calcium aluminates can be found in two forms, and while 5 CaO.3Al$_2$O$_3$ is brought to fusion at 1455°C. 3 CaO.5 Al$_2$O$_3$ fuses at 1700°C.

More interesting than the study of binary systems is the study of ternary systems. There are a series of binary and ternary compounds which can co-exist only for determinate combinations of oxide percentages and determinate values of temperature.

Reporting the ternary system graphically by the aid of a triangular diagram, (Figure 1) we notice that the areas in which a certain compound may exist are perfectly determinate and that therefore, once we know the percentage of the elements entering to make part of a cement and the temperature of clinkering to which they are subjected, we can by the aid of the diagram locate all the compounds that can be found in that cement. Taking thus for instance three different types of cement - Portland cement, aluminous cement, and high iron cement, we find that the areas occupied by each are those shown in Figure 2, areas determinate by the different percentage and the different temperatures of clinkering of those three types of cement.

Were Portland cement simply a product of three elements, calcium, silica and alumina, the solution of the problem of finding the constituent compounds would be easy - but unfortunately as we have said, there are to be considered iron, magnesia, sulphur, etc., which greatly complicate the solution. While in effect the study of binary and ternary systems is quite well along, the study of multiple element systems has scarcely been begun - so, we are left with rather exact observations as to the behavior of the element components of Portland when in groups of three, but without any help as to their behavior when in groups of a number higher than three. All we can do is to assume that what takes place whenever they are in ternary groups can be extended to multiple element systems. It is interesting to notice that the study of the ternary system, calcium,alumina, ferric oxide has shown clearly the possibility of formation of one ternary compound, tetra-calcium alumina ferrite, 4 CaO. Al$_2$O$_3$. Fe$_2$O$_3$, and that the study of

FIG. 1.

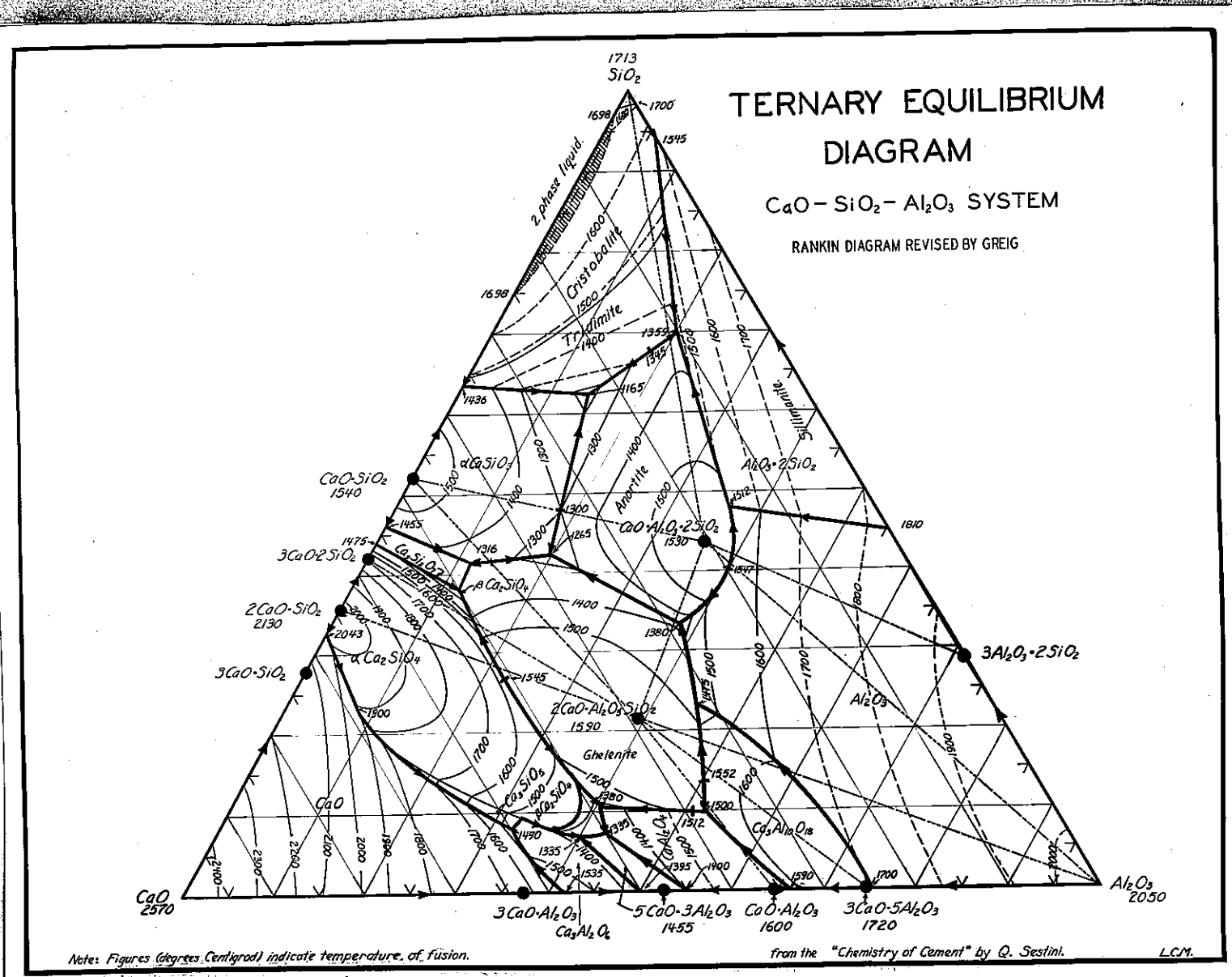
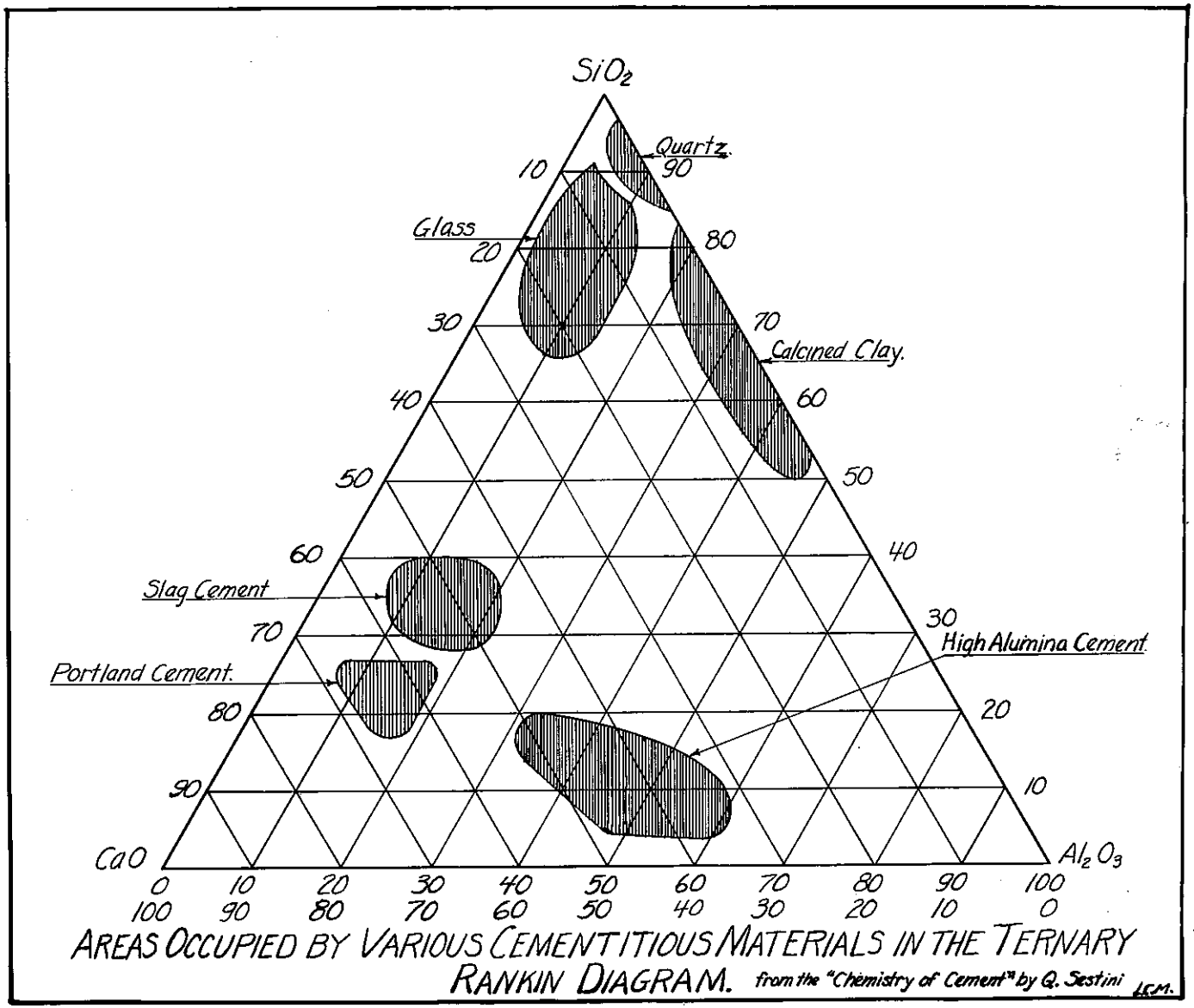

TERNARY EQUILIBRIUM DIAGRAM
CaO – SiO2 – Al2O3 SYSTEM
RANKIN DIAGRAM REVISED BY GREIG
1713 SiO2
2 phase liquid
Cristobalite
Tridimite
Sillimanite
Anorthite
Al2O3·2SiO2
CaO·Al2O3·2SiO2
1530
CaO·SiO2 1540
3CaO·2SiO2 1475
2CaO·SiO2 2130
3CaO·SiO2
αCa2SiO4
βCa2SiO4
2CaO·Al2O3·SiO2 1590
Gehlenite
3Al2O3·2SiO2 1810
Al2O3
CaO 2570
3CaO·Al2O3
Ca3Al2O6
5CaO·3Al2O3 1455
CaO·Al2O3 1600
3CaO·5Al2O3 1720
Al2O3 2050
Note: Figures (degrees Centigrad) indicate temperature of fusion.
from the "Chemistry of Cement" by Q. Sestini.
L.C.M.

FIG. 2.



AREAS OCCUPIED BY VARIOUS CEMENTITIOUS MATERIALS IN THE TERNARY RANKIN DIAGRAM. from the "Chemistry of Cement" by Q. Sestini J.C.M.

the ternary system, calcium, iron, silica has clearly shown no possibility of the formation of ternary compounds of calcium, iron, silica.

We have therefore, in the final clinker of Portland cement - first, the formation of tetra-calcium alumina ferrite, which seems to be the first compound formed; second, the formation of tri-calcium aluminate if there is alumina left available after the formation of the tetra-calcium alumina ferrite; third, as an alternative, the formation of di-calcium ferrite in case there is no alumina to enter into combination with both calcium and iron; and, finally, the formation of di-calcium and tri-calcium silicates, plus calcium sulfate when there is an addition of gypsum, the magnesia being assumed to be left in a free state, that is as MgO.

The calculation of the percentages of the various compounds is based on the study of R. H. Bogue. We shall therefore, not elaborate on this subject but proceed directly with the study of the chemical reactions which take place during the process of setting and hardening of Portland cement.

Before doing this however, it may be well to recall that the main compounds of cement have been assumed to form some well defined crystalline substance to which have been given the names Alite, Belite, Celite and Felite.

The crystals of Alite are formed mostly of tri-calcium silicate with perhaps an addition of tri-calcium aluminate. The crystals of Belite are formed of the di-calcium silicate, and the crystals of Celite are formed of tetra-calcium alumino ferrite, or of di-calcium ferrite when there is no alumina present. The crystals of Felite consist of materials of small or no hydraulicity.

The study of the chemical reactions which take place during the process of setting and hardening of Portland cement can be rendered easier by the study of the chemical reaction of each individual component compound of the cement with water, just the same as the study of the formation of these compounds was rendered easier by the study of the formation in determinate groupings. Beginning thus with the tri-calcium silicate we find that its hydration takes place very readily with a notable development of heat. After three hours, the water in which it is in suspension reaches a pH of 1228, which then remains constant. More than hydration, it undergoes a true hydrolysis because it decomposes into a silicate hydrate of lesser basicity and liberates free lime. If the product of hydrolysis is eliminated and new water is furnished, further hydrolysis takes place until the original tri-calcium silicate decomposes into silica hydrate and lime. But if di-calcium oxide liberated and transformed in calcium hydroxide is not eliminated, there is formation of a state of equilibrium between a low lime calcium silicate hydrate and calcium hydroxide, so that there is no possibility of further decomposition and therefore no formation of hydrated silica.

possibility of the formation of ternary compounds of calcium, iron, silica.

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DI-CALCIUM SILICATE

Of the two forms of di-calcium silicate the form beta, found in Portland cement shows signs of hydration after a few weeks in water, but the form gamma shows no sensible phenomena of hydration. In a lesser measure what has been said of the hydrolysis of the tri-calcium silicate applies also to the di-calcium silicate, although when the di-calcium silicate of Portland cement begins to hydrate, it finds itself in a more or less saturated solution of calcium hydrate originating from the hydrolysis of the tri-calcium silicate, therefore, unless the product of this hydrolysis is washed out there is very small likelihood of hydrolysis of the di-calcium silicate in Portland cement, and all that will take place will be simply a phenomenon of hydration.

MONO-CALCIUM SILICATE

This compound shows little or no change whatever in presence of water.

TRI-CALCIUM ALUMINATE

Tri-calcium aluminate reacts with water to form a hydrated calcium aluminate of a gelatinous form, which changes in time to a crystalline form and which answers to the formula $3\ CaO.Al_2O_3.X\ H_2O$, in which formula the number X of molecules of water of hydration varies with conditions. This same tri-calcium aluminate gives rise to the formation of hydrated tetra-calcium aluminate, if calcium hydroxide is present and takes part in the process of hydration. This reaction was assumed by Le Chatelier to be of the following type:

$$3\ CaO.Al_2O_3 + Ca(OH)_2 + 11\ H_2O = 4\ CaO.Al_2O_3.\ 2\ H_2O$$

This same reaction was claimed by H. Lafuma to take place according to the following formula:

$$2(Al_2O_3.3\ CaO)+19\ H_2O = Al_2O_3.\ 4\ CaO.12\ H_2O + Al_2O_3.2\ CaO.\ 7\ H_2O$$

Under the actual conditions therefore of the setting and hardening of Portland cement, in which during the process of hydrolysis of the tri-calcium silicate, calcium hydroxide is liberated there is bound to be the formation of tetra-calcium aluminate hydrate. This point is important on account of the extensive part played by the tetra-calcium aluminate in the disintegration of Portland cement in sea water.

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place according to the following formula:

$$3(Al_2O_3.3\ CaO)-12\ H_2O = Al_2O_3.6\ CaO.12\ H_2O + Al_2O_3.6\ CaO.7\ H_2O$$

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The reaction of the tri-calcium aluminate is rapid and is therefore accompanied by considerable heat and by quick setting.

MONO-CALCIUM ALUMINATE

This compound, found only in high alumina cements, reacts with water to form a di-calcium aluminate hydrate according to the equation of Lafuma:

$$2(Al_2O_3.CaO) + Aq = Al_2O_3.\ 2\ CaO.\ 7\ H_2O + Al_2O\ .\ Aq$$

The hydration begins after a few minutes and gives rise to the formation of a gelatinous mass.

TETRA-CALCIUM ALUMINO-FERRITE

This compound has remarkable hydraulic properties and does not give rise to any formation of free calcium hydroxide. The products of hydration are a tri-calcium aluminate hydrate and a calcium ferrite which does not hydrate.

DI-CALCIUM FERRITE

The di-calcium ferrite has no hydraulic properties whatever.

Passing from the study of the reaction with water of the single compounds to the study of the reaction with water of the cement as a whole, we find the following:

(a) The formation of a low lime calcium silicate hydrate,

(b) The formation of calcium hydroxide separating in crystals scattered through the colloidal mass of the hydrated silicates and slowly finding its way from the interior of the mass to the surface, and finally,

(c) The formation of tetra-calcium alumina hydrate and perhaps also the formation of tri-calcium alumina hydrate.

Owing to the different rates in which the hydration of the various compounds takes place, the reaction of Portland cement with water can be sub-divided into three progressive phases:

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Owing to the different rates in which the hydration of the various compounds takes place, the reaction of Portland cement with water can be sub-divided into three progressive phases:

(a) Initial set

(b) Final Set

(c) Hardening

which phases are derived from the ways and the time of formation of the various compounds.

Thus, we find, at first, internal hydration of the calcium silicates, aluminates and ferrites, a process which takes place within the cement grains, as R. Zollinger says in "Cement" of November 1933:

> "This internal hydration is rapidly completed since the necessary molecular structure is already present and the water can combine immediately with it. The second stage is the external hydration of the silicates corresponding to the liberated lime. Since there is no further silica available in the cement grains, the freed lime must seek out and combine with the cement grains, the freed lime must seek out and combine with silica of the materials added to the cement. The completion of this external hydration corresponds to the ultimate strength."

A theoretical presentation of the setting and the hardening phenomena is found in the book of Professor Q. Sestini, "The Chemistry of Portland", wherein he states:

> "In the first place there are crystalline formations of hydrated aluminates followed by the formation of colloidal matter of hydrated silicates. From the moment that the gelatinous substance predominates in the whole mass, the crystalline formations are deeply modified and assume the form of the empty space left throughout the gelatinous mass. Finally the formation of micro-crystals takes place in the micropores of the gelatinous substance. So far, it is not definitely ascertained whether the predominating gel of set Portland cement is formed by colloidal silica or by silicates of low basicity."

Concluding therefore, Portland cement which has set and hardened is not a homogeneous material but a colloidal mass composed mainly of hydrated calcium silicates interspersed with crystals of calcium hydroxide and crystals of hydrated calcium aluminate.

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All physical and chemical properties of Portland are derived from the ways in which the silicates, aluminates and the calcium hydroxide react to the action of physical and chemical agents.

As far as physical resistance is concerned we can state that in general the characteristic of initial strength is in direct relationship to the amount of tri-calcium aluminate present, the characteristic of early strength is in direct relationship with the amount of tri-calcium silicate present and the characteristic of strength increasing with time is in direct relationship with the amount of di-calcium silicate present.

As far as chemical resistance is concerned this characteristic is in direct relation to the quantities of tri-calcium aluminate and tri-calcium silicate present, as well as to the resulting free calcium hydroxides.

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C H A P T E R 3.

The Disintegration of Standard Portland Cement

By Chemical Agents.

We have seen in Chapter 2, that it is safe to assume that the modern Portland cement contains primarily tri-calcium silicate, di-calcium silicate, tri-calcium aluminate and tetra-calcium alumino ferrite with other compounds in very small proportions such as calcium sulfate, di-calcium ferrite, etc. Such being the case all chemical reactions which take place when mortar or concrete is immersed in a chemically aggressive liquid can be based on the reactions of each of these individual compounds with the various chemical agents.

Beginning with the tri-calcium silicate, the best authorities agree that this compound undergoes, in the presence of water, a process of hydrolysis rather than of hydration, that is, undergoes a process of partial decomposition during which the water decomposes the original compounds into hydrated silicate and hydrated lime according to the equation:

$$3\ CaO.SiO_2 + Aq = 2\ CaO.\ SiO_2.\ H_2O + Ca(OH)2$$

The calcium hydroxide separating in crystals of rather poor formation is scattered throughout the colloidal mass of the hydrated silicates. This process of hydrolysis of the tri-calcium silicates takes place at a rapid rate and appears to be quite complete at the end of 28 days.

The di-calcium silicate instead, remains practically unhydrolyzed under ordinary conditions and undergoes only a slow process of hydration, giving rise to the formation of additional colloidal hydrated silicate. It is not to be excluded though that in the presence of an excess of water the di-calcium silicate may also undergo a partial process of hydrolysis into lime which separates into crystalline formation and into calcium metasilicate which remains unhydrated and in a colloidal form.

The hydration of the silicates contained in standard Portland brings about, therefore, the liberation of a large quantity of calcium oxide, this quantity being in relation to the amount of calcium oxide contained originally in the cement, that is, being relative to the amount of tri-calcium silicate formed during the clinkering process.

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The calcium hydroxide formed from the liberated cal-
oxide and remaining as a free compound in set cement can-
constitute an element of chemical resistance. Through its
inity for other chemical compounds this free calcium hy-
-ide is a source of weakness in the set cement. Whenever
place set cement in contact with sea water, or any water
-taining sulfates, the calcium hydroxide is readily and
-ily transformed into calcium sulfate. Thus one element of
disintegration process is ready at hand in the calcium
-roxide always present in set Portland cement.

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water to form a hydrated tri-calcium aluminate of a gelatinous
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gives rise instead to the formation of hydrated tetra-calcium
aluminate, if calcium hydroxide is present and takes part in
the process of Hydration.

This reaction was shown by Le Chatelier to be of the
following type:

$$3\ CaO.Al_2O_3 + Ca(OH)_2 + 11\ H_2O = 4\ CaO.\ Al_2O_3.\ 12\ H_2O$$

Under the actual conditions, therefore, of the setting
and hardening of Portland cement in which during the process
of hydrolysis of tri-calcium silicate, calcium hydroxide is
liberated while the hydration of the tri-calcium aluminate
takes place, there is bound to be formation of hydrated tetra-
calcium aluminate. (This tetra-calcium aluminate plays an im-
portant part in the disintegration of Portland cement in sea
water.)

We find in other words, in the set Portland cement
mainly di-calcium silicate hydrate, tetra-calcium aluminate
hydrate, and free calcium hydroxide.

With this in mind, let us pass to the analysis of
the behavior of each of these chemical compounds when placed
in contact with aggressive waters.

In the summary of their studies on the action of sul-
fates in Portland cement, T. Thorvaldson, D. Wolochow, V. A.
Vigfusson, report that all the mortars expand and disintegrate
ultimately when exposed to solutions of magnesium or sodium

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dissolved impurities present in set Portland cement.
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ate to form a hydrated tri-calcium aluminate of a crystalline form
m, which changes in time to a crystalline form according to
e reaction:

$$3\ CaO.Al_2O_3 \cdot x\ H_2O \rightarrow 3\ CaO.Al_2O_3.6\ H_2O$$

The process of hydration was shown by the chemists to be of the
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In the summary of their reports on the action of sul-
fates in Portland cement, T. Thorvaldson, D. Wolochow, A. P.
Vivrusson, report that all the mortars of magnesium sodium
ultimately when exposed to solutions

sulfate, the rate of expansion increasing with the concentration of the solution. Also, the higher the lime content of the cement (i.e., the higher the percentage of tri-calcium silicate) the aluminum remaining the same, the lower is the resistance to the action of the sulfates.

Taking under individual consideration the three major components of Portland, these authors found that these "Three components were all attacked by both sodium and magnesium sulfate, the tri-calcium aluminate being the one most seriously attacked and the di-calcium silicate the one attacked most slowly." On page 304 of their 1927 report they state:

> "Assuming the accuracy of Rankin and Wright's conclusions as to the components of Portland cement one must conclude from the results given that disintegration of Portland cement in solutions of Na_2SO_4 is caused by the action of the salt on only one of the components present - namely, $3\ CaO.Al_2O_3$, while disintegration in solutions of $MgSO_4$ is the result of the action of the salt on all the three major components of the cement. It is true that the action of solutions of $MgSO_4$ on $3\ CaO.Al_2O_3$ is so rapid in comparison with its action on the silicates that it may appear to be the only action taking place. The difference in the action of the two salts however, suggests a possible explanation why a Portland cement may be more resistant to the action of Na_2SO_4 than $MgSO_4$ or why the resistance of two Portland cements does not vary the same way in solutions of Na_2SO_4 as in solutions of $MgSO_4$."

and in their summary they state that:

> "The mortars made from pure tri-calcium silicate and pure beta di-calcium silicate are not disintegrated in solutions of sodium but expand in solutions of magnesium sulfate," and that, "Mortars made from tri-calcium silicate or di-calcium silicate to which tri-calcium aluminate has been added, disintegrate rapidly in solutions of both sodium and magnesium sulfate."

This behavior of the components of Portland cement in these two kinds of sulfates leads us to think that there may be further difference between the action of individual sulfates and the action of sea water in which we find them mixed together,

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"Assuming the accuracy of Lerch and

clowly." on page 30 of their 1929 report they state:

attacked and the di-calcium silicate the one attacked most rate, the tri-calcium aluminate being the one most seriously components were all attacked by both sodium and magnesium sul- compounds of Portland cement in solution. These authors found that these three major

Taking under individual consideration the three major resistance to the action of the sulfates,

silicate) the aluminum remaining the same, the lower is the of the cements (i.e., the greater the percentage of di-calcium tion of the solution. Also, the higher the time constant

sulfate, the rate of expansion increases with the concen-

and in which, in addition we find chlorides and other chemical reagents. Going further into the difference between the action of sodium sulfate and that of magnesium sulfate, Thorvaldson, Harris and Wolochow in their study upon "The Disintegration of Portland Cement in Sulfate Waters", published in Industrial Engineering Chemistry, Volume 17, No. 5, Page 467, May 1925, say:

"Although the extent to which the silicates of calcium in a cement are decomposed in solution of sodium sulfate is apparently indicated by the development of alkalinity in the solution, this cannot be so when magnesium sulfate or other soluble magnesium salts are present. Here the liberated calcium hydroxide reacts with the magnesium sulfate forming the insoluble magnesium hydroxide and the slightly soluble calcium sulfate and the liquid remains nearly neutral as long as magnesium salts remain in the solution. Information as to the progress of the liberation of lime from the cement, however, may be obtained by following the rate of loss of magnesium by the liquid. A complete analysis of the liquid will also indicate the extent of the formation of calcium sulfate as well as any further reaction of the sulfate with the cement.

"As is to be expected, when magnesium sulfate is present in experiments such as the above, the extraction of lime from the cement is accelerated. This does not necessarily mean that the destruction of a block of concrete is more rapid when it is immersed in a solution of magnesium sulfate than in sodium sulfate of corresponding concentration, as the deposition of the products of the reaction in the pores of the block will affect the diffusion of the solution through the concrete. Field and laboratory tests indicate that the deterioration of concrete in solutions of magnesium sulfate is only slightly, if any, more rapid than in sodium sulfate."

Finally going into the phenomena of a mixture of the two sulfates they say:

"In mixture of sodium and magnesium sulfate, the magnesium sulfate disintegration controls as long as there is any of that salt present. Only after this is removed and the alkalinity rises can the sodium sulfate disintegration play its part."

On the other hand, Lerch and Bogue in their Bulletin on "The Chemical Action of Salt Solutions on the Constituents of Set Cement", state:

> "Increasing the content of tri-calcium silicate itself inert to sulfate action, means that the improved early strength resulting from increases in 3 $CaO.SiO_2$ content, may under some conditions, delay the rate of dissolution in sulfate solutions, but the increased alkalinity may give rise to more favorable conditions for the formation of the calcium sulfo-aluminate and so accelerate dissolution which otherwise might be slow."

On this subject of variable resistance of cement to sodium sulphate and magnesium sulphate, it is worth while to report the following taken from an article of F. Charles in "La Revue des Materiaux de Construction", year 1928, page 350:

1. "Contrary to the general opinion it has been found that the action of magnesium sulfate and of sodium sulfate upon cements differ fundamentally, and that some cements which highly resist solutions of one type of sulfate are very rapidly deteriorated in solutions of the other type. This explains the apparent contradiction between many tests which seemed to have been conducted in identical conditions.

2. "It has been found that the difference of concentration of the solutions have effects different upon different brands of Portland satisfying the required standards.

3. "It has been found that the conditions under which the mortar or the concrete is cured have a corresponding influence upon the resistance to the action of solutions of the two sulphates.

4. "It has been found that two cements may have the same resistance to the action of the same solution of sulfate if the specimens are made in mortar 1:10, and have a resistance relatively quite different in the same solution, if the specimens are made with mortar 1:3."

On the other hand, Lerch and Bogue in their bulletin on "The Chemical Action of Salt Solutions on the Constituents of Set Cement", state:

"Increasing the content of tri-calcium aluminate itself tends to sulfate action, i.e. it tends to increase the susceptibility to attack by sulfate solutions. This means that the improved early strength resulting from increases in C3A content may under some conditions, delay the rate of dissolution in sulfate solutions, but the increased alkalinity may give rise to more favorable conditions for the formation of the calcium sulfo-aluminate and so accelerate dissolution when otherwise might be slow."

On this subject of variable resistance of cement to sulphate and magnesium sulphate, it is worth while to report the following taken from an article of T. Charles in "La Revue des Materiaux de Construction", Year 1933, Page 350:

1. "Contrary to the general opinion it has been found that the action of magnesium sulfate and of sodium sulfate upon cements differ fundamentally, and that some cements which highly resist solutions of one type of sulfate are very rapidly destroyed in solutions of the other type. This explains the apparent contradiction between many tests which seemed to have been conducted in identical conditions.

2. "It has been found that the difference of concentration of the solutions have effects different upon different brands of Portland satisfying the required standards.

3. "It has been found that the conditions under which the mortar or the concrete is cured have a corresponding influence upon the resistance to the action of solutions of the two sulphates.

4. "It has been found that two cements may have the same resistance to the action of the same solution of sulfate if the specimens are made in mortar 1:3, and have a resistance relatively quite different in the same solution, if the specimens are made with mortar 1:2."

On the other hand, Professor O. Rebuffat in his article "I Solfoalluminati di Calcio e la Decomposizione delle Construcioni Marittime Eseguite in Cemento Portland" published in "Gazzetta Chimica Italiana", Volume 30, states:

> "Sea water energetically attacks the di-calcium silicates. The liquid immediately acquires a highly alkaline reaction and becomes larger in lime while some magnesia passes in the insoluble residue.
>
> "The solution of magnesium salts energetically attacks the di-calcium silicates. With the solutions of magnesium sulfate, the attack is rather slow and can be further slowed down through the addition of calcium sulfate."

We are left therefore, with a not very clear idea of how the silicates can effect the chemical resistance of a cement. Such being the case, in planning a series of tests on blended cements, it is worth while to split the series in two sub-divisions, that is:

1. A group based on a high lime clinker.
2. A group based on a low lime clinker.

Much more clear is the behavior of the free calcium hydroxide.

The pioneer in the field of research on the deleterious effects of free calcium hydroxide was Dr. W. Michaelis. In one of his first publications on the subject he said:

> "The Portland cements on the other hand, are less valuable from a chemical point of view because, like the Teil Lime, a very considerable quantity of calcium oxide striving for combination is produced in the process of hydraulic hardening.
>
> "It is easily understood that a body in which so considerable a quantity of quicklime (a substance of exceptionally strong affinity) becomes liberated, cannot be, in the chemical sense a stable compound. The free lime must work and react until, in one way or other, it forms a saturated compound. This occurs first from the surface downwards by the absorption of carbonic acid, when the cement is exposed to the air or to water containing carbonic acid; in sea water it is principally the soluble sulphuric acid compounds which react on the lime. First, the

The test made in the described way presented various practical difficulties. The tubes broke easily, not only when they were brought to a temperature higher than 100°C. but even when they were heated indirectly so that the determinations that we have reported are not even the fourth part of those begun, the others having been lost through the breaking of the tubes. It was on account of this that we modified the method of operation. What we did was to use a bowl or glass very resistant in which there was placed lime first and then pozzolana with a little water. This bowl could be closed by a rubber lid having only one opening through which entered a tube bent at right angles at one extremity. At the other end this tube was bent and terminated in a cylindrical base of about one meter high, almost full of mercury. In this way placing the bowl in a container with water and heating the whole thing, it was possible to obtain quite a high pressure in the interior of the apparatus which lent itself very well to the use for which it had been selected. We never tried to reach the pressure that could be obtained with closed tubes and furthermore we have placed the lime to react upon pozzolana for a rather short time (12 hours) obtaining therefore some percentages of lime liberated from pozzolana slightly smaller than those obtained with closed tubes, however, always high in relation to those which are obtained with the method of Vicat. The tests were always made in duplicate using for comparison the pozzolana of S. Paolo.

	1st Test	2nd Test	3rd Test	4th Test	5th Test
Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana
Pozzolana of S. Paolo	12.22	12.78	12.78	8.44	3.90
Pozzolana of Anzio	10.54	11.10	---	9.98	4.10
Pozzolana of S. Giovanni	---	---	12.92	---	---

From the above tests, we can derive that under pressure the quantity of lime liberated from pozzolana is much larger than that liberated in the test of Vicat, and therefore, it is our belief that we have reached the desired goal, namely of accelerating the action of lime upon pozzolana in such a way as to be possible to determine its effect during comparatively short time.

free lime changes, according to circumstances, into calcium carbonate or sulphate; next, into the form of the extremely unstable ferric oxide compound; thereupon follows the attack on the calcium aluminate and, lastly, on the silicate.

"Even the simple formation of calcium sulfate with two equivalents of water, causes a considerable increase of volume, and is sufficient for the destruction of the cohesion produced by the absorption of water. But with this formation of gypsum is connected the formation of Calcic Alumino-sulfate (see article on "The Cement Bacillus"), whose formation produces a formidable increase of volume, and, as a result, the total destruction of the cohesion. This double compound crystallizes with at least 30, probably with 60 equivalents of water; thus splitting up grain by grain, the hardest mortar with irresistable force to a completely disorganized mud, in which only the parts protected by the formation of calcium carbonate can maintain a certain degree of coherence."

Professor O. Rebuffat regarding this question of the reaction by the calcium hydroxide and chemical agents says in his study, "La Reazione Fre L'Idrato di Calcio e Il so Fato Sodico", published in "Giornale di Chimica Industriale e Applicata", XI. No. 12-1929:

"When specimens of mortar of Portland cement are immersed in a container full of a solution of sodium sulfate at 100 gr. per liter, no apparent phenomena are noticed at first, but in time the mortar becomes more porous, while the liquid takes a very strong alkaline reaction and keeps in solution notable quantities of silica, alumina and lime.

"If, instead of keeping the container well closed, it is left open, then the surface of the liquid becomes covered with thick scales of calcium carbonate.

"When 3 gr. of Portland cement of normal composition are allowed to react with 100 Cm.^{3} of a solution of sodium sulfate of 100 gr. per liter, taking care to agitate the mixture frequently, the filtered liquid contains, after two days:

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next, into the form of the extremely unstable
ferric oxide compound; thereupon follows the
attack on the calcium aluminate and, lastly,
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in solution notable quantities of silica, alumina
and lime.

"If, instead of keeping the container well
closed, it is left open, when the surface of
the liquid becomes covered with thick scales of
calcium carbonate.

"When 5 gr. of Portland cement or normal
compositions are allowed to react with 100 cm.
of a solution of sodium sulfate of 100 gr. per
liter, taking care to agitate the mixture fre-
quently, the filtered liquid contains, after
two days:

SiO_2	0.0042 gr.
Al_2O_3	0.0021 "
CaO	0.0582 "

and in reaching neutrality of reaction, consumes, in the presence of phenolphthalein:

116 $cm.^3$ of 1/10 normal solution of hydrochloric acid.

"These results show very clearly that the cement is disintegrated, because the lime (free or combined) passes into the solution of sodium sulfate, rendering it highly caustic.

"The reaction between the calcium hydrate and the solution of sodium sulfate (being the calcium hydrate partially dissolved and partially in suspension) is part of a reversible process:

$$Na_2SO_4 + Ca(OH)_2 \quad CaSO_4 + 2\ Na(OH)$$

which, in the reaction leading to the formation of calcium sulfate, determines an augmentation of the alkalinity of the liquid, because the sodium hydrate produced remains in solution. In the reaction leading to the formation of sodium sulfate it determines a diminution of alkalinity because the calcium hydrate set free remains in the insoluble state.

Conclusions

1. "The reaction between calcium hydrate and sodium sulfate proceeds rapidly, so that after one day, with temperatures between 15°C. and 20° C., it has almost reached the state of equilibrium.

2. "The quantity of sodium hydrate set free, or, what is the same, the quantity of sodium sulfate decomposed, increases when more diluted solutions are used. However, the quantity does not increase proportionally with the rate of dilution, but rather in a diminishing ratio, pointing to a maximum which would correspond to 60% of the theoretical quantity of hydrate for a solution of 20% of sodium sulfate. This is shown clearly in the following table:

SiO_2 0.0022 gr.

Al_2O_3 0.0021 "

CaO 0.0255 "

and in resulting neutrality of reaction, consumes, in the presence of phenolphthalein,

11.6 cm.³ of 1/10 normal solution of hydrochloric acid.

"These results show very clearly that the cement is disintegrated, because the lime (free or combined) passes into the solution of sodium sulfate, rendering it highly caustic.

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Solution of Sodium Sulfate (gr./liter)	Sodium Hydrate formed in % of Theoretical Quantity	Increase
101.1	21.0	----
50.5	36.0	15.0
33.7	48.6	12.6
25.25	52.2	6.6
20.2	60.0	4.8

in which the values for the 20% solution were obtained from a curve based upon the data of other experiences.

3. "Redoubling the quantity of calcium hydrate, or diminishing it by about one third, does not bring about (with the saturated solution of sodium sulfate) any variation in the quantity of sodium hydrate formed.

4. "The sulphuric acid in solution diminishes proportionally to the quantity of sodium sulfate decomposed.

5. "The quantity of CaO dissolved in the liquid is always within the limits of the coefficient of solubility.

6. "The solid part is formed by a mixture of calcium hydrate and calcium sulfate, and does not contain a basic calcium sulfate.

7. "The solid part does not contain large quantities of sodium sulfate; therefore any formation of a double salt of calcium and sodium is excluded.

Final Conclusion

"In the system:

$$Na_2SO_4 + Ca(OH)_2 \quad CaSO_4 + 2\,Na\,OH$$

the reaction proceeding from left to right corresponds to the disintegrating action that salt waters more or less rich in sodium sulfate exercise upon cementing masses. Such disintegration

Solution of Sodium Sulfate (gr./liter)	Theoretical Quantity	Sodium Hydrate formed in % of Increase
100.1	21.0	
50.5	36.0	15.0
33.7	46.0	12.0
25.25	52.8	6.8
20.2	60.0	7.2

in which the values for the 20% solution were obtained from a curve based upon the data of other experiments.

5. "Reducing the quantity of sodium hydrate, or diluting it by about one third, does not bring about (with the saturated solution of sodium sulfate) any variation in the quantity of sodium hydrate formed."

4. "The sulphuric acid in solution diminishes proportionally to the quantity of sodium sulfate decomposed."

3. "The quantity of CaO dissolved in the liquid is always within the limits of the coefficient of solubility."

6. "The solid part is formed by a mixture of calcium hydrate and calcium sulfate, and does not contain a basic calcium sulfate."

7. "The solid part does not contain large quantities of sodium sulfate; therefore any formation of a double salt of calcium and sodium is excluded."

Final Conclusion

"In the system:

$$Na_2SO_4 + Ca(OH)_2 \quad CaSO_4 + 2\,NaOH$$

the reaction proceeding from left to right corresponds to the disintegrating action which water's more or less rich in sodium sulfate exercise upon cementing masses. Such disintegration

is helped by the fact that the reaction is rendered easy by a moderate dilution of sulfate. The antagonistic reaction which could prevent the disintegration (reaction proceeding from the right to the left) has practically no effect whatever because it becomes important only for high concentration of sodium sulfate."

The French Chemist, E. Maynard, whose studies upon the diffusion of lime from the interior of a mass of set Portland cement mortar, have attracted considerable attention says in his article "Le Mecanisme de l'Action de Eaux de Diverse Natures sur les Mortiers et le Beton Arme", published in "Le Genie Civil" August 1927:

"When concrete is immersed in sea water the disintegrations are due to another order of phenomena; the water penetrating all the pores of the concrete is not renewed as the salts are dissolved except with extreme slowness, and possibly not at all. The lime of the cement dissolves and then diffuses in the external water, diminishing the cohesion of the mortar and increasing its porosity and this action continues actively, until the compounds of the cement: silicate, aluminate and calcium ferrite have become monobasic.

"The lime which liberates continuously from the concrete is transformed, through reaction with the magnesium sulfate, into calcium sulfate at the surface of the mortar, so that during all the time that this reaction takes place not one atom of magnesium sulfate penetrates within the concrete.

"The experiments of Le Chatelier on that subject have confirmed our own; on the other hand the calcium sulfate contained in sea water does not penetrate into the concrete except when the cement contains in solution a smaller quantity of it; but this penetration is always very slow and generally little noticeable, so that the role of the calcium sulfate of sea water in the phenomenon of disintegration is of small importance.

"At the same time sodium chloride accumulates in the cement until it attains the enormous quantity of 80 gr. per liter of mortar of pure cement; about half the amount of this salt - according to our researches - combines forming an unknown salt.

is helped by the fact that the reaction is hindered easy by a moderate dilution of sulfate. The antagonistic reaction which could prevent the disintegration (resolution proceeding from the right to the left) becomes important only through concentration of sodium sulfate."

The French Chemist, M. Lavaud, whose studies upon the dilution of lime from the interior of a mass of set Portland cement mortar, have attracted considerable attention here in his article "Le Mecanisme de l'Action de Eaux de Diverse Natures sur les Mortiers et le Beton Arme", published in "Le Genie Civil" August 1927:-

"When concrete is immersed in sea water the disintegrations are due to another order of phenomena; the water penetrating all the pores of the concrete is not renewed as the water is rapidly dissolved except with extreme slowness, and possibly not at all. The lime of the cement dissolves and then diffuses in the external water, diminishing the cohesion of the mortar and increasing its porosity; until the compounds of the cement; silicate, aluminate and calcium ferrite have become monobasic.

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"At the same time sodium chloride decomposes in the cement until it attains the amounts quantity of 80 gr. per liter of mortar of pure cement; about half the amount of this salt - according to our researches - combines forming an undrown salt.

"When the cement compounds are in a monobasic state, their disintegration by the action of water - with production of calcium hydrate, takes place with more difficulty and much more slowly, because the heat of formation of the monobasic salts reduces the action of water; the magnesium sulfate of sea water then penetrates little by little into the concrete, reacts upon lime and the magnesia deposits in the interior of the mortar in the shape of a multitude of whitish spots.

"On the other hand, the sodium chloride dissolves silica which leaves the mortar by diffusion. But, simultaneously, silica, alumina and ferric oxide hydrate thoroughly, and, inasmuch as the cohesion of the mortar is weakened by the liberation of lime, the mortar swells and disintegrates. Finally, the cement reconstitutes partially its primitive elements because in a cement totally decomposed is found some silicate of alumina, some ferric oxide, some calcium carbonate - either pre-existing or formed during the course of decomposition, and some magnesia deriving from the action of the salts of sea water.

"At the beginning of the immersion, and then little by little, some carbonate is formed, often at the surface of the mortar, in a crust - hard, adhesive and porous.

"Such is the mechanism of the action of sea water upon concrete, and there is no cement - however numerous may be those people who delude themselves upon this point - which can resist the action of sea water indefinitely. Its disintegration is simply a question of time."

One element above all in the mechanism of the disintegration seems to play the preponderant part. That element is the formation of magnesium sulfo-aluminate in the set cement. As Lerch and Bogue say in their study on "The Chemical Action of Salt Solutions on the Constituents of Set Cement":

"The failure of cements in sulfate waters appears to be due to the formation of calcium sulfo-aluminate and the resulting large increase in volume."

"When the cement compounds are in a monobasic state, their disintegration by the action of water - with production of solution and much more slowly, because the lack of contact of the monobasic salts reduces the action of water, the magnesium sulfate of sea water then penetrates little by little into the concrete, reacts upon lime and the magnesia deposits in the interior of the mortar in the shape of a multitude of minute spots.

"On the other hand, the aluminous silicates which leave the mortar by dissolution. But, simultaneously, silica, alumina and ferric oxide hydrate themselves, and, inasmuch as the content of the mortar is weakened by the dissolution of lime, the mortar swells and disintegrates. Finally, the cement recombines to regain its primitive elements because in a cement totally decomposed is found some silicate of alumina, some ferric oxide, some calcium carbonate - either precipitating or formed during the course of decomposition, and some magnesia deriving from the action of the salts of sea water.

"At the beginning of the immersion, and then little by little, some carbonate is formed, often at the surface of the mortar, in a crust - hard, adhesive and porous.

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"The reactions of concrete in sulfate waters appears to be due to the formation of calcium sulfo-aluminate and the resulting large increase in volume."

Of all those who have emphasized the role played by calcium sulfo-aluminate, the name of the Frenchman, H. Lafuma stands out as that of one who delved the deepest into the subject. In his book "Recherches sur les Aluminates de Calcium et sur leurs Combinaisons avec le Chlorure et le Sulfate de calcium" (Paris - 1932) Lafuma says:

> "It has been proved that the action of dissolved calcium sulfate upon the calcium aluminates is translated by the reactions:
>
> $Al_2O_3.4\ CaO.12\ H_2O + 3\ CaSO_4.2\ H_2O + Aq =$
>
> $= Al_2O_3.3\ CaO.\ 3\ CaSO_4.Aq + Ca(OH)_2$
>
> $3(Al_2O_3.2\ CaO.7\ H_2O) + 6\ CaSO_4.2\ H_2O$
>
> $= 2(Al_2O_3.3\ CaO.3\ CaSO_4.Aq) + Al_2O_3.Aq$
>
> "It is to these reactions that the action of sulfate waters upon cements containing alumina must be attributed.
>
> "The mortars of cements rich in lime and alumina swell up and increase in volume, very often in a considerable way, under the action of sulfate waters. It is merely to the reaction of the calcium sulfate upon the tetra-calcium aluminate that this effect must be attributed. Contrarily, if the cement is very rich in alumina and is poor in lime, like high alumina cements, for instance, the calcium sulfate reacts upon the di-calcium aluminate and in such a case the mortars do not evince either alterations or diminution of mechanical resistance. All the experimental works upon the disintegration of cements containing alumina have shown that the disintegration is much more evident whenever the alumina is found in greater quantity in relation to the lime. This shows that the presence of the tri-calcium aluminate hydrate in a set cement is deleterious while the presence of bi-calcium aluminate is without harmful consequences."

Le Chatelier had already shown how the hydration of the tri-calcium aluminate of Portland cement brings about the formation of a tri-calcium aluminate hydrate according to the equation:

$$Al_2O_3.3\ CaO + Ca(OH)_2 + 11\ H_2O = Al_2O_3.4\ CaO.12\ H_2O$$

Of all those who have emphasized the role played by calcium sulfo-aluminate, the name of the Frenchman P. Lefèvre stands out as that of one who delved the deepest into the subject. In his book "Recherches sur les Aluminates de Calcium et sur leurs Combinaisons avec le Chlorure et la Sulfate de Calcium" (Paris - 1933) Lefèvre says:

"It has been proved that the action of dissolved calcium sulfate upon the calcium aluminates is translated by the reactions:

$$Al_2O_3.\frac{1}{2}\,CaO.\frac{1}{2}H_2O + 3\,CaSO_4.3\,H_2O + Aq =$$

$$= Al_2O_3.3\,CaO.3\,CaSO_4.Aq + Ca(OH)_2$$

$$3(Al_2O_3.3\,CaO.Aq) + 8\,CaSO_4.3\,H_2O =$$

$$= 3(Al_2O_3.3\,CaO.3\,CaSO_4.Aq) + Al_2O_3.Aq$$

"It is to these reactions that the setting action of sulfate waters upon cements owing setting alumina must be attributed.

"The mortars or cements rich in lime and alumina swell up and increase in volume, very often in a considerable way, under the action of sulfate waters. It is merely to the reaction of the calcium sulfate upon the tetra-calcium aluminate that this effect must be attributed. Certainly, if the cement is very rich in aluminate and is poor in lime, like high alumina cements, for instance, the calcium sulfate reacts upon the di-calcium aluminate and gives rise to the formation of aluminium or mechanical resistances. In all the experiments we make upon the disintegration of cements containing alumina have shown that the disintegration is much more evident, whenever the alumina is found in greater quantity in relation to the lime. This shows that the presence of the tri-calcium aluminate by-crate in a set cement is deleterious while the presence of bi-calcium aluminate is without harmful consequence."

Le Chatelier had already shown how the hydration of the tri-calcium aluminate hydrate according to the equation of a tri-calcium aluminate of Portland cement brings about the formation of a bi-calcium aluminate hydrate according to the equation:

$$Al_2O_3.3\,CaO + Ca(OH)_2 + 11\,H_2O = Al_2O_3.\frac{1}{2}\,CaO.\frac{1}{2}\,H_2O$$

This finding of Le Chatelier has been corroborated by Lafuma who established the reaction taking place according to the formula:

$$2(Al_2O_3 \cdot 3\ CaO) + 19\ H_2O = Al_2O_3 \cdot 4\ CaO\ 12\ H_2O + Al_2O_3 \cdot 2\ CaO \cdot 7\ H_2O$$

In high alumina cements which are mainly composed of mono-calcium aluminates, Lafuma shows that their hydration produces di-calcium aluminate hydrate according to the equation:

$$2(3\ Al_2O_3 \cdot CaO) + Aq = Al_2O_3 \cdot 2\ CaO \cdot 7\ H_2O + Al_2O_3 \cdot Aq$$

which according to his findings, does not produce any increase of volume in the set cement.

> "It is possible to see", says Lafuma, "That there is not to be feared any action of calcium sulfate upon cement if there is no formation of tetra-calcium aluminate in the hydrated cement. A cement which contains a quantity of lime inferior to that indicated by the formula:
>
> $$X\ SiO + Y\ Al_2O_3 = (X + 2Y)\ CaO$$
>
> will furnish when hydrated, the compounds:
>
> $SiO_2 \cdot CaO \cdot 2.5\ H_2O$ and $Al_2O_3 \cdot 2\ CaO \cdot 7\ H_2O$
>
> without formation of tetra-calcium aluminate. The previous formula presents almost exactly the composition of the cements of which the index of chemical resistance, that is, the ratio:
>
> $$\frac{SiO_2 + Al_2O_3}{CaO}$$
>
> is equal to one (1). It is possible to see then that those cements of which the chemical resistance is equal or superior to one (1) will not be decomposed by the calcium sulfate. It is possible to go even further into the study of the action of calcium sulfate upon the calcium aluminates and to analyze the very mechanism of this action. That is, to connect to a more general principle the difference in behavior of the di-calcium aluminates and the tetra-calcium aluminates. This principle is the following:

This finding of Le Chatelier has been corroborated by Lerms who established the reaction taking place according to the formula:

$$3(Al_2O_3 \cdot 3\,CaO) + 18\,H_2O = Al_2O_3 \cdot 6\,CaO + CaO$$

$$18\,H_2O + Al_2O_3 \cdot 6\,CaO \cdot Y\,H_2O$$

In high alumina cements which are mainly composed of mono-calcium aluminates, Lerms shows that hydration proceeds these di-calcium aluminates according to the equation:

$$3(3\,Al_2O_3 \cdot CaO) + Aq = Al_2O_3 \cdot 3\,CaO \cdot Y\,H_2O + Al_2O_3 \cdot Aq$$

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"It is possible to see", says Lerms, "that there is not to be feared any action of calcium sulfate upon cement, if there is no formation of tetra-calcium aluminate in the hydrated cement. A cement which contains a quantity of lime inferior to that indicated by the formula:

$$x\,SiO_2 + y\,Al_2O_3 = (2x + 3y)\,CaO$$

will furnish when hydrated, the components:

$$x\,SiO_2 \cdot 2x\,CaO \text{ and } Al_2O_3 \cdot 3y\,CaO \cdot Y\,H_2O$$

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"The hydrated compounds which are formed with the dissolved salts do not bring about any change of the apparent volume of the mortar. The hydrated compounds formed from the solid salts develop instead disintegrating forces and bring about the destruction of the mortar. In other words, the action of the calcium sulfate upon the hardened cements is not to be feared except when the cement contains some tetra-calcium aluminate. Those cements for which the index of chemical resistance is equal or superior to one (1) harden without bringing about the formation of tetra-calcium aluminate and will not give rise to disintegration or swelling under the action of calcium sulfate."

Passing from the study of the action of calcium sulfate to the study of the action of sea water, he says:

"There is a very remarkable difference of action between sulfate waters and sea water. Cements which are decomposed with swelling in a few months time by sulfate waters may resist quite a few years the action of sea water.

"Magnesium sulfate of sea water placed in contact with lime of the cement gives rise to calcium sulfate liberating magnesia; this calcium sulfate gives birth to the calcium sulfo-aluminate which brings about the disintegration through swelling of the mass. But the chemical action is not the same as that in the case of sulfate waters.

"First of all, through reaction with the free lime of the cement, magnesium salts of sea water give birth to calcium salts and free magnesia, which brings about a diminution of the proportion of free lime in the cement. Afterwards, the sodium chlorides of sea water have a very remarkable chemical action upon the calcium aluminate of the cement.

"I demonstrated that if the solution in which the cement is placed contains 3% of sodium chloride, the tetra-calcium aluminate is completely decomposed, the bi-calcium aluminate alone remaining stable. If the quantity of sodium chloride increases - which is just what seems to take place in cements immersed in sea water, the sodium chloride combines with the calcium aluminate to give rise to calcium chloro-aluminate, this last salt

The hydrated compounds which are formed with the dissolved salts do not bring about any change of the apparent volume of the mortar. The hydrated compounds formed from the solid salts develop increased disintegrating forces and bring about the deterioration of the mortar. In other words, the solution of the calcium silicate upon the hardened cement compound is not to be feared except when the cement contains some tetra-calcium aluminate. These compounds for which the index of chemical resistance is equal or superior to one (1) harden without bringing about the formation of tetra-calcium aluminate and will not give rise to disintegration or swelling under the action of calcium sulfate."

Passing from the study of the action of calcium sulfate to the study of the action of sea water, he says:

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"As demonstrated there is the solution in which the cement is placed contains a lot of sodium chloride, the tetra-calcium aluminate is completely decomposed, the bi-calcium aluminate alone remaining stable. If the quantity of sodium chloride increases - which is just what seems to take place in cements immersed in sea water, the sodium chloride combines with the calcium aluminate to give rise to calcium chloro-aluminate, this last salt

is also born from the calcium chloride which derives from the magnesium chloride of sea water. Now, it is not upon the tetra-calcium aluminate that the calcium sulfate will react, but upon the bi-calcium aluminate and upon the calcium chloro-aluminate with which it will give calcium sulfo-aluminate. Therefore,

(a) If there is no free lime in the cement, the bi-calcium aluminate and the chloro-aluminate lets a little alumina go into the solution, the sulfo-aluminate is formed from the dissolved salts and there is no formation of swelling.

(b) If there is free lime instead, there is no formation of tetra calcium aluminate in presence of sodium chloride but both the bi-calcium aluminate and the chloro aluminate are insoluble, therefore there is no trace whatsoever of alumina in solution and the calcium sulfate reacts upon the solid salts in which case, there is noticed the formation of swelling.

"Resuming, the difference of action between sulfate waters and sea water, it reduces to this:

"That the calcium sulfate reacts upon the tetra-calcium aluminate in the first case and upon the di-calcium aluminate rendered insoluble by the free lime in the case of sea water. However, both in the case of sea water and in the case of sulfate water, it is possible to avoid disintegration through swelling by using cements with an index of chemical resistance equal or superior to unity. The di-calcium aluminate which is formed then in the absence of free lime, lets the alumina go into solution even in the presence of the salts of sea water. The sulfo-aluminate is formed then through the dissolved salts and its formation gives no rise to any swelling.

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Conclusion - "I have established in my work the existence of two calcium aluminate hydrates, that is, the di-calcium aluminate and the tetra calcium aluminate. These results bring about the possibility of explaining very simply larger difficulties brought about by the chemistry of cements containing alumina, that is, the action of the calcium sulfate upon these cements is much more remarkable if the quantity of alumina happens to be larger in relation to a larger quantity of lime.

"It is easy to understand then, why Portland with 6% or 7% of alumina is decomposed by sulfate waters and why the high alumina cements with a small quantity of lime can very well withstand the action of these waters, because in one case the calcium sulfates react upon the tetra calcium aluminate while in the other case, it reacts upon the di-calcium aluminate, or more exactly upon the alumina and the lime which this alumina lets pass into solution in the surrounding liquid."

We have concerned ourselves so far, with the behavior of the individual compounds, but it is interesting to notice that the general character of Portland cement, that is, its high basicity has been recognized by the leading cement chemist, Prof. F. Ferrari of the Royal University of Pisa, Italy as a very important element of weakness of this material.

Throughout his studies on the subject of cement disintegration published mainly in the "Giornale di Chimica Industriale et Applicata" he stresses the fact that all mortars containing aluminates or silicates of a highly basic nature are subject to a slow but constant disintegration, due to the action of sulfates and chlorides.

In one of these studies published in the year 1921, he states that the essential factor of the stability of a mortar or concrete exposed to aggressive water is the impermeability of the superficial stratum which originates from the slow formation of calcium carbonate. The variations of resistance of this superficial stratum on which depends the final diffusion of the lime from the inner mass of the mortar and the final penetration of the sulfates and chlorides in the same mass are due to the tensions arising from the formation of hydrates capable of expansion, like calcium alumino-sulfates, calcium hydrates, magnesia hydrates, etc. In all mortars, whatever their degree of basicity may be, the formation of calcium hydrates and magnesia hydrate in small lumps throughout the mass

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(resulting from the presence of free lime, that is, calcium oxide remaining uncombined) and the formation of calcium alumino-sulfates brings about steady and evident disintegration.

The hydration of calcium silicates and of the free calcium oxide gives origin to uniform tensions which in materials of high basicity, such as Portland cement mortar or concrete, succeed in time in modifying the structure of the superficial strata. These facts determine the fundamental qualities of a mortar to be used in maritime works, or in works in constant contact with water containing sulfates and chlorides. These qualities are:

(a) Reduced percentage of magnesium hydrates

(b) Lack of free bases.

(c) Lack of calcium aluminates.

In other words, Ferrari attributes as the largest element of resistance the reduction of the high basicity of the cement through a modification of its highly basic compounds as tri-calcium silicate and tri-calcium aluminate, in addition to a reduction of free calcium oxide. We therefore, have theory of increasing the resistance of Portland to sea presented in a new light, based on the advocacy of a radification of its structure.

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C H A P T E R 4.

The Problem of Producing a Chemically Resistant Cement

The solution of the problem of producing a chemically resistant cement is intimately linked to the possibility of eliminating all the objectionable features which characterize the behavior of the individual compounds of Portland in the presence of chemical agents without materially lowering their physical resistance.

It is necessary that the nature of the cement as a whole be changed from that of a highly basic to that of an acid substance.

Dividing the components of Portland into the two broad classes of acid and basic, we find that calcium oxide and magnesia represent the basic elements while silica and alumina represent the acid elements, so that whenever we speak of changing the nature of Portland from that of a basic substance to that of an acid substance we mean that we are aiming to increase the proportion of silica and alumina in relation to the proportion of lime and magnesia. This is in accordance with the ideas of Vicat, who contends that if it is possible to manufacture a cement of which the index of chemical resistance, that is, the ratio: silica plus alumina to lime plus magnesia - is larger than one (1), we will have obtained a chemically resistant cement.

From a superficial viewpoint, it would seem to be an easy matter to bring about this change in the proportions of the various constituents. When we recall however that these constituents are not found in the final product of Portland cement in their oxide state but are found instead in the form of very complex compounds and that it is exactly due to such compounds that all characteristics of Portland derive, we can appreciate the difficulty of the problem. If for instance, we begin by materially reducing the lime and increasing the silica in the materials which constitute the clinker we may obtain no formation whatever of tri-calcium silicate, perhaps no formation of di-calcium silicate and the only combination of lime and silica found is the mono-calcium silicate. But unfortunately, the mono-calcium silicate is not a hydraulic compound. Being thus an inert substance it cannot be an appreciable part of the cement without materially lowering the strength of the compound.

Working instead through an increase of the alumina content, Julius Bied brought about in France in 1908 the production of the aluminous cements, or what is called in French "Ciment Fondu" and in this type of cement the alumina content is equal and at times superior to the lime content, while the percentage of the silica is very small.

CHAPTER V.

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Following are three typical compositions of aluminous cements:

	1	2	3
SiO_2	5	10	15
Al_2O_3	45	40	35
Fe_2O_3	15	10	15
CaO	35	40	35

The principal compound found in such a type of cement is mono-calcium aluminate, the general chemical composition consisting mainly of one part of di-calcium silicate to two parts of mono-calcium aluminate.

Due to such a chemical composition, this type of cement is highly resistant to the action of sulfate or sea water, because the di-calcium silicate, in the process of hydration does not liberate free calcium oxide, and the mono-calcium aluminate forms hydrated di-calcium aluminate which, when placed in contact with sulfates, gives rise to a calcium sulfo-aluminate low in lime subject to no increase of volume. The reaction takes place, says Lafuma, according to the equation:

$$2(Al\ O\ .\ CaO) + Aq = Al\ O\ .\ 2\ CaO\ 7\ H\ O + Aq$$

An experimental proof of high resistance to sea water offered by aluminous cements was given by Feret in France, who reports in "Annales des Ponts et Chaussees", year 1922, that identical blocks of concrete made with standard Portland and with aluminous cement, after an immersion lasting for five years, behaved in an entirely different way. While the blocks made with standard Portland presented evident signs of disintegration within less than one year of immersion; the blocks made with aluminous cement were still intact at the end of the five year period.

It would seem therefore, that aluminous cements represent the desired solution of our problem. Unfortunately aluminous cements offer, apart from their high cost of production and the difficulty of their manufacture, great difficulties of practical use, for instance, they give rise to a very high heat of hydration, they cannot be mixed with any other type of cement and the water cement ratio must be extremely low. The forms and the mortar of concrete itself must be kept continuously wet, and the mass instead of hardening first at the surface, begins to harden in the interior.

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$$3(Al_2O_3 \cdot CaO) + 3H_2O = Al_2O_3 \cdot 3CaO + Al_2O_3 \cdot 3H_2O$$

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Paramount is the fact that the increase of the temperature of the whole mass during the setting process, which amounts to from 40°C. to 60°C., brings about an initial dilation and a subsequent contraction, accompanied by strains throughout the mass. J. Mallette in "Les Defauts des Mortiers et des Betons" quotes the following figures showing considerable contraction of a bar made of a mortar composed of 10 gr. of cement and 20 gr. of sand:

	HOURS					
Time.....	2	3	4	5	7	11
Contraction $cm.^3$.....	0.02	0.07	0.10	0.17	0.36	0.58

	DAYS				
Time	1	2	6	9	12
Contraction $cm.^3$	0.92	1.03	6.08	6.12	6.16

This great contraction, the tendency of the constituents of the concrete to separate during the pouring and the rapidity of the hydration process coupled with all the other undesirable features of which we have already spoken, render this cement of little practical help in the solution of our problem.

Eliminating thus any solution based on an increase of either the silica or the alumina content and a corresponding reduction of lime, no other solution (apart from a high iron cement seems to offer but that of blended cements. Of the high iron type of cement there are quite a few varieties mostly with German names such as: Sclackenzement; Huttenzement; Eisenportlandzement; and Ochofenzement. In Italy these cements are called by the general name of Ferro-Portland. The typical composition of a Ferro Portland cement is as follows:

SiO_2	23.17
Al_2O_3	1.49
Fe_2O_3	8.66
CaO	64.51
MgO	0.68
SO_3	0.59
Insoluble Silica	0.22
Alkalis	1.18
Total	100.00

Total	100.00
Alkalis	1.18
Insoluble silica	0.22
SO_3	0.26
MgO	0.89
CaO	15.19
Fe_2O_3	3.99
Al_2O_3	1.78
SiO_2	22.14

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Contraction cm.	0.22	1.03	0.08	0.12	0.19	
Time	1	2	3	6	12	
			D A Y S			
Contraction cm.	0.02	0.04	0.10	0.14	0.22	0.26
Time	2	3	4	5	6	11
			H O U R S			

Paramount is the fact that the increase of the hydration of a bar made of a mortar composed of 10 gr. of cement to 20 gr. of sand:

Hence, the following figures showing considerable con-
traction of a bar made of a mortar composed of 10 gr. of cement
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Ferrari in his study upon Ferro-Portland, published in "Giornale di Chimica Industriale et Applicata", year 1921 says:

"Concrete made with Ferro-Portland on account of its high basicity shows like all the cements of this type, having a high specific permeability and a high and ready resistance to physical agents, also a higher stability under the action of sulfates, a stability which is due to the lack of calcium aluminate.

"This stability on the other hand even though of an order entirely different from that of the Portland does not render Ferro-Portland the ideal cement for use in maritime works or in concrete works in contact with water containing sulfates. This stability of Ferro-Portland does not last long, but is subjected, after a lapse of time not excessively long, to a regress which cannot be deemed of small import.

"The cause of this phenomenon must certainly be referred to the high content of calcium oxide of the Ferro-Portland. The tensions which originate during the hydration of the Ferro-Portland (and I am not speaking here of the abnormal tensions due to the hydration of the free lime, but of the normal ones taking place during the setting, which stress in various ways the mass of the mortar), while they produce in the interior of the mass stable modifications of the crystal structure, resolve themselves at the surface in periodical alteration of the continuity of the superficial stratum.

"The diffusion of free lime from the interior of the mass takes place therefore, periodically, determining a diminution of compactness and with it a reduction of its mechanical efficiency. The light uniform, scale-like structure that the crystal mass of the mortars under observation has assumed after a certain number of years, the web of very fine cracks of which the surface results covered throughout, and the ascertained regress of the mechanical resistance justifies the rejection of Ferro-Portland alone as a sea water resistant cement.

Ferrari in his study upon Ferro-Portland, published in "Giornale di Chimica Industriale et Applicata", year 1921 says:

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"In other words, the mortars made with Ferro-Portland although free from the dangers which derive from the presence of aluminates of a highly basic nature are nevertheless subjected within rather large periods of time to a deterioration originating from the diffusion of free lime. This deterioration is due also to their high specific permeability and to the insufficient stability of their protective superficial strata. Disintegration is due in short to the characteristics which are conferred to Ferro-Portland by its high basicity."

Passing on from Ferro-Portland we next take up the study of blended cements. It is opportune at this point to recapitulate the conditions which blended cements must satisfy to present the desired solution.

According to many authorities they should be:

(a) High acid

(b) Devoid of any formation of a tetra calcium aluminate hydrate formed in their setting. (Consequently be free of tri-calcium aluminate.)

(c) Be free of calcium oxide, and consequently be free also of tri-calcium silicate.

It would appear however, that even these three conditions are not enough. Calling them the negative ones, there are in contrast the positive ones to be fulfilled, that is, there are some additional compounds that need to be part of the cement if it is to offer both physical and chemical resistance.

The first idea of a blended cement was born from the observation that the old Roman Mortars withstood the action of the elements for 2,000 years or more without in some instances showing any sign of disintegration. The mortars having the greatest physical and chemical resistance were apparently made with lime and pozzolana. It was natural to assume that by mixing Portland and pozzolana we might obtain a product presenting the characteristics of both. Also inasmuch as possolana is merely silica it was natural to assume that it might be possible to replace pozzolana with ordinary silica and obtain in the end the same results. In our study of the subject we must not lose sight of the fact that the behavior of a chemical element and the behavior of a compound of that same element are not necessarily identical. The reactions of calcium in its

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isolated state, for instance, and the reactions of calcium when part of calcium sulfate are entirely different in character and in results. The reactions of free, active silica and the reactions of silica when combined in the various silicates, constituting pozzolana present different aspects and produce different results.

This brings us to the fundamental question of: What is pozzolana? But before answering this question it is well to devote some time to a consideration of the nature of the blended cements so far on the market. These cements usually consist of 70% to 85% of standard Portland clinker mixed, before or after grinding, with 15% to 30% of the blend materials, be it silica or pozzolana. The problem is to ascertain whether or not the 15% to 30% of blend material can so modify the 70% to 85% of Portland clinker as to eliminate all of the undesirable characteristics.

No exhaustive analysis of the reasons for the chemical resistance of the old lime pozzolana mortars had been made when the use of blended cements was first advocated and put into practice. All that was known was that pozzolana or silica helped enormously to render the mortar or concrete less porous and more impermeable.

It is apparent that early disintegration of concrete frequently originates from the existence of pores, due to lack of density, where salts can deposit in crystalline formation. It was hoped that the use of a blended cement would insure a concrete practically free of pores and that an impermeable stratum would be provided on the surface of the concrete mass.

Concerning this point, Professor F. Ferrari in his studies upon Portland pozzolana mortars states:

> "The tensions to which the hydration of free lime gives origin in the internal part of the mortar, are translated in the interior of the mass - owing to the reaction of which this mass is capable - through a long period of time, in stable modifications of the crystalline elements, but at the surface resolve themselves in alterations of continuity of the superficial stratum. This explains why evem apparently impermeable mortars have shown the same failure as permeable mortars."

And J. Malette in his book "Les Defauts des Mortiers et des Betons", says in the chapter on "Decomposition par l'eau de Mer":

isolated state for instance, and the reactions of calcium when part of calcium silicate are entirely different in character and in results. The reactions of free, active silica and the reactions of silica when combined in the various silicates, constituting portland cement present different aspects and produce different results.

This brings us to the fundamental question of: What is portland? But before answering this question it is well to devote some time to a consideration of the nature of the blended cements so far on the market. These cements usually consist of 70 to 85% of standard portland clinker mixed, before or after grinding, with 15% to 30% of the blend materials, be it slitica or pozzolans. The problem is to ascertain whether or not the 15% to 30% of blend material can so modify the 70% to 85% of portland clinker as to eliminate all of the undesirable characteristics.

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Concerning this point, Professor R. Feret in his studies upon portland pozzolana mortars stresses:

> "The tensions to which the interior of free lime grains origin in the internal part of the mortar, are transferred in the interior of the mass - owing to the reaction of water - this mass is capable - through a long period of time, of considerable modifications of the crystalline elements, but of the average resistive capacity of the entire mass, it changes nothing essential. This explains why even apparently impermeable mortars have shown the same failure as permeable mortars."

And G. Michelis in his book "Les Defauts des Mortiers et des Betons", says in the chapter on "Decomposition par l'eau de mer":

"The phenomena of the decomposition of cements in sea water are at the mercy of a small crust impermeable and more or less expansive, a few tenths of a mm. of thickness. They are in other words at the mercy of the phenomena of production and destruction of this small crust which is in a state of perpetual transformation like a true living being, inasmuch as the lime liberated during the process of hydrolysis of the silicates is caused by diffusion to react upon the inner surface, while the magnesium salts of the sea water at the same time attack the exterior surface. Following this process, the sulfo-aluminate of calcium forms itself a little deeper in the same spot, following the alternative of the circulation of the lime and of the magnesium salts, occasioning wetting and cracking and facilitating therefore the penetration of sea water in large quantity."

And quoting from a report of Spanish Engineers to the 13th International Congress of Navigation in London we find:

"The idea of using impermeable concrete to reach unalterability is common. We constructed in this manner the beacon of the Serrapio of Gejon on a site so beaten by the seas that we were able to work only fifteen or twenty days during each year. A good result was obtained but we find that the impermeability is not by itself good quality. Impermeability is valuable only to delay the decomposition process, thus giving time enough to consolidate the natural external protection of a coating of carbonate of lime. A porous mortar on the other hand may present an unattackable mass. We have made an experiment with porous mortar in cement and lime through which we passed a strong jet of water to carry the lime away. The rest was afterwards submerged in concentrated sea water remaining without the least alteration. Possibly this is what happens with lime formed during setting, and this is the reason why those blocks taken out from the sea after many years of submersion are porous like a sponge although quite inalterable. In other words it may be the case of a mortar being good when porous and probably bad if impermeable.

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And quoting from a report of Spanish Engineers to the 15th International Congress of Navigation, in London we find:

"The idea of using impermeable concrete to resist variability is common. We construct- ed in this manner the dregon of the Serrapio of Ceton on a site so beaten by the seas that we were able to work only fifteen or twenty days during each year. A good result was ob- tained but we find that the impermeability is not by itself good quality. Impermeability is valuable only to delay the decomposition process, thus giving time enough to consolidate the natural external protection of the coating of carbonate of lime. A porous mortar on the other hand may present an unattackable mass. We have made an experiment with porous mortar in cement and lime through which we passed a strong jet of water to carry the lime away. The test was terminated without the least alteration. Possi- bly this is why happens with time formed during setting, and this is the reason why those places taken out from the sea after many years of sub- merged are porous like a sponge although quite impervious. In other words it may be the case of a mortar being good when porous and practically

"We have made in fact another essay with some briquettes with plenty of cement and very well rammed to make them impermeable. To the cement 40% of lime had been added, nevertheless the briquettes all failed in a 10% solution of sulfate of magnesia in spite of their impermeability."

Doubt relative to the validity of the assumption that density or the presence of an impermeable stratum at the surface could protect the whole mass led to the finding of a better explanation for the reason of being of blended cements and so the idea was advanced that if it is possible to provide a substance capable of combining with the free lime liberated during the process of setting and hardening and fix it in stable combinations, blended cements would be naturally the desired solution. We find this to be the common belief although Professor O. Rebuffat in his study entitled "The Analysis of Pozzolana Mortars" published in "Gazzetta Chimica Italiana", Volume 24, year 1896 disputes the claim on the ground that although there is such a combination through the first few years of the life of the mortar, still after about 20 years or so the lime disappears again, or in other words he contends there is no possibility whatever of making of free lime a stable and durable component of sea resistant mortar or any other mortar subjected to the action of highly ionized waters.

To demonstrate his point he made a comparative analysis of two pozzolana mortars, one 2,000 years old and the other 20 years old, showing that there was the possibility of determining that those mortars after 20 years or so of their immersion in sea water lose practically all their lime content. Summing up his studies he says:

"Two pozzolana mortars were analyzed, the first being taken from an old Roman Pier in the harbor of Pozzuoli near Naples about 2,000 years old. The second was taken from a maritime work 20 years old in the harbor of Naples. Part of the mortar was dried keeping it at a temperature of 100°C. and then was brought to red heat to determine the loss of weight. Another part instead was dried by keeping it at 100°C. and then immersed in hydrochloric acid, and kept at a temperature of 25°C. for three days (50 cubic centimeters of acid were used for one gr. of cement). From the solution was obtained iron, alumina, calcium and magnesia. From the insoluble part treated with sodium carbonate was obtained silica. The results of the comparative analysis are as follows:

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	Old Mortar	Modern Mortar
Insoluble	33.68%	52.18%
Silica	33.64	32.60
Alumina	32.61	28.38
Ferric Oxide	1.68	4.23
Calcium Oxide	5.66	6.67
Magnesia	3.56	2.35
Alkalis	5.15	4.68
Water	18.14	22.04
Total	100.45%	100.92%

> "About 20 years are required therefore to bring a pozzolana mortar in sea water to a limit state in which it has become practically inert to the action of the salts in sea water. The reason of this inertia is due to the fact that the mortar has lost all the lime and results in being constituted mainly of a hydrated silicate of alumina which owing to its composition is entirely indifferent to the action of salts in sea water."

In other words, according to Rebuffat, lime pozzolana mortars experience the same phenomena of disappearance of lime that takes place in time in Portland cement mortar or concrete.

The statement is frequently made that the fundamental reason for blended cement is the fixing of the free lime into a silicate compound which will fill all the pores and contribute to impermeability, strength and elasticity, which are the desirable characteristics of concrete exposed in sea water.

Blended cements may fulfill certain functions but there is no evidence to sustain the contention that they permanently fix the free lime.

If the only result of a silica admixture is an increase in density and possible increase in physical resistance the blended cement loses much of its excuse for being.

Dividing blended cements into two broad classifications of pozzolanic cements and high silica cements, we return to the question: "What is pozzolana?". This question must be solved before it is possible to treat of pozzolanic cements and to make an intelligent comparison of such cements with the general run of high silica cements.

	Old Mortar	Modern Mortar
Insoluble	33.68%	32.18%
Silica	33.64	32.80
Alumina	32.61	28.58
Ferric Oxide	1.68	4.23
Calcium Oxide	8.66	6.67
Magnesia	3.36	2.55
Alkalis	5.15	4.68
Water	18.14	22.04
Total	100.45%	100.92%

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C H A P T E R 5.

Natural Pozzolana

"Puteolamus pulvis,
si aquam attigit saxum
fit", Seneca, "Quaes-
tionum Naturalium."

What is pozzolana? To adequately answer this question we must refer to the original work done upon the study of pozzolana by the Italian chemists, inasmuch as Italy is the classical land of this material.

It is true that some clays or other siliceous substances having somewhat of a pozzolanic nature are found in many places throughout the world but it is doubtful if any of these substances can compete with the best grade of natural pozzolana in so far as hydraulic qualities are concerned.

Definition

Professor O. Rebuffat of the University of Naples, Italy dean of authorities on pozzolana, states in his article "La Pozzolana di Bacoli" published in Annali d'Ingegneria, Anno V. N. 10:

> "Pozzolana is a sandy rock of volcanic origin which, mixed with fat lime furnishes a hydraulic mortar. In this old definition the empirical part which is a fruit of the experience of centuries, takes the place of scientific knowledge acquired much later.
>
> "Not all volcanic sands however, can be effective pozzolanas. For a good pozzolana it is necessary that the sand present a vitreous structure and the chemical composition corresponding to that of the determinate lavic magma, trachytic or basaltic which contain as essential elements sanidime, leucite, nefeline and other alkaline silico-aluminates. In other words, pozzolana is constituted in its fundamental part of alkaline silico-aluminates in a vitreous state.
>
> "In a pozzolana, we may find various amounts of lime, magnesia and iron oxides but all these elements can be totally lacking without bringing about a diminution of the pozzolanic qualities. The alkaline sioico-aluminate must always be present however, if there is to be any pozzolanic action.

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"When the lavic magma is ejected suddenly into the atmosphere by the expulsion of steam, its particles undergoing a sudden cooling, remain in a vitreous state and acquire a reactivity of which the volcanic lava is singularly lacking in its ordinary state. In fusing and then suddenly cooling sanidine, leucite and orthoclase the resultant vitreous matter acquires pozzolanic properties.

"During the projection of the lavic magma into the atmosphere, the smallest particles, cooling off more rapidly remain in a vitreous state, while the larger particles, not being completely fused and also cooling more slowly assume a crystalline state. In this way a typical pozzolana ordinarily consists of a mixture of vitreous material (active) and crystalline materials (inert as to hydraulic effects.)"

From the above, we deduce that although pozzolana is constituted for the major part of silica (30% to 50%) its behavior, when mixed with hydraulic lime and subjected to the action of physical or chemical agents is fundamentally different from the behavior of the ordinary run of silica, either soluble or insoluble, or in an amorphous, colloidal, or gelatinous form. It is customary to attribute considerable hydraulic value to the soluble or colloidal form of silica. It is interesting therefore, to note how small a part the soluble or insoluble silica of the amorphous or colloidal form in pozzolana contributes to the part which pozzolana plays in its role of an hydraulic material. However, before going into the question of the influence of the physical characteristics of silica itself upon the hydraulic characteristics of pozzolana let us further emphasize the fact that although silica may be a material of very simple petrographic aspect, such is not the case of pozzolana. In the words of Professor G. Gallo of the University of Rome, Italy (see "The Microscopic Study of Pozzolanic Mortar" by G. Gallo, Gazzetta Chimica Italiana - Volume 38)*:

Pozzolanas, although constituted essentially of silica, alumina, ferric oxide, calcium oxide, magnesia, potassium and sodium oxides are materials of very complex petrographic aspect. Furthermore, their composition varies not only from one volcanic deposit to another but also from one stratum to another of the same deposit. Complete petrographic research on pozzolanas are still lacking. They remain therefore, actually a geological formation not well defined and whose general term "Pozzolana" is of dubious meaning.

*Appendix VI.

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"In general, they are constituted of volcanic laipIli in which it is possible to discover fragments of slag, pumice, lava, etc. and crystals of leucite, augite, mica, magnetite, and piroxene.

"But however the mineralogic composition of pozzolanas may vary it is nevertheless necessary to admit that in them there exists a common essence to which is manifestly due the property of setting under water, and that it is just the larger or smaller quantity of these essentially constituent parts present in a pozzolana that determines the higher or lower hydraulic value of a pozzolana."

The answer to the question hinges therefore upon finding what this constituent part of pozzolana is which plays the predominating role in its hydraulic properties. Professor Rebuffat has already said that part of the pozzolana is found in a vitreous state and part in a crystalline state. Stressing further the importance which this separation of pozzolana in two distinct physical states assumes, Professor G. Gallo says:

"It is possible to foresee a priori - anticipating in a way some of the findings which will be developed further on - that it is not possible to attribute in any way the hydraulic property of a pozzolana to its crystalline elements, because these elements constitute chemical compounds well defined and very stable which cannot undergo - when subjected to the action of the lime - a chemical transformation such as to make them contribute to the setting and hardening of hydraulic mortars."

Nor does the hydraulicity of a true pozzolana appear to be in any way dependent on the relative amounts of the chemical constituents.

We find, on comparing the analyses of numerous types of pozzolana, of varying degree of hydraulicity, that there is apparently no relationship between any single element or group of multiple elements and the hydraulic quality of the pozzolana. In fact, the chemical composition may vary in the most erratic way and still the pozzolana may be either hydraulically active or completely inert. This point is stressed by Professor Gallo in the study above referred to. He reports in fact the chemical composition of various types of pozzolana ranging from the so-called San Paolo Pozzolana which appears to be of the highest hydraulic value, passing through intermediate pozzolana types of decreasing hydraulic value, to the so-called Messina clays, lowest in hydraulic value.

"In general, they are characterized by volcanic lapilli in which it is possible to discover fragments of slag, pumice, lava, etc., and crystals of leucite, augite, mica, magnetite, and pyroxene.

"But however the mineralogic composition of porcellanes may vary, it is nevertheless necessary to admit that in them there exists a common essence to which is manifestly due the property of setting under water, and that it is just the larger or smaller quantity of these essentially constituent parts present in a porcellane that determines the higher or lower hydraulic value of a porcellane."

The answer to the question hinges therefore upon finding what this constituent part of porcellane is which plays the predominating role in its hydraulic properties. Professor Bechi has already said that part of the porcellane is found in a vitreous state and part in a crystalline state. Pressage further the importance which this separation of porcellane in two distinct physical states assumes, Professor C. Guglielmi says:

"It is possible to foresee a priori - and confirming in a way some of the findings which will be developed further on - that it is not possible to attribute in any way the hydraulic property of a porcellane to its crystalline elements, because these elements consist quite opposite compounds well defined and very stable when cannot undergo - when subjected to the action of the time - a chemical transformation such as to make them contribute to the setting and hardening of hydraulic mortars."

Nor does the hydraulicity of a type porcellane appear to be in any way dependent on the relative amounts of the chemical constituents.

We find, on comparing the analyses of numerous types of porcellane, of varying degree of hydraulicity, that there is apparently no relationship between any single element or group of multiple elements and the hydraulic quality of that porcellane. In fact, the chemical composition may vary in the most erratic way and still the porcellane may be either hydraulically active or completely inert. This point is stressed by Professor Gallo in the study above referred to. He reports the chemical composition of various types of porcellane ranging from the so-called San Paolo Porcellane which appears to be the best hydraulic value, passing through intermediate porcellane types of decreasing hydraulic value, to the so-called Messine clays, loved

Type of Pozzolana	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_3O	H_2O and Other Subt.	Author of Analysis
San Paolo	45.40	15.12	12.05	--	9.33	3.59	3.78	2.15	8.45	Prof. Cavarzi
Pratolungo	46.24	19.26	11.18	--	9.82	2.84	2.66	2.77	6.10	Prof. Agostinelli
Bacoli	64.71	20.03	4.98	--	4.39	0.96	1.77	3.07	0.09	Ital.R.R.
Portella	48.58	32.72	9.63	--	7.16	--	0.74	0.74	1.17	" "
Bassano	47.10	21.90	8.01	--	9.91	1.56	2.56	6.01	2.21	Prof. Rebuffat
Vesuvio	48.45	17.81	3.49	3.55	12.09	3.02	5.46	5.01	0.60	Giorgis & Gallo
Santorino	64.34	10.88	6.44		3.62	2.77	6.05	4.83	1.50	Vienna Polytechnic
Messina Clay	41.80	12.42	5.05		18.76	2.29	--	--	--	
								CO_2	16.81	Gallo

He compares all these analyses and says:

> "It is evident that from the chemical analysis of a pozzolana no conclusions can be derived regarding their hydraulic property, inasmuch as this property varies between wide limits even for pozzolana with the same chemical composition."

Two other investigators, G. Giorgis and U. Alvisi, of the Royal Engineering School in Rome, stress the same point when in their exhaustive study "Natural and Artificial Pozzolanas"* published in "Gazzetta Chimica Italiana", Volumes 29 and 30, they say:

> "It is well to call attention to the variable percentage of alkalis in pozzolanas because there has been an attempt on the part of some to base the hydraulic value of a pozzolana on the amount of alkalis present

*Appendix VII.

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Portella	48.58	32.72	9.63	--	7.16	--	0.74	0.74	1.17	"
Bassano	47.10	21.90	8.01	--	9.91	1.55	2.56	6.01	2.21	Prof. Hebarlat
Vesuvio	48.45	17.81	3.49	3.55	12.09	3.02	3.46	5.01	0.60	Giorgis Gallo
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									SO_3 16.81	Gallo

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assuming that their presence indicates an energetic and prolonged action of atmospheric agents, action which must have deprived the pozzolana of a considerable quantity of active elements. This observation is not without foundation but we must not give to it a greater value than it has in reality because it could lead us to erroneous conclusions.

"It happens that of two Roman pozzolanas one which has smaller quantities of leucite is of a higher hydraulic value than the other. However, if we take two different pozzolanas and from the quantity of potassium in one attempt to draw a conclusion, as to its superior or inferior hydraulic value, we will be led into error. We believe it very difficult to separate the constituent elements of pozzolanas into essential and accidental, because pozzolanas are highly complex, petrographic materials which vary not only from one volcanic center to another but also from cave to cave of the same field and often from stratum to stratum of the same cave. Unfortunately petrographic researches on pozzolanas are still missing and they remain as yet materials poorly defined and of vague meaning. However, although having in general throughout their mass, a variable physical aspect and also a variable chemical composition, it is possible nevertheless, to recognize macroscopically some recurring mineralogic elements as, for instance, leucite in the Roman pozzolanas and sanidine in Neapolitan pozzolanas.

Now it is evident that if the macroscopical observations can lead us into some general conclusions as to the character of the pozzolana the microscopic study may be of further help. Thus we find that Professor Gallo in his study says:

"If we bring under microscopic observation a thin section of each one of those pozzolanas of which we have given the chemical composition in Table 1, there is soon noticeable an essential difference between the constitution of pozzolanas known as satisfactory and those having very little or no hydraulic value. (Figures 1 to 6 of Appendix V., Page give an idea of their different constitution.)

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"The pozzolana of San Paolo and that of Pratolungo are constituted almost entirely of a granulous amorphous mass, which is a sign of a profound alteration. They are negative to polarized light and show only here and there small crystals of leucite or augite and of mica.

"Instead the pozzolana of Bassano and the ashes of Vesuvius have a composition completely different and essentially crystalline. The larger fragments show elements of two successive stages of consolidation, with crystals of piroxene, leucite, plagioclase and olivenite. All these elements are mixed with other substances more or less opaque and originating from small lamellae of black mica.

"In the pozzolana of Bacoli are prevailing instead, the leucites with symmetrical inclusions, a few augites, some large lamellae of altered mica of first consolidation and abundant small lamellae of mica of second consolidation, besides green piroxene and some olivenite with black rings.

"Santorino presents itself for the larger part constituted of a granulous, amorphous mass without any action upon polarized light and mixed with pumice and obsidian and also with fragments of crystals of feldspar, quarz, piroxene and volcanic lava.

"Regarding Santorino, it is interesting to learn that Mr. E. Heider was successful in separating from Santorino three different parts:

1. About 1/5 of light matter, floating in water, constituted pumice.

2. About 3/5 fine dust of a silvery gray color.

3. About 1/5 of fine sand almost always of a dark color, but sometimes red or yellow, constituted essentially of obsidian in its various forms.

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3. About 1/5 of fine sand almost always of a dark color, but sometimes red or yellow, constituted essentially of obsidian in its various forms.

"While the first and third part mixed with lime do not set under water, the second part which happens to be that appearing granulous and amorphous under the microscope, acquires the maximum of resistance. Furthermore, from the analysis of Feichtinger it appears that while the fundamental chemical composition of the various parts does not differ much, the behavior in presence of a concentrated solution of sodium hydrate is nevertheless very different because while only 5.2% of the silica of the first part is soluble in sodium hydrate and 3.4% of the third part, as much as 28.4% of the silica in the second part is soluble.

"From the experiments of Heider and from the knowledge which we now have of the behavior of the various crystalline compounds which enter into the composition of pozzolanas, we come to the conclusion that the active part of a pozzolana must be attributed uniquely to the granulous and amorphous part contained within the whole mass.

"It is natural therefore to assume that the hydraulic value of a pozzolana is proportional to the relative quantity of amorphous material and that the crystalline part cannot in any way take part in the phenomena of setting, but will remain simply interspersed throughout the hydrated parts in the hardened mass, contributing nothing to the hardening but rather establishing a solution of continuity of this same mass."

These remarks stress even further the importance of the granulous and amorphous part contained in the pozzolana. But so far no definite conclusion has been reached as to what constitutes the fundamental hydraulic element of a pozzolana.

Studying this material a little more in detail we find, quoting again from the article "Natural and Artificial Pozzolana" by Giorgis and U. Alvisi:

"The most important deposits of pozzolana are found in Italy and among them those of Rome and Naples lead in importance.

"The Roman pozzolana is frequently met with in the volcanic zones of the Roman provinces and especially in the neighborhood of Rome.

"While the first and third part mixed with lime do not set under water, the second part which happens to be that appearing granulose and amorphous under the microscope, acquires the maximum of resistance. Furthermore, from the analysis of Molfetta it appears that while the fundamental element is soluble in sodium hydrate and 5.4% of the first part is soluble in the second part as much as 25.4% of the third part, as much as 25.4% of the silica is soluble in sodium hydrate and 5.4% of the silica only 3.2% of the silica of the first part is soluble.

"From the experiments of Breiner and from the knowledge which we now have on the behavior of the volcanic compounds which enter into the composition of pozzolanas, we come to the conclusion that the active part of a pozzolana must be attributed mainly to the granulous and amorphous part contained within the whole mass.

"It is natural therefore to assume that the hydraulic value of a pozzolana is proportional to the relative quantity of amorphous material and that the crystalline part cannot in any way take part in the phenomena of setting, but will remain simply interspersed throughout the hydrated parts in the hardened mass, contributing nothing to the hardening but rather establishing a solution of continuity of this same mass."

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"The most important deposits of pozzolans are found in Italy and among them those of Rome and Naples lead in importance.

"The Roman pozzolana is frequently met with in the volcanic cones of the Roman province and especially in the neighborhood of Rome.

It can be divided into two distinct groups according to the conditions of the deposits. Limiting ourselves exclusively to their extreme characters and upon their geological formation we must hold that these Roman pozzolanas are derived from rocks of secondary formation constituted of very fine ash originating from the Tirrenean Volcanos and found first upon the Apennines and then washed out or carried with fragments of sedimentary rocks to lower levels by rain water. The disposition of these materials in immediate contact with pleocenic rocks corresponds to that of the oldest tufas of the Roman countryside which also rests directly upon pleocenic formation.

"The technical value of Roman pozzolanas has always been held to be very high. The red one of San Paolo above all is supposed to be the best and proposed as a basis of comparison in all technical tests upon pozzolanas. Even black Roman pozzolanas often give excellent results - as a matter of fact, nowadays it is believed that they are not inferior to the red ones.

"To Roman pozzolanas is usually assigned the density of 1.232. Following are analyses of some of the principal varieties of Roman pozzolanas which will give an idea of their composition beginning with that of San Paolo:

POZZOLANA OF SAN PAOLO	Analysis of Dufrenoy	Analysis of Ravier
Quarz	3.00	3.10
Silica	47.66	37.80
Alumina	14.33	19.40
Potassium Oxide	1.40	0.00
Sodium Oxide	3.73	3.40
Lime	7.66	9.80
Iron Perioxide	10.33	10.30
Magnesia	3.86	1.28
Water & Alkalis	8.03	12.74

It can be divided into two distinct groups according to the conditions of the deposits. Limiting ourselves exclusively to their extreme characters, we must hold that these Roman pozzolanas are derived from rocks of secondary formation upon the Apennines and then washed out by the Tyrrenean Volcanos and found later combined with fragments of sedimentary rocks carried by rivers, by rain or water. The disposition of these materials in immediate contact with pleocenic rocks corresponds to that of the oldest lavas of the Roman country, while also rests directly upon pleogenic formation.

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"To Roman pozzolana is usually assigned the density of 1.832. Following are analyses of some of the principal varieties of Roman pozzolana which will give an idea of their composition besides which test can be made:

POZZOLANA OF SAN PAOLO

Analysis of	Red	Analysis of	Gray
Silica	45.00		51.10
Alumina	17.25		19.40
Potassium Oxide	1.40		0.00
Sodium Oxide	3.13		3.40
Lime	7.00		3.80
Iron Peroxide	10.25		10.80
Magnesia	3.00		1.50
Water & Alkalies	13.02		10.80

POZZOLANA OF SAN PAOLO.

(Analysis of Professor Cavazzi (126)

	Elements Soluble in hydrochloric acid	Insoluble Residue	Total
Silica	0.525	44.975	45.500
Alumina	14.925	0.200	15.125
Lime	8.498	0.838	9.336
Magnesia	3.172	0.423	3.595
Ferric Oxide	11.200	0.850	12.050
Potassium Oxide	2.154	-----	2.154
Sodium Oxide	3.782	-----	3.782
Water & Traces of other substances.	8.458	-----	8.458
	52.714	47.286	100.000

THREE TYPES OF ROMAN POZZOLANA

Elements	I.	II.	III.
Silica	40.25	40.25	35.20
Alumina	14.70	13.45	15.95
Ferric Oxide	12.85	15.90	12.55
Lime	7.97	8.62	6.91
Magnesium	2.50	1.45	2.32
Matter insoluble in hydrochloric acid	7.90	6.10	13.65
Alkalies, Water, etc	13.83	14.23	13.42
	100.00	100.00	100.00

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Regarding the Neapolitan pozzolanas, the same authors say:

"One of the best, and as a matter of fact judged indeed excellent, is that of the cave of Bacoli near Pozzuoli which extends for more than a kilometer and whose stratum presents a thickness of about 40 meters, constituted of a kind of volcanic ash of a clear gray color resting on a substratum of ashes, pumice and other volcanic ejections. This cave is near the coast line between Baja and Bacoli. Of the analyses which were made of it, we report the two following:

"The first is a memoir of L. Luiggi and V. Cardi and the second in a note of Professor O. Rebuffat:

Analyses

	I.	II.
Silica	56.20	52.77
Alumina	19.30	17.00
Iron Sesquioxide	8.70	4.84
Magnesia	0.25	1.35
Sodium Oxide	2.90	4.94
Potassium Oxide	3.45	7.65
Lime	2.90	3.28
Water	3.90	Loss by Ignition 7.25
Calcium, Sulphate, Chlorine, etc.	2.40	----
Total	100.00	99.08

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Potassium Oxide	3.48	7.65
Lime	2.90	3.28
Water	3.90	Loss by Ignition 1.28
Calcium, Sulphate, Chlorine, etc.	2.40	—
Total	100.00	99.08

"Not far from Bacoli is found the pozzolana of Baja of which Prof. Favilli of the University of Naples gives the following description and analysis:

"This pozzolana is a substance of a whitish color which adheres to the tongue and which has produced through mechanical separation almost 46% of a sand formed of small fragments of pumice and other substances of volcanic origin, and almost 54% of clay material. Its density is 2.074 which is much greater than the density of Roman pozzolanas. Five gr. of Baja pozzolana is liberated of the lime from 10 cubic centimeters of lime water after two days of contact. Its percentage of composition is:

PERCENTAGE OF COMPOSITION

Water	3.50
Silica	55.10
Alumina	18.30
Ferric Oxides	7.60
Magnesia	0.40
Lime	6.55
Sodium Oxide	2.95
Potassium Oxide	2.80
Other elements, Mg.,Chl.,Etc.	2.80
	100.00

"Professor F. Ferrari in an article of "Special Cements in Connection with the Action of Aggressive Waters" gives for the pozzolana of Baja, the following composition:

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PERCENTAGE OF COMPOSITION

Water	3.50
Silica	55.10
Alumina	18.30
Ferric Oxides	7.60
Magnesia	0.40
Lime	0.55
Sodium Oxide	3.95
Potassium Oxide	2.80
Other elements, Mg, Chl, Fe	0.80
	100.00

"Professor F. Ferrari in an article of "Special Cements in Connection with the Action of Aggressive Waters" gives for the pozzolana of Baja, the following composition:

Loss thru calcination	6.27
SiO_2	57.02
Al_2O_3	18.85
CaO	3.18
MgO	0.65
Na_2O	3.51
K_2O	2.78
Fe_2O_3	6.90

"Professor Rebuffat gives the following results from a pozzolana of Baja:

	Screened through 100 mesh sieve	Un-screened
Loss thru calcination	4.82	4.21
SiO_2	54.16	53.18
Al_2O_3	19.14	19.80
Fe_2O_3	3.51	3.40
CaO	5.12	5.50
MgO	1.05	1.86
K_2O	9.35	9.04
Na_2O	2.89	2.73
	99.84	99.72

"This last analysis proves that the coarse materials and the fine ones have about the same percentage composition. Another type of pozzolana is that of Vesuvius found near Torre del Greco, at 13.3 kilometers from Naples and about 70 m. from the shore. The cave is named, the cave of Bassano and the pozzolana is found immediately under the vegetable earth, at a depth of about m. 0.40.

Results from a Dozzolane of Pets:
Professor Hedgling gives the following

Fe_2O_3	2.80	
K_2O	2.23	
Na_2O	2.21	
MgO	0.92	
CaO	2.18	
Al_2O_3	12.82	
SiO_2	24.05	
Loss with calcination	0.24	

This cave shows two distinct strata; the thickness of the first stratum is of about m. 2.80; the thickness of the second is of about m. 3.50. These two strata are separated by smaller alternate layers of sandy clay and black lapilli (fragments of pumice and slag). From an analysis of this pozzolana made by Professor Rebuffat we obtain:

Loss by ignition	2.21
SiO_2	47.10
Al_2O_3	21.90
Fe_2O_3	8.01
CaO	9.91
MgO	1.56
K_2O	6.01
Na_2O	2.56
	99.35

"It is worthy of notice that the Neapolitan pozzolanas present in general a content of lime much larger than that of the Roman."

From this general analysis it will be seen that no criterion has been derived from which to judge the quality of the various pozzolanas based on chemical analysis. Recurring to tests we notice that continuing the microscopic study of a pozzolanic mortar, Professor Gallo says:

"If particles of a pozzolana have a tendency to aggregate in lumps and if when they are in a free state and not compressed in mass they have a tendency toward an increase of volume and if furthermore this swelling is emphasized at once and reaches its peak in a short time, about 20 days, we have in it a criterion of the constitution of a good pozzolana. Perhaps a better test lies in the fact that when a good pozzolana is boiled with water for ten minutes a quantity of silica and alumina separates in a colloidal state. This quantity reaches 0.57% for the pozzolana of San Paolo.

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Loss by ignition	2.21
SiO_2	47.10
Al_2O_3	21.90
Fe_2O_3	2.01
CaO	9.41
MgO	1.56
K_2O	6.01
Na_2O	2.56
	99.36

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Comparing these tests with that proposed by the famous Palladio:

> "If a pozzolana has good hydraulic value it is supposed to leave no mark on a linen cloth when compressed in it by hand,"

we notice an improvement in the technique of determining the hydraulic value of a pozzolana. However, both these tests, as well as the tests which are presented in Appendix are not entirely satisfactory. Although they furnish us with some indication of the hydraulic value of a pozzolana they are not a safe guide in all cases.

It is possible that by studying the genesis of pozzolanas we may be able to derive some indication as to their hydraulic value. Professor G. Gallo says:

> "Pozzolana evidently originate from materials carried by volcanic ejections from deep geological strata of essentially clayey composition; materials that during eruption must have undergone a calcination such as to bring about a complete de-hydration and a profound chemical alteration of the mass. But this alteration has not proceeded so far that the entire mass has been brought to a complete degree of fusion. It is pertinent to enquire why if the pozzolanic property is due to the action of atmospheric agents which have contributed to materially modify the materials of volcanic eruption why it is that the ashes of all the volcanoes active or dead are not found to evince after a certain period of time pozzolanic properties? If this does not happen, it means simply that from the beginning the constituent materials have a different chemical composition and that furthermore the action that the volcano has exercised upon them is fundamentally different.
>
> "In the case of pozzolanas which have been subjected through numerous centuries to the action of atmospheric agents which in turn have brought about a slow and progressive modification of silica and alumina already in a free state, a modification takes place which consists essentially of an intimate hydration of the single particles, this hydration being in relation to the quantity of water of composition contained in the good pozzolanas. Owing to such

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hydration these pozzolanas coming in contact with lime water find themselves in very opportune condition to form some high forms of hydrates, swelling up and dissolving little by little, and giving rise finally to the phenomena which determine the setting of pozzolana. It is interesting to notice that this property of being subject to hydration is in a strict relationship with the quantity of water necessary for the mixing, a quantity which is a maximum for the good pozzolana and the minimum for the bad ones (inert).

"On the other hand, it is well known that pozzolanas subjected to calcination partially or totally lose their property of setting under water, because through calcination we eliminate the essential element which determines their hydraulic value, that is, the absorbed water of hydration and make both silica and alumina unable to hydrate at the surface and to react with lime water.

"Calcination destroys also that intimate molecular composition resulting from age. The microscopical examination shows that the active part of a pozzolana is found equally distributed throughout its various particles. When pozzolana is used finely ground, all the active parts coming in contact with lime water hydrate readily, therefore, the swelling and the setting take place during a relatively short time.

"Using pozzolana in its natural state, hydration does not take place with the same intensity and although the swelling can still be observed, it never results in the maximum volume that can be obtained through the action of lime water upon finely ground pozzolana."

From the above, it appears that no safe criterion of the hydraulic value of good pozzolana can be formed at the present state of our knowledge unless we pay attention to the behavior of pozzolana in the phenomena of hydration.

Beginning with the studies of Professor Rebuffat we find in the above referred article "La Pozzolana di Bacoli" Nei Lavori Marittimi, that:

hydration these pozzolanas coming in contact with lime water tend themselves in very opportune condition to form some kind forms of hydrates, swelling up and dissolving little by little, and giving rise finally to the phenomena which determine the setting of pozzolana. It is interesting to notice that this property of being subject to hydration is in a strict relationship with the quantity of water necessary for the mixing, a quantity which is a maximum for the good pozzolanas and the minimum for the bad ones (Imoff).

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"During pozzolana in its natural state, hydration does not take place with this same intensity and although the hydrating can still be observed, it never reaches in the maximum volume that can be obtained through the motion of lime water upon finely ground pozzolana."

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Beginning with the studies of Professor Report we find in the above referred article "la Pozzolane di Recoli" of Favorit Hermitime, that

"Pozzolana in presence of calcium hydroxide or in presence of a solution of calcium saccaronate unites with all the calcium oxide which is in solution.

"Finally, pozzolana placed to react with slaked lime decomposes into an active part of high solubility even in weak acids, and to an inert part not attacked by ordinary acids.

"The main reaction taking place in the process of hydration of pozzolana is the reaction of the alkaline silica-aluminates with the calcium hydroxide.

"The result of the reaction is the liberation of the alkalis and the formation of a hydrated calcium silica-aluminate. The compound thus formed has no claim of chemical stability higher than the stability of ordinary cements. It is in fact like them attacked by the carbonic anhydride of the atmosphere with change of the calcium oxide into calcium carbonate and is also equally decomposed by mineral acids of various strengths. But - what constitutes the highly important difference - when some saline solutions more or less ionized act upon a pozzolanic mortar which has set and hardened, this mortar - evincing a different behavior than that evinced by Portland cement mortars - loses all the lime without disintegrating."

"The main reaction according to Professor Rebuffat is a very slow reaction.

"It has been noticed that ancient pozzolanic mortars older than one thousand years still contain in the interior of the mass some free lime which phenomenon is to be attributed to the fact that their setting is not yet completed."

According to Professor Gallo this setting can be subdivided into two parts and is to be explained in the following way:

"The calcium hydrate, which is part of the composition of pozzolana mortars, brings about the hydration of silica and alumina which swell so as to occupy all the space already occupied by water and air, giving rise to the formation of an impermeable mass which contributes highly to the resistance of the mortar. Next follows the formation of a soluble calcium aluminate which finding itself in the presence of an ex-

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"The main reaction taking place in the process of hydration of pozzolans is the neutralization of the alkaline silica-aluminates with the calcium hydroxide.

"The result of the reaction is the formation of a hydrated calcium silica-aluminate. The compound thus formed has no claim of chemical stability higher than the stability of ordinary cements. It is in fact like them attacked by the carbonic anhydride of the atmosphere with change of the calcium oxide into calcium carbonate and is also equally decomposed by mineral acids of various strengths. But - what concerns us the highly important difference - when once set the solutions more of less ionized ecc ipons possessing movant which has set and hardened this movant avoiding a different behavior when it evinced by Portland cement mortars loses all the time without disintegrating."

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"The calcium hydrate, which is part of the composition of pozzolans mortars, diffuses about the hydration of silica and alumina which swells so as to occupy all the spaces already occupied by water and at the same time to the formation of an impermeable mass which contributes highly to the resistance of the mortar, next reacts with the hydroxide.

cess of lime, and therefore in a super-saturated solution, precipitates and crystallizes and in its consolidation connects together the various particles which enter to form the matrix of the crystals. This represents the first part of the setting. The surface of the flocculent parts are seats of capillary tensions, through which silica attracks lime in its pores and gives rise to a nucleii solution within which the lime slowly giving up its water of hydration crystallizes to the state of calcium mono-hydrate, bringing about a complete bond of the various parts in such a way that the total mass transforms itself into a unit highly resistant and very compact. This is the second period of the setting when all these phenomena manifest themselves in the interior of the mass kept moist and protected externally by an insoluble stratum of calcium carbonate.

"The setting of pozzolana is therefore due partly to a general phenomenon of formation of a super-saturated solution which characterizes the setting or hardening under water and partly due to a purely physical phenomena of swelling.

"Consequently, the more rapidly a pozzolana reaches its maximum swelling, the better will be its setting, because the mortar becoming impermeable to water is not subjected to the deteriorating action that water can exercise, action which causes a greater havoc with a greater substitution of water in the interior of the mass. It is therefore in this way that it is possible to explain the slow process of the setting of pozzolana mortar; the silica present in fact cannot absorb more than a certain quantity of lime, the excess lime liberated crystallizes then forming a deposit of calcium hydrate crystallized. It is not to be excluded though that between the silica and lime so intimately mixed, a chemical reaction might take place which will give birth to some well defined compounds even if the formation of these compounds has not been so far confirmed by actual observations."

From the above quotations we derive a fairly good idea of the conclusions reached by Italian scientists relative to the process of setting and hardening of a pozzolanic mortar. It appears that there is in pozzolana mortars a chemical compound of the character of an alkaline silico-aluminate which keeps itself unaltered in time, however active may be the surrounding medium in which it finds itself. A good pozzolana possesses a greater hydraulic quality and a consequent greater possibility of forming a large quantity of insoluble compounds in the set and hardened material.

Following this thought, it may be interesting to recall that Feret believes that the readiest way to find the hydraulic value of a pozzolana is that of determining the percentage of lime fixed from lime water by a determinate weight of finely ground pozzolana. This test results from the fact that the calcium silico-aluminate found in pozzolana is a compound poor in lime content, which shows a tendency to further absorption of lime, and when placed in contact with water and lime at the same time, shows a tendency to transform itself into a calcium silico-aluminate hydrate of higher lime content.

But on the subject of this test, Professors Giorgis and Alvisi (see Gazzetta Chimica Italiana, Volume 30, page 1) contend that the quantity of lime fixed is too small, requires too long a time and is affected by the presence of extraneous materials.

A better method appears to be the one proposed by Professor Gallo who observing the time taken for the hydration of various types of pozzolana says:

> "All good pozzolanas begin hydration immediately, reaching a maximum volume - which is for instance ten times larger than the initial one for the San Paolo pozzolana - at a period of time which can be held in the average to be equal to about 20 days. After this time, even changing the lime water frequently, the volume shows a tendency to remain constant, furthermore after two months or more it shows a tendency to diminish. I believe that the slow diminution of volume after the maximum volume is reached is connected with the crystallization and the formation of calcium aluminate which compound occupies a smaller volume than its components. The microscopic observations of the lumps shows after this period of time the abundant presence of crystals of calcium aluminate.
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> "All good pozzolanas begin hydration immediately, reaching a maximum volume which is for insurance ten times larger than the initial one, for the best pozzolana - at a period of time which can be held in the average to be equal to about 30 days. After this time, even changing the lime water frequently, the volume shows a tendency to remain constant, furthermore after two months or more it shows a tendency to diminish. I believe that the slow diminution of volume after the maximum volume is reached is connected with the crystallization and the formation of calcium aluminate which compound occupies a smaller volume than its components. The microscopic observations of the lumps above after this period of time the abundant presence of crystals of calcium aluminate."

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ated solution, the various materials are left in contact with the same lime water, the swelling which takes place at the beginning never reaches the maximum value which is reached when the solution of calcium hydrate is renewed from time to time. It is also interesting to verify the relation of the increases of volume to the technical value of known pozzolanas. Thus, clay, the Pozzolana of Bassamo, the vegetable earth and the ashes of the Vesuvius, materials which have little or no hydraulic value, vary little from a straight line parallel to the abscissa axis. The pozzolana of Bacoli is shown through this test to be inferior to Roman pozzolanas and such a consequence can be deducted also from the microscopic observation of the pozzolana itself, which is in a large part composed of crystalline elements. The quantity of lime absorbed by the various pozzolanas after eight days remains about constamt in the various determinations and for the length of time under consideration. The quantity averages as follows:

CaO Absorbed by 100 gr. of Pozzolana:

San Paolo	2.52 grms.
Pratolungo	2.26
Santorino	2.38
Portel la	1.82
Bacoli	1.68
Bassano	0.75
Ashes of Vesuvio	0.12

"Note how these values are in a strict relationship with the observed increase of volume. For the clay it is noticed that there is not as rapid a swelling as for the good pozzolanas, but that this swelling is gradual and progressive until it reaches the maximum value of 37 cubic centimeters. Furthermore the quantity of calcium oxide absorbed is 1.4% during the first few days while the density of the solution remains constamt afterwards.

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CaO Absorbed by 100 gr. of Porcellane:

San Paolo	2.52 grms.
Frate Unge	2.39
Sanberino	2.18
Portella	1.89
Zecolli	1.83
Passano	0.78
Ashes of Vesuvio	0.75

"Those new theses values are in a perfect relationship with the observed increases of volume. For the clayey is hotness that there is now rapid a swelling action for the good porcellanes, but that this swelling is gradual and progressive until it reaches the maximum value of 25 cubic centimeters. Furthermore the quantity of calcium oxide absorbed is 1.46 for the first few days while the quantity of the solution remains constant

"For the vegetable earth, although there is no increase of volume whatever, the quantity of lime which is fixed is about 2.78% in the first few days (superior that is, to the quantity of lime fixed by the best pozzolanas as had been already observed by Giorgis and Alvisi) but the quantity of lime fixed diminishes little by little until it disappears altogether after a few days.

"If then instead of repeating the test of Vicat in the usual conditions, that is, leaving the pozzolana always in contact with the same lime water, this is constantly renewed, the total quantity of lime water which the pozzolana can fix is much larger than that which at the same time is taken away by a given amount of pozzolana from a solution of lime which is never renewed."

Having thus obtained an idea of the hydraulic value of a pozzolana through the total quantity of lime that it can fix we are in possession of one element of determination of the hydraulic value. The other element consists in knowing more exactly the state in which silica and alumina must be present in a good pozzolana.

It is the generally accepted view that silica and alumina must be present in a soluble state, and that, consequently, the amount of soluble silica can furnish a safe indication of hydraulic value of a pozzolana.

Were this true, we would be very close to the solution of the problem of finding the hydraulic values of various kinds of pozzolanic materials. All we would have to do in effect would be to find the percentage of soluble and insoluble silica without paying any further thought to the morphological structure of the material, its physical properties, chemical composition, etc. Unfortunately this easy method appears unreliable for the purpose.

Professor Gallo in the above mentioned study writes:

"Hydrochloric acid does not exercise any sensible decomposition upon silica and alumina of the granulous and amorphous part of a pozzolana, that is, upon its active part."

And in a later study:

"Even this test (Rivot's) in its new modification does not solve the problem of finding

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> the technical value of pozzolana, the percentage of silica soluble in potassium hydrate being not at all in relationship with the hydraulic quantity of the substance from which it was experimented. The soluble silica of the pozzolana of the cave called Portella was the highest of all, although it is well known to be a very mediocre pozzolana."

These words which were written twenty-five years ago have here received support from the most recent researches of the German Society for Testing Materials upon that variety of pozzolanic material called Trass. Investigating a method of analysis which would furnish an adequate indication of the pozzolanic quality of this material, the German researches apparently demonstrate that:

> "Neither the complete chemical analysis nor the soluble silica content gives a positive indication of the quality of Trass in a mortar."

see Tonindustrie Zeitung, Vol. 56, Pages 993-5; also Study on Pozzolanas published by the Buildings Research Board of England wherein it is stated on Page 8 of Volume 2:

> "Further investigations show that there is no distinct relationship between "soluble silica" and pozzolanic activity, at least in natural pozzolanas."

These conclusions are of the highest importance in so far as they apparently disprove the theory that it is possible to fix the hydraulic value of a pozzolana by the amount of soluble silica and alumina. They leave us, however, still without any positive help toward a knowledge of the state in which both silica and alumina must be present in a good pozzolana. Further studies are necessary to tell us more about the possibility of recognizing, under the microscope or through simple tests, those characteristics of silica and alumina which play such a predominating part in the hydraulic value of a pozzolana.

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C H A P T E R 6.

Artificial Pozzolanas

The scarcity of available natural pozzolana coupled with the abundance of materials which when subjected to treatment show some pozzolanic qualities has brought the subject of artificial pozzolanas to the front.

Since the Roman times we find side by side, the extensive use of natural pozzolanas and the occasional use of artificial pozzolanas obtained through the grinding of calcined bricks or tiles. However, the only mortars which have withstood the test of time have apparently been those of lime-natural pozzolanas. This naturally prejudices the case against artificial pozzolanas.

However, with the beginning of the 19th century, the French Engineer, L. J. Vicat attempted to eliminate the use of Italian natural pozzolana in French construction works by substituting artificially prepared pozzolanic materials, indigenous to the French regions. In bringing about the fulfillment of his aim he had in mind the possible reproduction of those characteristics of chemical resistance peculiar to natural pozzolana mortars.

Vicat had very little knowledge of what constitutes the true nature of a pozzolana. It is only in the last thirty years that the first comprehensive studies upon natural pozzolanas have been published. Therefore, Vicat had no other rule to guide his researches than a limited knowledge of the superficial characteristics. Thus, although his insight was truly exceptional, he lacked the element most necessary to the successful outcome of his attempts. Had he known what pozzolana is in reality; had he known to what element the pozzolanic action is due; had he known the nature, the extent and the outcome of the chemical reactions originating from the combination of lime with pozzolana in the presence of water, he would have been in a much better position to solve the problem of producing a good artificial type of pozzolana. Of all the people who have endeavored to solve this problem none have been better equipped by study and through natural gifts than Vicat - however, with a limited and faulty knowledge of the basic principles, the foundations of the edifice which he attempted to raise was faulty.

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Through a long series of years lasting half a century or more, he followed every known road to the manufacture of materials which, in the phenomena of setting and hardening under

water when mixed with slaked lime, would reproduce the characteristics of natural pozzolana. He experimented with all types of clays, all temperatures of calcination, all possible proportions of mixture - always baffled by unsatisfactory results. In the end he died convinced that there must be a solution to the problem of manufacturing artificial pozzolana and that, although his proposed solution had not up to that time proved entirely satisfactory, it would nevertheless prove the forerunner of more successful work along the same lines.

Since Vicat died, no sensible progress appears to have been made towards a successful solution. All those that have experimented upon natural pozzolanas have done nothing more than to repeat the work of Vicat in modified forms, so that today all we know is that to produce a substance which resembles natural pozzolana, it is necessary to calcine siliceous material of the clay group to temperatures variable with their composition but generally of 800°C. or thereabouts.

Regarding the exact type of siliceous material we know practically next to nothing, that is, we do not know which of the numerous natural materials at our disposal are the best suited to the purpose. Some people have insisted that inasmuch as silica is the major component of pozzolana, the siliceous material which would contain the greatest amount of silica would be the most adapt. According to many of the best authorities, however, it is not silica per se which is the essential factor of a pozzolanic action. This action is due rather to a silica compound - properly a calcium alumino-silicate. Silica is a generic name which denotes a variety of materials like quartz, tridymite, crystobalite, etc., which have different physical and chemical properties. While some materials containing high percentages of silica have shown the lack of pozzolanic properties, there have been others, with far lower content of silica, which have shown much greater pozzolanic activity.

There is no very solid foundation for the conclusion that an calcined siliceous material mixed with slaked lime is able to set under water and be resistant to the action of chemical agents during the first few years of contact, nor is there ground to believe that those characteristics of physical and chemical resistance peculiar to natural pozzolana can be reproduced in any artificial material. Such characteristics are apparently due to the presence in each type of natural pozzolana of some fundamental chemical compounds peculiar to that type of material. Before we can claim to have successfully solved the problem of manufacturing artificial pozzolana we must be able to reproduce artificially those natural compounds found in pozzolanas in their original state. This involves a knowledge of natural pozzolana much deeper and much more extensive than what we have at present. While the study of oxide composition is quite well elaborated, the study of compound composition is in its

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water when mixed with slaked lime would reproduce the chara-
ties, there have been observed pozzolanic activity.
percentages of silica have shown the lower content of silica,
and chemical properties. Quite a number of natural pozzolans
triginite, crystobalite, etc., which have different physical
ezic name which denotes a variety of materials like quartz,
compound - properly a natural alumino-silicate. Silica is an
of a pozzolanic action. Pure silica, or silica as an amor-
however, it is not silica per se that is the matter to a silica
be the most acidic. According to many chemists the present theory
material which would contain the great amount of silica
as silica is the major component of pozzolans, the siliceous
suited to the purpose. Some people have insisted that between
of the numerous natural materials at our disposal are the best
know precisely why to durable, that is, we do not know which
Regarding the latest type of siliceous material we
position but generally of 800°C. or thereabouts.
lat of the clay group temperatures variable with the com-
natural pozzolans, it is necessary to calcine artificially to-
day all we know is that to produce a pozzolana material more
than to depend the work of nature in modified forms, so that
have experimented upon natural pozzolans have done nothing
have been made towards a successful solution. All those that
Since that date, do besides presenting papers by
the Rosenmuller type accessful work along the same lines
tive proved entirely satisfactory. It would nevertheless prove
tion to the problem of manufacturing artificial pozzolana
sulfes. In the end be dried ignited red hot on to dust
proportions of mixture always better there must be so-
types of clays, all temperatures boiled by unsatisfactory re-
note ignited of natural pozzolans of calcination, all possible
water when mixed with slaked lime would reproduce the chara-

infancy and petrographical analysis is hardly under way.

We are faced at the start with a lack of a thorough understanding of the essential composition of a natural pozzolana thus hampering the development of a suitable substitute in the form of an artificial pozzolana.

Whenever the physical and chemical characteristics, morphological structure, etc., of a true natural pozzolana are thoroughly understood, then a rational program may be mapped out to reproduce artificially all those properties and all those characteristics. Until such time however, all work done on this subject is work done blindly. The purpose of this study is to review what is at present known of the subject with the hope that it may be of some assistance to others in arriving at a solution of the problem.

The first discovery of Vicat worth mentioning is that the pozzolanic property is essentially due to the silicate of alumina present in the pozzolana (see Vicat - Note sur les Pouzzolanes Artificielles - Ann. Ponts et Ch., T 4, p. 135, S. 2). This discovery is in line with the latest discovery of Rebuffat upon the nature of the silicate of alumina forming the matrix of a pozzolanic material. Next we find a statement advanced by Rivot and Chatoney worthy of notice. This statement is to the effect that artificial pozzolanas which already contain lime compounds in stable combinations cannot set when mixed with slaked lime or, at least, give a very poor set. Their statement reads as follows:

> "Ferruginous and calcareous clays subjected to a prolonged calcination cannot be considered as pozzolanas because they already contain combinations of lime with silica and with alumina, although at the same time they have clay with which lime can react." (See Chatoney-Rivot - Considerations Generales, ecc. ecc., Comptes Rendues, t. 43, p. 373.)

From generic description of the characteristics of the material to be rendered pozzolanic Vicat passed to the description of the composition of a good pozzolana. He says that the clays to be used for the purpose of producing an artificial pozzolana must contain in 100 anhydrous parts from 20 to 45 parts of alumina and from 80 to 55 parts of silica; they can also contain some quarz and some quantities of iron oxides and must be mixed with lime in the proportion of 15 to 18 parts of lime for each 100 parts of pozzolana. (See Vicat in "Des Ciments ecc. ecc., Compte Rendues, t. 45, p. 198.)

Passing from the studies of Vicat to those of Re- we find the opinion that the essential element of the ...nic property is the silicate of alumina 2 SiO_2.Al_2O_3. and that accordingly, artificial pozzolanas should be ...ified as more or less useful in relationship to the ratio ...lica to alumina.

Rebuffat found that of three different artificial ...anas one made from Kaolin was the most active because in ...material the ratio of silica to alumina was equal to 1.29, ...lue very near that of 1.19 which, according to theory, would the value of the molecular ratio of the silicate of alu- ...mentioned. (See - A Study of Artificial Pozzolana - Re- ...fat - Gazzetta Chimica Italiana - Year 1900, Volume 30, Part .)

Some of the conclusions of these studies are worth ...rting in full because they point to a better understanding the problem of artificial pozzolanas than the knowledge ...forded by other studies. These conclusions are:

1. The silicate of alumina 2 SiO_2. Al_2O_3. 2 H_2O brought to a temperature of 700°C to 800°C. loses water and ac- quires pozzolanic property.

2. The pozzolanic property which clays acquire when calcined at 700°C. to 800°C. as shown by Vicat, must be attri- buted to the silicate 2 SiO_2. Al_2O_3. 2 H_2O. There remains to investigate though, whether other silicates of alumina can manifest the same reaction.

3. The silicate 2 SiO_2. Al_2O_3. 2 H_2O cannot again acquire directly the water of hydration lost through heating at 700°C to 800°C.

4. The same silicate either at 700°C. or 800°C. does not become more easily decomposed by hydrochloric acid but be- comes readily soluble in the diluted solutions of alkaline hy- drates.

5. The silicate 2 SiO_2. Al_2O_3, combined with lime in the presence of water forms the compound of 2 SiO_2. Al_2O_3.3 CaO. 10 H_2O. The formation of this compound brings about the setting of the mortar of pozzolana, of Kaolin, or of any other pozzolana made with clay, calcined at 700°C. to 800°C.

6. The silicate 2 SiO_2. Al_2O_3. 3 CaO. 10 H_2O is readily decomposed by acids, and by solutions of ammonium or magnesium salts. These salts liberate all the lime leaving a hydrate silicate of alumina 2 SiO_2. Al_2O_3.4 H_2O equal as far as its chemical properties are concerned to some varities of Haloysite.

passing from the oxidies or Type to those of the
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Finally we find two statements in a study of G. Gallo upon the microscopic study of pozzolana mortars published in Gazzetta Chimica Italiana, Volume 38, which are worth reporting, the first because it points to the general belief of a possibility of producing artificial pozzolanic substance, the second because it expresses a warning which cannot be too strongly emphasized against the too ready acceptance of calcined clays as natural pozzolanas.

From the works of Vicat, Fremy and others, Gallo says:

"It is known that while clay in its natural state does not manifest any pozzolanic property, it acquires following calcination at about 700°C. the property of producing a certain setting under water.

"For all that it is not to be believed that calcined clay can furnish a good pozzolana, because if such were the case, this excellent hydraulic material would have found too many competitors and it is a fact that the numerous attempts of Vicat and others have not succeeded in producing artificially good pozzolanas."

These few quotations and the various studies on artificial pozzolanas which form part of the Appendix at the end of this study indicate the deficiency of our knowledge of the true pozzolanic essence.

The subject should be followed up with original research comparing mainly the behavior of various siliceous materials and best grades of Italian pozzolana. The phenomena which arises these various materials are mixed either with lime or Portland cement, both in their uncalcined and calcined state should be used to obtain a clear idea of the extent of the modifications produced by the calcination. Finally, by bringing about the manufacture of an ideal artificial pozzolana and an ideal pozzolana cement, find out what are the elements which distinguish actions of natural pozzolana with lime and water, natural pozzolana with Portland cement and water, artificial pozzolana with lime and water, artificial pozzolana with Portlamd cement and finally pozzolanic cement and water.

C H A P T E R 7.

Natural Pozzolana Blended Cements

Speaking of pozzolanic cements the first thought recurs to the old Roman lime-pozzolana cementitious materials. We shall, however, restrict the terminology of this Chapter by defining as pozzolanic cements those substances obtained through the intimate mixing of Portland cement and natural pozzolanic materials.

The history of pozzolanic cement, as defined above, does not of course begin until the development of Portland and the need of modifying Portland for marine structures became felt. Thus, it happens that the history of this product is rather brief, and we find nowadays only a couple of such types of cements in existence. The need of modifying Portland cement and the knowledge of the hydraulic qualities of pozzolana has been mainly responsible for the development of natural pozzolanic cements.

It was only logical to assume that the best results could be obtained through a combination of Portland with a natural pozzolana.

As we have seen, the principal need of modifying Portland apparently arises from the necessity of reducing its high basicity. We have seen also that this reduction is not simple because the only two acid elements of Portland on which we can work to reduce basicity are silica and alumina.

Now we cannot increase the percentage of alumina without going into the special process of manufacture of high alumina cement, with all its difficult characteristics and all its difficulties of usage. We have also seen that we cannot materially increase the silica content of the original clinker without bringing about a complete change in the composition and the percentage of the calcium silicates, compounds which impart to Portland its principal physical and chemical characteristics. At the same time we have seen that pozzolanas are acid substances, with high hydraulic qualities, these qualities originating from the affinity of pozzolana for slaked lime. Therefore, addition of pozzolana to Portland cement clinker, besides reducing the basicity of the original clinker, may also bring about a combination of stable compounds of the free lime liberated by the hydration of the calcium silicates. There is reason to believe that the addition of pozzolana in the manufacture of pozzolanic cement is a step in the right direction. It appears however, that the true solution is still far off. Before further considering that phase of the subject however, let us enquire a little more closely into the development of pozzolanic cements.

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Beginning with the definition of a pozzolanic cement we find first, the definition of the Department of Public Works of Italy:

> ".....pozzolanic cement is meant the product obtained through grinding without addition of inert material, an intimate and homogeneous mixture of pure clinker of cement and of pozzolana presenting acid reaction. The clinker can be obtained also through the clinkering of limestone and pozzolana."

The definition of the French Standardizing Body, L'Association Francaise de Normalisation", is much more brief:

> "Pozzolanic cements are mixtures of hydraulic cement and pozzolana, other than blast furnace slags."

Perhaps the best definition is that found in the study of Dr. C. Vittori, "I Progressi Compiuti dal Cemento Pozzolanico" (The Progress of Pozzolanic Cement) published in "L'Industria Italiana del Cemento", February, 1932. This definition says:

> "Pozzolanic cement is that cement which results from an intimate mixture obtained by the regrinding of two constituents, each having maximum hydraulic properties, that is, pozzolana which has been appositely treated and rationally calculated for quantities, with adequate clinker of slow setting cement, of which the free lime liberated during the process of setting and hardening, is fixed by the acid elements of the pozzolana."

The above quoted authorities evidently consider it essential to add a certain percentage of pozzolana to the clinker before final grinding to bring about the formation of a pozzolanic cement. On the other hand, it is possible to produce a pozzolanic cement in which the pozzolana has undergone a process of calcination during the clinkering of the original clinker. We find this second method followed by one of the two Italian manufacturing plants engaged at present in the manufacture of pozzolanic cement. The progress of manufacture of this special cement can be followed from the studies of Dr. Vittori.

Reporting from the article, "I Cementi Pozzolanici Razionali di Segni" (Rational Pozzolanic Cements di Segni) from the proceedings of the Congress of the N.A.I.E.M. held in Zurich, September, 1931:

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"The study of the chemical, physical and mechanical behavior of hydraulic cements through the process of time brings about the possibility of classifying them in two categories:

a. "Cementitious materials which due to their chemical composition exhaust their hydraulic activity in a period of time more or less brief. The mortars and the concretes obtained with such cementitious materials assume in a short time noticeable states of hardening but the successive increases of resistance, decrease until they disappear altogether, and sometimes are transformed into marked retrogressions. Typical cementitious materials of such a category are Portland cements in which the exhaustion of the hydraulic activity corresponds to the final crystalline formation, reached at the end of the hardening process.

b. "Cementitious materials which, owing to their chemical composition prolong through time their hydraulic activity and consequent capacity of hardening beyond any period of time that can be practically foreseen. This second category is formed almost exclusively (in so far as we know) from the cementitious materials of pozzolanic character, like pozzolanic cements, properly called, Trass cement, Gaize cement, Santorino cement, Mo-ler cement, etc.

"In a completely different way from what happens in Portland cements, the final crystalline solidification of these materials is distributed over an exceptionally long period of time, this characteristic being imparted to them by the presence of the pozzolanic element.

"The addition to Portland cement of a hydraulic material like pozzolana has always been made for the purpose of fixing the lime liberated by hydrolysis through formation of compounds chemically stable and capable of great hardening, obtaining thus very much better resistance to air and to water and their indifference to the action of sea water.

"Great apostles of pozzolanic cement have been Vicat in France and Michaelis in Germany; the first

"The study of the chemical, physical and
mechanical behavior of hydraulic cements
through the process of time offers about the
following possibility of classification into two cases:

a.) Cements from materials which can be
brought into a short time equilibrium with
their environment. The mortar and the concrete
obtained with such cements exhibit a constant
behavior in a period of time more or
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process.

b.) Cements from materials which, owing to
their chemical composition or process of
manufacture, only after a relatively long time
be practically terminated. This second
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"Great qualities of pozzolana to resist
rior in saline and mixtures to cement mortars

assigned also the terms of its composition with the characteristic index for cements chemically resistant:

$$\frac{SiO_2 + Al_2O_3}{CaO} = 1$$

recently brought to the fore again and analyzed by Lafuma who proposed to call it "Index of Chemical Resistance" - a definition which we fully endorse.

"At the beginning of its manufacture pozzolanic cement answered very well the exigencies of mechanical resistance because of the narrow requirements of the construction technique of the times and also because they gave no greatly different results from those of Portland cement. But with the increased needs of modern construction Portland has been brought to offer physical resistance always greater especially in the pozzolanic cement, as was known by Vicat and Michaelis, shows at a disadvantage because it cannot furnish in the early stage of hardening the greater mechanical resistance required.

"The reason of this deficiency is uniquely due to the constituents of pozzolanic behavior, constituents which, due to their varied and sometimes unadapt morphologic composition and the not always constant pozzolanic activity, confer to the cementitious material a property of reaction very variable in their first contact with water, beside offering values of compressive strength highly inconstant and generally too weak esepcially in the first stages of hardening.

"Owing to these technical deficiencies manufacturers have the alternative of either producing cementitious material having very slight pozzolanic addition and, therefore, hardly deserving the name of pozzolanic cements (although offering quite a high value of physical resistance) or of manufacturing a true pozzolanic cement which will answer the requirements of Vicat but not the technical requirements of modern construction technique.

assigned also the terms of its composition with the characteristic index for cement chemically resistant:

$$\frac{SiO_2}{CaO} + Al_2O_3$$

"At the beginning of its manufacture, Portland cement rapidly answered very well the exigencies of mechanical resistance because of the extreme refinements of the construction technique of the time and also because they gave to structures different results from those of Portland cement. But with the increased needs of modern construction has been brought to clear chemical resistance always greater especially in the pozzolanic cement, as was known by Vicat and Michaelis, owing to a disadvantage because it cannot furnish in the early days of hardening the greater mechanical resistance required.

"The reason of this deficiency is mainly due to the constituents of pozzolanic behavior, constituents which, due to the varied and sometimes unsteady morphologic composition and the not always constant possibility activity, confer to the cementitious material a property of reaction very variable in their relationship with water, besides altering values of compressive strength highly important and generally too.

"Owing to these technical deficiencies many researchers have the alternatives of either producing chemical addition and, therefore, partly operating the rules of pozzolanic cements (although offering quite a high value of chemical resistance) or of manufacturing a true pozzolanic cement which will answer the requirements of Vicat but not the technical requirements of modern construction technique.

"Compelled to face this alternative in the plant of Di Segni, we set for ourselves the goal of manufacturing a pozzolanic cement which would be a true one from the chemical standpoint and would still possess sufficient initial strength.

"We therefore, made extensive researches and experiments upon pozzolanas with the aim of eliminating, if possible, all of their deficiencies, endeavoring thus to reproduce the quality of the original pozzolanic cements.

"The first result of these studies has been the discovery and adoption of pozzolanas of older origin, practically deprived of alkalis through the profound alteration of the compounds from which they originate; pozzolanas essentially amorphous of which the average composition is the following:

Loss	9.10%
SiO_2	46.40%
Fe_2O_3	11.40%
Al_2O_3	22.36%
CaO	10.30%
Ind.	0.44%

"After an appropriate granulometric separation, these pozzolanas are subjected to a thermic process of calcination and of tempering - processes which are more or less completed according to the State, physical and chemical, in which the various compounds of silica and alumina are found in the natural material.

"The calcination modifies profoundly the physical state of the pozzolana, and the successive tempering rendering stable the physical structure thus acquired, confers to the product an unstability of intrinsic equilibrium which translates itself into a high chemical sensitiveness for lime. This profound physical transformation is rendered evident to the microscope by the complete inactivity to polarized light of the treated pozzolana, inactivity which can be taken as an index that it contains no hydraulically inert particles

"Another variety of pozzolana used in the manufacture of the rational pozzolanic cement is substituted for clay in the formation of the original clinker mixture. This pozzolana of high alkalinity, owing to its high content of Leucite, KAL $(SiO_3)_2$ has the following typical composition:

Loss	8.75%
SiO_2	40.90%
Fe_2O_3	10.10%
Al_2O_3	20.00%
CaO	10.50%
Alkalis	10.05%

"The alkalis of this pozzolana added at the beginning of the clinkering process, having fulfilled during such process, like the iron compounds - the function of catalytic agents, become volatile at high temperature, leaving the clinker comparatively purer of vitreous formations and much richer in hydraulic crystals, than the clinkers obtained from common clay.

"The second additional pozzolana is the pozzolana which has been subjected to a process of calcination; its addition is proportioned in full agreement with the formula of the index of chemical resistance of Lafuma which we have reported. It happens thus that in the hardened material there is no possibility of having free basic elements, and the possible exceeding acidity remains as a safety factor especially useful for all works submerged in water.

"It is thus that the pozzolanic cement which we call "Cementi Pozzolanici Razionali" can be defined: "The products of the intimate mixture obtained through grinding of two substances, each one of them evincing hydraulic properties, that is, pozzolana which has undergone a thermic treatment and has been rationally proportioned with clinker of slow setting cement, of which the lime liberated during the hardening process is fixed in stable combinations by the acid elements of the pozzolana.

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"As an index of the average behavior of a rational pozzolanic cement we report in the following table (Table 1) the resistance to tension and compression, specimens of 1-3 mortars made with ten types of cements (see pages 80-81).

"Any value set forth in the table is the average obtained by breaking six specimens. The ten cements have been chosen following the criterion of dealing with substances having initial similar resistance. Basing a deduction from the average of the 10 values for each breaking period, we have drawn the curves reported in the following diagram (see p. 83-84) where also we show similar curves drawn with the average values of 5 good types of Portland cement of equal value.

"From the examination of these curves, it is evident that the progression of the values of resistance for the shortest curing time, shows a much slower progression in the case of pozzolanic cement than that indicated in the case of Portland cement.

"Noticing the inflexion of these curves, we find that the more abrupt inflexion points to a rapid exhaustion of hydraulic energy, which is also demonstrated by the successive progression of the curve which very early reaches the asymptote while the much less pronounced inflexions of the pozzolanic cement point to an ascending progression almost uniform in time and to ultimate values which highly counteract the low values of the early stages.

"To be able to appreciate the phenomenon it is possible to assume that the area comprised between the abscissa axis and the corresponding tension and compression curves of the two types of cement can be made to represent their hydraulic capacity of hardening. This being the case, it is easy to deduct how those portions of deficient areas of the early stages are entirely compensated by the areas of the later stages.

"The continued increase in strength of the pozzolanic cement indicates that there is at all times some residual hydraulic activity to be developed while the tendency of the curves of Portland cement can at best be interpreted as evidencing a good retention of the developed hydraulicity but not an always greater amount of this sams hydraulicity.

"As an index of the average behavior of a
reinforced concrete column we report in the
following table (Table 1) the ratios of
maximum and compressive specimens of 1-3
mortars made with ten types of cements (see
pages 80-81).

"The value set forth in the table is the
average obtained by testing six specimens.
The ten cements have been chosen to show
the criterion of testing with substances having
initial similar resistances. Seeing a deduction
from the average of the 10 values for each
period, we have drawn the curves re-
ported in the following diagram (see p. 82-3).
Where also we show similar curves drawn with
the averaged values of 5 good types of Portland
cement of equal value.

"From the examination of these curves it
is evident that the progression of the values
of resistance for the mortars during time
shows a much slower progression in the case of
pozzolanic cements than that indicated in the case of
some of Portland cement.

"Noticing the duplication of these curves, we
find that the more strong initial reactions points to
a rapid combination of available quantity, which
is also demonstrated by the successive progression
of the curve which very early receives the progression
note while the much less pronounced initiations
of the pozzolanic cement point to an accounting
progression almost uniform in time and to attri-
bute values which nicely counterpoise the low values
of the early stages.

"It do able to appreciate the phenomenon it
is possible to assume that the arcs comprised
between the abscissa axis and the corresponding
section and compression curves of the two types
of cement can be made to represent their hydraulic
capacity of hardening. This being the case, it
is easy to deduce from these portions of the joint
areas of the early stages entirely compensated
by the areas of the latest stages.

"The combined increase in strength of the pozzo-
lanic cements indicates that there is all this
some retarded hydraulic activity to be developed
while the tendency of the curves of Portland cement
can at best be interpreted as evidencing a good
retention of the developed hydraulicity but not
an always greater amount of the same hydraulicity.

TABLE 1.

	TENSION										COMPRESSION									
No.	Da.	Da.	Da.	Da.	Yr.	Yr.	Yr.	Yr.	Yr.	Yr.	Da.	Da.	Da.	Da.	Yr.	Yr.	Yr.	Yr.	Yr.	Yr.
1.	21.5	32.	34.4	36.6	38.5	40.2	41.1	43.1	45.	46.8	251	418	496	505	529	560	590	611	630	655
2.	22.5	29.5	31.	33.6	36.1	39.5	41.1	43.3	45.8	47.3	240	406	469	527	545	565	589	610	625	648
3.	20.8	27.9	33.	35.5	37.	38.1	39.7	43.8	42.9	44.9	251	397	415	441	495	535	555	622	600	627
4.	18.5	28.5	32.8	38.1	41.	43.1	45.	47.	49.	50.1	255	359	417	484	502	529	550	571	583	613
5.	18.1	26.3	32.	36.9	42.2	46.2	50.	51.	55.	55.1	256	426	469	489	515	541	565	588	610	630
6.	27.	36.8	37.	38.7	39.	40.	41.2	43.3	46.2	48.8	297	407	454	525	581	620	652	677	702	725
7.	20.4	26.2	36.	41.	43.	44.2	46.	47.9	49.	51.5	353	424	500	485	570	635	660	682	710	728
8.	25.8	29.5	37.	37.5	41.5	40.2	41.	43.1	46.	48.2	249	374	411	420	527	541	563	590	611	647
9.	20.9	29.	31.3	40.	41.9	42.2	45.1	47.5	48.3	51.9	224	346	381	460	502	550	598	629	694	725
10.	22.9	29.	33.7	35.	35.1	37.	39.5	41.1	41.6	44.5	222	337	402	511	450	555	561	581	630	657
Avg.	20.8	29.3	33.7	37.2	39.5	41.	42.9	45.1	46.8	48.7	260	389	432	485	521	562	588	616	638	665

NOTE: All values in $Kg/cm.^2$

TABLE 1.

COMMENTS

| | | |

T A B L E 2.

	COMPRESSION									TENSION									
No.	7 Days	28 Days	84 Days	184 Days	1 Year	2 Year	3 Year	4 Year	5 Year	6 Year	7 Da.	28 Da.	84 Da.	184 Da.	1 Yr.	2 Yr.	3 Yr.	4 Yr.	5 Yr.	6 Yr.
1	3570	5940	7050	7180	7525	7960	8390	8690	8960	9320	306	455	489	521	548	572	584	613	640	666
2	3410	5770	6670	7500	7750	8000	8380	8680	8900	9228	320	420	441	478	514	562	584	616	652	673
3	3570	5640	5900	6270	7040	7620	7900	8850	8540	8920	296	397	469	505	526	542	565	623	610	638
4	3625	5110	5930	6880	7140	7520	7820	8120	8300	8720	263	406	466	542	584	612	640	668	697	713
5	3640	6060	6670	6960	7330	7700	8040	8360	8680	8960	258	374	455	525	600	658	712	725	782	783
6	4220	5790	6460	7470	8260	8820	9270	9630	9980	10310	384	524	526	550	554	569	586	616	657	694
7	5000	6000	7120	6900	8100	9040	9380	9700	10100	10350	290	373	512	584	612	628	654	681	697	733
8	3540	5320	5850	5975	7500	7700	8000	8400	8700	9200	367	420	526	554	590	572	583	613	654	686
9	3160	4920	5420	6540	7140	7820	8500	8950	6875	10340	297	413	445	569	596	600	642	676	686	738
10	3140	4790	5700	7270	6400	7900	7980	8260	8960	9350	326	413	479	498	499	526	562	584	592	633
Avg	3700	5530	3040	6900	7410	8000	8370	8750	9080	9460	296	417	480	530	562	583	610	642	666	683

All Quantities in Pounds per Square Inch.

TABLE.

No.	COMPRESSION										TENSION									
	7 Days	28 Days	84 Days	184 Days	1 Year	2 Year	3 Year	4 Year	5 Year	6 Year	7 Da.	28 Da.	84 Da.	184 Da.	1 Yr.	2 Yr.	3 Yr.	4 Yr.	5 Yr.	6 Yr.
1	3570	5940	7050	7180	7525	7960	8390	8690	8960	9320	506	455	489	521	548	572	584	613	640	666
2	3410	5770	6670	7500	7750	8000	8380	8680	8900	9228	320	429	441	478	514	562	584	616	652	673
3	3570	5640	5900	6270	7040	7520	7900	8850	8540	9320	296	397	469	505	528	542	565	623	610	638
4	3635	5110	5930	6880	7140	7520	7820	8120	8500	9720	363	405	466	542	584	612	640	668	697	715
5	3640	6060	6670	6960	7330	7700	8040	8360	8680	8960	258	374	455	533	600	658	712	725	782	735
6	4220	5790	6460	7470	8360	8820	9270	9630	9980	10510	384	524	526	550	554	569	586	616	657	694
7	5000	6060	7120	6900	8100	9040	9380	9700	10100	10850	390	373	513	584	612	623	654	661	697	735
8	3540	5320	5850	5975	7360	7700	8000	8400	8700	9200	367	420	526	534	590	572	583	613	654	666
9	3160	4920	6420	6540	7140	7820	8300	8950	6875	10340	297	413	443	569	596	660	642	676	636	738
10	3140	4790	5700	7270	6400	7300	7980	8260	8960	9350	326	413	479	498	499	526	562	584	592	633
Avg.	3700	5330	6040	6960	7410	8000	8370	8750	9080	9460	296	417	480	530	562	583	610	642	666	683

All Quantities in Pounds per Square Inch.

T A B L E 3.

Penetration in mm. of:

Specimens	Cured In	Sodium sulphide after 120 days of immersion after a previous curing of: 84 Days	180 Days	1 Year	2 Years	3 Years	4 Years
N. 1	(Water	Tot.	6.4	3.6	2.8	1.1	0.6
	(Air	"	8.2	6.6	4.4	2.7	1.4
N. 2	(Water	"	7.2	3.9	3.1	1.2	0.5
	(Air	"	8.6	6.6	5	2.8	1.6
N.3	(Water	"	6.3	3.5	2.9	1.1	0.7
	(Air	"	7.9	6.8	5	2.6	1.7
N. 4	(Water	"	7.1	3.1	3	1.2	0.4
	(Air	"	8.1	6.2	5.3	2.7	1.5

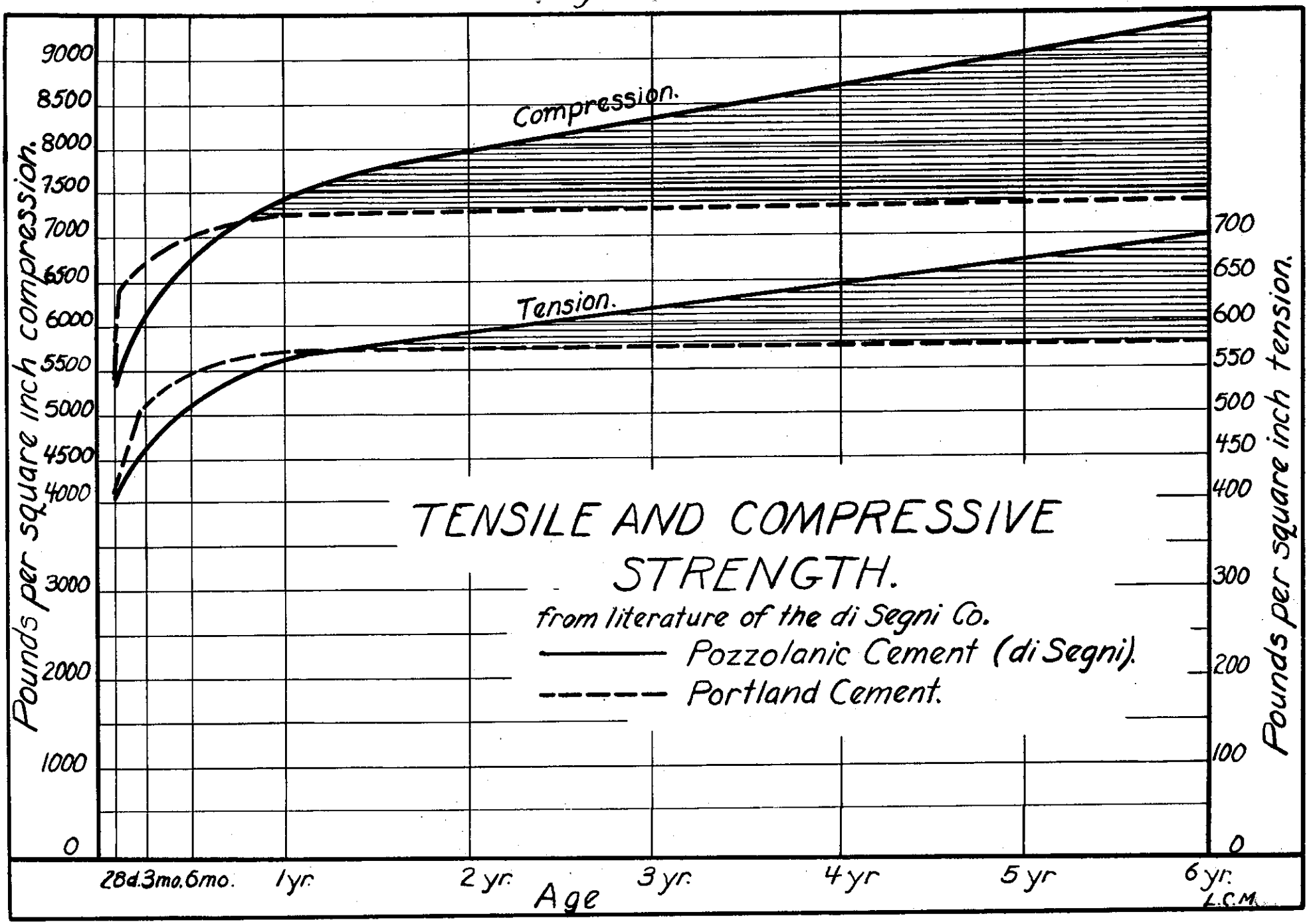
TABLE 3

Penetration in mm. of

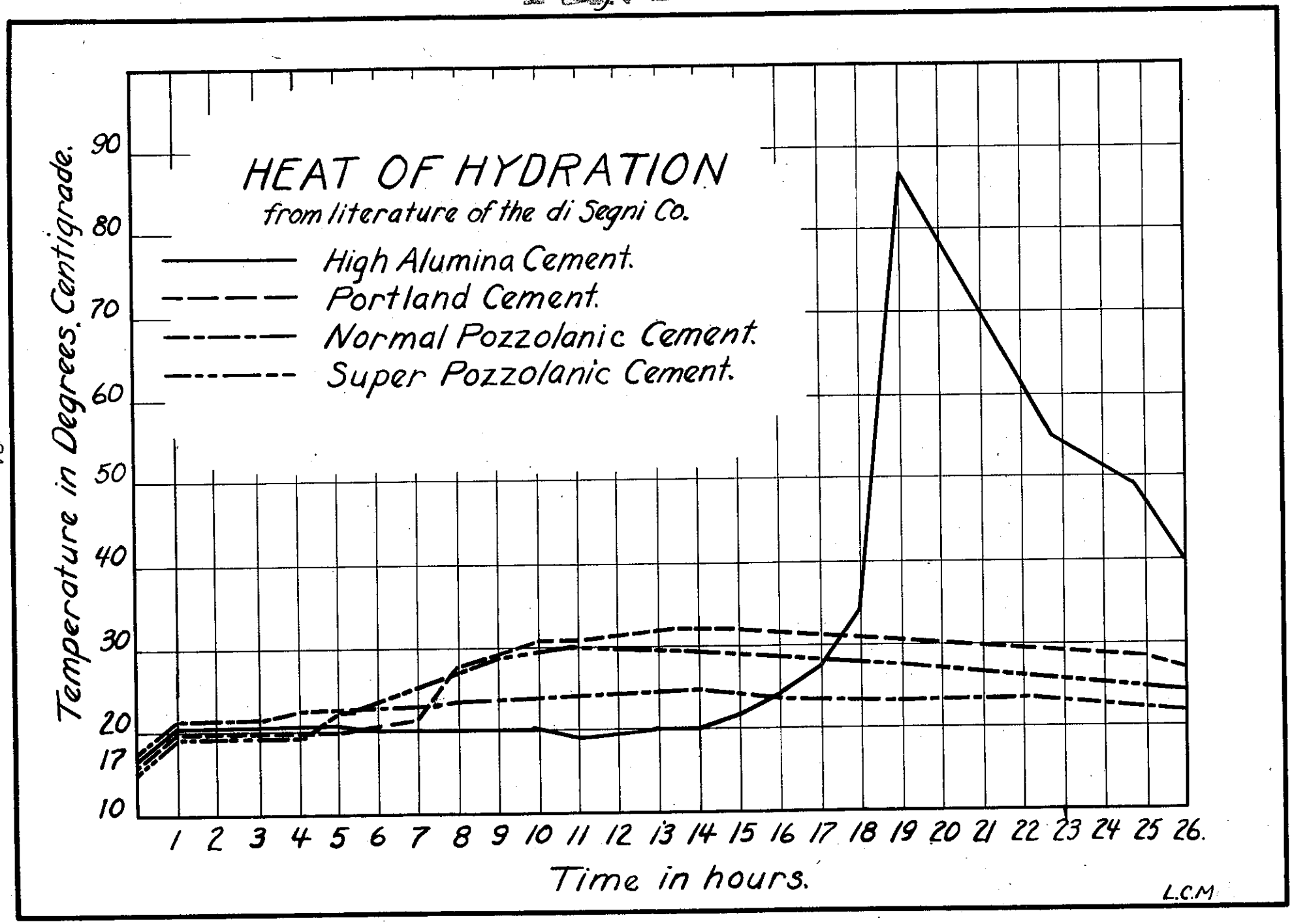
Specimens	Cured in	Sodium sulphide after 120 days of immersion after a previous curing of: 84 Days	180 Days	1 Year	2 Years	3 Years	4 Years
M. 1	Water	Tot.	5.4	5.6	2.8	1.1	0.6
	Air	"	8.2	6.6	4.4	2.7	1.4
M. 2	Water	"	7.3	5.0	3.1	1.2	0.5
	Air	"	6.6	6.6	5	2.8	1.6
M. 3	Water	"	6.5	5.5	2.0	1.1	0.7
	Air	"	7.2	5.8	3	2.6	1.7
M. 4	Water	"	7.4	5.1	3	1.2	0.4
	Air	"	8.1	6.2	6.3	2.7	1.5

PLATE

Fig. 3 E


Compression.
Tension.
TENSILE AND COMPRESSIVE STRENGTH.
from literature of the di Segni Co.
Pozzolanic Cement (di Segni).
Portland Cement.
Pounds per square inch compression.
Pounds per square inch tension.
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3000
2000
1000
0
700
650
600
550
500
450
400
300
200
100
0
28d. 3mo. 6mo. 1yr. 2 yr. 3 yr. 4 yr 5 yr 6 yr.
Age
L.C.M.

Plate


HEAT OF HYDRATION
from literature of the di Segni Co.
High Alumina Cement.
Portland Cement.
Normal Pozzolanic Cement.
Super Pozzolanic Cement.
Temperature in Degrees. Centigrade.
90
80
70
60
50
40
30
20
17
10
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26.
Time in hours.
L.C.M

"The smaller inflexions in the first part of the tension and compression curves of pozzolanic cement are due to the moderating influence of the pozzolanic part of the cementitious material upon the speed of reaction of the Portland component. This moderating influence of the initial development of physical resistance is due in turn to the beginning of auxiliary combinations of the liberated lime with pozzolana, combinations which evidence values of mechanical resistance logically much weaker.

"Owing to the consolidation of the pozzolanic compounds the Portland component receives in the process of hardening an always greater help, and the ascensional tendency of the second part of the tension and compression curves is due thus on one hand to the progression of the hydration of the Portland component and on the other hand to the reaction of the liberated lime with pozzolana with formation of compounds of always greater mechanical resistance with the progression of time.

"The assumption, therefore, appears justified that pozzolanic cements may always increase in strength with time instead of the retro-gressions evidenced by many other cementitious materials.

"The value of the ratio of tensile strength to compressive strength has assumed a notable importance in the study of cementitious materials, since the time that the majority of experts have based a classification of the various types of cement upon the value of this ratio.

"As a result of a long series of experimental tests, Feret came to the conclusion that the value of compressive strength is more exact - as index of the physical resistance of a mortar - than the value of tensional strength.

"A classification of cementitious materials based upon this criterion brought him to assign the highest value to aluminous cements and the lowest value to pozzolanic cements.

"Feret shows in his most recent study upon the comparison of the various types of stress in mortars and concretes that the cause of the high increase

"The smaller inflections in the first part of the tension and compression curves of pozzolanic cements are due to the moderating influences of the pozzolanic part of the cementitious materials upon the speed of reaction of the Portland component. This moderating influence of the initial development of physical resistance is due in turn to the beginning of auxiliary combinations of the liberated lime with pozzolans. Combinations which evidence values of mechanical resistance lowering with weather.

"Owing to the consolidation of the pozzolanic compounds the Portland component receives an increase of hardening as always greater help. And the secondary tendency of the second part of the tension and compression curves is due thus on one hand to the processing of the hydration of the Portland component and on the other hand to the reaction of the liberated lime with pozzolanic combining with formation of compounds of always greater resistance with the progression of time.

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"Feret shows in his most recent study upon the comparison of the various types of stress in mortars and concretes when the causes of the time increase

of the tensional values of modern cements is a fictitious cause inasmuch as such an increase is due to the formation of a superficial stratum of high lime calcium compounds, which stratum is proportionally more resistant than the remaining section.

"The studies that we have made upon this argument confirm the deductions of Feret regarding the increase of tensional strength but at the same time show how erroneous is the conception of basing a classification of the hydraulic capacity of all cementitious materials simply on this phenomenon, without distinguishing between those having fundamentally basic constitution and those having a fundamentally acid one.

"Very different is the origin and also the composition of the superficial stratum of a highly basic mortar like the one of Standard Portland and the superficial stratum of a pozzolanic mortar which is always of acid character. In the first case that superficial stratum consists mostly of lime, which through a phenomenon of displacement from the interior of the mass toward the outer part, deposits itself at the surface where it is subjected to carbonization due to the action of carbonic anhydride. There it forms a very frail film chemically unstable owing to the possibility of undergoing bi-carbonization and therefore of becoming soluble.

"In pozzolanic mortar instead, it is always the case of a superficial stratum of acid origin, chemically stable and mechanically resistant which is produced through the development of the gels of the active elements of a pozzolana. These gels, which especially at the earlier periods of curing can present themselves in impure surface carbonization, constitute a very dense acid tissue surrounding the crystalline formation already taken place and the elements of the successive crystalline formations which will develop in new gels in the interior of the preceding ones, thus increasing the density of that cellular tissue. Inasmuch as the development of these gels takes place only through absorption of lime water, when they crystallize they will give place to the formation of calcium alumina compounds and of calcium silica compounds which will effect a cementing process of the inert part of the mortar, conferring at the same time, to

of the regional values of modern deposits is a fluctuation whose importance as much as 12 degrees is due to the formation of a superficial stratum of high lime calcium compounds, which stratum is progressively more resistant than the remaining sediment.

"The studies that we have made upon this argument concerning the deduction of facts regarding the changes of temperature during the same time show how erroneous is the conception of basing a classification of the hydraulic property of all cementitious materials simply on this phenomenon, without distinguishing between those having fundamentally basic composition and those having a fundamentally acid one.

"Very different is the origin and also the composition of the superficial stratum of a highly basic mortar like the one of standard Portland and the superficial envelope of a pozzolanic mortar which is always of acid character. In the first case that superficial stratum consists mostly of lime, which through a phenomenon of dissociation from the interior of the mass toward the outer part, deposits itself on the surface where it is subjected to carbonization due to the action of carbonic anhydride. There is formed a very thin chemically unalterable coating to the possibility of undergoing bi-carbonization and therefore of becoming soluble.

"In pozzolanic mortar instead, it is always the case of a superficial stratum of acid character, chemically stable and mechanically resistant which is produced through the development of the gels of the active elements of a pozzolana. These gels, which especially at the earlier periods of carbonization present themselves in impure surface combinations, constitute a very dense solid insoluble and unalterable, covering the original volume and the elements of the successive crystalline formations which will develop in new gels in the interior of the preceding ones, thus increasing the density of that original mass. Inasmuch as the development of these gels takes place only through absorption of lime water, when they crystallize they will give place to the formation of calcium aluminum compounds and of calcium silico compounds which will effect a renewing process of the inert part of the mortar, conferring at the same time, to

the mortar with the corresponding mechanical energies a very high degree of impermeability. The crystallization of the gels of mortars takes place in a centrifugal direction beginning from the innermost zones, inasmuch as these zones are those enjoying higher thermical protection, as well as higher relative stability.

"What we have said is proved in the following table in which are reported the penetration of a 10% sodium sulfide (Na_2S) solution - according to Le Chatelier - on mortars of pozzolanic cement experimented upon in our laboratory.

"The specimens were of prismatic shape, 4 cm. wide and 7 cm. high. The measurement of the penetration of sodium sulfide (which, through the action of iron, colors the mass through which it penetrates, a greenish black) has been obtained by cutting in half the resulting cubes perpendicularly to the surface. (See table 3, page 82)

"This impermeability of mortars of pozzolanic cement is also rendered practically evident even when the inert part does not answer to the best criterions for a maximum of compactness; it is also rendered equally evident by the chemical resistance which they present to the action of aggressive waters. Consequently, if it is true that the values of tensional strength of the mortars of a pozzolana cement are increased as in Portland by the formation of a superficial stratum more resistant than the central nucleus, it is nevertheless true that in the case of a pozzolanic cement this stratum is of a different nature and remains in the state of a thin crust only temporarily, differing in this from the superficial stratum of lime which cannot go very deep.

"If we are not interested in the long time strengths of all pozzolanic cements we should at least admit that the formation of the highly compact acid crust confers to this cement technical properties of such value as to render them superior at least to basic Portland, which in this respect shows negative properties.

"Another characteristic worth remembering is the very small development of heat during hydration of pozzolanic cements.

"On page 84, Figure 4, we report the curves of the temperatures developed during the first hours of the setting comparing them with the corresponding curves of an aluminous cement and of a Portland cement, which have been all experimented upon under equal conditions of laboratory technique. This diagram clearly shows the difference between the maximum temperatures of the different cements, especially the aluminous cements. This advantage is not to be disregarded when we consider the advantage of using a cement with less heat of hydration in mass construction.

"From what we have mentioned above, it is apparent that the best cement is that cement which gives rise to substantial and quick physical strength so as to fully satisfy the needs of the construction industry and which at the same time will guarantee with chemical resistance impermeability and continued hardening with age.

"In our opinion, pozzolanic cements satisfy these requisites in a satisfactory manner and of the pozzolanic cements the rational one appears to be the prototype of unsurpassed value."

Additional information on the same subject can be obtained from another study of Dr. Vittori "I Progressi Compiuti dal Cemento Pozzolanico" (The Progress made by Pozzolanic Cement) published in "L'Industria Italiana del Cemento", February, 1932.

"All pozzolanas contain in general alkali bases under the form of sodium and potassium salts and this is much more true of the Roman pozzolanas rich in leucites which would have brought in pozzolanic cements a too high percentage of alkalis.

"We began therefore, to look for pozzolanas offering a modified form of leucite, which, due to a long exposure to external influences, had lost the alkali base, leaving in place of the crystals of silicate of alumina and potassium only an amorphous, colloidal, skeleton of silicate of alumina. It was found that these pozzo-

"Another observation is worth remembering is the very small development of heat during hydration of pozzolanic cements.

"On page 64, figure 6, we report the curves of the temperatures developed during the first hours of the setting comparing them with the corresponding curves of an aluminous cement and of portland cement, which have all experimented under under equal conditions of laboratory technique. This diagram clearly shows the difference between the maximum temperatures of the different cements, especially the aluminous cement. This advantage is not to be disregarded when we consider the advantage of using a cement with less heat of hydration in mass construction."

"From what we have mentioned above, it is apparent that the best element is that cement which gives rise to substantial and quick physical strength so as to fully satisfy the needs of the construction industry and still at the same time will eliminate with chemical resistance impermeability and continued hardening with age.

"In our opinion, pozzolanic cements satisfy these requisites in a satisfactory manner and of the pozzolanic cements the ratioval one appears to be the prototype of unsurpassed value."

Additional information on the same subject can be obtained from another study of Dr. Vittorio "I Progressi Compiuti dal Cemento Pozzolanico" (The Progress made by Pozzolanic Cement) published in "L'Industria Italiana del Cemento", February, 1938.

"All pozzolanas contain in general silicic bases under the form of sodium and potassium salts and this is another cause of the known pozzolanic action in leaches which would have brought in pozzolanic cements a too high percentage of salts.

"We began therefore, to look for pozzolanas offering a modified form of leuciti, which, due to a long exposure to external influences, had lost the silicit base, leaving in place of the crystals of silicate or alumina and potassium only an amorphous, colloidal, skeleton of silicate of alumina. It was found that these pozzo-

lanas were the most adapt and, therefore, all further study was made upon them. The only drawback seemed to be that they appeared unadapted to be used in the state they were taken from the quarry.

"Their morphologic composition always quite variable did not normally guarantee a good and uniform hydraulicity throughout the mass of pozzolanic material. They contained, it is true, the leucites in a deeply altered form, but to polarized light they revealed some characteristics of double refraction of the crystalline compounds, which are least adapted to readily fixing the lime.

"Furthermore, throughout the various points of the same quarry, the amorphous and the crystalline parts were distributed in the pozzolanas in highly variable percentages and, consequently, brought to the cements a corresponding variability of hydraulic behavior, which was revealed during the period between initial and final set and was generally weaker with the more crystalline forms of pozzolana.

"Other reasons of deficiency and hydraulic variability were found to be due to variation in the material in the same deposit. In the same quarry, it was possible to find "lapilli" of strong tenacity and tufas of variable consistency from a tender and crumbling texture to a texture easily reduced to a lamellar form, or yet, portions made up of disconnected grains absolutely incoherent and resembling volcanic ashes. Also the ferric compounds were often met differing in the degree of oxidation, with colors ranging from dark red to deep grey, through a full gradation of pink, violet, etc.

"It is not enough, therefore, to have found that the pozzolanas having a very small and almost unimportant content of alkalies are to be preferred; it is necessary to study how to eliminate the above causes of hydraulic variability, and, principally, to study the way to augment the hydraulic property, so that the pozzolanas may enter readily into reaction with the lime of the cements, which in turn have to satisfy the

lands were the most easily and, therefore, all further study was made upon them. The only drawback seemed to be that they appeared unadapted to be used in the state they were taken from the quarry.

"Their mineralogic composition always quite variable did not normally guarantee a good and uniform hydraulic property throughout the mass of pozzolanic material. They contained, at the same time, the reactives in a deeply altered form, unfit to polarize light, they severed some objectionable compounds. Under the microscope, the amorphous and the crystalline parts were distributed in the pozzolanes in highly variable percentages and, consequently, the same quality of hydraulic behavior was foreseen as probable to the cements a corresponding variability of hydraulic behavior during the period between initial and final set was generally greater with the more crystalline forms of pozzolanes.

"Other reasons of deficiency are hydraulic variability were found to be due to variation in the material in the same deposit. In the same quarry, it was possible to find "lenticles" of strong pozzolan and veins of variable consistency from a tender and crumbling structure to a texture easily reduced to a familiar form, of yet, portions made up of disconnected crystalline specimens incoherent and resembling volcanic sands. Also the petric compounds were often met dispersed in the degree of alteration, with colors ranging from dark red to deep grey, through a full gradation of pink, violet, etc.

"It is not enough, therefore, to have found that the pozzolanic pozzolana is a very small and almost unimportant content of alkalies are to be preferred; it is necessary to study how to eliminate the above causes of variability and, principally, to study the way to eliminate hydraulic variability. To study the way to eliminate the hydraulic property, so that the pozzolanes may enter, in much greater proportion of the time, the domain of pozzolanic materials with the more crystalline forms of pozzolanes.

higher and quicker strengths required, still remaining true pozzolanic cements as far as chemical composition is concerned.

"There was begun thus a whole series of experiments methodically and carefully organized, so that whatever was thought to be useful to the aim to be reached, was to be attempted, and, possibly realized.

"It was decided thus to operate along the following directions:

(a) "Study of granulometric composition and classification of the various materials composing the pozzolanas.

(b) "Study of the various temperatures and pressures in the various treatments and length of the same.

(c) "Study of torrefaction and tempers more or less rapid in all kinds of surroundings.

"It was the thermic treatment under the form of torrefaction and successive temper which gave the best result and which, since the beginning approached more closely the aim towards which all the numerous works were aiming.

"With such a treatment, the characteristic of double refraction presented by the material to the polarizing microscope disappeared entirely, and the material showed to be uniformly amorphous and, therefore, practically all of a hydraulic nature. Its affinity for lime in the first three days was revealed to be almost four times as great as that which characterized it at the time of extraction from the quarry, and both the color and the physical condition was equalized in all the various masses.

"The good results offered by pozzolanic cement are not only due to the treatment of the selected special pozzolana containing no alkalis. Some very numerous tests had already, in fact, given us the certainty that the ordinary clinker of standard Portland could not fulfill two purposes at one time, would not, in other words, be

higher and quicker strength is required, still remaining true porcelain, a composite as far as chemical composition is concerned.

"There was born then a whole series of experiments methodically and carefully organized, so that whatever was thought to be useful to the aim to be reached, was to be altered, and, possibly realized."

It was decided thus to operate along the following directions:

(a) Study of gradually changing composition and classification of the various materials composing the porcelains.

(b) Study of the various temperatures and pressures in the various treatments and length of the same.

(c) Study of coloration and tempers more or less rapid in all kinds of surroundings.

"It was the general treatment under the form of fusion and successive temper which gave the best result and within, since the beginning, established more clearly the aim towards which all the numerous works were aiming.

"With such a research, the characteristic or double refraction presented by the materials by the polarizing microscope disappeared entirely, and the material showed to be uniform, amorphous and, therefore, practically all of a uniform nature. It is clearly for time in the first three days was revealed to be almost four times as great as that which obtained for the time of exhibition like quartz, and soon the color and the various condition was equalized in all the various masses.

"The good results offered by porcelanic cement are not only due to the treatment of the selected special porcelains containing no clay, in fact, some very numerous tests had already given us clear certainty that the ordinary clinker as standard formula could not furnish two pieces at one time, would not, in other words, be

the right material both for the production of standard Portland and pozzolanic cement. It was a fact that pozzolana, especially after its treatment of intensification of its hydraulic properties, could not be considered to be an element fulfilling simply a secondary function in pozzolanic cements, but instead, a very primary one, and, in a certain way, a more important one of that fulfilled by the clinker.

"It appears highly necessary that the very pronounced acidity of pozzolana in contrast to the high basicity of the component clinker could find in it those elements and those appropriate conditions to begin at once its hydraulic action owing to which the liberation of lime and its fixing is followed and completed by the phenomena of jellification of the silico-aluminates, which give to the mortars those characteristics of strength, tenacity and impermeability so highly valued.

"All this brought into being a new series of experiments with the aim of determining the best clinker which could fulfill the requisites of producing rational pozzolanic cements absolutely undecomposable chemically, and also, at the same time, offering high and quick mechanical resistance. Keeping in mind the new characteristics of pozzolana rendered, by special process, of still higher hydraulicity, a new series of clinkers was experimented upon; beginning with a clinker of very low hydraulic modulus, or from those poorest in vitreous magma to the richest, and from those of less to those of more concentration in a certain element.

"The result was that the most adapt were the clinkers of high basicity, and form them it was then necessary to study special cares and artifices for their best clinkerization.

"In this type of clinker the hydraulic modulus is always larger than the siliceous modulus, and from this characteristic derive qualities contrary to those of the almost total number of clinkers for Portland cement in which the hydraulic modulus is always smaller than the siliceous modulus.

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"A type of research which required plenty of work and which often showed up the conclusions of the experiment was the study of the physical state of the free lime scorified in the clinkers and of its behavior when placed in contact with pozzolana.

"Finally, the best method of preparation of the clinker before combining with the pozzolana during the grinding, required very extensive experiments.

Recapitulating:

"For the manufacturing of rational pozzolanic cements, before it was possible to arrive at the final solution, it was necessary to solve the following problems:

(a) Choice of the right pozzolana, according to its chemical composition and its physical and morphological state.

(b) Its thermic treatment and its successive temper for higher hydraulic activity.

(c) Chemical composition of the clinkers best adapted for mixing with pozzolana, also their process of heating and their successive temper."

Following are typical analyses of two types of pozzolanic cement manufactured by the Di Segni Plant. The first called "Supercemento Pozzolanico" develops a compressive strength of 10,000 pounds and a tensile strength of 650 pounds at one year and shows the following chemical composition:

CaO	42.30%
SiO_2	42.68%
Fe_2O_3	2.10%
Al_2O_3	5.50%
SO_3	1.54%
Loss to Calcination	5.00%
Indeterminate	0.88%

"A type of recession which required plenty of work and which often showed up the conditions of the experiment was the study of the physical steps of the climber's end of the line carried in the climber's end of the belayer when placed in contact with powerful lens.

"Firstly, the best method of preparation of the climber before combining with the ocean lens during the climbing is used very extensive experiments.

Recapitulation:

"For the resurgence of national power, many centuries before it was possible to arrive at the final solution, it was necessary to solve the following problems:

(a) Choice of the right polarity according to its chemical composition and its physical state.

(b) Its thermic resistance and its susceptive temper for higher hysteretic activity.

(c) Chemical occupation of the sitmere best adapted for mixing with cosolute, since their purpose of heating and their superative temper."

Following are typical analyses of the types of ocean-land cement manufactured by the Ohio Cement Plant, the test called "Temperemento Fosforamico" develops a compressive strength of 10,000 pounds and a tensile attempt of 600 pounds at one year and shows the following chemical composition:

Insoluble	0.08%
Deterioration	0.20%
Loss on ignition	1.66%
SO3	0.30%
Fe2O3	3.10%
Mn3O4	3.10%
Al2O3	22.00%
CaO	64.00%

with an index or chemical resistance of:

$$\frac{SiO_2 + Al_2O_3}{CaO} = 1.13$$

The second type of pozzolanic cement is a special cementitious material manufactured to present very high resistance to sea water, consequently its index of chemical resistance is the highest ever encountered which means that the cement is of particularly high acidity. Its analysis shows:

CaO	24.08%
SiO_2	39.90%
Fe_2O_3	5.65%
Al_2O_3	12.49%
Loss by Calcination	14.08%
Indeterminate	3.08%

The justification of the manufacture of such a type or cement so poor in lime content is treated in a memoir of the Di Segni Plant:

"It is well known that the richer an hydraulic cementitious material is in lime, the smaller is the resistance which it can offer to the disintegrating action of salts contained in the water in which it is immersed. It is a fact that insofar as the chemical composition of hydraulic materials is concerned, maritime structures are in conditions diametrically opposite to structures above water. These last, to shorten the construction time and to diminish the mass of the structurel members require cements of high physical resistance and of quick hardening. Both these qualities are nowadays normally obtained by the increase of the lime content. Hydraulic and maritime structures instead can very well dispense with rapid and high physical resistance although they have absolute need of the lowest possible basicity. The chemical characteristic of the lowest basicity of the cementitious materials used is the secret of long life for hydraulic structures, even if these structures are immersed in very ag-

gressive waters, while the high basicity of modern cements happens to be the determining cause of the rapid deterioration of hydraulic works.

"Now the lime found in the pozzolanic cement for maritime works is not found under the form in which it is found chemically in Portland cements, that is, it is not part of high lime compounds obtained at very high temperature but instead is prepared and found in the cement in the anhydrous state in a condition of reactivity at ordinary temperature.

"From this it follows that in the process of hydration and during the phenomenon of hardening of the mortars, the lime combines readily and intimately with the pozzolanic substance which forms the essential basis of this material. The pozzolanic substance on the other hand has been in turn previously treated and heightened in its acid qualities so as to complete its integration with the lime of the cement into a very harmonious chemical formation of well defined and stable compounds which will guarantee an absolute resistance of the structures to the deleterious action of sea water.

"In other words, this special pozzolanic cement for all that it has to do with chemical resistance (specific and essential quality of all stable cementitious materials) finds itself in ideal conditions not only owing to its low basicity but also because it contains in a slight excess the acid elements which can neutralize all the lime that the original cement may contain.

"Another source of greater stability of this material to the action of aggressive waters is due to the velocity and the magnitude of hardening of which this material is susceptible. Its qualities are due in turn to the state of high reactivity in which are found its basic and acid components when placed in intimate contact.

"The prevailing conception that the hardening of ordinary cementitious materials is in direct relationship to their basicity is exact inasmuch as this basicity is bound in turn to combinations

obtained in thermic conditions for which the temperature is essentially higher than the temperature of the mediums in which the cementitious material will be used. This special pozzolanic cement instead, inasmuch as it is a product of low temperature reactions, is a material exactly opposite to the cements of high physical resistance due to high basicity. Another characteristic, although not always strictly necessary but nevertheless to be considered not less precious is the progressive gradual hardening in time due to the formation at ordinary temperature of hydraulic compounds always much more stable and defined.

"This characteristic excludes any possibility of retrogression of strength which is so easy to happen with ordinary Portland cement, and even with high alumina cements.

"Through the above properties, we have the formation of an impermeable crust at the surface of the structures built with this special pozzolanic cement and immersed in sea water. This impermeable crust does not allow the washing out of the cementing elements and the penetration of salts in the interior parts of the mass, and brings about therefore, a condition such that the mortar can offer to the action of aggressive waters, in addition to the chemical resistance, a physical-mechanical resistance which can safeguard still better the chemical reactions of the compounds formed during the slow but always growing hardening of the mortars themselves."

Having secured a fairly good description of pozzolanic cements let us recapitulate the reasons which brought about their manufacture. These reasons are given as:

1. Need of lowering the high basicity of Portland

2. Need of taking care of the lime liberated from the hydrolysis of the high lime calcium silicate compounds of Portland cement.

3. Need of eliminating compounds like tri-calcium aluminate which are paramount agents in the formation of a disintegrating process.

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3. Need of eliminating compounds like tri-calcium aluminate which are paramount agents in the formation of a disintegrating process.

4. Need of bringing about a greater degree of hydration and consequently higher resistance to the deteriorating effect of aggressive water.

Having thus recapitulated the needs to be fulfilled let us pass to an inquiry into the way in which any commercial pozzolanic cements fulfill these needs.

For such an inquiry, we should know in advance:

(a) The chemical composition of the original clinker.

(b) The chemical composition of the pozzolana added.

(c) The percentage in which they are mixed.

(d) The compounds which are formed, if any, in the anhydrous state.

Unfortunately there are no data available on these items, inasmuch as they are kept secrets by the various manufacturing plants. We are left therefore, without information essential for a sound judgment. However, let us take all the various needs which we have enumerated and find if possible just how a true pozzolanic cement may fulfill them. Beginning with the last of all it is apparent that with a true pozzolanic cement we can reach a much greater degree of hydration. Owing to the affinity of pozzolana for lime, the lime liberated in the first stage of the hydration of the cement from the hydrolysis of the tricalcium silicate reacts immediately with the pozzolana giving origin to an additional process of hydration of the pozzolanic elements which take place at the time of the secondary stage of hydration of the Portland element and continue indefinitely through time. This is evidently an advantage not to be overlooked and which has been stressed by the manufacturers of pozzolanic cements who have shown that the curve characteristic of the increase of physical resistance in time is of the hyperbolic type, that is, does not approach the asymptote for finite values of time.

But we must not lose sight of the fact that pozzolanic cements were born from, and their reason of being subsists upon, the need of offering a greater chemical resistance. Of interest in this regard is the following statement by the dean of all pozzolana experts, Professor O. Rebuffat of the Royal University of Naples (see: La Pozzolana di Bacoli, nei Lavori Marittima", published in "Annali d'ingegneria", Anno. V. - N. 10):

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"When we speak of the use of pozzolana it is also necessary to say something about the addition that is made of this material to ordinary cements with the aim of bringing about a bettering of their qualities. Very little clearness of ideas exists nowadays upon this argument among engineers and builders and therefore it is necessary to make a distinction of the various cases in which the blended cements can be employed.

"It was an old proposal of Michaelis, the one of introducing trass in mortars or concretes of Portland cement to render them stable to the action of sea water, but that proposal was completely fallacious because, as we have already explained, pozzolana (or trass) has not the property of fixing lime in an insoluble state in sea water.

"Instead, as it is the case of works meant to be placed in fresh water or in damp places, the addition of pozzolana can lead to a noticeable economy in the use of cement without damage of the quality of the work, because the lime liberated during the hydration of the cement is used then to activate the pozzolana."

In the face of such a statement, we must acknowledge that we may be still very far from having found the solution sought. If it is true, in fact, that in highly ionized waters, as for instance sea water containing aggressive sulphate ions, pozzolana cannot fix in stable compounds the lime of the Portland cement, then this same lime, after having activated the pozzolana, that is, after having brought about its setting and hardening, disappears again bringing about the transformation of the calcium silicates of alumina, which form the main elements of the set pozzolana, into hydrated silicates of alumina devoid practically of all lime. In other words, the common binder which bound the Portland element to the pozzolanic element is lost in time again and the two parts of the cementitious material, which during a certain number of years had formed one integral substance, begin to separate again and behave from then on according to laws of their own.

That is, the hardening of the Portland cement element will proceed up to a certain period and then will end; the hardening of the pozzolanic element however at the time that the hardening of Portland is virtually through, is perhaps only in its initial stages. The different phases of hardening may give origin throughout the mass to internal stresses which may resolve themselves into a rupture of the formation colloidal-crystalline of the mass itself. At the same time we have the formation of high

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lime content calcium sulpho-aluminate in the Portland element, through the formation of the tetra-calcium alumina hydrate, shown by Lafuma to take place in the hydration of Portland (which is an essential element in the formation of the calcium sulpho-aluminate). In other words, even granting the fact that pozzolanic cement fulfills some of those needs, that is even granting that pozzolana can in the initial stages of the hydration process offset the high basicity of Portland; that it can fix the free lime liberated by the hydrolysis of the silicates and that it can furnish a superficial stratum of high impermeability, also that it still remains that in time the lime fixed may disappear; that Portland and pozzolama may separate again into their constituent elements; that calcium sulpho-aluminate may be still formed whenever there is alumina present in the Portland element, and that owing to their peculiarities of behavior in the hardening process, Portland and pozzolana may in the end take part in a disruptive process due to internal strains.

Professor F. Ferrari of the Royal University of Pisa, Italy, is another cement expert who has expressed himself relative to what he considers the deficiencies of the Portland pozzolana mixture. Quoting from one of his studies on the subject published in "Giornale di Chimica Industriale e Applicata" year 1920, we find:

"Owing to their peculiar acidity, pozzolanic materials constitute the natural moderator of the excessive basicity of hydrated Portland cement. It is possible in fact to obtain through the addition of such materials, that goal toward which the concrete technique must aim, that is, to have the lime which is liberated during the process of hydration fixed in combinations which result practically insoluble. During the contact of a pozzolanic material with calcium hydrate, the acid elements of the former become combined with the calcium to form compounds of very small solubility and permeability.

"Once we establish a combination of the various materials which shows a full integration of the components, it is possible to obtain after the complete hydration a mortar made of elements of the same order, of negligible solubility, homogeneous and impermeable in any of its sections. Its disintegration under the action of fresh water will be limited at the surface and even there will be hardly noticeable on account of the formation of those hydrated silicates which cannot be subjected to further decomposition, constituting a colloidal mass almost indifferent to the attack of fresh water.

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"The application of the mixture of Portland cements and pozzolanic materials appears fully justified therefore in such cases as the materials showing pozzolanic nature constitute a natural correction of the excessive basicity of hydration of the mortars made with Portland cement, which basicity is the origin of the specific permeability of those mortars.

"But the mixture of Portland and pozzolanic materials owing to their greater or less content of calcium aluminates of highly basic nature of the Portland, do not present to the action of sea water or water containing sulfates, the stability which has always been vouched for them. This fault being due to the slow but constant disintegration, that the sulfates and the chlorides originate in all mortars containing aluminates of a highly basic nature. The various amounts according to which these aluminates enter into the various mortars in relation to the smaller or larger content of CaO combined in those mortars, explain the noticeable and sometimes very large variations of the resistance of these mortars.

"Mixtures of Portland-Pozzolana result instead of absolutely rational use in all water works or in all works which in any event are bound to be in constant contact with sulfates or chlorides.

"Mortars of Portland-pozzolana and sand, at full integration of their components (that is, calculated so that the quantity of lime freed from the hydration of the Portland corresponds to the quantity of lime which can be fixed by pozzolana and sand), can substitute in every work (not in aggressive waters) completely and successfully, the concrete made of Portland, presenting, when compared to the deficiencies of this concrete (great specific permeability and resistance to physical agents degrading in time) an impermeability practically absolute and a mechanical resistance superior and growing with great regularity until it reaches a constant value."

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We are left thus with a material which apparently can be used for all purposes but the purpose for which it was meant, that is, for sea water, sulfate waters, alkali waters and all

chemically aggressive waters in general.

In the manufacture of a true pozzolanic cement it is apparently not enough to mix Portland clinker and pozzolana indiscriminately but it is necessary that:

(a) The clinker itself be opportunely modified.

(b) The pozzolana must undergo a special process of preparation.

(c) The material must be accurately gauged as to granulometric composition.

(d) The percentage of the two elements, Portland pozzolana must be in a determinate relationship deriving from their actual chemical composition.

In the book "Lime and Cements" of L. Mazzocchi we find this warning:

> "It cannot be called a rational pozzolanic cement, a cementitious material which contains an addition, not exactly calculated, of pozzolanic elements (either deficient or excessive quantity) with a clinker which, due to its nature and its hydraulic index, would require a quantity of pozzolana relatively larger or smaller to reach, during the hydration and the hardening, the necessary equilibrium for its chemical stability."

The dean of pozzolana experts in France, R. Feret in charge of the laboratory of Bridges and Roads at Boulogne-sur-mer in his study "Recherches sur la Nature et la Progression de l'Action Pouzzolanique" (Researches upon the nature and progress of the pozzolanic reaction) published in Revue des Materiaux de Construction et de Travaux Publics, February and March, 1933, says on this subject:

> "From the fact that a material is highly pozzolanic it does not necessarily follow that its introduction in a mortar or in a concrete should be advantageous <u>if to obtain the desired consistency this addition brings about the use of an excessive quantity of water.</u> This excessive quantity in fact diminishes the compactness and the resistance and increases the ten-

generally aggressive waters in general.

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In the book "Time and Cements" of L. Vassconi we find this warning:

"It cannot be called a rational pozzolanic cement, a cementitious material which contains an addition, not exactly regulated, of pozzolanic elements (either deficient or excessive quantity) with a clinker which, due to its nature and its hydraulic index, would require a quantity of pozzolane relatively larger or smaller to react, during the hydration and the hardening, the necessary equilibrium for its chemical stability."

The dean of pozzolane experts in France, A. Perret in charge of the Laboratory of Bridges and Roads at Boulogne-sur-Mer in his study "Recherches sur la Nature et la Préparation de l'Action Pouzzolanique" (Researches upon the nature and preparation of the pozzolanic reaction) published in Revue des Materiaux de Construction et de Travaux Publics, February and March, 1953, says on this subject:

"From the fact that a material is highly pozzolanic it does not necessarily follow that its introduction in a mortar or in a concrete should be advantageous if to obtain the desired consistency this addition brings about the excessive quantity of water. This excessive quantity of water diminishes the compactness and the resistance and increases the tendency

dency to retrogression of strength and the tendency to be subjected to various alterations.

"The industrial addition of pozzolanas to cements to the end of increasing their resistance to chemical decompositions must therefore be subordinated at the same time not only to the choice of a material sufficiently hydraulically active but also must be subordinated to the determination of the optimum proportions and to a grinding fine enough to allow a good development of the pozzolanic energy without nevertheless requiring an excessive amount of mixing water susceptible in weakening the mechanical resistance and the compactness."

And in the study "Effect of Sea Water upon Concrete and Mortar" forming Chapter XVI. of the treatise on concrete by Taylor and Thompson, Feret writes:

"It is conceivable however, that the substances which in the pozzolanas appear as acids are less energetic in their action upon the lime of the cement than the sulphuric acids of sea water, and that therefore, in the end they will be displaced by the latter with the consequent decomposition of the mortar. This method cannot then be looked upon as giving absolute security against deterioration although it has been proved to be useful."

Practically the same conclusion was reached at the Fifteenth International Congress of Navigation. We find in fact in the report by P. Periani on "The Use of Concrete and Reinforced Concrete in Maritime Works":

1. "The best mortar for making concrete to be used in maritime works is that composed of rich lime and pozzolana.

2. "The addition of Portland cement to the above mentioned mortar accelerates the setting without changing its resistance to the action of sea salts.

3. "The use of concrete made with Portland cement and all other kinds of cement having a chemical composition rich in lime is not advisable for the construction of maritime works, especially those which are subject to alternate submersion and emersion by sea water.

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2. "The use of concrete made with Portland cement and all other kinds of cement having a chemical composition other than that set forth as advisable for the construction of marine works, especially those which are subject to alternate submersion and emersion by sea water, is not to be advised."

3. "The addition of Portland cement to the above mentioned mortar accelerates the setting without changing its resistance to the action of sea salts."

4. "The addition of Portland cement to the above mentioned mortar accelerates the setting without changing its resistance to the action of sea salts."

5. "The use of concrete made with Portland cement and all other kinds of cement having a chemical composition other than that set forth as advisable for the construction of marine works, especially those which are subject to alternate submersion and emersion by sea water."

6. "The tendency to retrogression of strength and the tendency to be subjected to various alterations."

"The industrial addition of pozzolanas to cements to the end of increasing their resistance to chemical decompositions must therefore be coordinated at the same time not only to the choice of a material suitably hydraulic actively but also must be subordinated to the determination of the optimum proportions and to a grinding fine enough to allow a good development of the pozzolanic energy without nevertheless requiring an excessive amount of mixing water susceptible in weakening the mechanical resistance and the compactness."

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1. "The best mortar for making concrete to be used in maritime works is that composed of Trion lime and pozzolana."

4. "The mere adding of ground natural pozzolana to the above mentioned cement mortars is not sufficient for preserving concrete against the action of sea salts.

Finally, we find in a technical book of G. Rizzi on hydraulic cementitious materials, a warning against the indiscriminate admixture of pozzolana to Portland in the following words:

"For the integration of Portland cement in mortars or in concrete of lime and pozzolana, it is necessary that the cement be well preserved, does not contain gypsum and be ground to extreme fineness."

C H A P T E R 8.

Other Types of Blended Cements.

Among other types of blended cements are included all cements in which the admixture materially differs from the natural Italian pozzolana, although even these other types of blended cements are frequently referred to as pozzolanic cements.

It is customary to attribute to all blended cements, including those in which natural pozzolana is used, the virtues of lime-pozzolanas as evidenced by their durability throughout the centuries extending back at least to Roman times. Many of the best authorities contend however that no Portland cement plus pozzolana of any kind can be manufactured which will acquire the durability in the presence of sea water that is attained by a true lime-pozzolana due to very material differences in compound combinations and resistance to chemical reagents.

Even restricting the term pozzolanic cement to the intimate mixing of Portland cement and natural pozzolanic material as we have done in Chapter Seven, we must not lose sight of the fact that these true pozzolanic cements are not identical with the old Roman pozzolana-lime mortars. Much less, therefore, are any other types of blended cements, using as admixture substances, differing radically from the natural pozzolanas, entitled to automatically claim the attributes of the old Roman pozzolanic cementitious materials, without additional proof of similarity and for the sake of clearness of understanding and accuracy they should not be called pozzolanic cements at all. The term "Blended Cement" is more fitting and they are therefore hereinafter referred to by that name.

The impracticability of obtaining natural pozzolanas in all cases and the belief that the better grades of artificial pozzolanas are the equal of natural pozzolana has led to the development of blended cements.

Henri Le Chatelier in his study "La Tenue des Ciments a la Mer" (The Behavior of Cement in Sea Water) states:

> "The addition of pozzolanic materials, particularly of calcined clay and of trass of good quality confers to all hydraulic products a great supplement of chemical resistance. By fixing the lime in insoluble combinations, this substance avoids its elimination through the fusion and the correlative porosity of mortars."

PART B.

Other Types of Blended Cements.

Among other types of blended cements are included all cements in which admixture materially differentiation natural Italian pozzolans, although even these other types of blended cements are frequently referred to as pozzolanic cements.

It is customary to apply the term blended cements including those in which natural pozzolans be used, the virtues of the pozzolanas as evidenced by their durability centuries exhibiting back even to Roman times. Many of the best authorities contend however that Portland cement plus pozzolan of any kind can be manufactured which will acquire the durability in the presence of sea water that exhibited by a true lime-pozzolana due to very material differences in compound combinations and resistance to chemical reagents.

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Henri le Chatelier in his study via Terre des Turpenes e la Mer, (The Formation of Cement in Sea Water) stated:

"The addition of pozzolanic materials, particularly of calcined clay and of trass of good quality conveys to all hydraulic mortars a great augment of chemical resistance. By mixing the lime in theolyte combinations, pozzolanic cements are given the same durability of mortars."

Since Le Chatelier wrote this thirty years ago, the idea that siliceous admixtures could fix the lime liberated by the hydrolysis of the silicates in stable chemical combinations has become general. So, it is not uncommon to find in the most recent literature dealing with the subject of siliceous additions statements like the following:

> "Finely divided silica is capable of combining chemically with the lime at a rate which depends upon the curing temperature and upon the condition of the silica."

Granting for the time being, that these statements can be substantiated and that there is proof of combinations having taken place between lime and siliceous materials under the ordinary conditions of temperature which characterize the process of hydration of Portland cement, let us inquire the probable nature of the reactions which take place when this additional element is introduced into the hydrated Portland.

First as to physical resistance, we are interested in knowing whether the addition increases or decreases the tensile and compressive strength.

If the siliceous admixture has hydraulic properties of its own, equal to a good grade of natural Italian pozzolana, then it follows that owing to the increase of hydration, higher ultimate strength can be anticipated. With a siliceous material such as a pure silica sand for instance, which is completely inert from the hydraulic standpoint, there is no ground upon which to base the assumption that its addition will automatically bring additional strength; whereas if instead of the inert silica we use a good natural pozzolana, the free lime liberated from the hydrolysis of the silicates activates the pozzolana, setting up a series of chemical reactions which bring about the formation of cementitious material.

In the most recent book on "The Technology of Portland Cement" which has received most favorable comment from cement experts (see T. T. Salerno "The Technology of Portland Cement", reviewed in Cement and Cement Manufacture, September 1932) we find the following:

> "If Portland cement is ground with inert sand in proportions up to 50% of the original clinker, a product results which has mechanical qualities which can be compared to the qualities of the original Portland. The results which are obtained are in true relationship with the fineness and the homogenity reached in the process of grinding. The re-

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sistance offered from specimens of cement paste is often superior with these mixtures to that of Portland without admixture."

If increase of physical resistance is to be expected with any type of inert sand, it is reasonable to believe that the same or even greater increase is to be expected from the addition of siliceous admixtures slightly pozzolanic and containing a large part of soluble silica held by common consent to be the active part of the siliceous admixture. R. Zollinger in "Cement" for 1933, states:

"The addition of chemically active silica, previously only used from the point of view of protection against acids is also destined to solve the problem of the attainment of greater ultimate strength since by this means the free lime can be brought into combination with silica. At the present, the only objection is the combination of free lime as mono-calcium silicate. Future work must attempt to produce di-calcium silicate in the cement by combination of the free lime and active silica with the object of improving the resistance to acids and accelerating the attainment of ultimate strength. Success in this direction - towards which trass cement is perhaps the first step - would be of great interest to the cement industry and would bring lime to a position of importance once more. It would possibly revolutionize the present conception of cement, replacing modern cement by a composition of lime containing the highest possible content of highly active silica and ultimate strength of such lime-silica mortars might even exceed that of the best present day cements."

Authorities therefore, seem agreed that increased strength in fact has been proven to take place whenever we add a siliceous admixture to Portland cement. What has not been proved however, is that mono-calcium silicate has been formed, such as all are agreed is formed by the combination of chemically soluble silica and liberated lime. On the other hand, Monath and Lorenz contend that combinations of lime with silica (be it soluble or insoluble) do not take place below a temperature of 700°C. and Dr. Hans Kuhl in his "Systematic Calculation of the distribution of lime" (See: Cement Chemistry in Theory and Practice by Dr. Hans Kuhl, page 13) places the first formation of calcium silicate ($CaO.SiO_2$) at 800°C. And in Chapter 14 of the same work he says:

"We have already seen that at 800°C. only mono-calcium aluminate and mono-calcium silicate are present. The latter begins to change into di-calcium silicate at 900°C. and this reaction continues as the temperature increases."

And alfred B. Searle in his book on the Chemistry of Clay says:

"Calcium silicates may, according to Cobb, be formed at as low a temperature as 800°C. if they are in intimate contact, the action taking place below the melting point of the eutectic without any signs of fusion.

"The formation of mono-calcium silicate remains therefore, at present a pious hope under the conditions of temperature and pressure of the ordinary hydration process. Furthermore, as P. Periani says in his most exhaustive report to the Fifteenth International Congress of Navigation on "The Use of Concrete and Reinforced Concrete in Maritime Works": "There is no ground whatever on which to base the belief that the liberation of lime and its combination with silica are phenomena which can take place at the same time. Furthermore, mono-calcium silicate is an hydraulically inert compound which cannot add anything at all to the strength deriving from the hydration of the other two calcium silicates....."

"We incline to believe rather that the silica remains in a colloidal, gelatinous state around the grains of free lime, protecting them from further hydration and consequently from possible dissolution. As a matter of fact the opening of old mortars has proved the existence of grains of lime still unhydrated after many years."

Summing up, we are left with the knowledge that an admixture of siliceous material may bring about an increase in strength without knowing exactly to what factor this increase of physical resistance is due. This beneficial result is apt to make us lose sight of the fact that the main reason of being of blended cements is fundamentally the same as that of pozzolanic cement, that is, they are born from the need of providing greater chemical resistance.

Such being the case, the question arises, "Does this increase of physical resistance bring along with it a corres-

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Such being the case, the question arises, "Does this increase of physical resistance bring along with it a corres-

ponding increase of chemical resistance?" A satisfactory answer to this question can only be secured through durability tests in all types of aggressive waters.

To repeat what has been previously stated, there are, according to leading authorities on the subject, four fundamental points to be satisfied before a cementitious material can be said to be chemically resistant to a high degree:

(a) The cement must have an index of chemical resistance equal or larger than one.

(b) The cement must be totally free of the presence of binary compounds of calcium aluminates of highly basic nature.

(c) The lime liberated through the hydrolysis of the calcium silicates must give rise to further hydration during which additional compounds are formed.

(d) The superficial stratum of a mortar or concrete must be of an essentially acid nature and possess those characteristics of chemical resistance described in the studies of F. Ferrari.

We have seen in the previous chapter that Portland cements mixed with natural pozzolana apparently fulfill three of these four conditions; that is, they possess an index of chemical resistance equal or greater than one (1); they present during the process of hydration the phenomena of a group of reactions taking place between the liberated lime and the pozzolana, giving birth to additional hydraulic compounds; and finally, they give assurance of the formation of superficial stratum highly acid in character and chemically resistant. But unfortunately they give no assurance of the elimination of the deleterious calcium aluminates of highly basic nature formed in the Portland element whenever the original clinker contains alumina. Also it is contended that the lime activating the pozzolana element may disappear in time, thus weakening the binding of Portland and pozzolana compounds until such a time that the transformation of the calcium silicate of alumina of the pozzolana element into hydrated silicate of alumina, devoid of lime, had been completed.

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Nevertheless even with such deficiencies the natural pozzolana Portland blended cements appear in theory at least to other types of blended cements.

Beginning with the first requisite we should recall that Vicat, in establishing the ratio

$$\frac{SiO_2 + Al_2O_3}{CaO} = 1$$

did not mean that to the silica quantity entering into such a relation we can add the silica of the admixtures. What he had in mind was that in any fractional quantity of the cementitious material that ratio should, hold true.

This does not appear to be the case when we add siliceous admixtures to the silica of the original clinker, unless these admixtures are clinkered in the manufacturing process of the cement.

Vicat tried to lower the basicity of Portland by changing the highly basic calcium silicates and aluminates rather than by changing the total quantity of silica and alumina. In other words, he tried modifying the compounds composition rather than modifying the oxides composition. Silica added to the clinker at the end of the clinkering process, either before or after grinding, cannot be held to rightly enter into a modification of the index of chemical resistance (although the addition before grinding appears to be more effective than after grinding).

Passing to the second item, it is doubtful if the addition of silica, soluble or insoluble, can bring about a transformation of the deleterious tri-calcium aluminate of the Portland element. The objection may be raised that it is not the tri-calcium silicate per se which is to be avoided, but that it is rather the formation of the tetra-calcium aluminate hydrate formed during the process of hydration from the tri-calcium aluminate and water in presence of lime that we must avoid.

It is claimed, that if it is true that the siliceous admixture fixes the free lime, there should be no possibility of the formation of tetra-calcium aluminate hydrate, and therefore, of that calcium sulfo-aluminate of highly expansive nature stated by Lafuma to be the greatest agent of deterioration of cements in waters containing sulfates. The question hinges therefore, again upon the point whether the siliceous admixture fixes the free lime or not, and further if it fixes it with a rapidity such as to prevent the formation of hydrate tetra-calcium aluminate. This is connected with the fulfillment of the third requisite - that is, the development of additional hydraulic compounds through the reaction of the liberated lime upon the admixture.

In this regard all we know for certain is:

(a) There is no formation of 100% hydraulic compounds for substances not pozzolanic.

(b) Only silica gel appears up to the present to be able to combine with lime, giving rise to the formation of a gelatinous substance which presents nevertheless no characteristic of a true chemical compound.

(c) While mono-calcium silicate is not attacked, the formation of gelatinous silica-lime is attacked by acids.

Both the second and third prerequisites are thus not satisfied and regarding the fourth, that is the presence of an acid crust at the surface, this crust can derive only from the presence of the acid substance of the cementitious material.

We are left thus without any assurance that apart from an increase of physical resistance there may be a permanent increase of chemical resistance. Although the same held true of natural pozzolanic cement, there still exists a difference between natural pozzolana cements and other blended cements, which is of great importance inasmuch as it has to do with those phenomena of hydration which in the last analysis are the main elements responsible for hydraulic cementitious properties. Perhaps the best explanation of the difference between natural pozzolanic cement and other blended cements is given by Dr. C. Vittori in his article "Portland Corretti e Cementi Pozzolanici Razionali" (Modified Portland and Rational Pozzolanic Cements) published in "L'Industria Italiana del Cemento" December, 1932.

> "It is evident", he says, "that if pozzolanic cements should be considered according to the criterion of a modified Portland, that is, if the phenomena of hardening was dependent entirely upon the constituent clinker the addition of pozzolana in large proportions should be condemned because only a small part of it would be hydraulically utilized through the fixing of the free lime liberated from the hydrolysis of the calcium silicates, while the largest part of it would remain practically inert.

"But in pozzolanic cements not only that part of pozzolana soluble in acids and in alkalis is hydraulically active, but the whole mass of a pozzolanic material takes part in the reactions and undergoes a transformation in contact with the liberated lime.

"The rapid formation of gels constitutes one of the main characteristics of the hardening of pozzolanic cements. These plastic gels uniformly distributed throughout the whole mass, weld together the heterogeneous elements of the system, conferring to the hardened cement a particular morphologic configuration from which are derived those physical-chemical characteristics which differentiate pozzolanic cement from Portland cement.

"In pozzolanic cements, the hydration takes place in the presence of large quantities of pozzolana, and this pozzolanic condition alters the whole character of the physical-chemical transformations taking place during the hardening of Portland or modified Portland like high silica cements. The grains of clinker which have not undergone hydrolysis during the first stage of the hardening process are in a short time surrounded by the pozzolanic gels. These pozzolanic gels begin their drying through the action of internal tensions, on account of their affinity for water shown by the grains of clinker not yet hydrated. In a second time, the gels fix additional lime and liberate water, drying progressively until complete hardeming.

"The process of hydration and crystallization takes place and develops therefore, in a different way from what happens in Portland clinker, be it standard, modified or even mixed with additions hydraulically inert."

All that we have said above and all that we have reported from studies of experts on the subject have not been corroborated by any actual tests which have come to our attention. These tests could well be included in a research program designed to determine the:

(a) Hydraulic value of different natural pozzolana.

(b) Hydraulic value of different artificial pozzolana.

(c) Hydraulic value of different siliceous materials.

(d) Strength of lime-natural pozzolana mortars.

(e) Strength of lime-artificial pozzolana mortars.

(f) Strength of lime-siliceous material mortars.

(g) Chemical resistance of lime-natural pozzolana mortar.

(h) Chemical resistance of lime-artificial pozzolana mortars.

(i) Chemical resistance of lime-siliceous material mortars.

(j) Strength of Portland cement-natural pozzolana mortars.

(k) Strength of Portland cement-artificial pozzolana mortars.

(l) Strength of Portland cement-siliceous admixture mortars.

(m) Strength of Portland cement-natural pozzolana mortars.

(n) Chemical resistance of Portland cement-artificial pozzolana mortars.

(o) Chemical resistance of Portland cement-siliceous admixture mortars.

These tests together with additional information on the characteristics of volume change, heat of hydration, porosity etc., would be of material assistance in arriving at a correct conclusion as to what may be expected from each type of modified Portland cement.

Before closing this chapter, it may be well to devote a little thought to the question of the grinding of siliceous admixtures. If it is true that there is a possibility of formation of an intimate mixture of silica gel and lime, the greater the colloidal nature of the silica of the admixture the greater the formation of an intimate mixture with calcium hydroxide.

Colloidal substances have grains of very small size, therefore no siliceous admixture can be claimed to furnish a colloidal substance unless it is extremely fine. But, on the other hand, apart from this characteristic of fineness, colloidal substances are characterized by an amorphous morphological structure. A crystalline substance no matter how finely ground, will probably not fill the place of an admixture which forms a gel.

Professor C. Mazzetti of the Royal University of Rome, Italy, writing on "The Setting and the Hardening of Portland Cement" in Giornale di Chimica Industriale e Applicata, year 1920, No. V., says:

(a) Chemical resistance of Portland cement-siliceous admixture mortars.

(b) Chemical resistance of Portland cement-natural pozzolans mortars.

(c) Strength of Portland cement-natural pozzolans mortars.

(d) Strength of Portland cement-artificial pozzolans mortars.

(e) Chemical resistance of lime-natural pozzolans mortars.

(f) Strength of lime-natural pozzolans mortars.

(g) Strength of lime-artificial pozzolans mortars.

(h) Variously value of different silicates materials.

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Before closing this chapter, it may be well to devote a little thought to the question of the grinding of siliceous admixtures. If it is true that there is a possibility of formation of an intimate mixture of slaked lime and fine-ground the colloidal nature of the silica of the admixture has created the impression of "an intimate mixture with colloidal hydrous silicates".

Colloidal substances have grains of very small size, therefore no siliceous admixture can be claimed to impart a colloidal substance unless it is extremely fine. But, on the other hand, apart from the character, texture, colloidal substances are characterized by an amorphous-noncrystalline structure. A crystalline substance no matter how finely ground will probably not fill the place of an admixture which forms a gel.

Professor G. Massecti of the University of Pavia, Italy, working on pure beet mud and the hardening of Portland cement in chlorate of Vanadium laboratories, says,

"Substances which are properly called colloids never show a neat crystalline form, because this state presupposes a certain mobility of the substance within the solvent, be it liquid or gaseous."

This means that the selection of the right kind of siliceous admixture is not only linked to a very fine grinding but is also linked to the need of obtaining a material of amorphous morphological structure. Furthermore, it appears that having selected a siliceous admixture in an amorphous state there is one other item to be considered, and that is, the characteristic of the relative solubility of that siliceous substance in the solution of calcium oxide formed during the process of hydration of the Portland element from the hydrolysis of the silicates.

As Professor C.Mazzetti says in the above mentioned study:

"It appears that if a substance is finely ground it can exist and maintain itself in a colloidal state only if it is rigorously insoluble, otherwise, even, if its solubility is negligible it may maintain itself colloid for a little time, but it will end with giving with the liquid, a solution super-saturated from which matter will be deposited in a crystalline state; the crystals being more or less large according to the higher or lower solubility of the material."

From the above it is therefore apparent that the selection of the right kind of admixture is much more important than may seem at a first glance, apart from the difficulty of obtaining particles fine enough to have a safe guarantee that the substance added be of a colloidal nature. We can obtain an idea of the extremely small dimensions of the particles when we read a statement like the following, taken from the same study of professor Mazzetti:

"Between dimensions of the order of 5 ten thousandths of millimeters and those of colloidal matter there is still a notable chasm."

In other words, to hope that the formation of gel of the siliceous admixture will be an actual fact, and therefore, that the fixing of the free lime will be actually brought about, it is necessary to grind the admixture to a fineness of the order of hundredths of microns. It is necessary that the sub-

stance present an amorphous morphological structure and that it present the characteristics of being insoluble in a saturated solution of lime water. Once all these requirements are fulfilled one step in the production of siliceous material blended cements has been accomplished; but whether or not this step will lead in turn to an increased chemical resistance remains to be proven.

C H A P T E R 9.

Pozzolana Blended Cements

vs.

Silica Blended Cements

In this chapter we shall concern ourselves mainly with a comparison between the two extreme types of blended cements, that is, blended cements in which the admixture is a pozzolana hydraulically active throughout and blended cement in which the admixture consists of a siliceous material completely inert.

To more exactly define our terms when we speak of a material hydraulically active throughout, we mean a material which placed in contact with slaked lime gives origin to a series of chemical reactions, the outcome of these reactions being a complete transformation of the original physical and chemical characteristics of that material.

Contrarily, when we speak of a material hydraulically inert, we mean a material which placed in contact with slaked like gives rise to the formation of a mortar which does not set or harden under water, and which presents the characteristics of maintaining unaltered the physical and chemical properties of the constituent elements.

We are fully aware of the fact that there probably is no such thing as a pozzolana 100% hydraulically active or a siliceous material completely inert. Even the best natural Italian pozzolanas contain a large percentage of inert matter, roughly corresponding to its insoluble part. We say roughly because there is apparently no direct relationship between the hydraulic quality of a pozzolana and its solubility in a certain acid or alkali, and therefore the insoluble part is not necessarily a safe indication of the total amount of the inert part, and may very often lead to erroneous conclusions. (See Chapter V., Page 88 - 89).

Assuming however for the sake of comparison that the pozzolana added is 100% hydraulically active we have as one term of comparison, a material which will all be transformed by the lime liberated during the hydration of the Portland element into a cementitious mass. And assuming, also for the sake

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of a more forceful comparison, that the siliceous material added is 100% hydraulically inert, we have as another term of comparison a material which will remain entirely unaffected by the lime liberated during the hydration of the Portland element.

Let us now consider the successive phases of the process of hydration of a Portland cement.

According to Vittori:

"The first effect of water upon the constituents of the clinker is a decomposition of the high lime compound with subsequent liberation of lime. When the Ca(OH)2 dissolved reaches a certain proportion, the hydrated calcium aluminate becomes stable, while the silicates do not reach equilibrium even when the water is still richer in calcium hydroxide. These silicates keep on furnishing lime to the water of solution in which they crystallize until such a time as the hydraulic compounds of the clinker are completely hydrolyzed. It thus results that the cement during the time of its hydration cannot be considered as a substance in chemical equilibrium especially if it finds itself in presence of a sufficient quantity of water." (See "Progress of the Industry of Hydraulic Binders" by Dr. C. Vittori, Page 14.)

While this process of liberation of lime is under way, the reaction of lime with us see what happens in the two types of blended cements considered, and also for the sake of a more comparative study, us see what happens in a third type, in which the admixture ists of silica gel derived from the action of hydrochloric upon sodium silicate (water glass).

In the case of pozzolana blended cements, as soon as iberation of lime is under way, the reaction of lime with olana begins to take place, this reaction consisting of eration of the original structure of the compounds present into hydrated forms generally and transformation of the three phenomena, liberation of calcium hydroxide into calcium pozzolana with transformation the calcium hydroxide with pozzolana ner in lime content. From a certain time on, during ess of hydration of the Portland element is practically, transformation of the calcium hydroxide with pozzolana and reaction of the Portland element is practically at the same time, poraneous. Although they take place at the same time, a different speed of reaction, so it happens that when the hydration of the liberated lime plete the series of reactions of the liberated lime ime is still under way. (See statements of P. is report to the Fifteenth International Congress in the difference of phases existing between the lib- and the pozzolanic reaction and statements of G. Gallo upon the length of time taken

pozzolana mortar to reach its definitive state of equilibrium).

The product of a cementitious material is due therefore in pozzolanic cements to a twofold process; 1. The cementing action brought about by the hydration of the calcium compounds present in the original clinker, and, 2. The cementing action brought about by the reaction of the liberated lime upon the pozzolana.

We will thus have at each particular stage of the cementing process of pozzolanic cements a complex of conditions of somewhat the following order:

First stage, hydration of the calcium silicates and aluminates of the Portland element, with subsequent liberation of lime; second stage, similar to the first, but in addition, lime begins to react upon pozzolana; third stage, a state of equilibrium of the solution silicates - lime water in presence of pozzolana has been finally reached, owing to which no further hydration of the silicates takes place; fourth stage, the lime liberated is partly continuing its reaction with pozzolana and partly crystallizing as free calcium hydrate during the transformation of the colloidal formation of the hydrate mass into a crystalline structure; fifth stage, no free calcium hydrate is present, having been all used in the reaction with pozzolana; sixth stage, (for pozzolanic cements immersed in highly ionized waters only) the lime of combination of the pozzolanic compounds is being dissolved again, these compounds transforming themselves into hydrated combinations deprived of lime.

Provided therefore that enough pozzolana is added, that enough time has elapsed and that the pozzolanic cement is not immersed in highly ionized water, the ultimate stage of the hydration process guarantees a complete fixing of the liberated lime in stable chemical compounds, guarantees also an intimate binding of the Portland and the pozzolanic elements, and a complete transformation of the pozzolanic substance into cementitious material. Regarding the quantity of pozzolana to be added to a certain quantity of Portland we must recall that "The quantities of lime that various pozzolanas can fix and the velocity with which the reaction takes place depend in general upon the quality of the pozzolana and is notably superior for the activated pozzolana (that is, pozzolana subjected to thermic treatment) and, always speaking of good pozzolanas or pozzolanas treated thermically, it is possible to reach values of the order of 50 to 60 grams of CaO for 100 grams of pozzolana." (See "Modified Portland and Rational Pozzolanic Cements" by Dr. C. Vittori, published in "L'Industria Italiana del Cemento", December 12, 1933).

Passing now to blended cements in which the admixture used is silica gel, silica gel like pozzolana removes the possibility of a thorough hydrolysis of the Portland element by keep-

possible means to reach the desired extra of equilibrium.

The process of a cementitious material is due therefore to pozzolanic cements of a hybrid process: 1. The cementing action brought about by the hydration of the setting compounds present in the original clinker, and 2. The cementing action brought about by the reaction of the liberated lime upon the pozzolana.

The two steps have at each particular stage of the cementing process of pozzolanic cements a compliment of combining to some other following order:

First stage, liberation of the calcium silicates and aluminates of the Portland element, with subsequent liberation of time; second stage, similar to the first, but in addition time begins to react upon pozzolana; third stage, a phase of equilibrium of the solution silicates - lime water in presence of pozzolana has been finally reached, owing to which no further hydration of the silicates takes place; fourth stage, the lime liberated is partly combining its reaction with pozzolana and partly crystallizing as free calcium hydrate during the transformation of the colloidal solution of the hydrate mass into a crystalline structure; fifth stage, no free calcium hydrate is present, having been all used in the reaction with pozzolana; sixth stage, (for pozzolanic cements limestone in finely ionized water only) the lime or combination of the pozzolanic compounds is being dissolved again, these compounds transforming themselves into hydrated combinations deprived of lime.

Provided therefore that enough pozzolana is added, the enough time has elapsed and that the pozzolano cement is not immersed in highly ionized water, the fifth stage of the hydration process guarantees a complete fixing of the lime in stable chemical compounds, guarantees also an increase of the tensile strength and the possible elements, and a complete transformation of the pozzolanic substance into cementitious materials. Regarding the quality of pozzolana to be added to a certain quality of Portland we must recall that the various kinds of lime that pozzolana can in and the velocity with which the reaction takes place depend in general upon the quality of the pozzolana and is notably superior for the activated pozzolana (that is, pozzolana subjected to thermic treatment) and, always, keeping of good pozzolana or pozzolanas treated thermically, it is possible to reach values of the order of 50 to 60 grams of CaO for 100 grams of pozzolana." (See "Publicazioni sui cementi Pozzolanici Comunali" by Dr. C. Viola, published in "Ricerche" - Istituto del Cemento, December 15, 1939).

Regarding now to Dietzen comments in which the admixture used is silica gel, stated that pozzolana removes the deposition of a through hydrolysis of the Portland element by keep-

ing the concentration of lime in the solution below that necessary to present continued hydrolysis. (See: "Studies on the Action of Sulfates on Portland Cement" by T. Thorvaldson, V. A. Vigfusson, and D. Wolochow in Canadian Journal of Research, 1929, Volume 1, Pages 385-389). This is due to the property that silica gel evinces of fixing the free lime by forming with it a gelatinous product in which particles of lime have no further freedom of ulterior reactions.

Furthermore, by removing the lime as it is liberated by the scission of the high lime compounds, the added silica gel seems to remove the possibility of formation of the deleterious tetra-calcium aluminate hydrate formed whenever the tri-calcium aluminate present in Portland cement is hydrated in presence of free lime. (See H. Lafuma, "Recherches sur les Aluminates de Calcium", Paris, 1932).

Now, as we have said in Chapter 3, the possibility of formation in Portland cement mortars immersed in sulfate solutions of a greatly expansive calcium sulfate of alumina, crystallizing with a high molecular content of water, is dependent from the previous formation of tetra-calcium aluminate hydrate. Once the possibility of formation of that compound is removed the resistance to sulfates necessarily greatly increases. We find in fact a statement in the above mentioned study of Thorvaldson, Vigfusson and Wolochow to the effect:

> "The most striking effect of the presence of a sufficient quantity of silica gel in a Portland cement mortar is to render it very resistant to the action of solutions of sodium and calcium sulfates."

Silica gel therefore, seems to fulfill in part the necessary requisites of a modified Portland chemically resistant. But we must not overlook the fact that silica gel is not a natural material, and that it is at present a rather costly substance to obtain, and that consequently, it does not represent the right type of admixture for a commercially successful product of a blended cement chemically resistant. Passing then from the consideration of silica gel to the consideration of a natural siliceous material admixture we must reckon that the silica added besides being hydraulically inert - as assumed at the start - may present either an amorphous or a crystalline morphological structure, may be also either fully soluble or partly soluble in hydrochloric acids, and may be finally either ground to the dimensions of colloidal matter or ground to the order of ordinary cement fineness. At this point an objection may be raised regarding the apparent discrepancy existing between the admission of a certain percentage of soluble silica in the siliceous ad-

mixture and the possibility that the material may be hydraulically inert. The answer to this objection is found in the comprehensive study of Professor Gallo upon the microscopic study of pozzolana, quoted in the previous chapter. From this study it appears that the amount of soluble silica present is in no determinate relationship to the hydraulic quality of a pozzolanic material because this hydraulic quality rests mostly with the granulous amorphous substance which it contains, and the amorphous part of a pozzolana, that is, its active part, remains unaffected by hydrochloric acid, and whatever soluble silica it may contain, this soluble silica has very little to do with the hydraulic and cementitious qualities of the pozzolana (See Chapter 5, Pages 88 and 89). Having thus removed the apparent incongruity in the definition of the characteristic properties of the siliceous admixture, let us examine what their effect will be in the series of phenomena constituting the hydration process of the Portland clinker blended with such a type of admixture.

Repeating once more the progression of the various stages of this process we find:

(a) The first effect of the reaction with water is the scission of the calcium compounds of the Portland element with liberation of free lime.

(b) The next stage is characterized by the absence or the presence of a reaction of the free lime upon the admixture.

We have seen that in the case of a natural pozzolana admixture this reaction brought about: First, a complete transformation of the original physical and chemical properties of the pozzolanic material; Second, the integration of the lime and pozzolana elements into one cementitious mass; Third, the binding of this additional cementitious mass with the original one due to the Portland element.

We have seen also that as a consequence of this reaction of lime with pozzolana there is to be expected a continuous increase of physical resistance in time, and also an increase of chemical resistance provided this type of blended cement is not placed in contact with highly ionized waters.

We have seen that in the case of a silica gel admixture the reaction with lime brought about the formation of a gelatinous mass in which the grains of lime were surrounded by the colloidal particles of silica gel, without bringing about however, a change of the physical and chemical properties of the silica gel.

We have seen also that in the case of a silica gel admixture there is to be expected quite an increase of chemical resistance although practically no sensible increase of physical resistance.

Finally, we have seen that in the case of hydraulically inert siliceous admixture the lime liberated does not give origin to any series of reactions with the admixture and the cementing action remains simply a result of the hydration of the compounds contained in the original clinker. But assuming that the silica added is in a fully soluble amorphous and colloidal state there is good ground to believe that there is to be expected, during the hydration process, that a colloidal formation will take place in which the grains of free lime will be enveloped by the particles of silica in a way somewhat similar to the silica gel admixture. The resemblance however, is only superficial because the mechanical tensions arising within the cementitious mass during the hydration of the Portland element lead ultimately to a disruption of this colloidal formation when in time all the mass is gradually transformed (and finds itself in a final state of equilibrium) into a crystalline structure. Furthermore, the supposition that the silica added is fully soluble, that is, chemically active throughout, presents an amorphous morphological structure and is ground to dimensions of colloidal matter, are assumptions which find very small probability of actual realization. The fact that colloidal matter has particles of dimensions averaging hundredths of a micron makes us realize how small is the chance to bring about those ideal conditions. Finally, we must not forget that:

> "In the case of a natural pozzolana it is not only the part soluble in acids and alkalis which is hydraulically active, but it is the whole mass of the pozzolanic substance which takes part in the reaction and is transformed under the action of the lime." (See: "Modified Portland etc....." by Dr. C. Vittori).

Thus it happens that passing from an inert insoluble crystalline and coarse siliceous material to the good hydraulic natural pozzolana there is an abyss which can hardly be bridged by intimate mixtures of natural materials which have not been produced under the conditions which made possible the physical and chemical composition of natural Italian pozzolanas.

Apart from the fundamental difference derived from the way in which the added material reacts with liberated lime there are other points which, as we have said in Chapter 4, have to be considered for the production of a chemically resistant cement. Beginning with the need of providing a suitable resistant film at the surface of a mortar or concrete, it is well to recall once more the important part played by the superficial crust.

According to Le Chatelier, Ferrari and others, the extent and the amount of chemical disintegration is partly dependent upon the formation of this crust. According to them there appears to be a decided difference between the types of superficial crust formed with Portland pozzolana cements and the crust with Portland silica cements. In the case of Portland pozzolana mortars the superficial crust is, on the authority of Dr. C. Vittori, of an acid character produced by the development of the gels of the active elements of the pozzolana, whereas, in the case of Portland silica cements this crust is formed by the lime that has not been restrained by the siliceous admixture from continuing its process of displacement from the interior of the mass to the exterior, and which deposits itself at the surface forming a thin film in a continuous state of transformation. This accumulation of lime is highly unstable owing to the continuous reaction taking place on both its inner and outer surface and also owing to the possibility of absorbing carbonic anhydride and therefore becoming soluble.

Besides this difference in characteristics of the superficial crust we must consider other equally important secondary factors. Amont these first place must be assigned to the fulfillment of the relationship of Vicat for the index of chemical resistance. When Vicat set forth the importance of such a relationship he had in mind principally an alteration of the percentage composition of the various elements of the cementing part alone. He never meant that still keeping unaltered the excessive percentage of basic elements of the cementing substance, an increase of the index of chemical resistance could be achieved by simply adding an extraneous substance of acid nature which was not part of the cementing material.

On the other hand, there is ground for believing that the natural pozzolana addition can be considered as an integral part of the cement itself because of the fact that pozzolana apparently joins with the liberated lime in an auxiliary cementing process. The inert added silica however, cannot be considered as contributing to the hydraulic cementing properties of the original Portland element, and must therefore be considered simply as an admixture which cannot reduce its high basicity. From this we may deduce that while the relationship of Vicat expressing the value of the index of chemical resistance may be fulfilled by Portland-pozzolana cements, it is not fulfilled by Portland-silica cements.

Accessory properties of cements such as heat of hydration, amount of water to produce a certain value, etc., are also quite important elements to be considered. Portland-pozzolana cements present a minimum coefficient of thermic dilation. This is probably due to the fact that the development of heat brought about by the hydration of the Portland element is offset by the absorption of heat from the reaction of the lime or the

according to the Portland Cement Association, the cement and the amount of chemical disturbance is partly dependent upon the duration of the grind. According to these experts to be a decided difference between the types of Portland cement mixed with pozzolana cements and the cement with Portland silica cements. In the case of Portland pozzolana mortars the superficial crust is on the authority of U. S. Vibert, or an acid character produced by the development of the gels of the active elements of the pozzolana, whereas, in the case of Portland silica elements this crust is formed by the lime that has not been neutralized by the silicosis admixture from continuing its process of displacement from the interior of the mass to the exterior, and which deposits itself as the surface forming a film like a continuous state of crystallization. This accumulation of lime is highly unstable owing to the continuous reaction taking place with the carbonic anhydride and therefore becoming soluble.

Besides this difference in characteristics of the pozzolanic cement we must consider other equally important secondary factors. Among these first place must be assigned to the fulfillment of the requirements of water for the index of chemical resistance. When just enough the importance of such relationship be had in mind primarily an alteration of the percentage composition of the various elements of the cementing part alone. It never means that still leaving unaltered the excessive percentage of basic elements of the cementitious substance an increase of the index of chemical resistance could be obtained by simply adding an excessive surcharge of said nature which was not part of the cementing material.

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clinker with the pozzolana. On the other hand the heat of hydration of a pozzolana silica blended cement may not be less and is often greater than the heat of hydration of straight Portland. While the Portland-pozzolana blended cements require no greater amount of water for hydration than is required by standard Portland, Portland-silica blended cements on the other hand appear to require a larger volume of water with a consequent possible lowering of density and strength.

Summing up therefore, the conclusions of the authorities quoted we reach the following comparison between the essential characteristics of a true Portland-pozzolana cement and the ordinary Portland-silica cement:

Portland-Pozzolana	Portland-Silica
1. LIBERATION OF LIME	
The lime liberated is united chemically to the pozzolana admixture.	The lime liberated is united mechanically to the silica admixture.
2. REACTION OF LIME	
The reaction consists of a complete transformation of the physical and chemical properties of the pozzolana substance.	The reaction consists of superficial adhesion of the particles of silica to the grains of calcium hydrate.
3. RESULTING EFFECTS OF THE LIME REACTION	
An auxiliary hydraulic cementing mass.	No hydraulic cementing material is formed.
4. INCREASE OF PHYSICAL RESISTANCE	
The lime pozzolana reaction continues for a long period of time bringing about an increasing physical resistance.	The lime-silica reaction ends with the ending of the hydrolysis of the calcium silicates of the Portland element. No increase of physical resistance is to be expected.
5. HYDRATION OF THE PORTLAND ELEMENT	
Hydration is carried only up to the time when the lime in solution has reached a concentration compatible with the presence of pozzolana.	Hydration goes on indefinitely until the silicates have been transformed to plain silica thereby losing all of the lime.

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Hydration is carried only up to the time when the lime in solution has reached a concentration compatible with the presence of pozzolana.	Hydration goes on indefinitely until the silicates have been transformed to plain silica thereby losing all of the lime.

6. CHARACTER OF THE SUPERFICIAL CRUST

The superficial crust is of an acid nature and is derived from the formation of gels of the pozzolana element.	The superficial crust is of a basic nature and is formed, as in Portland cements, of free lime which has found its way from the interior of the mass to the surface.

7. INDEX OF CHEMICAL RESISTANCE

This compound is present whenever the original clinker contained tri-calcium aluminate unless the pozzolana has been so activated by thermic treatment or otherwise as to combine with liberated lime at the rate of formation of tetra-calcium aluminate hydrate in the original Portland element.	This compound is always present, whatever amount of silica is added to the original Portland clinker, if this clinker contains any substantial amount of tri-calcium aluminate.

8. CHEMICAL RESISTANCE

Is greatly increased except when this type of blended cement is immersed in a highly ionized water.	There is no assurance that the mechanical combination of lime-silica will stand the action of chemically aggressive reagents.

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C H A P T E R 10.

The Chemistry and Manufacture of a Chemically Resistant Cement

The discussion presented in this Chapter is based on the assumption that the production of a cement perfectly resistant to weathering action of any kind, remains an unsolved problem and that there is no positive proof that a pozzolana-Portland cement or any other types of blended cement possesses the desired quality.

Many eminent authorities contend that natural pozzolana blended cements do not bring about the elimination of the high lime calcium aluminates of the Portland element nor do they give any guarantee of permanency to the combination of the Portland and the pozzolanic elements when the blended cement is in contact with highly ionized waters. On the other hand, the blending of Portland with a natural pozzolana apparently increases hydration with corresponding increased physical resistance which physical resistance continues during the entire period of the lime-pozzolana reaction. In theory a cement of this type has a low heat of hydration, probably on account of the utilization of the heat developed by the Portland element in the lime-pozzolana reaction. It is claimed to be a cementing material in which no elements are found in a free state but are instead combined in well defined chemical compounds.

It is further contended that Portland inert silica blended cements in addition to the deficiencies of natural pozzolana blended cements possess other deficiencies as important and perhaps even more deleterious. These deficiencies are defined as:

(a) Lack of definite chemical combinations of the free lime with the silica admixture.

(b) Lack of increased hydration.

(c) Lack of additional chemical compounds besides those due to the original Portland clinker.

(d) No assurance of complete hydrolysis of the calcium silicates of the Portland element.

(e) Non-fulfillment of the Vicat requisite for the indes of chemical resistance.

(f) Consequent formation of a basic crust of lime at the surface.

(g) No reduction of heat of hydration, and finally,

(h) Need of an increased water cement ratio for normal consistency.

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(d) No assurance of complete hydrolysis of the calcium silicates of the Portland element.

(e) Non-fulfillment of the Vicat requisite for the index of chemical resistance.

(f) Consequent formation of a basic crust of lime at the surface.

(g) No reduction of heat of hydration, and finally,

(h) Need of an increased water cement ratio for normal consistency.

Other types of blended cements range in quality between the completely inert silica blended cements and the natural pozzolana blended cements.

Without admitting that all of the above conclusions are sound, let us nevertheless consider the possibility of manufacturing a modified Portland cement through the addition of an admixture to the original clinker in a different manner from that followed in the production of the type of blended cements so far discussed with the aim of producing a material with the physical characteristics of a true Portland cement and at the same time the durable characteristics of a true pozzolana-lime mortar.

Inasmuch as the qualities of the cementitious materials are derived from the presence of certain well defined chemical compounds, the ideal cement should present in its composition compounds which are part of modern standard Portland cements and compounds which are part of natural pozzolana (these compounds to be selected according to their desirability, that is, according to the role which they play in the formation of a material highly resistant both physically and chemically).

The field covered by this new super-cement in the ternary Rankin diagram is a field covering in part the area of standard Portland and extending out of this area toward the region of those calcium silicates of alumina forming the matrix of natural pozzolana.

The problem of developing a chemically resistant cement may thus be in the formation, during the process of clinkering, of chemically resistant compounds ultimately resulting in a greater degree of hydration with continuously increasing physical strength.

One phase of the problem has to do with the possible complete ultimate elimination of the tri-calcium silicate present in ordinary Portland. A second phase consists in the formation of hydraulic compounds like calcium silicates of alumina, low in lime content and of a pozzolanic nature, which with their tendency toward hydration with absorption of lime may add elements of physical strength and chemical resistance lacking in the original Portland clinker.

Having outlined the theoretical composition of this new cement, let us give some thought to the practical problems involved in its manufacture.

Starting with a standard Portland cement clinker of either low or high lime content it is not feasible to modify the composition through some variation of temperatures during the manufacturing process. The final temperature is determined by the necessity of completing the surface reaction plus lime-silica so that no free calcium oxide will be present in the final pro-

Other types of blended cements range in quality between the completely inert silica blended cements and the natural pozzolana blended cements.

Without admitting that all of the above conclusions are sound, let us nevertheless consider the possibility of manufacturing a modified Portland cement through the addition of an admixture to the original clinker in a different manner from that followed in the production of the type of blended cements so far discussed with the aim of producing a material with the physical characteristics of a true Portland cement and at the same time the durable characteristics of a true pozzolana-lime mortar.

Inasmuch as the qualities of the cementitious materials are derived from the presence of certain well defined chemical compounds, the ideal cement should present in its composition compounds which are part of modern standard Portland cements and compounds which are part of natural pozzolana (these compounds to be selected according to their desirability, that is, according to the role which they play in the formation of a material highly resistant both physically and chemically).

The field covered by this new super-cement in the ternary Rankin diagram is a field covering in part the area of standard Portland and extending out of this area toward the region of those calcium silicates of alumina forming the matrix of natural pozzolana.

The problem of developing a chemically resistant cement may thus be in the formation, during the process of clinkering, of chemically resistant compounds ultimately resulting in a greater degree of hydration with continuously increasing physical strength.

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Having outlined the theoretical composition of this new cement, let us give some thought to the practical problems involved in its manufacture.

Starting with a standard Portland cement clinker of either low or high lime content it is not feasible to modify the composition through some variation of temperatures during the manufacturing process. The final temperature is determined by the necessity of completing the surface reaction plus lime-silica so that no free calcium oxide will be present in the final pro-

duct, and the course of the intermediate run of temperatures cannot be varied at will with the present process of manufacture.

Though the role played by temperature is important, of equal if not greater importance, is the addition of some suitable admixture to the original clinker during the manufacturing process. The qualifications of the admixture are determined by some of the conditions that must be fulfilled. These added substances must be such as to modify the character of Portland from basic into acid. This means that inasmuch as the principal acid elements of the cementitious material are silica and alumina and inasmuch as any addition of alumina would bring us into the field of high alumina cements, we are limited to addition of silica. But an addition of silica at the beginning of the clinkering process would simply mean the formation of an increased percentage of di-calcium silicate. On the other hand the addition of silica at the end of the clinkering process and without further heating or other treatment can be considered, for the reasons set forth in the previous chapter, simply as admixture, and therefore assumed as not fulfilling the purpose.

We are left therefore, with the consideration of the addition of silica to the original clinker at an intermediate stage of its clinkering process, a stage at which there is a possibility of the transformation of some of the original compounds in the clinker and the formation of additional compounds of a pozzolanic nature.

Reviewing the temperature ranges between which the various compounds are formed we find that in the range between 750°C. and 850°C. some compounds are formed which are not present in the final standard Portland cement clinker.

The first compound formed whenever the added silica is in presence of additional lime is mono-calcium silicate. This mono-calcium silicate according to the researches of Professor O. Rebuffat, published in Gazzetta Chimica Italiana, Volume 28, combines with the calcium aluminates to form a calcium silicate of alumina low in lime and of high hydraulic qualities. Therefore, through the formation of mono-calcium silicate we eliminate all of the tri-calcium aluminate, most of the tri-calcium silicate and form a ternary compound of calcium silicate of alumina of hydraulic quality presenting also decided affinity for absorption of lime. The next and perhaps most important result is the lowering of the high basicity of standard Portland through the reduction of the original high lime compounds. A possible way of obtaining the above results may be that of adding a certain quantity of highly reactive silica to the clinker during the process of manufacture, after having

duct, and the course of the intermediate run of rotary cutter is varied at will with the manufacturing process.

Though the tools played by temperature is important, of equal if not greater importance, is the addition of some suitable admixture to the original clinker during the manufacturing processes. The qualifications of the admixtures are determined by some of the conditions that must be fulfilled. The added substances must be such as to modify the character of Portland cement into acid. The most usual admixtures as the principal acid elements of the compositions material are silica and alumina and gypsum as any addition of alumina would bring us into the field of high alumina cements. Limits to addition of all these, but an addition of silica, at the beginning of the clinkering process would simply mean the formation of an excessive percentage of di-calcium silicate, on the other hand the addition of silica at the end of the clinkering process and with their burning or other treatment can be obtained, for the reasons set forth in the previous chapter, simply as admixture, and therefore assumed as not fulfilling the purposes.

We are back therefore with the consideration of the addition of silica to the original clinker at an intermediate stage of the clinkering processes, a stage at which there is a possibility of the transformation of some of the original compounds in the clinker and the formation of additional compounds of a pozzolanic nature.

Reviewing the temperature regions between which the various compounds are formed we find that in the cases between 750°C. and 900°C. some compounds are formed which are not present in the final established Portland cement clinker.

The first compound formed whenever the added silica in the presence of added coal lime is mono-calcium silicate, mono-calcium silicate according to the researches of Professor O. Rebuffat, published in Gazzetta Chimica Italiana, Volume 28, combined with the calcium aluminates to form a calcium silicate of a lower lime and higher acidic quality. Therefore, through the creation of mono-calcium silicate all of the tri-calcium aluminate, most of the tri-calcium silicate and form a ternary compound of calcium silicate of lower basicity quality presenting also decided solubility not accepting the next and perhaps most important result is the lowering of the binding capability of Portland cement by the reduction of the original high lime compounds. A possible way of obtaining the above results may be the method of adding a secondary material to the clinker during the process of manufacture, after burning

reached the upper limit temperature and keeping the added silica and the original clinker at a temperature between 700°C. and 850°C. for a period of time long enough to allow the desired reactions to take place between the clinker and the added silica.

The first effect is a partial dissociation of the tri-calcium silicate with subsequent release of calcium oxide and formation of additional di-calcium silicate. The second effect is the reaction of the free lime with the added silica with formation of mono-calcium silicate. In theory, this mono-calcium silicate reacts with the calcium aluminates of the original clinker with formation of a calcium silicate of alumina of a pozzolanic nature. At the end of the reaction we have a material which will react as follows in the presence of water. The initial set will be furnished by the first reaction of the various hydraulic compounds with water although owing to the total absence of calcium aluminate and the reduced quantity of calcium silicate the cement will probably be rather slow setting.

During the process of hardening whatever lime was originally free or is further liberated by hydrolysis of the silicates will be used up in the reaction with the calcium silicate of alumina. At the same time, the hydrolysis of the silicates does not proceed indefinitely and a state of equilibrium will be reached soon after the small amount of tri-calcium silicate is transformed into hydrated di-calcium silicate. No further liberation of lime will thereafter take place than that which has already taken place and which will have reacted with the calcium silicate of alumina. We shall have reached therefore the composition of an ideal cement devoid of tri-calcium aluminate, low in tri-calcium silicate, rich in di-calcium silicate with in addition, mono-calcium silicate, and calcium silicate of alumina; a cement of essentially acid nature presenting greater hydration possibilities than ordinary, greater strength with time, and finally, a cement of high chemical resistance, this resistance being derived from the lack of highly basic compounds and the total absence of calcium aluminates and of free lime.

Having developed the process of manufacture theoretically necessary to bring about the desired result, we find that in the first stage the material is subjected to temperatures up to 1500°C. with production of compounds originating from reactions taking place at these temperatures, and in the second stage the added material is subjected to temperatures much lower (of the order of 750°C. to 850°C.) with production of compounds whose formation takes place only within such a range of temperatures.

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Having developed the process of manufacture theoretically necessary to bring about the desired result, we find that in the first stage the material is subjected to temperatures up to 1500°C. with production of compounds originating from reactions taking place at these temperatures, and in the second stage the added material is subjected to temperatures much lower (of the order of 750°C. to 850°C.) with production of compounds whose formation takes place only within such a range of temperatures.

Next let us devote some thought to the character and the amount of the material to be added in the second stage of manufacture.

In Chapter 5, we stated that one of the characteristics of a good pozzolanic material is its morphological structure which, in the case of a good pozzolana, is in greater part granulous and amorphous. There is reason to believe that crystalline substances are not very well adapted to become a part of that colloidal formation which characterizes the early stage of the process of hydration of Portland, also that the possibilities of reaction of substances presenting themselves in well defined crystalline structure are very slight. We have therefore in these limitations an indication of the type of material suitable for the secondary stage of the manufacturing process. We must next determine the amount to be added. This involves in turn a knowledge of the clinker composition because it involves a knowledge of the amount of lime to be liberated by the calcium silicates. This amount will vary according to conditions, although as a general rule, it can be stated that it must bring about the fulfillment of the requirement of Vicat for the index of chemical resistance, that is, in the final composition of the cementitious material the acid elements must at least balance the basic ones.

One of the main differences between this proposed new type of cement and the pozzolanic or other blended types of cements lies in the way in which the requirement of Vicat is fulfilled.

It is reasonable to conclude that in the new cement the relationship of Vicat is verified along the true lines of Vicat's thought for the quantities of acid and basic elements entering into that relationship are of elements forming integral parts of the original cement compounds.

Therefore, it may be said that the added silica in the new cement plays a role so radically different from that which it plays in other types of blended cements as to justify the assumption that the new cement is an integrally blended cement essentially different from other blended cements like ordinary high silica or pozzolanic cements.

Thus we find that while in an ordinary high silica cement, the compounds in the final product are those already present in the original Portland clinker, in the new cement the compounds in the final product are partly the same and partly different from those present in an ordinary Portland clinker.

In this new cement we are not simply taking care of a certain deficiency of Portland by physical means as in silica blended cements or by chemical means as in natural pozzolana

blended cements, but rather producing as an integral part of the cementitious material and during the clinkering process, chemical compounds which are characteristic and essential elements of a natural pozzolanic substance.

Blended cements represent only a partial solution at best of the problem of chemical resistance, while the new cement through the modification of Portland brought about by:

(a) The change of the ratio of percentages of acid to basic elements.

(b) The splitting of the clinker process into two stages.

(c) Introduction of part of the material to be added at the beginning of the first stage and part at the beginning of the second stage.

(d) The selection of the material to be furnished in the first stage as composed of the basic elements producing an ordinary standard Portland high lime clinker.

(e) The selection of the material to be furnished in the second stage as granulous, amorphous siliceous material, rich in active silica and poor in extraneous substances.

Not only takes care of the fixing in a chemical way of the free lime liberated by the hydrolysis of the calcium silicates but is productive of a material offering:

(a) An index of chemical resistance not smaller than one.

(b) A chemical composition substantially free of binary compounds of calcium and alumina.

(c) A chemical composition of which the tri-calcium silicate is a very small part.

(d) A chemical composition which presents, in addition to tri-calcium silicate and di-calcium silicate, a substantial amount of mono-calcium silicate.

(e) A chemical composition in which are present ternary combinations of calcium, silica and alumina of a pozzolanic nature.

(f) An area in the ternary Rankin diagram which covers partly the field of Portland and lies partly outside of it.

(g) An increased hydration.

(h) A practically total hydraulic activity of the whole cementitious material.

(i) A double cementing process, the auxiliary one taking birth from the reaction of the liberated lime with the calcium silicate of alumina.

(j) The characteristic of progressive hardening and consequently a physical resistance continuously increasing in time.

(k) A formation of a superficial crust devoid of free lime and of essentially basic acid nature.

Such in brief are the characteristics that may be found in the new cement. Further extensive research is necessary to either confirm or disprove the theory advanced. This report is closed with this tentative exposition of a theoretically ideal type of blended cement which may furnish the solution of the problem of chemical resistance.

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A P P E N D I X I.

Plants Manufacturing Pozzolanic Cement in Italy

1. "Societa Calci e Cementi Di Segni, Rome", manufacturing the following types of pozzolanic cement:

	TENSION Kg. per sq. Cm.			COMPRESSION Kg. per sq. Cm.		
(a) Special super-cement.....	*(356) 25	(427) 30	(498) 35	(4270) 300	(5690) 400	(9250) 650
(b) Super-cement type 500.....	(284) 20	(356) 25	(427) 30	(3560) 250	(4980) 350	(7820) 550
(c) Special cement type 425.....	--	(284) 20	(356) 25	---	(3560) 250	(6050) 425
(d) Normal cement type 325.....	--	(256) 18	(313) 22	---	(2560) 180	(4630) 325
(e) White Cement ...	--	(284) 20	(356) 25	---	(3560) 250	(6050) 425
(f) Special cement for maritime Works	--	(256) 18	(313) 22	---	(2560) 180	(4630) 325

*All figures in parenthesis represent pounds per square inch.

2. "Societa Italcementi, Bergamo, manufacturing a pozzolanic cement with high iron Portland clinker, a cement called (Mare) of which the composition has been studied so as to obtain with it the greatest resistance to the action of sea water. And, finally, a white cement very low in iron, manufactured by the same method as Portland but with special provisions for lowering the temperature of clinkering and avoiding any coloring due to small quantities of iron.

APPENDIX 1.

Plants Manufacturing Pozzolanic Cement in Italy

1. "Societa Calci e Cementi di Segni, Roma", manufacturing the following types of pozzolanic cement:

	TENSION Kg. per sq. cm.			COMPRESSION Kg. per sq. cm.		
(a) Special super-cement	*(356) 25	(427) 30	(428) 35	(4270) 300	(5690) 400	(9230) 650
(b) Super-cement type 500	(234) 20	(356) 25	(427) 30	(3560) 250	(4980) 350	(7820) 550
(c) Special cement type 425	--	(234) 20	(356) 25	--	(3560) 250	(4650) 425
(d) Normal cement type 325	--	(256) 18	(313) 22	--	(2560) 180	(4650) 325
(e) White Cement	--	(234) 20	(356) 25	--	(3560) 250	(6650) 425
(f) Special cement for maritime works	--	(256) 18	(313) 22	--	(2560) 180	(4650) 325

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2. "Societa Italcementi, Bergamo, manufacturing a pozzolanic cement with high iron Portland clinker, a cement called (Mare) of which the composition has been studied so as to obtain with it the greatest resistance to the action of sea water. And, finally, a white cement very low in iron, manufactured by the same method as Portland but with special provisions for lowering the temperature of clinkering and avoiding any coloring due to small quantities of iron.

A P P E N D I X 11.

Standard Tests and Specifications for Cementitious Materials Issued by the Italian Government, July 1933

1. Classifications and Definitions:

Cementitious materials are distinguished as:

(a) Limes:

1. Hydraulic lime
2. Lime eminently hydraulic

(b) Cements:

1. Portland cement
2. High alumina cement
3. Slag cement
4. Pozzolanic cement

(c) Cementitious Mixtures:

1. Fast setting
2. Slow setting.

2. Definition of Pozzolanic Cement:

As pozzolanic cement is meant the material obtained through grinding, without addition of inert substances of an intimate and homogeneous mixture of pure clinker of cement and pozzolana, presenting acid reaction. The clinker may also be obtained through the clinkering of limestone and pozzolana.

Whenever pozzolanic cement reaches a compression strength of 600 kg. per square cm. (8534 lbs. per sq. inch) upon normal mortar (1:3) after 28 days of curing, it acquires the qualification of high strength cement.

APPENDIX II

Standard Tests and Specifications for Cementitious Materials Issued by the Italian Government, July 1933

1. Classifications and Definitions

Cementitious materials are distinguished as:

(a) Limes:

1. Hydraulic lime
2. Lime eminently hydraulic

(b) Cements:

1. Portland cement
2. High-alumina cement
3. Slag cement
4. Pozzolanic cement

(c) Cementitious Mixtures:

1. Fast setting
2. Slow setting

2. Definition of Pozzolanic Cement

As pozzolanic cement is meant the material obtained through grinding, without addition of inert substances of an intimate and homogeneous mixture of pure clinker of cement and pozzolana, presenting acid reaction. The clinker may also be obtained through the clinkering of limestone and pozzolana.

Whenever pozzolanic cement reaches a compression strength of 500 kg. per square cm. (8534 lbs. per sq. inch) upon normal mortar (1:3) after 28 days of curing, it acquires the qualification of high strength cement.

3. Minimum Requisites to be Fulfilled by Pozzolana Cement:

Maximum residue on the sieve of 900 open:/cmq.(100 mesh sieve) 2%
" " " " " " 4900 " " (200 " ")15%

Maximum specific gravity - 2.90.

Time of Set:

Initial not less than 1 hour
Final between 6 and 10 hours

Tensile Strength (1:3 mortar)

3 days	- 20 kg./cmq.	(284 lbs./sq. in.)
7 "	- 30 " "	(426 " " ")
28 "	- 35 " "	(498 " " ")

Compressive strength of (1:3 mortar)

3 days	- 250 kg/cmq.	(3560 lbs./sq.in.)
7 "	- 450 " "	(6400 " " ")
28 "	- 600 " "	(8534 " " ")

Pozzolanic cement shall contain a quantity of calcium carbonate not higher than 5%. The pozzolana employed in the manufacture of pozzolanic cements must fulfill all the prescribed prerequisites for pozzolana.

A P P E N D I X 111.

Analysis of a Pozzolana
By Professor O. Rebuffat.

Following are the results of the analysis of a variety of pozzolana of Bacoli.

This pozzolana of a clear gray color, has all the characteristic properties of the good trachytic pozzolanas, was subjected to chemical analysis following the method which had already been used other times for similar research. By sieving through a sieve of 100 openings per square centimeter, the finer pozzolana was separated from the coarser, and from each one of these parts I made the quantitative analysis following the method in use for silicates partially decomposed by acids. The part not decomposed by hydrochloric acid (freed through a boiling solution of sodium carbonate of the silica liberated by the decomposed silicates) was attacked with fluodridic acid for the determination of the bases and with sodium carbonate for the determination of silica. The results obtained were the following:

POZZOLANA OF BACOLI - CANNETO CAVE

	FINE PART			COARSE PART		
	Total	Decomposed in HCL	Undecomposed	Total	Decomposed in HCL	Undecomposed
Loss thru calcination	4.82	3.93	0.89	4.21	3.18	1.03
SiO_2	54.16	21.37	32.59	53.18	21.46	31.72
Al_2O_3	19.14	8.73	10.41	19.80	9.05	10.75
Fe_2O_3	3.51	2.43	1.08	3.40	2.22	1.18
CaO	5.12	2.15	2.97	5.50	2.65	2.85
MgO	1.05	0.48	0.57	1.86	0.86	1.00
K_2O	9.35	4.67	4.68	9.04	4.17	4.87
Na_2O	2.89	1.16	1.73	2.73	1.17	1.56
	99.84	45.12	54.72	99.72	44.76	54.96

APPENDIX III.

Analysis of a Pozzolana
By Professor C. Beuffat.

Following are the results of the analysis of a variety of pozzolana of Bacoli.

This pozzolana of a clear gray color, has all the characteristic properties of the good trachytic pozzolanas, was subjected to chemical analysis following the method which had already been used other times for similar research. By sieving through a sieve of 400 openings per square centimeter, the finer pozzolana was separated from the coarser, and from each one of these parts I made the quantitative analysis following the method in use for silicates partially decomposed by acids. The part not decomposed by hydrochloric acid (freed through a boiling solution of sodium carbonate of the silica liberated by the decomposed silicates) was attacked with fluedridic acid for the determination of the bases and with sodium carbonate for the determination of silica. The results obtained were the following:

POZZOLANA OF BACOLI - CONTENTS

	Total	Decom-posed	Undecom-posed	Total	Decom-posed	Undecom-posed
Loss thru calcination	4.82	3.95	0.89	4.21	3.18	1.03
SiO_2	54.16	21.37	32.59	53.18	21.46	31.72
Al_2O_3	12.14	8.73	10.41	19.80	9.05	10.75
Fe_2O_3	3.31	2.45	1.68	3.40	2.22	1.18
CaO	5.12	2.16	2.97	3.50	2.65	2.85
MgO	1.05	0.48	0.57	1.86	0.86	1.00
K_2O	3.55	4.67	4.68	9.04	4.17	4.87
Na_2O	2.89	1.16	1.73	2.73	1.17	1.56
	99.84	45.12	54.72	99.72	44.76	54.96

An examination of the obtained values leads to the following conclusions: First, the fine part and the coarse part of pozzolana have both the same percentage composition and behave in the same manner with hydrochloric acid. Second, the percentage composition considered as a whole does not differ noticeably from that of other pozzolanas of the same region. For instance from the two following pozzolanas which I have analyzed with the same method:

	Fine Salemma		Fine Canneto	
Loss thru calcination	7.25		4.82	
SiO_2	52.77		54.16	
Al_2O_3	17.00		19.14	
Fe_2O_3	4.84		3.51	
CaO	3.28		5.12	
MgO	1.35		1.05	
K_2O	7.65)		9.35)	
	)	12.59	)	12.24
Na_2O	4.94)		2.89)	

Third, when we consider the behavior of the same substance with hydrochloric acid we find very marked peculiarities.

	SOLUBLE		INSOLUBLE	
	Canneto	Salemme	Canneto	Salemme
SiO_2	21.57	10.04	32.59	42.73
Al_2O_3	8.73	9.00	10.41	8.00
Fe_2O_3	2.43	1.69	1.08	3.15
CaO	2.15	2.06	2.97	1.22
K_2O	4.67	N.D.	4.68	N.D.
Na_2O	1.16	N.D.	1.73	N.D.
Loss thru calcination	3.93	4.85	0.89	2.40
	45.12	29.78	54.72	70.22

An examination of the obtained values leads to the following conclusions: First, the fine part and the coarse part of pozzolana have both the same percentage composition and behave in the same manner with hydrochloric acid. Second, the percentage composition considered as a whole does not differ noticeably from that of other pozzolanas of the same region. For instance from the two following pozzolanas which I have analyzed with the same method:

	Fine Salemme	Fine Canneto
Loss thru calcination	7.25	4.83
SiO_2	52.77	34.16
Al_2O_3	17.00	19.14
Fe_2O_3	4.84	5.51
CaO	5.23	3.12
MgO	1.35	1.05
K_2O	7.65	9.35
Na_2O	4.84	2.89
	12.79	12.24

Third, when we consider the behavior of the same substance with hydrochloric acid we find very marked peculiarities.

SOLUBLE				INSOLUBLE
Canneto	Salemme	Canneto	Salemme	
SiO_2	21.07	10.04	32.00	42.73
Al_2O_3	8.73	9.00	10.41	6.00
Fe_2O_3	2.45	1.69	1.08	6.18
CaO	3.15	1.06	2.97	1.22
K_2O	4.67	N.D.	4.88	N.D.
Na_2O	1.16	N.D.	1.73	N.D.
Loss thru calcination	3.95	4.85	0.80	2.40
	45.12	29.73	51.72	70.32

From this table it can be seen that while the Salemme pozzolana only shows 30% of attackable part, the Canneto pozzolana shows 45%, and this is so much more noticeable inasmuch as the Canneto pozzolana is much richer in silica than the Salemme. Equally noticeable is the diversity of the ratios $\frac{SiO_2}{Al_2O_3}$ which for the Canneto pozzolana happens to be about three, either for the soluble or the insoluble part, while in the Salemme pozzolana they pass from the value of one of the soluble part to the value of five of the insoluble part.

It is rather difficult to account for such diversity of behavior unless it can be attributed to the presence of various mineralogic species in rocks of the same type and in a large part in a vitreous state. It appears therefore necessary to find out to what extent the phenomena of alteration of a pozzolana through the effect of atmospheric agents can be made to determine the diversity of behavior.

The largest difference which is found between the two pozzolanas lies in the loss from calcination, which is 4.82 for the Canneto pozzolana and 7.25 for the Salemme pozzolana.

Now the loss from calcination is mainly due to elimination of the water of hydration and to the elimination of small quantities of carbonate anhydride, substances which in pozzolana as well as in all volcanic rocks in general, are present initially in very small amounts but with progress of time increase continually due to the action of atmospheric agents.

It is usual to indicate with the generic name of kaolinization the decomposition of feldspar and similar rocks through the action of atmospheric agents, although it is known that the products which derive from this decomposition vary according to the composition of the original rocks. But in general, it is possible to affirm that kaolinization leaves in place of an aluminous alkaline silicate the hydrate silicate of alumina, and therefore there is thus brought about in the case of pozzolanas, the diminution of substance which can be attacked by hydrochloric acids in the course of the method usually followed for the analysis of the materials.

Following this way of thinking, it is possible to ...ive from the examination of pozzolanas some very useful de...ions from the comparisons between the loss from calcination ... the behavior with hydrochloric acid.

It has been held by some that pozzolanas acquire ...raulic property only after a prolonged exposure to atmospheric ...ts but this opinion which is decidedly contradicted by the ...ical traditions centuries old, which still regulate nowadays

the use of these materials, has no scientific basis whatever. If we were to hold this opinion as true, we should consequently state that the ideal pozzolanas were a mixture of hydrated silica and silicate of alumina - which is absurd. We must hold therefore, that pozzolanas are - all other conditions being equal - so much better the less they are altered through the action of atmospheric agents.

The following table taken from the study of "Artificial and Natural Pozzolana" by Giorgis and Alvisi in Gazzetta Chimica Italiana, Volume 29, gives a very clear idea of the effect of atmospheric agents upon pozzolanas:

POZZOLANA OF SAN PAOLO

Analysis of L. Luiggi and V. Cardi

Silica	30.00
Alumina	24.00
Lime	13.00
Iron Oxide	23.50
Water	8.50
Magnesia	1.00
	100.00

Table showing how pozzolanas lose their hydraulic activity when exposed to atmosphere.

	Penetration to Vicat needles in mm.			Tensile Strength Kg./sq. cm. at one year.
	1 mo.	2 mo.	3 mo.	
1 lime - 2 Roman pozzolana stored for 3 years free of the action of atmospheric agents	5	2	-	8,500
1 lime - 2 Roman pozzolana stored for 3 yrs. in contact with atmospheric agents	7	5	2	4,500
1 lime - 2 Roman pozzolana used soon after its excavation	5	-	-	7,200
1 lime - 2 Bacoli pozzolana stored for 3 yrs. in closed containers	6	3	-	7,100
1 lime - 2 Bacoli pozzolana stored for 3 yrs. in contact with atmospheric agents	8	4	3	3,100
1 lime - 2 Bacoli pozzolana used soon after exaavation	4	-	-	8,250

1 time - Second mortgage
used case first examination ..... $ 500

1 time - Second mortgage
written chattel mortgage ..... $ 100

1 time - Second mortgage
stored for 3 yrs. in closed
containers ..... $ 100

1 time - Second portions
stored for 3 yrs. in closed
vault ..... $ 500

1 time - 3 Month postponements
need each after the exam-
ination ..... $ 500

1 time - 3 Month postponements
after chattel mortgage ..... $ 500

1 time - 3 month postponements
stored for 3 yrs. in vault
agents ..... $ 500

1 time - 3 month postponements
stored for 3 yrs. in closed
the action of atmospheric

1 time - 5 Second postponements
stored for 3 yrs. in vault
written chattel mortgage

1 time - 5 Second postponements
used case first examination

1 mo.	2 mo.	3 mo.	one year

Inspection by Local Committee

Complete Storage

Table showing new Postponements upon Automatic Renewal

Analysis of 1 Second and 1 Third

Files	30.00
Examine	25.00
Times	15.00
Item Price	25.00
Letters	5.00
Agents	1.00
	100.00

atmospheric agents upon postponements.

Interest, Volume 25, gives a very clear idea of the effect of

and Retinal Postponements" by Florels and Alvarl in Eccelette Chemical

The following table taken from the study of "Artificial Retinal

action of atmospheric agents.

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Meetings, that postponements are - all other conditions being

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avoids that the ideal postponement would a mixture of hydrated

to we were to hold this opinion as true, we should eliminate

the use of these materials has no foundation. Here theory

Table showing how the grinding of pozzolana affects the strength of a 1:2 mortar of lime-Roman pozzolana:

Type of Pozzolana	Tensile Strength Kg/Cm.^{2} 3 m.	6 m.	18 m.
Commercial type mixed by hand.....	4,100	5,100	9,050
Ground to pass the sieve of 400 open:/cm.^{2}..	5,200	9,000	12,050
Ground to pass the sieve of 121 open:/cm.^{2} and not 225 sieve	3,800	4,900	8,000
Ground to pass the sieve of 81 open:/cm.^{2} and not 121	3,800	4,200	6,100
Ground to pass the sieve of 16 open:/cm.^{2} and not 81	2,200	2,900	3,200
Commercial type mixed by machine	4,600	8,100	11,900

A P P E N D I X IV.

Technical Tests upon Natural Pozzolanas
from the
study
"Natural and Artificial Pozzolanas"
by
Giorgis & Alvisi

To the builder who must avail himself of pozzolana, the problem of the valuation of its technical qualities presents itself under a dual aspect; first, he must see if the pozzolana has been artificially or naturally adulterated; second, he must determine the hydraulic value.

Adulteration of Pozzolanas

The material which is most commonly used in the adulteration of pozzolanas, is clay - therefore, red pozzolanas are more difficult to adulterate because it is less easy to find a clay of their same color, while the black and the gray pozzolanas lend themselves very well to such an adulteration.

Since very remote times, builders were careful about adulteration of pozzolana. Palladio states that a pozzolana can be judged favorably if it does not leave any spot upon a linen cloth.

Luiggi* who occupied himself with the study of pozzolanas in connection with the works of Genoa Harbor (166) regarding adulteration with clay proposes to subject pozzolana to a test of calcination, a test which is also among those proposed by Dardenne (215) for natural pozzolanas and for trass.

When we consider that whatever the nature of the soil ground or mixed with pozzolana, it must in general contain organic matters, some test should be made to detect their presence. The qualitive test only is necessary as the quantative determination of organic matter is of little importance.

In addition to the other tests noted above, additional tests of value are: tests for sieve analyses; determination of the fineness; specific gravity; apparent density, and the water of combination. Although the results of chemical analyses are rather ambiguous, nevertheless, it is rather interesting to determine on one hand the proportion of silica and alumina solu-

*(one of the most famous of modern Italian engineers.)

*(one of the most famous of modern Italian painters.)

determine on one hand the proportion of silica and alumina combined chemically; on the other, the proportion of carbonate of lime, magnesia, oxide of iron and alumina which are simply mixed mechanically with the silicates. The former constituents are essential; the latter are not. Hydraulicity depends on the quantity of the former which is present in the cement. The quantity of the latter may vary within very wide limits without affecting the hydraulicity.

In addition to the other tests mentioned above, additional tests of value are: tests for sieve analysis; determination of specific gravity; apparent density; and time of setting. Specific gravity is a factor in rather interesting comparisons. Hydraulic cements of commercial fineness and time of setting have specific gravities ranging from 3.1 to 3.25. Pozzolanas have specific gravities ranging from 2.1 to 2.9. Apparent density is a factor in determining the proportioning of concrete mixtures. Pozzolanas are very light and voluminous and require much more material by weight to fill a given space than do cements. Time of setting is a factor in determining the suitability of a cement for use under certain conditions. Pozzolanas are slow setting and require much more time to harden than do cements.

Tests for tensile strength are made on briquettes of standard form and dimensions. The usual method of making the test is to clip the ends of the briquette in the jaws of a testing machine and apply a steadily increasing pull until the briquette breaks. The tensile strength is then computed by dividing the total pull by the cross-sectional area of the briquette. Tensile tests are usually made on briquettes composed of one part cement and three parts standard sand. Tests are also made on briquettes composed of one part cement and one part sand, and on neat cement briquettes. Pozzolanas usually develop relatively high tensile strength when mixed with three parts of sand, but develop relatively low strength when mixed with one part of sand or when used neat. Cements usually develop relatively high strength when mixed with one part of sand or when used neat.

Tests for compressive strength are made on cylinders of mortar or concrete. The usual method is to break the cylinders in a testing machine by applying pressure to the ends of the cylinder. Pozzolanas usually develop relatively low compressive strength when mixed with three parts of sand, but develop relatively high strength when mixed with one part of sand or when used neat. Cements usually develop relatively high strength when mixed with one part of sand or when used neat.

Tests for soundness are made on pats of neat cement or pozzolana. Pozzolanas usually develop relatively low soundness when mixed with three parts of sand, but develop relatively high soundness when mixed with one part of sand or when used neat. Cements usually develop relatively high soundness when mixed with one part of sand or when used neat.

Tests for fineness are made on sieves of standard form and dimensions. Pozzolanas usually develop relatively low fineness when mixed with three parts of sand, but develop relatively high fineness when mixed with one part of sand or when used neat. Cements usually develop relatively high fineness when mixed with one part of sand or when used neat.

Tests for time of setting are made on pats of neat cement or pozzolana. Pozzolanas usually develop relatively long time of setting when mixed with three parts of sand, but develop relatively short time of setting when mixed with one part of sand or when used neat. Cements usually develop relatively short time of setting when mixed with one part of sand or when used neat.

Tests for specific gravity are made on pats of neat cement or pozzolana. Pozzolanas usually develop relatively low specific gravity when mixed with three parts of sand, but develop relatively high specific gravity when mixed with one part of sand or when used neat. Cements usually develop relatively high specific gravity when mixed with one part of sand or when used neat.

Tests for apparent density are made on pats of neat cement or pozzolana. Pozzolanas usually develop relatively low apparent density when mixed with three parts of sand, but develop relatively high apparent density when mixed with one part of sand or when used neat. Cements usually develop relatively high apparent density

ble in acids and alkalis and on the other hand the proportion of insoluble matter.

Regarding the sieve analysis and surface fineness in relation to pozzolana, this test has not very great importance inasmuch as pozzolana is a material which is ordinarily used in the state in which it is found in nature, although it is sometimes sieved through large screens to free it of coarse particles larger than 5 mm. in size.

We must always remember though that pozzolanas are very complex materials constituted of various mineralogic parts which can even be rendered more complex by possible alterations, therefore, to pozzolanas can never be applied the criterions and the determinations which characterize cement in general and Portland in particular, which can in a certain way always be regarded as a well defined compound, at least technically speaking.

But even if these tests could furnish a useful criterion to judge the hydraulic value of a pozzolana, it would still be necessary to establish the conditions according to which it is necessary to proceed to the various determinations, especially insofar as it has to do with the apparent specific weight.

For our tests we have chosen a series of pozzolanas of which we practically knew the technical value, the best being the pozzolana of San Paolo. Regarding the apparent specific weight we have determined it in two conditions, that is, first, in the grade of fineness in which it is practically used, and, second when reduced to a very fine powder which leaves no residue larger than 25% or 30% when passed through the sieve of 5,000 openings per square centimeter. Of the same pozzolana we have determined the water of combination, which in trass, according to dordenne is in direct relation with its hydraulic particles, by operating upon the pozzolanas briefly dried to a temperature variable between 100° and 110° and then determining their loss of weight due to the furnace.

We report in the following table, the results of the various tests.

Types of Pozzolana	Treatment with Potass. Hydrate	Apparent Density of Pozzolana		Specific Weight	Water of Comb. Loss by Ignition	Carbonic Anhydride
		Nat. St.	Ground			
1.	Limpid liquid	1.164(1)	1.044	2.352(2)	5.92	----
2.	Id.	1.113	0.943	----	5.88	----
3.	Id.	0.997	0.9936	----	5.59	----
4.	Id.	1.149	1.006	2.439	5.88	----
5.	Id.	1.129	1.006	----	5.23	----
6.	Id.	1.187	1.0506	----	5.15	----
7.	--	----	----	----	3.13	----
8.	Limpid Liquid	----	----	----	5.50	----
9.	Id.	1.124	1.057	----	4.65	----
10.	Gray Color	0.942	----	2.174	12.50	6.70
11.	Yellow Color	0.957	----	----	8.13	2.19
12.	Id.	----	----	----	9.30	----
13.	Gray Color	----	----	----	17.26	4.98
14.	Yellow Color	----	----	----	15.90	10.20

(1) Luiggi and Cardi (166-a) found: 1.13 - 1.15

(2) Prof. Cavazzi (126) found: 2.285

Type of Potassium Hydrate	Treatment with Potassium Hydrate	Apparent Density Nat. St.	Apparent Density Ground	Specific Weight	Water of Comb. Loss by Ignition	Bar-Ionic Grade
1.	Limpid Liquid	1.164(1)	1.044	2.33(2)	5.92	----
2.	Id.	1.113	0.643	----	5.88	----
3.	Id.	0.997	0.9936	----	5.59	----
4.	Id.	1.149	1.006	2.439	5.58	----
5.	Id.	1.129	1.008	----	5.23	----
6.	Id.	1.167	1.0606	----	5.15	----
7.	--	----	----	----	3.13	----
8.	Limpid Liquid	----	----	----	5.50	----
9.	Id.	1.124	1.057	----	4.65	----
10.	Gray Color	0.942	----	2.174	12.50	6.20
11.	Yellow Color	0.957	----	----	8.13	3.19
12.	Id.	----	----	----	9.50	----
13.	Gray Color	----	----	----	17.26	4.96
14.	Yellow Color	----	----	----	15.90	10.20

(1) Liquid and Cards (166-a) found: 1.13 - 1.15

(2) Prof. Cavazzi (126) found: 2.285

From the above it is readily seen that the treatment of pozzolanas with a diluted solution of potassium hydrate and the test of clarification are sufficient data to differentiate the true pozzolana from those which were adulterated with earthen materials.

The same thing cannot be said with regard to the density be it real or apparent, because these densities do not vary much in the different pozzolanas although they have a different technical value in various cases. Although it is true that pure clay has an apparent density of about two and therefore, whenever it is mixed with pozzolana theoretically increases its density, nevertheless in all adulterations it is never a question of pure clay, but always a case of clayey earth which contains in turn many impurities which lower its density very close to that of pozzolanas. It is also worth while to notice that those pozzolanic deposits like that of the cave of S. Giovanni, of Coriano Sicoli and others to which we made reference in the first part of our work, were transported by winds rather far from the crater of ejection. They are constituted in general of elements very fine and light, owing to which their density is diminished.

The apparent density is always greater for pozzolanas in their natural state than for ginely ground pozzolanas. In other words, it appears that we meet the same phenomena with pozzolanas as with cements - above all with Portland cements in which the apparent density diminishes with the fineness of grinding, explained by the contraction which has taken place through the high temperature of clinkering.

Concerning the determination of the water of combination while this determination reveals quite well the presence of vegetable matter or of clay, it is not related to the technical value of the various pozzolanas, first because the percentage is too small to offer characteristic gradations; second, because in all pozzolanas studied, although they were quite different as regards the technical value, this percentage varied little with the exception of the pozzolana of Paliano or better yet that of Vicovaro, which differs from the Roman in that it has a larger quantity of base soluble in acids.

It is also noticeable that in the true pozzolanas carbonic anhydride is very seldom found unless in very small quantities, while it is found in remarkably large quantities in all adulterated pozzolanas, clays, etc.

The proposed tests to determine the value of pozzolanas are those of Vicat and Chatoney-Rivot and appear to be the only ones of their kind.

VICAT TEST

The principle upon which this test is based is stated by Vicat as follows (35):

"The energy of a pozzolana is directly proportional to the quantity of lime water which it is capable of fixing during a determinate time." (Vicat used a solution of lime in water but inasmuch as the solubility of lime in water is rather small (128) he substitutes a solution of sugared water which has a much larger dissolving power for the calcium hydrate). "This test must be made in comparison with a pozzolana of known technical value, and is conducted in the following manner:"

"A determinate weight (20 gr.) of pozzolana to be examined and an equal weight of the comparative one are each placed in a (100 cm.) solution of calcium hydrate in sugared water, a solution which is tested with hydrochloric acid. The calcium oxide which we have used to prepare all the tests which we have described was a very pure substance, which at the furnace gave a loss of only 3.76% of which 0.74% was carbonic anhydride (CO_2). This lime in the sugared solution left an insoluble residue of 1.18%. It contained very little traces of magnesia and was also entirely exempt from the presence of alkalis. We could perhaps have found some calcium oxide purer than that or we could have prepared it ourselves, but we thought to use a material of construction prepared with precautions which must be followed for a technical product instead of a product of a laboratory which if on one hand is purer does not present on the other hand those qualities which render it well adapted for technical tests.

"Regarding the quantity of sugar to be used for the solutions, from our tests we have found that the maximum solubility of calcium oxide (CaO = gr. 2.5%) in sugared water is obtained by dissolving a kilogram of sugar in about 10 liters of water. This solution can be further

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diluted, but to see that this happens in the right way, it is necessary to take precautions to first hydrate the lime and after the hydration has taken place it must be placed in contact with sugared water and filtered after being left in it ten or twelve hours, being careful to shake it from time to time. The whole is filtered upon a dry filter and an aliquot part is brought again in contact with a normal solution of hydrochloric acid. It is thus possible to calculate all the lime which is liberated by the solution from the pozzolana.

"We have made a test upon pozzolana of the fineness used in practice and upon the same pozzolanas when reduced in a very fine powder, using as a means of comparison the pozzolanas of S. Paolo. We have also observed the behavior of earth, clay and some natural silicates.

NATURAL POZZOLANA

Sugar Solution 1.53% of CaO

Pozzolana	DURATION OF IMMERSION	
	48 Hours	10 Days of 24 Hours
	CaO taken from 100 P. of Pozzolana	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo (Cave Mezzetti)	1.71	1.88
Pozzolana of S. Sebastiano	1.18	1.60
" " Porta Maggiore ...	1.29	1.20
" " the Pigno	1.04	1.20
" " Vicovaro	1.05	1.26
Pozzolana of Anzio	1.18	1.54
Pozzolana of Pagliano	1.32	1.48
" " S. Giovanni	1.64	1.48
" " Goriano Sicoli ...	2.17	2.07
Vegetable Soil	3.16	3.44
Pozzolana of S.Paolo(Tre Fontane)	1.65	1.90

PULVERIZED POZZOLANA

Sugar Solution 1.99% of CaO.

Pozzolana	DURATION OF IMMERSION	
	48 Hours	10 Days of 24 Hours
	CaO taken from 100 P. of Pozzolana	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo (Cave Mezzetti).....	2.114	2.114
Pozzolana of the Pigno ...	1.094	1.094
Vegetable Soil	2.254	2.226

PULVERIZED POZZOLANA

Sugar Solution 1.54% of CaO.

Pozzolana	DURATION OF IMMERSION
	Four days of 24 Hours
	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo	1.68
Pozzolana from Cave Sette Camini	1.51
Pozzolana from the Pigno ..	0.97
" of S. Giovani ..	1.50
" of Goriano Sicoli.	2.06
Clay of Bari	0.84
Vegetable Earth	2.27
Wollastonite(1)	0.04
Leucite(1)	0.00

(1) These are 2 natural silicates with which we thought to experimemt at the same time we experimented with natural pozzolana.

Sugar Production 1.Jan. to 31 Dec.

Sugar Production 1.Jan. to 31 Dec.

Sugar Production 1.Jan. to 31 Dec.

"As will be noted from the table which represents the results of the third test, we have experimented with the action of a sugar solution upon two natural silicates, Wollastonite and Leucite. Wollastonite does not set with lime and Leucite is found frequently, though always Kaolinized, in pozzolanas - especially those of the Roman type, while it is very seldom found unaltered like the pozzolana of Pigno. Making a mortar in the proportions of one part of Leucite to two parts of lime in volume and making an analogous type of mortar with the pozzolana of S. Paolo, we placed both mortar specimens under water. After a few days, the pozzolana had set while the Leucite had not. After about three months we noticed a certain superficial set even in the Leucite mortars. This set is easily explained if account is taken of the action of water and carbonic acid of the air upon the lime and the Leucite. The final result of these actions is the kaolinization of the leucite followed then by its setting. But these actions are very slow and this explains the behavior of Leucite at the Vicat test.

"From the three tests made, it is possible to notice that the length of immersion beyond a certain time has little influence, although such a statement deserves to be verified by a greater number of tests than those which we have made.

"Also, it is certain that the quantity of lime which is fixed by the pozzolanas is always very small - even if the test is prolonged for many hours - to be able to get any kind of index.

"To this must be added another objectionable feature of greater importance which can lead to many mistakes and which is rendered manifest by the observations of the percentage of lime absorbed by common earth which is so much large than that of the pozzolana of S. Paolo. Of this on the other hand we can very easily find an explanation, when we consider that lime combines with humus (65) giving rise to insolu-

ble compounds. From this it follows that more or less of this substance can considerably alter the results of the test and lead to mistakes. This is confirmed by the percentage absorbed by the pozzolanas of S. Giovanni and of Gorlano Sicoli as well as by that of the Clay of Bari which is much less than that of earth containing smaller quantities of humus.

"One thing seems noticeable, though, whenever the humus substances are lacking altogether the test gives results that do not always conform to the truth. In effect, the pozzolana of S. Paolo in all the tests is above any other which follow it in the order of their technical value as known in practice. From this we are brought to the agreement with Professor Rebuffat (174-c) who says in a study upon the technical analysis of pozzolanas:

> "To have a good method of technical analysis of pozzolanas, it is convenient simply to accelerate the action of lime upon pozzolana in such a way as to be able to determine its effect in a practically short time."

TESTS OF RIVOT

This test is described by Rivot himself (203) in the following way:

"Take 5 gr. of the substance brought about by grinding to the degree of fineness adopted in practice for the manufacture of mortars, and submit to the action of pure concentrated nitric acid; leave the acid to react upon the silicate for about 24 hours at a temperature of 50°C. to 60°C. Evaporate the solution and treat again by a diluted solution of nitric acid. From the liquid part, there is obtained the alumina, the iron oxide, the lime, the magnesia, and the alkalis. The insoluble part is first calcined, then weighed, then placed in a weak solution of potassium hydrate brought to a temperature of about 40°C. and left in this solution for 12 hours. The insoluble part

in this alkaline solution is washed out with great care, is dried, calcined and then weighed. The difference between the two weights is considered as representing the silica which becomes soluble through the successive action of acids and alkalis. In this determination of soluble silica rests the important result of the analysis because it is the best basis of comparison of values of pozzolanas. It is useful to complete the analysis by determining the composition of that part of silicate which has not been a part of the two reagents in the wet process, therefore, it is mixed intermittently with an equal weight of lime perfectly pure and brought to the temperature of bright red. After cooling, it is subjected to the action of nitric acid and then the determination is made of the silica and the bases. One must take care in this test to add in the weight of the lime, the weight of that particular base which has been added to render the silica of easy attack. As we have done for the test of Vicat we report in the following table, also for the test of Rivot the results obtained with various pozzolanas, with earth, with clay and some silicates.

Pozzolana	Water Hygroscopic	Water of Combination Loss through Ignition	Part Soluble in HNO_3	Part Soluble in Potassium Hydrate	Part Insoluble
Pozzolana of S. Paolo	4.60	5.92	40.03	31.42	28.55
" from the Cave of the Sette Camini	5.88	5.88	39.39	31.37	29.24
Pozzolana of S.Giovanni	6.85	12.50	38.07	22.55	39.38
Pozzolana of Goriano Sicoli	6.31	8.13	47.42	24.90	27.68
Clay of Bari	4.52	17.26	44.58	12.43	42.99
Vegetable Earth	11.77	9.30	57.16	25.81	17.03
Wollastonite	0.17	4.26	51.47	46.40	2.13
Leucite	0.12	0.13	39.60	24.71	35.69

"The principle upon which this test is based seems to somewhat beg the question, because it consists in examining the action of strong reagents upon pozzolanas, reagents like nitric acid and potassium hydrate. Now to obtain some degree of comparison between the results, it is necessary to operate always in the same way with reagents always in the same degree of concentration and within limits almost rigorously equal in time and temperature."

"The student is then told that he is to
assume atoms to somewhat behave like spheres
because it consists in examining the action
of strong reagents upon particular reagents
like nitric acid and potassium hydrate. How
to obtain some degree of comparison between
the results, he is necessary to give the
student the same way with reagents always
in the same degree of concentration and tem-
and temperature."

A P P E N D I X V.

Contribution to the Study of Pozzolana and of its Technical Value.

By
G. Giorgis & U. Alvisi.
in
Gazzetta Chimica Ital.
Year 1906, Volume 36.

Notwithstanding the researches and studies that have been so far made upon pozzolana this material still presents some unknowns, both as to the nature of its physical and chemical constitution and the phenomena of setting when mixed with lime. To this must be added that while for other materials of construction we are in possession of laboratory tests from which it is possible to ascertain their technical value, we have nothing similar for pozzolana. Tests so far proposed do not solve the problem. An accelerated test would of course be of considerable value inasmuch as the setting of this material requires a rather long time owing to which it is impossible to obtain any results of the tests of physical resistance until after months or years. Because of the difficulties presented by the problem, it is highly improbable that such a solution can be obtained at once, therefore all the studies of the attempts which are made along those lines, even if they do not bring about a definite result, cannot fail to be a useful contribution.

Among the pozzolanas found in the Neapolitan countryside we must distinguish the old ones which originate from the volcanos of the Flegreian fields and the modern which originate from Vesuvius.

The ancient pozzolanas must be divided into trachytic and leucofritic while the modern are all leucofritic. One of these last pozzolanas is that of the cave of the Cardinal of the following analysis:

Silica	48.00
Alumina	17.53
Ferrous Oxide	2.03
Ferric Oxide	5.09
Calcium oxide	11.19
Magnesia	3.60
Potass. Oxide	8.47
Sodium Oxide	2.56
Water of Comb.	1.54
Total ..	100.01

We have experimented with the technical value of this pozzolana comparing it with a specimen of pozzolana of Bacoli, and specimens of volcanic sand deriving from the ashes of Vesuvius from three successive eruptions. The following are the chemical analyses of the three types of sands:

	I. Eruption of 1878	II. Eruption of May, 1900	III. Eruption of Nov., 1900
SiO_2	48.45	47.94	47.40
SO_3	0.60	0.56	0.66
Fe_2O_3	3.49	0.69	3.76
FeO	3.35	3.35	3.65
Al_2O_3	17.81	21.31	21.31
CaO	12.09	8.89	9.71
MgO	3.02	1.65	1.73
K_2O	5.01	5.12	5.02
Na_2O	5.46	7.33	6.38
Water of Combination	0.60	0.06	0.20
Total	100.08	99.90	99.82

It can be seen that from the comparison of the chemical analyses no conclusion of any value can be reached inasmuch as their composition does not differ from that of common pozzolanas, although an exception must be made for the percentage of water of combination, which is much lower than that found in such pozzolanas - also, it must be noted that this percentage is slightly higher in the sand derived from the 1878 eruption, which sand has been exposed for a longer time to the action of external agents.

On this matter it appears interesting to us to see which modifications the prolonged action of water and carbonic anhydride could have produced upon these sands inasmuch as those two substances are the principal agents which are active upon pozzolanas in their natural state.

To such purpose 100 gr. of each of the three types of sand in their natural state of fineness were weighed, then were placed in three glasses filled with water and through these glasses a current of carbonic anhydride was made to pass, taking good care of agitating the glass from time to time.

The test was prolonged for two months. At the end of these two months, the liquid was filtered and the materials remaining unfiltered were maintained in the sun until they had reached a degree of dryness equal to the initial one. They were then again analyzed chemically. The following table shows the chemical analysis:

	I.	II.	III.
SiO_2	46.12	48.78	47.56
SO_3	0.57	0.65	0.62
Fe_2O_3	4.30	3.83	3.08
FeO	3.62	4.14	3.65
Al_2O_3	18.43	20.60	23.36
CaO	15.09	9.95	9.92
MgO	2.14	1.47	1.35
K_2O	5.73	5.67	6.44
Na_2O	3.95	4.33	3.93
Water of Comb.	0.43	0.17	0.21
Total	100.38	99.49	100.12

It is unfortunate that no practical deduction can be obtained from the comparison of these analyses with those of the sand in its natural state, and this was perhaps to be expected if one thinks of the relatively short time that they were subjected to the action of carbonic anhydride and water. The test of Vicat upon the two types of pozzolana and the three types of sand gave the following values:

Pozzolana	Duration of Immersion: CaO Liberated from 100 P. of Pozzolana 52 Hours	Duration of Immersion: CaO Liberated from 100 P. of Pozzolana 27 das. of 24 Hrs.
Pozzolana of Bacoli	0.56	1.204
Pozzolana of Cardinal Cave	0.20	0.41
Sand from Vesuvius No. 1	0.28	0.980
" " " " 2	0.14	0.868
" " " " 3	0.14	0.868

to each [illegible] 100 cc. of each of the [illegible] of urea solutions of [illegible] strengths were placed, [illegible] ture closed in water [illegible] placed with [illegible] Vapors and [illegible] Change [illegible] allowed a current of carbonic anhydride was made to pass [illegible] tion of one [illegible] per minute [illegible] time.

The [illegible] was prolonged for two hours. At the end of [illegible] the mercury, the [illegible] was filtered and the [illegible] [illegible] by weighed tests [illegible] used in the [illegible] I may [illegible] [illegible] place a series of [illegible] added to the [illegible] one. They were [illegible] again weighed [illegible]. The following [illegible] above [illegible] analysis:

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

The test of Rivot gave the following results:

Pozzolana	Hygroscopic Water	Water of Combination Loss by Calcination	Part soluble in HNO3%	Part Soluble in Potassium Hydrate	Insoluble Part
Pozzolana of Bacoli	2.11	5.04	14.21	4.53	81.26
" of Cardinal	0.36	1.54	27.02	17.94	55.04
Sand From Vesuvius No. 1	0.41	0.60	38.05	27.76	34.19
" " " No. 2	0.17	0.06	37.71	25.19	37.10
" " " No. 3	0.13	0.20	38.32	22.81	38.87

These results confirm what we said in our first study upon the value of the tests of Vicat and Rivot (G. Giorgis and U. Alvisi, "Pozzolane Naturali ed Artificiali", Gazzetta Chimica Italiana, Volume 30, Part 1.)

We therefore modified the test of Rivot in the following way for the purpose of determining the disintegrated silica and perhaps even the alumina rather than the fixed lime.

We brought pozzolana to react with lime in such proportions that there was present a higher percentage of lime in relation to pozzolana than is usually employed in practice - that is, 3 gr. of fat lime were mixed after being slaked with 10 grs. of pozzolana. These proportions correspond in volume to about seven volumes of lime to eight volumes of pozzolana. The temperature of the experiment was at about 140°C. which corresponds to a pressure of about 4 atmospheres and the duration of the experiment was of about 12 hours. The substance was left to cool and then placed in a glass bowl and treated with a current of carbonic anhydride for the purpose of decomposing the calcium silicate and the calcium aluminate and to liberate both silica and alumina. Having allowed the carbonic anhydride to react for about 24 hours, the material was heated to eliminate whatever carbonic anhydride was dissolved, after which it was treated with a 30% solution of potassium hydrate. The amount of silica on a filtered portion treated with hydrochloric acid was determined. The following table furnishes some data on the percentage of soluble silica found in the solution of potassium hydrate:

Pozzolana	% Silica soluble in Potassium Hydrate	% Alumina soluble in Potassium Hydrate
Pozzolana of S. Paolo	5.05	1.34
" " Bacoli	2.26	
" of Cardinal Cave	2.82	
" " Portella Cave	5.36	
Sand from Vesuvius No. 3	1.27	
Clay from the Valley of the Inferno, Rome	1.11	

Even this test in its new modification does not solve the problem of finding the technical value of pozzolana, the percentage of silica soluble in potassium hydrate being not at all in relationship with the hydraulic quality of the substance tested. This is apparent when we notice that the soluble silica of the pozzolana of the cave called Portella was the highest of all, although it is well known to be a very mediocre pozzolana. To further substantiate our conclusions we have experimented with the attack upon some pozzolanas of a concentrated solution of potassium hydrate following the method of Professor O. Rebuffat (See: O. Rebuffat, "Studio sulla analisi tecnica delle pozzolane" Rend. Acc. Scienze Fisiche e Mat., Napoli, 1896, Aprile, Fasc. 4).

This method is followed to ascertain exactly the quantity of silica passed in solution. The following table furnishes the results obtained:

Pozzolana	% of Soluble silica in Potassium Hydrate	% of Soluble alumina in Potassium Hydrate
Pozzolana of S. Paolo	12.928	0.571
" " Bacoli	12.115	
" " Cardinal Cave	5.598	
" " Portella Cave	13.467	0.627
" " Tor Marancia	9.693	

Reagent	Potassium Hydrate	Potassium Carbonate
Ponceau 2 R. Color	15.00	0.00
" " Paste	15.00	0.00
" " Certified Dye	0.00	0.00
" " Portella Dye	15.00	0.00
" " Ice Scarlet	0.00	

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" " Paste 15.00
" " Certified Dye 0.00
" " Portella Dye 15.00 0.00
" " Ice Scarlet 0.00

From all these tests one thing appears evident and that is that it is wrong to suppose that a criterion of the hydraulic quality of a pozzolanic material can be based solely upon the quantity of silica soluble in potassium hydrate either by a previous attack with an acid or with the direct action of the potassium hydrate itself.

In saying this however, we do not pretend to say any new thing because this has already been said by Fuchs and Rose (See: Fuchs, Ueber die Eigenschaften, Bestandtheile, und ecc. Dingl.J., T. 49, P. 241), (H. Rose: "Sur les Different Etats de l'Acide Silicique"- Annales de Chimie et Physie - Vol. 58 1860, page 163.)

As a matter or fact, as Fuchs observes, we find that Wollastonite gives with acids gelatinous silica soluble in potassium hydrate, while at the same time it does not set up when mixed with lime. And furthermore, it is not only gelatinous silica which is soluble in potassium hydrate, but there are many silicates which attacked by acids give silica soluble in potassium hydrate - the silica being either in powder form or in a gelatinous state according to the different way in which silica separates itself from the silicates when subjected to the action of acids. Bishoff, discovered that the silica either in a powdered or a gelatinous state has always the same density of 2.2, which is the density of amorphous silicic acid, and came to the conclusion that silica is contained in silicates under two different states, the crystalline state always having a density greater than 2.6).

This idea was also favored by Landrin who, as it can be ascertained from his studies upon hydraulic silica*, in his second note, written as an answer to Le Chatelier, having noticed that the silica which is dissolved by hydrofluoric acid, is not hydraulic, says:

"I maintain that silica, be it amorphous or gelatinous, soluble or insoluble, exists always in a free state in all the hydraulic compounds."

We must therefore, stress the fact that if a solution is to be found of the problem of the determination of the technical value of pozzolanas by means of laboratory tests, it is useless to try this way because through it, it will never be possible to obtain a result which is both practical and reliable.

Landrin: "Sur la Silice Hydraulique et sur le Role qu'elle Joue ... la Prise des Composes Hydrauliques", Compt. Rend., 1883, 1st ... Tom., 96, Page 156. Landrin: "Sur la Silice Hydraulique ... ponse a M. Le Chatelier, 1883, 1 Sem. Tom. 96, Page 379.

A P P E N D I X VI.

The Microscopic Study of Pozzolana Mortars
By - G. Gallo in Gazzetta Chimica Ital. Volume 38.

The use of pozzolana mortars goes back to the oldest times. Six hundred years before the birth of Christ pozzolana was used for important works and Seneca Isidoro, Oratius, Plinius, Vitruvius and Sidonus Apollinaris praise the cementitious power of mortars made with pozzolana. Successively, throughout the centuries, almost until our own times, pozzolana together with trass and santorino has been the only hydraulic material employed in hydraulic works.

Even though after the discovery of artificial hydraulic cements, the use of pozzolana has diminished, the appreciation of its high hydraulic value has nevertheless remained universal.

Even today however, it is preferred to other cementitious materials in many maritime works, in Italy as well as aborad, inasmuch as it is a well proved fact that very often artificial cements do not present in maritime works that resistance presented by pozzolana mortars. The old Roman constructions still remaining testify that the resistance of these mortars render them capable of withstanding safely through centuries the physical violence of elements, and the chemical disintegrating action of sea water.

Italy is the classical land of these volcanic products. The best and the most extended deposits are those which derive from the volcanos of the Glegreian fields near Naples.

Pozzolanas, although constituted essentially of silica, alumina, ferric oxide, calcium, magnesia, potassium and sodium, are materials of very complex petrografic aspect. Furthermore, their composition varies not only from one volcanic deposit to another, but also from one stratum to another of the same deposit. Complete petrographic researches on pozzolana are still lacking. They remain therefore, a geological formation, not well defined, whose general term "pozzolana" is of dubious meaning. In general, however, they are constituted of volcanic "lapilli" in which it is possible to discover fragments of slag, pumice, lava, etc. and crystals of leucite (KAl(SiO3(2), augite, mica, magnetite, piroxeme, etc.

The Microscopic Study of Pozzolana Mortars

By - G. Sallo in Gazzetta Chimica Ital.

Volume 08.

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However, no matter how much the mineralogic composition of a pozzolana may vary, there exists a common essence to which is manifestly due the property of setting under water. The percentage of this essential constituent determines the hydraulic value.

Anticipating some of the findings which will be developed further on, it is not possible to attribute the hydraulic property of a pozzolana to its crystalline elements, because these elements constitute well defined and very stable chemical compounds which cannot undergo, when subjected to the action of lime, a chemical transformation such as to contribute to the setting and hardening of the hydraulic mortar.

Various hypotheses have been advanced by different authors regarding the causes which determine the setting of pozzolana mortars. These hypotheses never are based upon facts developed through research. They were derived from the chemical composition of pozzolana or from its behavior when placed in contact with some chemical reagents, or, finally, from analogy with facts observed in other artificial hydraulic materials, which present a well defined chemical composition of constant proportions. It is on account of this discrepancy between what was assumed and what is the true state of things, that the hypotheses advanced up to the present time upon the nature of pozzolana are to be considered as having the same value as those made by the first chemists experimenting with the setting of artificial hydraulic materials.

Smeaton, an English engineer, was the first to make known in 1796 the presence of clay in materials capable of furnishing, after clinkering, a product with hydraulic qualities. This observation was the starting point of a great number of researches all aimed at a determination of the function fulfilled by the various elements which, in the composition of hydraulic mortars, enter into the phenomena of setting and hardening.

In 1813 Collet-Descotils attributes the characteristic property of hydraulic materials to the presence of silica only (Annales des Mines, t.34, p. 308) while Vicat in 1818* directs attention to the role of alumina. It is to Vicat that the larger part of our theoretical and experimental knowledge of mortars is due. He affirmed that the setting was due to the chemical action that the elements of the mortar (silica, alumina and lime) exercise upon each other. According to Vicat the more the combinations of lime-pozzolana approach well defined proportions (whose values are for that matter still not exactly known) the stronger becomes the mass of the mortar.

*Annales des Mines - 1 Serie, T. 7, p. 445.

However, Iohn in the article "Sur la Chaux et les Mortiers" in Annales des Chimie et Physique, Serie 1, t. 19, p. 15, contrary to Vicat, holds that the setting of pozzolana mortars is not due to a chemical action, but to an absorption of lime from the porous mass of pozzolana. Berthier (see Annales des Mines 1822, 1 Serie, t 7, p. 483) though holding to the hypothesis of Iohn relative to the setting of pozzolana mortars, holds with Vicat that the setting of artificial hydraulic materials is truly due to a chemical combination of silica with lime.

After Berthier, Rivot his successor to the position of professor of inorganic chemistry to the School of Mines in Paris, made some researches which led him to the conclusion that during the clinkering of cements the following binary compounds are formed:

$$2\ CaO.SiO_2 \quad \text{and} \quad 3\ CaO.Al_2O_3$$

and that setting results from the simple hydration of

$$2\ CaO.SiO_2.6\ H_2O$$

and

$$3\ CaO.Al_2O_3.6\ H_2O$$

(Annales des Mines, 5 Serie, t. 9, P. 405)

According to Rivot there is an essential difference between Portland cement mortars and pozzolana mortars. In the first, the hydration of the silicate and the aluminate determines the setting, whereas in the pozzolana mortars, the hydrated silicate and hydrated aluminate are formed entirely through the action of the slaked lime upon the multiple silicate which constitutes the pozzolana.

But the theory of Rivot is no more than a simple hypothesis which owes its success more to the name of its author than to the experimental proofs upon which it is based.

The argument was thoroughly studied by Fremy in 1865 (Recherches Chimiques sur les Ciments Hydrauliques) Annales de Chimie et Physique, Ser. 4, t. 7, page 69. Fremy following his numerous experiments came to the conclusion that the hydraulicity is due not only to a phenomenon of hydration - as it appears from the theories of Vicat and Rivot, but, essentially to two distinct chemical actions, that is, to the hydration of calcium aluminates which are the main hydraulic agents of cement and to a pozzolanic action during which the calcium hydrate combines directly with the silicates of alumina giving rise to very stable compounds.

These results are highly interesting and it is impossible to overlook them in a study of hydraulic products. But Fremy has not proved that these reactions are the only ones which are produced in cements and in pozzolana mortars nor has he proved that these reactions actually take place in cements, inasmuch as he experimented only with artificial mixtures of silica and lime and alumina lime.

According to Michaelis, pozzolana, trass and santorino are volcanic products which have been subject to the action of hydrochloric acid, and, following that, to the action of water, which processes brought about the elimination of the larger part of the bases, leaving only some soluble silica, capable of reacting with lime and determining its setting. He rejects the idea of Feichtinger according to whom the setting of hydraulic materials is due to an absorption of carbonic anhydride by the free lime which slowly changes to the state of calcium carbonate. He states that, although he believes that the setting is due to the formation of a calcium silicate, he has never been successful in discovering the presence of such a compound in the crystalline state.

Landrin, in 1882 (in Comptes Rendues, t. 96, p. 156) contends that the setting of hydraulic products is due to what he calls "hydraulic silica" obtained by decomposing an alkaline silicate with an acid and he believes that it is found under special modifications in all hydraulic products and in the pozzolana.

At a later date he held that the setting of pozzolana is due to a lent modification of the bases combined with the hydraulic silica under the action of the lime. By studying then the quantity of lime absorbed by various qualities of siliceous materials placed in contact with a solution of lime, he comes to the conclusion that almost all siliceous materials have a tendency to absorb a quantity of lime corresponding to the compound:

$$3\ SiO_2.4\ CaO$$

to which he gives the name "pozzo-portland" and which, according to him, would be the constituent element of hydraulic materials. Having then prepared this compound artificially by fusion, following the observation that such a compound could set in water through the intervention of carbonic anhydride, he comes to the conclusion that carbonic acid is a main factor of the setting, and the only agent which determines the final hardening.

A material contribution to the bibliography on artificial cementitious materials was made in 1887 by Le Chatelier (Recherches Experimentales sur la Constitution, etc. - Annales des Mines - Series 8, t. 11, p. 345) who attempted to study the

chemical reactions which take place during the clinkering of the material and during the hardening thereof. In these studies Le Chatelier used the microscope with valuable results. In this way he studied some silicates prepared artificially by fusion including a calcium metasilicate - $CaO.SiO_2$, similar to the Wollastonite and a dicalcium silicate - $2\ CaO.\ SiO_2$ which dusts easily (neither silicates setting under water) and finally, a tri-calcium silicate - $3\ CaO.SiO_2$, which exists in cement, but is not well defined and shows a tendency to decompose with elimination of one molecule of lime. According to the views of LeChatelier this last compound is the principal element of hydraulicity of a cement. Under the action of water it decomposes into free lime and crystallized calcium silicate hydrate answering to the formula:

$$CaO.\ SiO_2.\ 2.5\ H_2O$$

according to the reaction:

$$3\ CaO.\ SiO_2 + Aq = CaO.\ SiO_2.\ 2.5\ H_2O + 2\ Ca(OH)_2$$

However, when Le Chatelier attempted to obtain this compound through the action of lime upon hydrated silica, he found that the chemical composition of the resultant product was not well defined. This explains the various formulae attributed to this compound by Berthier, Rivot and Landrin. In effect tri-calcium silicate loses with water both lime and silica until it transforms itself into pure silica while the precipitate does not crystallize.

Next to the silicates, the calcium aluminates appear to present a secondary importance; of them, the dicalcium and the tricalcium possess hydraulic properties. Both, during hydration, form supersaturated solutions, from which they ultimately precipitate in a crystalline state.

Le Chatelier then extended his studies upon Portland cement, both before and after its hydration, and from his studies concluded that the setting of Portland is due to the hydration of tri-calcium silicate into

$$CaO.SiO_2.\ 2.5\ H_2O$$

and of tri-calcium aluminate into tetracalcium aluminate hydrate

$$4\ CaO.Al_2O_3.12\ H_2O$$

Tornebohm, through the application of the microscope to the study of hydrated cements, confirms, in general, the observations of Le Chatelier with some modification upon the constitution of the hydrated cement. He acknowledges the presence of essential minerals to which he assigns the following names and the following composition:

chemical precipitate would take place during the alkalizing of the material and during the hydrolyzing thereof. In these studies a chemical was used which reacted with various reagents by producing a colored precipitate. This was then compared with a standard chart which identified the material. Such a chart was made by reacting a calcium chloride solution with sodium carbonate, sodium hydroxide and a calcium silicate - $CaSiO_3$. Upon exposure to the atmosphere (natural silicates contain water) and finally a tri-calcium silicate - Ca_3SiO_5, which exists in cement, but is not well defined and shows a tendency to decompose with elimination of one molecule of lime: According to the views of Bogue, quoted by Lea, the hydration of a cement under the action of water is represented by the following equations:

$$2(3CaO.SiO_2) + 6H_2O = 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

According to the reaction:

$$3CaO.Al_2O_3 + 6H_2O = 3CaO.Al_2O_3.6H_2O$$

However, when the observer attempted to obtain this compound through the action of lime upon hydrated alumina, he found that the chemical composition of the resultant product was not well defined. This explains why various formulas were assigned to the compound by different authors and investigators. In effect, it is quite possible that a calcium silicate does not exist, but rather a calcium silicate loosely combined with water. Lea states that

<u>Cement mixed into a paste with water sets and hardens.</u>

Setting is attributed to the calcium aluminates present, which rapidly precipitate in a crystalline state.

He observed that the setting of cement was retarded when a small amount of sugar was added. This was found to be true also in the case of tri-calcium aluminate into tetracalcium aluminate hydrate.

$$2(3CaO.Al_2O_3) + 21H_2O = 3CaO.Al_2O_3.6H_2O + 3(CaO.Al_2O_3.12H_2O)$$

One of the tri-calcium aluminates hydrates, $3CaO.Al_2O_3.6H_2O$, is cubic in crystallization and is not affected by sulphate waters. Another hydrate, $CaO.Al_2O_3.12H_2O$, is hexagonal in crystallization and is attacked by sulphate waters. Mixtures of these hydrates are intermediate in their behavior. In the study of hydrated cements, Le Chatelier, in general, the observations of Candlot on the mode of solution upon the constituents of cement. Candlot found that the tri-calcium aluminate hydrate, $3CaO.Al_2O_3.6H_2O$, dissolved in water, and the following compounds:

Alite: $X(3\ CaO.SiO_2) + 9\ CaO.Al_2O_3$

Belite: $X(2\ CaO.SiO_2) + 3\ CaO.Al_2O_3$

Celite: $3\ Ca(FeAL)_2\ .03\ .\ 2\ SiO_2$

Felite:

and, finally, a vitreous residue.

During the hardening of a cement the only active element is "alite" but even "Alite" is attacked at the surface only because due to the action of water, a gelatinous substance is formed which surrounds the grains, preventing any further hydra- (from which is born the need of a very fine grinding of cement).

This rapid resume of the various theories proposed relative to the constitution and setting of hydraulic materials, shows how divergent are the opinions held and shows on the other hand the difficulties presented by the following study. The publication of the present work is justified even though I do not claim to have completely solved the problem in question, but have tried to bring to general knowledge a series of facts which may be useful some day in establishing the complete theory of hydraulic mortars.

Following the mircoscopic study which I undertook upon the setting of lime-sand mortars, I conceived the idea of applying the same means of investigation to the study of lime-pozzolana mortars upon which - after the microscopic observations begun on Portland cements by Le Chatelier, Tornebohm, Feret Clifford, Richardson, etc., - no similar researches had been made.

Accordingly, I have chosen a certain number of pozzolanas whose hydraulic value is practically known, either because proved by many years of application or because derived from mechanical tests by various testing laboratories, and, finally, some inert materials.

The materials upon which I worked were the following:

1 - Red Pozzolana of "San Paolo", deriving from the group of Roman volcanos.

2 - Red pozzolana of "Pratolungo" deriving from the same volcanic group.

3 - Pozzolana of Bacoli, from the volcanic group of the Flegreian Fields.

4. Gray-colored pozzolana of the cave of Portella in the Roman countryside.

Alite: $3(3\,CaO.SiO_2) + 3\,CaO.Al_2O_3$

Belite: $2(2\,CaO.SiO_2) + 3\,CaO.Al_2O_3$

Celite: $3\,Ca(Fe,Al)_2.O_3 + 3\,SiO_2$

Felite:

Aft, finally, a vitreous residue.

During the hardening of a cement the only active element is "alite" but even "alite" is attacked by the surface only because due to the action of water, a gelatinous substance is formed which surrounds the grains, preventing any further hydration (from which is born the need of a very fine grinding of cement).

This rapid resume of the various theories proposed relative to the constitution and setting of hydraulic materials, shows how divergent are the opinions held and shows on the other hand the difficulties presented by the following study. The publication of the present work is justified even though I do not claim to have completely solved the problem in question, but have tried to bring no general knowledge a series of facts which may be useful some day in establishing the complete theory of hydraulic mortars.

Following the microscopic study which I undertook upon the setting of lime-sand mortars, I conceived the idea of applying the same means of investigation to the study of lime-pozzolana mortars upon which - after the microscopic observations begun on Portland cements by Le Chatelier, Forneboum, Feret, Clifford, Richardson, etc., - no similar researches had been made.

Accordingly, I have chosen a certain number of pozzolanas whose hydraulic value is practically known, either because proved by many years of application or because derived from mechanical tests by various testing laboratories, and, finally, some inert materials.

The materials upon which I worked were the following:

1 - Red pozzolana of "San Paolo", deriving from the group of Roman volcanos.

2 - Red pozzolana of "Pretolungo" deriving from the same volcanic group.

3 - Pozzolana of Racotic from the volcanic group of the Flegreian Fields.

4 - Grey-colored pozzolana of the cave of Portella in the Roman countryside.

5 - Pozzolana of "Torre del Grew" near Naples from the Vesuvius.

6 - Ashes of the eruption of the Vesuvius of the year 1878.

7 - Santorino

8 - Clay from Messina

9 - Vegetable soil.

The chemical composition in weight percentages of these materials is shown in the following table:

CHEMICAL COMPOSITION OF VARIOUS TYPES OF POZZOLANA

Type of Pozzolana	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	H_2O and other Subst.	Author Analysis
S. Paolo	45.50	15.12	12.05	--	9.33	3.59	3.78	2.15	8.45	Prof. Cavazzi
Pratolungo	46.24	19.26	11.18	--	9.82	2.84	2.66	2.77	6.10	Prof. Ostinelli
Bacoli	64.71	20.03	4.98	--	4.39	0.96	1.77	3.07	0.09	Italian R. R.
Portella	48.58	32.72	9.63	--	7.16	--	0.74	0.74	1.17	"
Bassano	47.10	21.90	8.01	--	9.91	1.56	2.56	6.01	2.21	Prof. Neubuffat
Vesuvio	48.45	17.81	3.49	3.55	12.09	3.02	5.46	5.01	0.60	Giorgis Gallo
Santorino	64.34	10.88	6.44		3.62	2.77	6.05	4.83	1.50	Vienna Polyt.
Messina Clay	41.80	12.42	5.05	--	18.76	2.29	--	--	--	
									CO_2 16.81	Gallo

From the chemical analysis of pozzolanas no conclusions can be derived regarding their hydraulic property, inasmuch as this varies between rather wide limits even for pozzolanas with the same chemical composition.

Under microscopic observation of a thin section of each one of these materials, an essential difference is noticeable between the constitution of the pozzolana known as satisfactory and those which have a hydraulic value very small or next to nothing. Figures 1 to 6 give an idea of their different constitution.

The pozzolana of San Paolo and that of Pratolungo are constituted almost entirely of a granulous, amorphous mass, which is a sign of a profound alteration. They are inactive to polarized light, and show only here and there small crystals of leucite, of augite and of mica.

Instead, the pozzolana of Bassano and the ashes of Vesuvius have a composition completely different and essentially crystalline. The larger fragments show elements of two successive stages of consolidation, with crystals of piroxene, leucite, plagioclase and olivenite. All these elements are mixed to products of alteration, more or less opaque and originating from small lamellae of black mica.

In the pozzolana of Bacoli are found the leucites with symmetrical inclusions, a few augites, some large lamellae of altered mica of first consolidation and abundant small lamellae of mica of second consolidation, besides green piroxene and some olivenite with black rings.

Santorino is constituted for the larger part of a granulous, amorphous mass without any action upon polarized light and mixed with pumice and obsidian and also with fragments of crystals of feldspar, quarz, piroxene and volcanic lava.

Regarding santorino it is interesting to remember that Mr. E. Heider was successful in separating from the santorino three different parts, that is; first, about 1/5 of light matter floating in water, constituted of pumice; second, about 3/5 of fine dust of a silvery gray color; third, about 1/5 of fine sand, almost always of a dark color, but sometimes red or yellow constituted especially of obsidian in its various forms. Now, while the first and the third part mixed with lime do not set under water, the second part, which under the microscope appears to be of a granulous and amorphous texture, acquires a maximum of resistance.

Furthermore, from the analysis of Feichtinger while the fundamental chemical composition of the various parts does not differ much, their behavi or in presence of a concentrated

solution of sodium hydrate is, nevertheless, very differemt because, while the first part abandons 5.2% of silica and the third 3.4% from the granulous part, sodium hydrate separates from the second part 28.4% of silica.

From the experiments of Heider and from the information which we already have upon the behavior of the various crystalline compounds which enter into the composition of pozzolana, we come, to the conclusion that the active part of a pozzolana must be the granulous and amorphous part contained within the whole mass.

It is natural therefore, to assume that the hydraulic value of a pozzolana is proportional to the relative quantity of amorphous material and that the crystalline part, cannot in any way, take part in the phenomenon of setting, but will remain simply interspersed throughout the hydrated parts in the hardened mass, contributing nothing to hardening, but rather establishing a solution of continuity of this same mass.

It remained now to establish the true chemical constitution of this amorphous mass and what is its behavior when placed in contact with lime. For this purpose mortarx were mixed in proportions of one part of lime and 3 parts of the various materials finely ground. The mixtures were first thoroughly mixed in the dry state and then mixed slowly with distilled water in a quantity sufficient to obtain a plastic mix, which would mold readily under the pressure of the hand. A small mortar cylinder 10" high and 1" in diameter was then made. The specimens were kept first in moist air for two days, and then immersed for three hours in distilled water to eliminate the largest part of air, and finally introduced into a graduated pipe, closed at one end and kept vertical, full of distilled water and with the open end immersed in a container of distilled water.

From these specimens very thin sections were cut every three days during the first month, and thereafter every ten days. The observations were prolonged through eight months, and corroborated at the same time by other observations and tests which had for their aim to extend the study to various aspects of the problem.

All the mortars made according to the described method soon presented to the microscopic observation a neat border of calcite (Fig. 7) of very small thickness (not more than 1/10 mm.) which remained almost constant, in the course of time, for all the good pozzolana. This superficial stratum of calcium carbonate, very uniform, well compacted and an integral part of the mortar, is formed as soon as the mortar has been mixed and is left in the open air during the period of drying. This stratum presents the great advantage of protecting the mortar from a rapid infil-

tration of water in the interior of the mass. Were this infiltration not checked, all the lime would in a short time be dissolved and eliminated, especially in those constructions in which water would be in a state of continuous movement. Furthermore, this stratum makes it possible that the reactions which determine the setting take place slowly in the interior of the mass.

Very soon, though, the good pozzolanas differentiate from the inert ones because the small grains of the amorphous part, which have at first well defined contours, separate into needles which penetrate between the surrounding grains. The resultant flocculent part remains partly reddish on account of the presence of iron (Fig. 10) and towards the end assumes a decisively white aspect. Owing to these phenomena, the small grains, losing their aspect little by little, appear as if they are surrounded by a reddish-white cloud. The flocculent mass then assumes the aspect of a compact sieve. This fact cannot be observed in the ashes of Vesuvius, or in vegetable earth and can only be observed to a very limited extent in the pozzolana of Bassano, which have a smaller quantity of amorphous substance. All of the crystalline parts which enter into the composition of the various materials keep their contours clear and well defined.

To be better able to witness the formation of these flocculations, and to at the same time follow their development, I have treated the various materials, finely ground, with slaked lime in a microscopic glass container, having a hollow bottom. The mixture in an extremely small quantity was deposited in the hollow bottom of this glass, the glass was filled with distilled water, and the whole covered, taking care that no air bubles remained within the mass. With such conditions, besides having been able to observe very well the slow diffusion of the lumps of pozzolana I have been able to notice that when the lime, in the process of hydration, assumes a flocculent aspect, in the shape of large lumps, that is in such a way as to present the aspect of very small grains, held together by very fine threads, the lumps of pozzolana and those of lime intersect each other in all directions, and increase in volume little by little so that for the good pozzolanas, the cavity is very soon completely filled.

I have been able to observe the Brownian movements every time I have treated either pozzolana or lime finely ground with water. But, while this movement can be observed when the two substances, lime and pozzolana, are separated, whenever they are mixed together, the movement begins and lasts but a few seconds, because the particles of pozzolana and of lime although suspended in the liquid, exercise a mutual attraction which renders the molecular movement impossible. While a pozzolana mani-

fests its movement with any liquid whatsoever, even for instance with hydrochloric acid, if a lime solution is added to the liquid containing the particles of pozzolana in movement, the movements gradually diminish in intensity, until they stop altogether.

This process of increase of volume of the amorphous, granulous part of the pozzolana due to the action of the lime reminds us that this is a property peculiar to silica and alumina when these two substances are found in some determinate allotropic modifications.

It is well known, from the experiments of Le Chatelier that treatment of a solution of colloidal silica with an excess of lime water gives birth to a precipitate of such large volume that one grain occupies the volume of two liters.

Furthermore, experiments of Michaelis show that under the action of lime water, silica and alumina swell, forming hydrated compounds extraordinarily rich in water, so that dried through compression, they can still contain 48 molecules of water in the case of silica, and 58 molecules of water in the case of alumina.

If, then, the particles of pozzolana have a tendency toward a diffusion in lumps and if, when they are in a free state and not compressed in mass, they have a tendency toward an increase of volume, it is natural to hold that silica and alumina enter, for the largest part in the constitution of the amorphous, and, at the same time - active part of a pozzolana. Furthermore if this swelling is manifested at once, and reaches its peak in a short time, about 20 days, this is another criterion of the constitution of pozzolana.

When, instead, pozzolana and lime are mixed together and then compressed, owing to the great tenacity of the lumps which are formed, there is no manifestation of an increase of volume, inasmuch as these lumps, during the progressive hydration are subject to a diffusion which increases until they occupy the whole space occupied by the water which they absorb, rendering at the same time, the mass of the mortar extraordinarily compact.

A proof of the compactness that the mortar assumes is furnished by the fact that throughout this peculiar process of swelling, the last molecules of air which could still remain enclosed within the mass, are displaced. In fact, as long as this process lasts it is possible to see small air bubles separate themselves from the mortar, and this production of air bubles stops when the swelling has reached its zenith. The quantity of air which is liberated from two equal quantities of pozzolana, cannot always give a sure indication of the quality of pozzolana,

even if the series of operations takes place in identical conditions, but is, in all cases, in a certain relation with the magnitude of the swelling. And inasmuch as these lumps increase continuously, they subdivide so that the size observed becomes smaller; the threads of activated materials follow through the mass of inert matter an increasingly crooked trajectory and from their relative position make a structure almost cellular, (See Fig. 10 & 10 bis.) which contains in its interior the particles of lime and pozzolana not yet attacked. This peculiar cellular structure is truly characteristic of all the good hydraulic pozzolana.

All this can be observed within the space of almost a month. During this time the pozzolana of Bassano, the clay, the vegetable earth, and the ashes of the Vesuvius, which had all conferred to the water a reaction constantly alkaline (rendered visible from a solution of fenolftaleina) had completely disintegrated, without showing any modification, while the lime which separated at the surface of the liquid, passed successively into calcium carbonate.

Proceeding further in the examination of the mortars which had remained integrated after about two months from their mixing, it was possible to see, at first in a very hazy way, and then more and more clearly, some crystalline nucleii and some needles diverging from a central point in such a way as to form a spheroidal mass. Little by little the needles united together to form small blades, and the whole thing assumed the form of a small flower with many petals, until the crystalline formation visible in Fig. 8 was clearly shown.

This crystalline formation was a complex of extremely thin blades all superimposed, and rotated a few degrees with respect to each other, often containing irregular formations of lumps of hexagonal shape, presenting an angle of 120 degrees inactive to light polarized in the direction of their optical axis, and active in the other direction. Similar crystals of very beautiful form, and perfectly complete, could be observed in the treatment of the pozzolanas in the small glass of the microscope, where the mass being not compressed allowed the free formation of crystals.

The question that naturally arose was that of the constitution of those crystals which were successively formed in the various pozzolanas, and of which, although being of different dimensions in the differemt pozzolanas, the crystalline system and the optical properties were always the same. Subjected to the action of the various reagents under the microscope, the crystals behaved in the following way:

1- With a concentrated solution of sodium hydrate they are attacked in a very short time, and some insoluble grains (probably of lime) separate from the total mass at the same time.

2- They are also slowly decomposed by pure water, separating out small gelatinous lumps.

3- With hydrochloric acid they dissolve slowly without liberation of gas and separate out some small grains which are in time dissolved.

4- A solution of ammonium chloride attacks them with liberation of gelatinous lumps.

These characteristics were sufficient to establish that the crystals belonged to a calcium compound, probably a silicate or an aluminate or a combination of the two.

Inasmuch as it was not possible to proceed naturally to the separation and the analysis of these crystals within the total mass, I tried to prepare them artificially, guided by the observation that they were formed from the flocculent mass, constituted of silica and alumina.

Already Le Chatelier had succeeded in preparing a hydrated silicate of lime through the action of lime water upon colloidal silica. He obtained an abundant flocculent precipitate which under the action of water liberated lime, leaving a residue of pure silica. Furthermore, even after a contact of six months with lime water, the precipitate remained constantly in a flocculent state. This silicate, which owing to its analogy with the barium silicate, received from Le Chatelier, the chemical composition:

$$CaO.SiO_2.Aq$$

has nevertheless, a variable composition according to the time in which the washing out of the lime is stopped.

The same Le Chatelier also prepared a hydrated calcium aluminate by treating the solution of an anhydrous aluminate with lime water. The precipitate thus obtained when observed under the microscope showed numerous needles grouped around a central point in the form of spherical groups, similar to those observed in the crystallization of all saturated solutions. The calcium aluminate thus obtained, decomposed easily under the action of water, and Le Chatelier from the average of his analyses, attributed to it the formula: $4\ CaO.Al_2O_3.12\ H_2O$.

I began by treating;

(a) A solution of an alkaline silicate with lime water.

(b) A solution of an alkaline aluminate with lime water.

(c) A mixture of a silicate and an aluminate with lime water.

In the first case, after some time, a turbidity becomes noticeable in the solution. This turbidity increases day by day, until it becomes an abundant precipitate, which remains constantly in a flocculent state.

In the second case, the precipitate presents all the characteristics observed by Le Chatelier.

In the third case, it is possible to notice phenomena resulting from the combination of the first two cases.

Now in none of these treatments could I obtain the crystals observed in the pozzolana.

I then treated as had been done by Le Chatelier, gelatinous silica and also gelatinous alumina with lime water, and finally the mixture of the two with lime water. I separated with ammonium chloride gelatinous silica from a solution of an alkaline silicate with ammonium chloride and ammonium. I precipitated the hydrate of alumina from a solution of nitrate of alumina. The two gelatinous precipitates after thorough washing were treated separately with a saturated solution of lime (0.127%), which was frequently renewed with fresh solution; the bottles being often agitated by hand. In a third bottle I placed the mixture of silica, alumina and lime water. Finally I made a fourth test by treating gelatinous alumina with a small quantity of magnesium hydrate in presence of water.

All four precipitates were subjected to a daily microscopic observation, while from a small part of the liquid was measured the quantity of lime absorbed. The precipitate of gelatinous silica although absorbing some lime from the solution, manifested itself readily as possessing a flocculent aspect of a cellular structure (Fig. 11) similar to that found in the flocculent mass of pozzolana.

This particular structure of gelatinous silica had already been observed by Rohland, who attributed to it the property of silica and other colloidal substances of fixing solid matter. It is also interesting to notice that it maintains itself without alteration, even after four months from its preparation.

The gelatinous alumina, although it presented at the beginning a flocculent aspect, slowly assumed a crystalline form, visible after six or seven days to the naked eye. This crystalline formation is made of extremely thin lamellae which, during the agitation of the liquid, present the same light effects as silk tissues. Viewing this crystallization with the microscope it is observed that the first formation is in the shape of needles which arrange themselves in lumps around a central point, giving rise to spherolites analogous to those observed by Le Chatelier for calcium aluminate. Little by little as the needles are united at their ends, they acquire contours clear and distinct, and give rise to the formation of small blades of hexagonal shape, superimposed and very characteristic, having the identical form and optical behavior of the crystals observed in pozzolanas.

These first crystals in pozzolana were then constituted of calcium aluminate, and, inasmuch as I had it also prepared in a separate test, perfectly pure, I could submit it to analysis. I must admit though, at this point, that the analysis is not as simple as it may appear at first.

In the first place, the filtration takes place very slowly because the smallest particles entering into the pores of the filter clog it in a short time, and in the second place, the time required for the filtration is such that a large part of lime water readily absorbs the carbonic anhydride of the atmosphere, transforming itself into carbonate.

Furthermore, these crystals are stable only in presence of lime water. With pure water they decompose (as Le Chatelier observed.)

The precipitate was then simply gathered upon a filter, without washing it, and then left for an hour in the open air, to allow the complete transformation of free lime into calcium carbonate, and was finally thoroughly dried.

The dry residue was then weighed with a small Fresenius apparatus and was subjected to the determination of carbonic anhydride by treating with hydrochloric acid 10% normal solution, with ebullition, which appears sufficient to the complete solution of the aluminate.

From the quantity of carbonic anhydride I determined the corresponding quantity of lime in the state of carbonate. Therefore, in the hydrochloric solution, proceeding to the determination of the alumina - and the lime - I determined from this last one the quantity that was supposed to be in the state of carbonate. The analyses made in this way gave me percentages

such that divided by the respective molecular weights, lead to the following results:

		I.	II.	III.
Al_2O_3	=	1.15	1.12	1.20
CaO	=	2.91	3.07	3.15
H_2O	=	10.06	10.51	9.98

From the results of these analyses I hold myself authorized to attribute to the compound formed during the setting of pozzolana, the formula:

$$3\ CaO.Al_2O_3.10\ H_2O$$

At this point it is opportune to notice that Candlot contrary to Le Chatelier, has demonstrated that one of the main agents in the setting of cements is the formation of a calcium aluminate of the formula:

$$3\ CaO.\ Al_2O_3.\ 10\ H_2O$$

which is formed through direct hydration of the anhydrous tricalcium aluminate and not through addition of lime, as Le Chatelier believed.

As a complement of these observations I may add that also treating gelatinous alumina with hydrated magnesia, it is possible to give rise to the slow formation of isomorphous crystals with the crystals of calcium aluminate - but the presence of these crystals does not become manifest until after about a month of contact. I believe that this characteristic must be in a strict relationship with the smaller solubility of magnesia compared to lime. In effect, while lime is soluble in the ratio of one part lime to 760 parts of water, magnesia is only soluble in the ratio of one to 50.000. Therefore, the quantity of magnesia which can remain dissolved and can react with the soluble alumina to crystallize together, is small compared to the lime, from which follows the slowness of the formation of crystals.

Proceeding further in the examination of the mortars which had remained coherent in water, and which had undergone a perfect setting, it was possible to observe that after a period of time varying from four to seven months, according to the various pozzolanas, crystalline needles deposited slowly within the

texture of the flocculemt mass, and, properly in the small pores found in it. The needles were oriented in all directions of a slightly double refraction becoming obscure under polarized light in the direction of their length (Fig. 10 bis. and Fig. 12).

These crystals have constituted the reef against which all my activity has broken so far, not having been able to dedice with certainty their exact composition. They present analogy with those observed by Le Chatelier during the setting of cements; crystals to which he assigned - without proving it - the formula:

$$SiO_2 . CaO . 2.5\ H_2O$$

The facts however are that treating colloidal silica with water, Le Chatelier never could obtain the formation of similar crystals, also the whole mass remained flocculent and amorphous. Furthermore, as I have already said, the mass was decomposed by water, liberating lime and leaving a residue of pure silica. In the various preparations, which I have kept now for about four months, of alkaline silicate with lime water, and of gelatinous silica with lime water, still presenting a flocculent aspect, and a characteristic cellular structure I have been unable to discover the presence of similar crystals.

While I was working on these researches, I tried to check the observations previously made upon older pozzolana mortars. My researches extended especially upon a pozzolana mortar placed in the harbor of Leghorn in the year 1854. Of this mortar I have taken away a few samples from a block immersed to a depth of 5 meters below sea level, the 22nd of March 1907. Esamining those samples under the microscope, I noticed the presence of crystals of calcium aluminate, and also very clearly the characteristic cellular structure covered by the formation of such crystals.

The mass, with the enclosed crystals, subjected to various reagents behaves in the following way. A diluted solution of potassium hydrate is without action; a concentrated solution attacks and disintegrates the flocculent mass in a brief time, but leaves, almost intact the crystals presenting double refraction. Separating the alkaline solution, treating it with a drop of hydrochloric acid, and heating it lightly, it is possible to observe the separation of small lumps of silica. I assume that the silica does not enter to form part of the constitution of the crystals, inasmuch as these have kept their form almost equal and uniform and have not lost their property of double refraction.

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While I was working on these researches, I tried to check the observations previously made upon older pozzolana mortars. My researches extended especially upon a pozzolana mortar placed in the harbor of Leghorn in the year 1864. Of this mortar I have taken away a few samples from a block immersed to a depth of 3 meters below sea level, the 22nd of March 1907. Examining those samples under the microscope, I noticed the presence of crystals of calcium aluminate, and also very clearly the characteristic cellular structure covered by the formation of such crystals.

The mass, with the enclosed crystals, subjected to various reagents behaves in the following way. A diluted solution of potassium hydrate is without action; a concentrated solution attacks and disintegrates the flocculent mass in a brief time, but leaves, almost intact the crystals presenting double refraction. Separating the alkaline solution, treating it with a drop of hydrochloric acid, and heating it lightly, it is possible to observe the separation of small lumps of silica. I assume that the silica does not enter to form part of the constitution of the crystals, inasmuch as these have kept their form almost equal and uniform and have not lost their property of double refraction.

Hydrochloric acid and acetic acid, even if diluted, completely disintegrate the crystals in a relatively short time, leaving the general structure unattacked. But this solubility is not complete, and some very small grains are left, which are impossible to exactly identify. A solution of ammonium chloride also disintegrates the crystals, which lose their property of double refraction, and, at the same time, develop small quantities of gas which might be ammonia.

The analogy of optical behavior observed between these crystals and those which I had noticed in my previous works upon ordinary lime-sand mortar led me to believe that these crystals are made of crystallized calcium hydrate.

Furthermore, it was noticed that ancient pozzolana mortars, older perhaps than 1000 years, contain in the interior of the mass some free lime, which phenomenon is attributed to the fact that their setting is not yet complete.

I would incline therefore to hold, with some reservations and until contrary proof, that these crystals are constructed of calcium hydrate crystallized, and in such a case I would concur with the hypothesis advanced by Chevreul, Fremy and Michaelis, according to which the setting of pozzolana mortars would be due simply to a physical phenomenon of capillary attraction of lime from the silica and the alumina.

Resuming the results already described, the setting of pozzolana mortars is to be explained in the following way:

"The calcium hydrate which is part of the composition of pozzolana mortars brings about the hydration of the silica and alumina, which swell so as to occupy all the space already occupied by water and air, giving rise to the formation of an impermeable mass which contributes highly to the resistance of the mortar. Successively takes place the formation of a soluble calcium aluminate, which finding itself in presence of an excess of lime, and, therefore, in a supersaturated solution, precipitates and crystallizes under the form of:

$$3\,CaO,\ Al_2O_3.10\,H_2O$$

and in its crystallization connects together the various particles which enter to form the matrix of the crystals. This represents the first period of the setting. The surfaces between the flocculent part and the empty spaces are seats of capillar tensions, owing to which silica attracks lime in its pores and gives rise to the formation of nucleii within which the lime, giving up slowly its water of hydration, crystallizes to the state of calcium monohydrate, determining a complete adherency of the various parts,

in such a way that the total mass transforms itself into a whole unit highly resistent and very compact, even if between lime and silica are not formed very definite compounds but only variable mixtures. This is the second period of the setting, when all these phenomena manifest themselves in the interior of the mass kept moist and protected externally by an insoluble stratum of calcium carbonate."

The setting of pozzolana is, therefore, due partly to a general phenomenon of formation of a supersaturated solution which characterizes the setting of those materials hardening under water, and partly due to a purely physical phenomenon of swelling.

Consequently, the more rapidly a pozzolana reaches its maximum swelling, the better will be its setting, because the mortar becoming impermeable to water is not subjected to the deteriorating action that water can exercise; action which causes a greater havoc with a greater substitution of water in the interior of the mass.

It is therefore in this way that it is possible to explain the slow process of the setting of pozzolana mortars - the silica present, in fact, cannot absorb more than a certain quantity of lime; the excess of lime liberated then crystallizes forming a deposit of calcium hydrate crystallized.

It is not to be excluded, though, that between the silica and the lime so intimately mixed a chemical reaction might take place which would give birth to some well defined compounds, even if the formation of these compounds has not been so far, confirmed by actual observation.

Contemporaneous with the microscopic researches above described, I have proceeded for the various pozzolanas to analytical tests of comparison, which have the aim of confirming the observations made by the microscope rather than the aim of determining the technical value of pozzolanas.

As it is well known the tests which are presently applied to judge the hydraulic value of a pozzolana, are not sufficient to give in a relatively short time a safe index of the technical value of these materials. It appears therefore, highly desirable that a practical chemical or physical test be developed for determining the hydraulic value of a pozzolana.

Already in a previous work in collaboration with Prof. Giorgis* we set forth a series of experiments from which it is possible to deduce that the variation of electric conductivity of a pozzolana mortar is in a direct relationship to the progression of the setting process.

* Giorgis & Gallo: Gazz. Chim. Ital. Vol. 36, 1906, p. 137

The method has furnished some very satisfactory results especially in discovering actual adulterations of pozzolana with vegetable soil, but, on account of the fact that the measurements are of an extreme delicacy, they are too highly influenced by accidental circumstances that very often escape direct observation.

The tests which offer the greater reliability are still the mechanical tests, provided that the experiments are made in well determined and constant conditions, and the tests are prolonged for about two years.

A chemical test to determine the active part of a pozzolana would be sufficient to solve the problem, but, unfortunately we are still far from this solution.

Feret believes that the most logical way to find out the hydraulic value of a pozzolana is that of determining the percentage of lime fixed from lime water by a determinate weight of finely ground pozzolana. This is the old method already proposed by Vicat, which is still used, notwithstanding the numerous researches made on this subject by Professors Giorgis and Alvisi (see Gazzetta Chimica Italiana, Vol. 30, P. 1, 1900), which have shown that the quantity of lime fixed is too small, requires too long a time and is affected by the presence of extraneous materials.

To obtain more conclusive results Manzella proposes to diminish the quantity of pozzolana or to increase the quantity of lime water, employing, that is, about 3 cmq. of silica for 100 cm^3 of lime water. This condition had been already fulfilled by Landrin (see Gazzetta Chimica Italiana, Vol. 36, P. 113) who in his study of the quantity of lime fixed by various hydraulic siliceous materials, used 3 cmq. of silica for each 100 $cm.^3$ of lime water; and by Feret and Zamboni who used gr. 0.75 of pozzolana for 150 $cm.^3$ of lime water.

According to my findings upon the setting of pozzolana mortars, this greater facility of pozzolana of fixing lime under the conditions set forth above is due to the presence of an excess of lime compared to the amount of pozzolana, owing to which silica and alumina as we have seen, can absorb and fix (physically as for the silica, chemically as for the alumina) a certain quantity of lime only when this element is present in excess.

On te other hand, water not saturated with lume, exercises a disintegrating action upon the calcium aluminate already formed, and, finally, the swelling due to the hydration of the silica and the alumina reaches its maximum only when it takes place in presence of saturated lime solution.

To be able to obtain a measure and a comparative value of the increase of value observed through the microscope when treating the pozzolana with lime water, I have made some graduated cylinders, of the capacity of 50 $cm.^3$, and of an internal diameter of 2 cm., and a height of 20 cm. graduated on the basis of half $cm.^3$ and hermetically closed.

One gram of the materials subjected to the microscopic examination, minutely ground, and sieved through the 4000 mesh sieve (4000/$cm.^2$), was each time introduced in similar cylinders, perfectly dry, and afterwards treated with lime water containing 1.27 g. of CaO per liter and hermetically closed. The small cylinders were every so often mechanically agitated, and every day after one hour of rest from the last agitation, the volume of the mass was checked and recorded. Every two days 25 $cm.^3$ of the clear liquid above were substituted with new saturated lime water, and from those 25 g. was obtained the quantity of lime dissolved.

The increase of volume which took place with the various materials in a period of time of 30 days is rendered evident by the curves reported in Table 1., which have been obtained by regarding the volumes as ordinates, and the time durations as abscissae. From the examinations of these curves it is possible to discover that the good pozzolanas begin their hydration immediately reaching a maximum volume (which is, for instance ten times larger than the initial one for the San Paolo pozzolana) after a period of time which can be held in the average to be equal to about 20 days; after this time, even changing the lime water repeatedly, the volume shows a tendency to remain constant; furthermore, after two months or more it shows a tendency to diminish, as verified by Feret.

I believe that the slow diminution of volume, after the maximum has been reached is connected with the crystallization and the formation of calcium aluminate on account of the fact that this compound occupies a smaller volume than its components. The microscopic observation of the lumps shows exactly after this period of time the abundant presence of crystals of calcium aluminate.

If instead of substituting a new saturated solution every two days for original lime water, the various materials are left in contact with the same lime water, the swelling which takes place at the beginning never reaches the maximum value which is reached when the solution of calcium hydrate is renewed from time to time.

It is also interesting to verify how the single increases of volume are in relation with the technical value of

known pozzolana; thus clay, the pozzolana of Bassano, the vegetable earth and the ashes of the Vesuvius, materials which have a hydraulic value very small or entirely negligible, vary very little from a straight line parallel to the abscissa axis.

The pozzolana of Bacoli shows through this test, to be inferior to all Roman pozzolanas and such a consequence can be deduced also from the microscopic observation of the pozzolana which is in a large part crystalline.

The quantity of lime absorbed successively by the various pozzolanas every 8 days remains about constant in the various determinations and for the length of time under consideration; and precisely, for each one of them, that quantity averages the following values:

CaO absorbs by 100 gr of pozzolana:	
San Paolo	2.52
Pratolungo	2.26
Santorino	2.38
Portella	1.82
Bacoli	1.68
Bassano	0.75
Ashes of Vesuvius	0.12

Note how these values are in a strict relationship with the observed increases of volume. For the clay it is noticed that there is not a rapid swelling as for the good pozzolana, but that this swelling is gradual and progressive until it reaches the maximum value of 37 $cm.^3$. Further, the quantity of calcium oxide absorbed is 1.4% during the first few days, while the density of the solution afterwards remains constant. For the vegetable earth, although there is no increase of volume whatever, the quantity of lime which is fixed is about 2.78% in the first few days (superior that is, to the quantity of lime fixed by the best pozzolana, as it had been already observed by Giorgis and Alvisi) but the quantity of lime fixed diminishes little by little until it disappears altogether after a few days, in conformity to the observation of Manzella. If then, instead of repeating the test of Vicat under the usual conditions, that is leaving the pozzolana in contact with the unrenewed lime water, the water is constantly renewed, the total quantity of lime water which the pozzolana can fix, is much larger than that which at the same time is taken away by a given amount of pozzolana from a solution of lime which is never renewed.

known pozzolana; thus clay, the pozzolana of Bassano, the vegetable earth and the ashes of the Vesuvius, materials which have a hydraulic value very small or entirely negligible, very very little from a straight line parallel to the abscissa axis.

The pozzolana of Pacoli shows through this test to be inferior to all known pozzolanas and such a consequence can be deduced also from the microscopic observation of the pozzolana which is in a large part crystalline.

The quantity of lime absorbed successively by the various pozzolanas every 8 days remains about constant in the various determinations and for the length of time under consideration; and precisely, for each one of them, that quantity averages the following values:

Cad absorbs by 100 gr of pozzolana

San Paolo	2.52
Pratolungo	2.36
Santorino	2.28
Portella	1.82
Pacoli	1.58
Bassano	0.75
Ashes of Vesuvius	0.12

Note how these values are in a strict relationship with the observed increases of volume. For the clay it is noticed that there is not a rapid swelling as for the good pozzolana, but that this swelling is gradual and progressive until it reaches the maximum value of 37 cm. Further, the quantity of calcium oxide absorbed is 1.4 during the first few days, while the density of the solution afterwards remains constant. For the vegetable earth, although there is no increase of volume whatever, the quantity of lime which is fixed is about 2.78 in the first few days (superior that is, to the quantity of lime fixed by the best pozzolana, as it had been already observed by Giorgis and Alvisi) but the quantity of lime fixed diminishes little by little until it disappears altogether after a few days, in conformity to the observation of Manzella. If then, instead of repeating the test of Mica under the usual conditions, that is leaving the pozzolana in contact with the unrenewed lime water, the water is constantly renewed, the total quantity of lime water which the pozzolana can fix is much larger than that which the same time is taken away by a given amount of pozzolana a solution of lime which is never renewed.

In accordance with the microscopical observations is the fact that from the various analyses of pozzolana separating on one hand the part which is soluble in acids from that which is insoluble, it is always possible to find in the good pozzolanas a remarkable quantity of alumina in the soluble part. Thus, for instance, from the analyses of the soluble and the insoluble parts of the pozzolana of San Paolo in hydrochloric acid, made by Prof. Cavazzi, it is possible to discover that the quantity of alumina contained in the insoluble residue is about 0.20%, while in the soluble part it is possible to find as much as 14.92%.

Now it is true that this alumina can derive also from compounds easily decomposable by the action of acids, but it is just these soluble principles which offer us a criterion for judging the larger or smaller facility of pozzolana to enter into reaction.

To verify whether all the alumina which enters into combination with lime is in a state of easy attack by diluted acids, or if lime acts upon it by bringing about such a transformation as to render it more easily soluble, I have subjected the various materials in their natural state to boiling treatment with hydrochloric acid 10% for 10 minutes, and in the filtered liquid I have next proceeded to the precipitation of iron and alumina and, eventually, of the quantity of silica dissolved through ammonium chloride and ammonia. From the weight of the precipitate thus obtained, I have treated in the identical way the same materials after they had remained for three months in contact with saturated lime water. The results of the determinations are tabulated hereinafter:

	$Al_2O_3 \cdot SiO_2$ of materials in their natural state.	$Al_2O_3 \cdot SiO_2$ after 2 months of contact with lime water	Difference
San Paolo	13.30	20.46	7.16
Pratolungo	12.98	19.66	6.68
Bacoli	2.28	3.58	1.30
Bassano	4.18	3.60	0.58
Portella	4.22	5.96	1.74
Santorino	3.46	8.97	4.57
Clay	2.16	2.18	0.02
Vesuvius	1.76	1.71	0.05
Earth	8.58	8.60	0.02

From the comparison of these values it is noticed that the quantity of alumina and of silica which can be dissolved in a diluted acid solution is in all good pozzolanas greater when these pozzolanas have reacted with lime than when they are in their natural state.

This is easily explained by the fact that through the action of the lime, alumina and silica are subject to a hydration which renders them more soluble, and that, successively alumina is partially dissolved to give rise to calcium aluminate crystallized which is decomposed by hydrochloric acid N/10%. The quantity of silica and alumina dissolved, instead by hydrochloric acid in the inert materials remains about constant, before and after the treatment with lime water.

Besides the treatment of the various materials in their natural state, and after the action of lime water, with hydrochloric acid, I have tried to determine also the action of solutions of alkaline hydrates of various concentration. Rivot, Landrin, Signorile, Michaelis, Rebuffat, Lunge, Millberg and Feret have experimented upon the action of alkaline hydrates and carbonates upon pozzolanas and their researches have proved that the quantity of pozzolana which can be dissolved varies with the nature and the degree of concentration of the reagent.

Lunge and Millberg have reached the conclusion that quarz finely ground can be in large part attacked through prolonged boiling with a solution of sodium hydrate of 30% concentration, and that, on the other hand, a solution of 5% sodium hydrate placed to react with a mixture of quarz and calcined gelatinous silica, allows an almost complete separation between quarz and soluble silica.

They believe also that trass and pozzolana contain silicates easily decomposable, owing to which they propose to decompose first the material with hydrochloric acid, and then to subject the residue to the action of an alkaline hydrate, a test which had been proposed by Rivot without concrete results.

They come to the conclusion "that it is possible to obtain the hydraulic value of a pozzolana from the quantity of silica and alumina which it can release through heating during six hours in a solution of 30% sodium hydrate.

The experiments of Rebuffat, Giorgis and Alvisi and of Feret who uses, instead, a solution of NaOH 15% proved clearly that the results thus obtained are entirely arbitrary and do not allow for any deduction.

To be able to better define the composition of that part of pozzolana which appears granulous and amorphous, I have

made various tests of comparison, and, have experimented with:

1 - The action of a 1% solution of sodium hydrate during one half hour upon the materials in their natural state.

2 - The action of a 1% solution of sodium hydrate during one half hour upon the same materials after having been 75 days in contact with lime water.

3 - The action of a 5% solution of sodium hydrate during fifteen minutes upon the materials in their natural state.

4 - The action of a 5% solution of sodium hydrate during fifteen minutes upon the same materials after having remained for 75 days in contact with lime water.

5 - The action of a 5% solution of sodium hydrate during fifteen minutes, upon the dry residue of the treatment of the materials in their natural state with hydrochloric acid.

The results of all these determinations are gathered in the following table:

	1st Exp.		2nd Exp.		3rd Exp.		4th Exp.		5th Exp.	
	SiO_2%	Al_2O_3%	SiO_2%	Al_2O_3%	SiO_2%	Al_2O_3%	SiO_2%	Al_2O_3%	SiO_2%	Al_2O_3%
S. Paolo	4.53	2.78	4.31	2.67	14.51	5.80	13.85	6.31	14.28	6.58
Pratolungo	3.41	2.15	3.70	2.36	12.29	6.15	13.45	6.81	14.77	6.63
Bacoli	2.10	1.88	1.95	2.20	6.51	3.27	6.70	3.12	8.94	3.15
Portella	2.88	1.87	2.25	1.71	6.15	4.82	5.11	3.05	6.34	4.21
Santorino	2.15	1.08	1.91	1.05	5.47	2.15	6.41	3.55	6.27	4.88
Bassano	0.97	0.82	0.85	0.60	2.10	1.30	2.35	1.21	10.17	4.55
Clay	0.38	0.12	0.22	0.31	0.91	0.70	0.21	0.65	0.37	0.13
Earth	1.75	1.34	1.15	1.65	6.12	2.31	5.73	2.46	6.64	4.55
Ashes	0.52	0.15	0.25	0.32	1.71	1.65	1.68	1.53	10.16	4.37

| | | |

From the examination of the reported values it is possible to make some observations of interest.

In the first place the 1% solution of sodium hydrate and the 5% solution bring the larger part of active silica and alumina present in pozzolana into a soluble state, and such quality is maintained in the good pozzolana almost constant even in the case of previous treatment of materials with hydraulic acid, while for the poor hydraulic materials, like the ashes of the Vesuvius and the Bassano pozzolana, the previous decomposition with hydrochloric acid brings into solution a much larger quantity of silica and alumina.

Clay, in these conditions is not attacked except in a very small way. The vegetable earth instead (on account of the fact that it is a material easily decomposed) cannot give any safe indication.

Another fact appears evident from the examination of the above table, and that is: comparing the quantities of silica and alumina soluble in the 5% solution of sodium hydrate the Roman pozzolanas are much superior to the best Neapolitan pozzolanas, of which the Bacoli pozzolana forms the prototype.

From the described tests it is possible, furthermore, to notice that if for some materials the previous treatment with hydrochloric acid brings into solution a larger quantity of silica and alumina, this does not take place, for the good pozzolanas. This means that hydrochloric acid does not exercise any sensible decomposition upon these materials. It is possible thus to arrive at the conclusion that, in all probability, the amorphous and granulous part of pozzolana, which is its active part, results from a mixture of silica and alumina in a free state, in a special allotropic manifestation brought about by the action of atmospheric agents, or, at the most, in the state of silicate of alumina easily decomposed.

Another proof, finally, of this constitution of the active part of these materials lies in the fact that a good pozzolana abandons through boiling with water during 10 minutes, a certain quantity of silica and alumina in a colloidal state, and this quantity reaches 0.57% for the pozzolana of San Paolo. This behavior besides confirming what we have seen, explains also in a very convenient way how pozzolanas left for long time exposed to the action of atmospheric agents are subject in time to a degeneration of their hydraulic value.

It is now opportune to mention the controversial issue whether the use of pozzolanas in their natural state or else finely ground is to be preferred.

From the experiments of Feret, Luiggi and Cardi, the finely ground pozzolanas give to mechanical tests better results than those given by the pozzolanas used in their natural state, but the difference is not so great as it is believed, and, furthermore, diminishes in time. All this brought Rebuffat to express himself without hesitation in favor of the use of pozzolana in its natural state.

Without going into too many details, it is possible to see, at the microscopical examination, that the active part of a pozzolana is found equally distributed throughout its various particles. So it happens that when finely ground pozzolana is used, all the active part coming in contact with lime water, hydrates readily, therefore the swelling and the setting takes place during a relatively short time.

Using pozzolana instead in its natural state, the hydration does not take place with the same intensity, the swelling still can be observed, but never reaches the maximum volume that can be obtained through the action of lime water upon finely ground pozzolana. Nevertheless, the active part of the pozzolana reacts during the hydration, but more slowly, even in the interior of the particles, and the gelatinous lumps are diffused toward the exterior of the mass, where, meeting the excess of lime, they give rise to the setting through the formation of calcium aluminate and the separation of calcium hydrate crystallized. But as the lime cannot penetrate toward the interior to complete the setting of the whole mass, it results that while at the surface the particle is of the whitish color of the mortar, and highly resistant, in the interior it keeps the color of pozzolana still unaltered, because in the interior of the mass there has been no action of the lime.

From all this we can state that through fine grinding the pozzolana reaches much sooner the limit of setting and the maximum of resistance, and also shows a better behavior under mechanical tests, but, that on the other hand, using the pozzolana in its natural state, although it gives rise to the formation of particles with an unhydrated nucleus, these particles are, nevertheless, protected at the surface by a very hard and resistant stratum which adheres perfectly to the surrounding particles, and the incoherency of the nucleus does not produce a solution of continuity. Owing to the aforesaid, whenever there is not absolute need of reaching the maximum of resistance in a short time even the pozzolana used in its natural state can give satisfactory results.

At the same time also from the microscopic observation it results that the truly active part of a pozzolana presents itself as granulous and amorphous.

From the works of Vicat, Fremy and others it is known that while clay in its natural state does not manifest any pozzolanic property, it acquires instead, following calcination at about 700°C. the property of setting under water to a certain extent.

It is easy to prove, says Fremy that the calcining of clay sets at liberty a certain quantity of silica and of alumina. In effect, while clay in its natural state is not attackable by acids, following calcination, it forms with them a gelatinous substance, giving up in solution a remarkable quantity of alumina.

And inasmuch as it has been proved by the experiments of Vicat that silica and alumina in their free state and in a particular allotropic condition, exhibit high pozzolanic qualities, it is easily explained how clay, under thermic action is transformed into pozzolana.

Clay, in fact, is nothing more than a hydrate silicate of alumina. There is a large number of hydrated salts in which water enters as integral part of the constitution of the molecule and in which the simple process of de-hydration determines the deepest decomposition. Such seems to be the case of calcined clay.

On the other hand I have found that while natural clay does not undergo more than a light swelling under the action of lime water, following calcination at between 700°C. and 800°C. clay when placed in contact with lime water can reach a volume of about five or six times larger than the initial one, indicating in this way that while the hydration could not take place before calcination, after the same, silica and alumina set free can easily become hydrated and increase in volume.

For all that it is not to be believed that calcined clay can furnish a good pozzolana, because if such were the case, this excellent hydraulic material would have found too many competitors, and it is a fact that the numerous attempts of Vicat and others did not succeed in producing artificially good pozzolanas.

Although the composition of calcined clay and of pozzolana is approximately the same, it is not possible to establish a comparison between a material of which calcination is of recent date and another material instead, whose calcination goes back hundreds of centuries and upon which atmospheric agents have long acted.

We are thus, enabled to put forward an hypothesis upon the genesis of pozzolanas:

Pozzolanas must, evidently originate from materials carried by volcanic ejections from deep geological strata of es-

sentially clayey composition, materials that, during the eruption must have undergone a calcination such as to determine a complete de-hydration and a profound chemical alteration of the mass. But this alteration has not proceeded so far that the mass has been entirely fused as in the case of crystalline elements.

If the pozzolanic property is simply due to the action of atmospheric agents, which have contributed to deeply modify the materials of volcanic eruption, why is it that the ashes of all the volcanoes active or dead are not found to exhibit pozzolanic properties after a certain period of time.

If this does not happen it means simply that from the beginning, the constituent material had a different chemical composition, and that, furthermore, the action that the volcano has exercised upon it, is fundamentally different.

In the case of pozzolanas, they once deposited, were subject, through numerous centuries, to the action of atmospheric agents, which have determined a slow and progressive modification of silica and alumina already in a free state, modification which consists essentially of an intimage hydration of the single particles, this hydration being in relation to the quantity of water of composition contained in the good pozzolanas. Owing to such hydration these pozzolanas, coming into contact with lime water find themselves in a proper condition to form some higher forms of hydrates, swelling up and dissolving little by little, giving rise finally, to the phenomena determining the setting of pozzolanas.

It is interesting to notice that this property of being subject to hydration is in a strict relationship with the quantity of water necessary for the mixing; a quantity which is maximum for the good pozzolanas, and minimum for the bad ones (inert).

On the other hand, it is well known that pozzolanas subjected to calcination lose partially or totally their property of setting under water, because with such an operation we eliminate the essential element which determines their hydraulic value, that is, the absorbed water of hydration, thus making both silica and alumina unable to hydrate at the surface and to react with lime water. Finally, calcination also destroys that intimate molecular composition which had been determined in them by the long process of time.

And, finally, such constitution of pozzolana is related strictly to the fact observed through many centuries of the extraordinary resistance that pozzolana mortars offer to the disintegrating action of sea water.

The disintegration of cementitious materials in sea water is a phenomenon which has highly interested, and still interests, scientists and engineers, to explain the numerous disasters to which it has given rise, and to obviate such possibilities.

In general it is believed that the disintegrating action of sea water is due to the fact that the magnesium sulphate in presence of free lime gives rise to the formation of magnesium hydrate and to calcium sulphate, which, crystallizing, increases in volume and exercises a pressure capable of disintegrating the mass. A pozzolana mortar, should, therefore, find itself in an opportune condition to be attacked by sea water - nevertheless, this assumption is denied by actual facts.

Besides the insoluble surface stratum of calcium carbonate, and the density which the mass assumes, another factor influences its preservation. If it is true that the active part of a pozzolana consists of silica and alumina in a free state, these two substances under the action of lime water on hydrating give rise to the formation of a gelatinous mass (which is in larger quantity, the better the pozzolana is). This gelatinous mass completely envelopes the crystals of calcium aluminate and of free lime in the mortar.

This silica in such an allotropic condition, and, eventually, the alumina also, are part of a category of substances which exhibit special properties, long since known, and which are referred to in many researches of general chemistry.

Van t'Hoff derived his ingenious theory of diluted solutions founding it upon the osmotic pressure exercised from salt solutions of various concentration, immersed in a pure solvent and separated from it by a semi-permeable membrane, that is a membrane which leaves free passage to the molecules of the solvent, and not to those of the material in solution.

This property is characteristic of some colloidal substances like hydrate iron oxide, gelatinous alumina and gelatinous silica whose intimate structure very nearly approaches the cellular structure of animal and vegetable tissues. If then the active hydraulic elements of pozzolanas are truly constituted of alumina and silica in a colloidal state, and if silica remains in a free state, this means that it is going to manifest to a high degree its property of semi-permeability, and is therefore going to prevent the diffusion of the salts of sea water within the mass of the mortar, thus preventing those chemical disintegrating actions which have been the cause of so many failures of artificial cementitious materials in sea water.

A corroboration of the above statement can be found in the experiments made by Le Chatelier upon the diffusion of colored salts in specimens manufactured with various types of hydraulic mortar. From these experiments, it is possible to learn that while in pure cements the diffusion of those salts is complete, in pozzolana mortars, the diffusion is smaller or, almost negligible, although they contain a much larger quantity of water.

From all the previous discussion it is possible then, to conclude that pozzolana mortars represent an hydraulic material superior to artificial hydraulic materials.

G. G A L L O

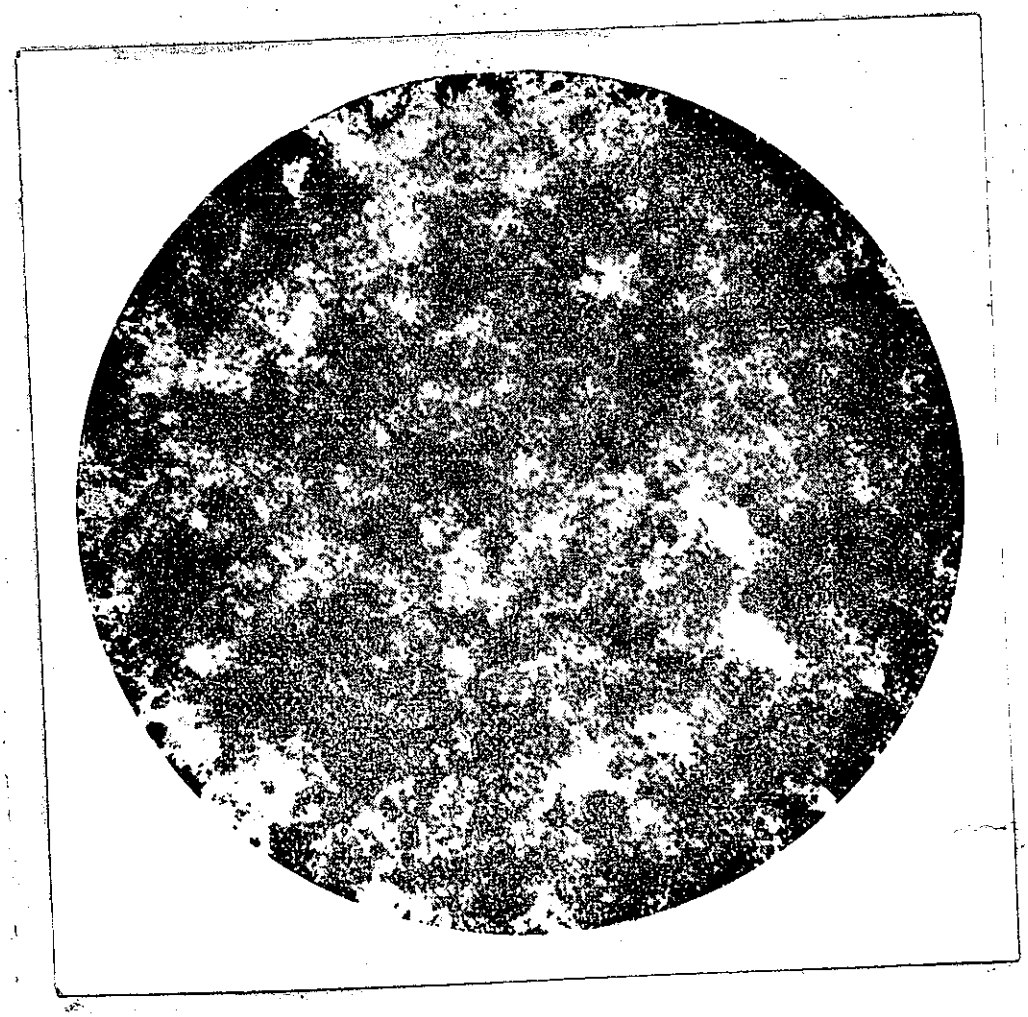


FIG. 1
POZZOLANA OF SAN PAOLO

Fig. 2
POZZOLANA OF PRATOLUNGO

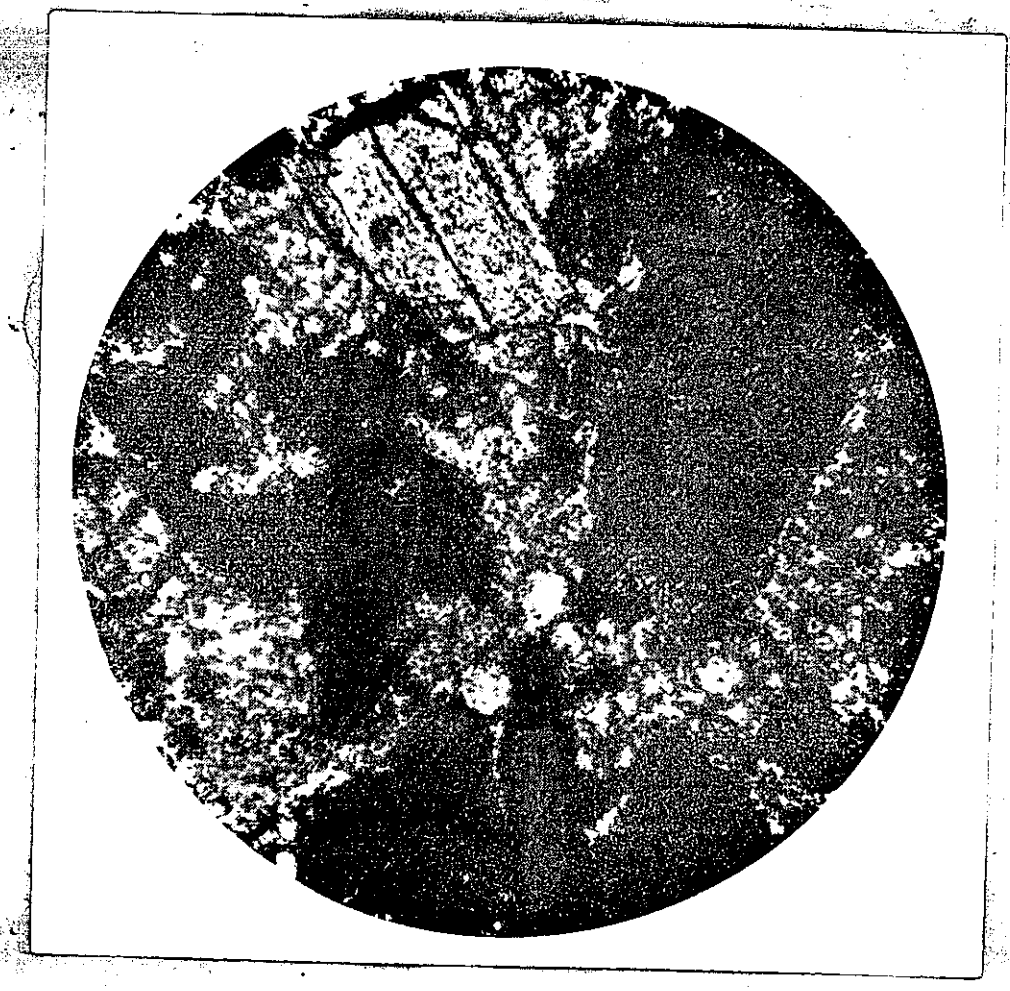


FIG. 3
POZZOLANA OF BASSANO

Pirotana

Banano

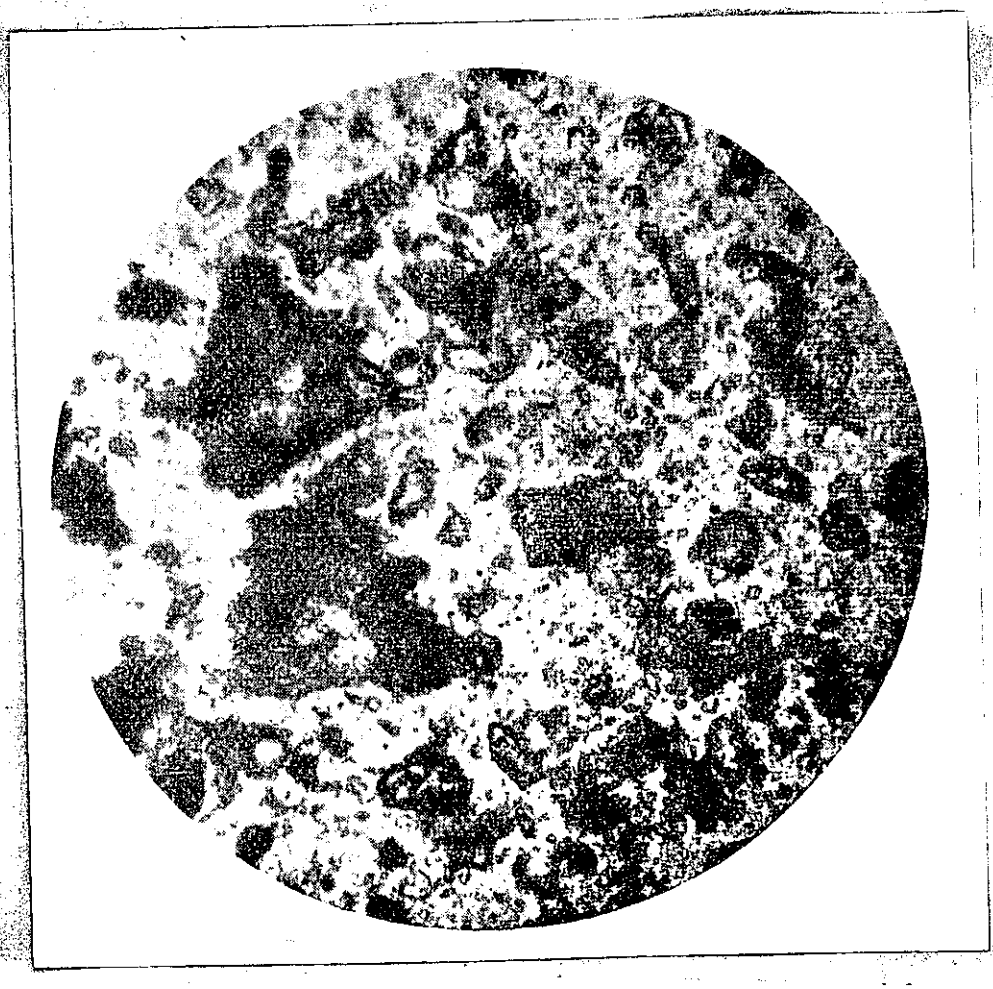
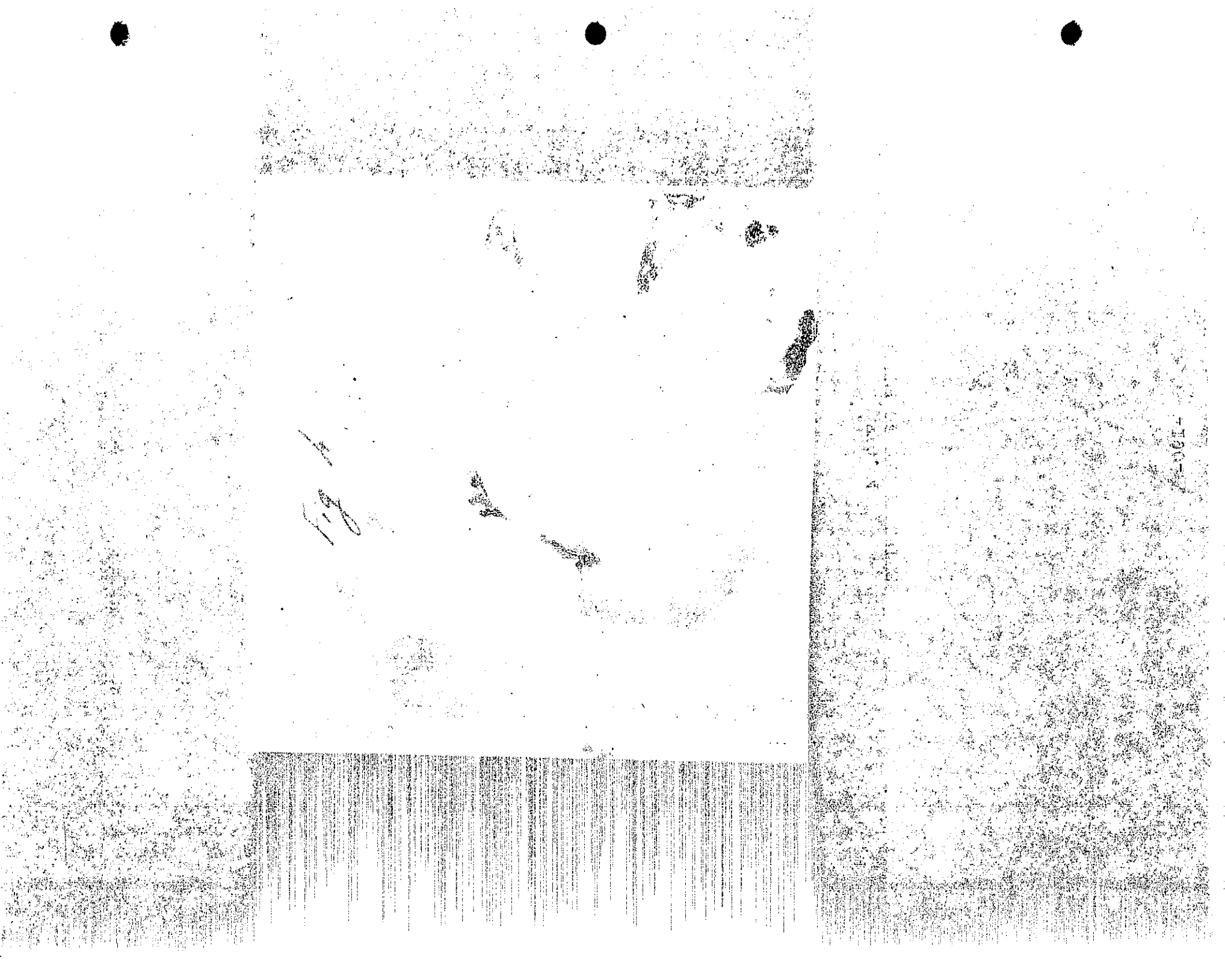


FIG. 4
ASHES OF THE VESUVIUS



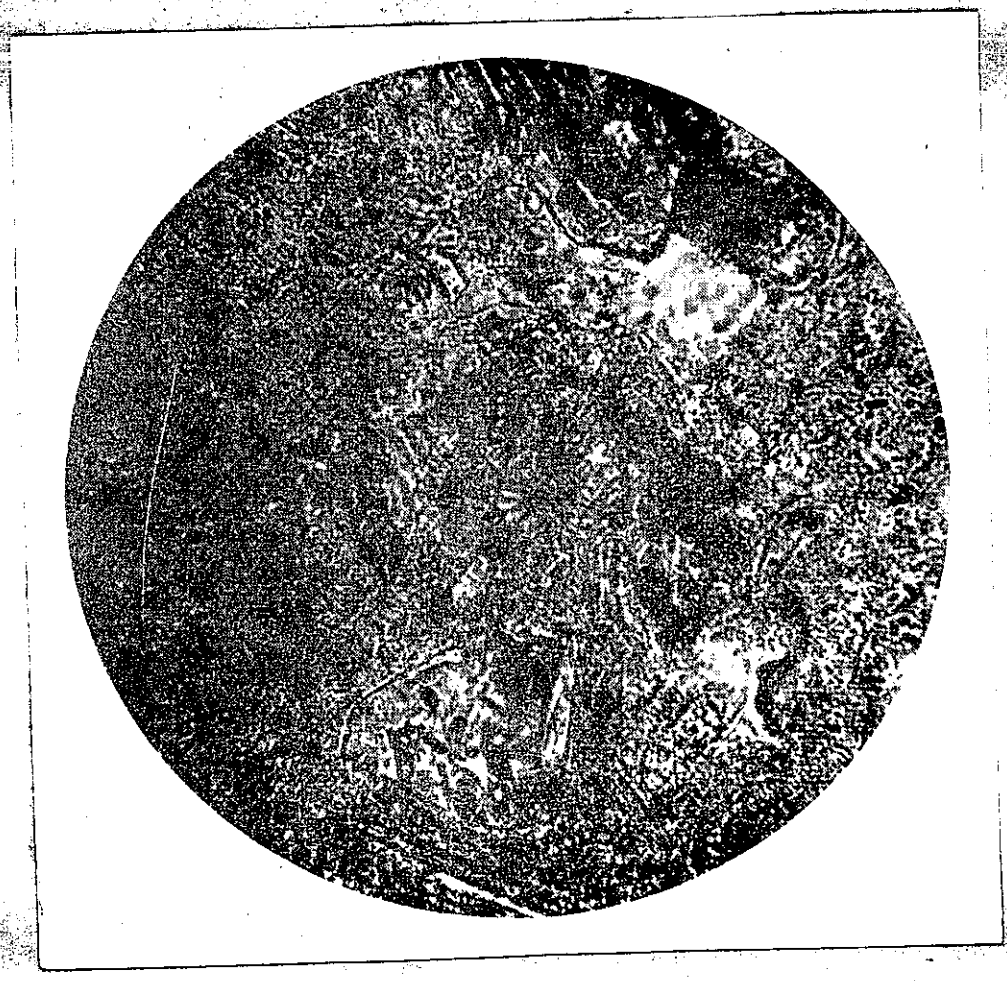
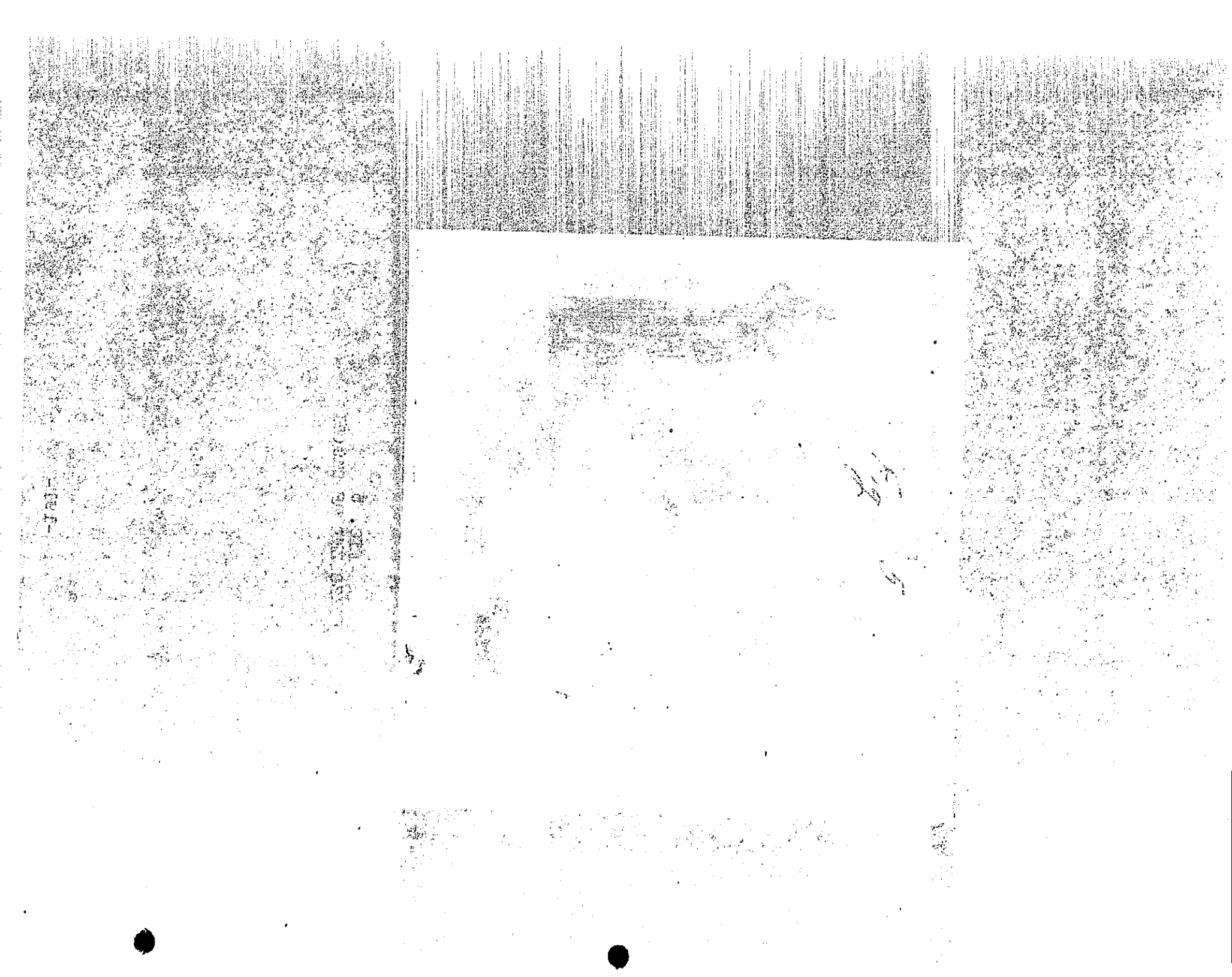


FIG. 5
POZZOLZNA OF BACOLI



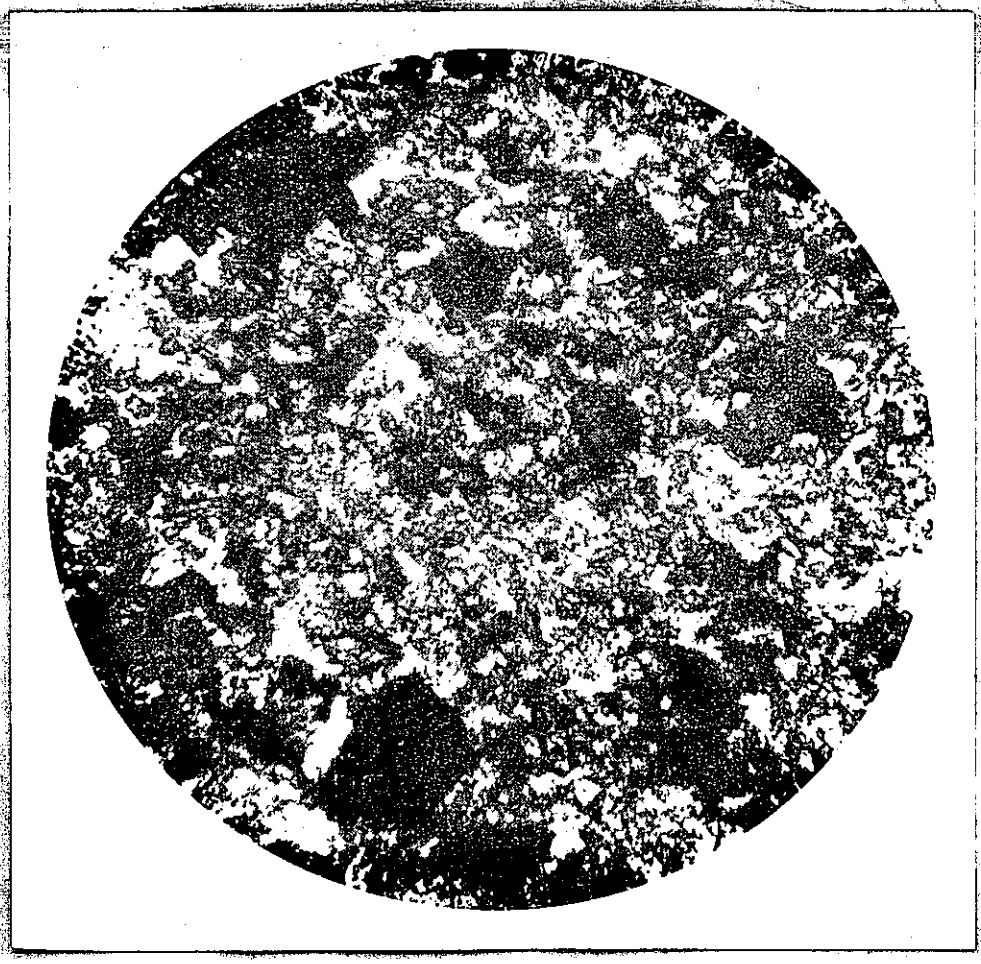


FIG. 6
SANTORINO

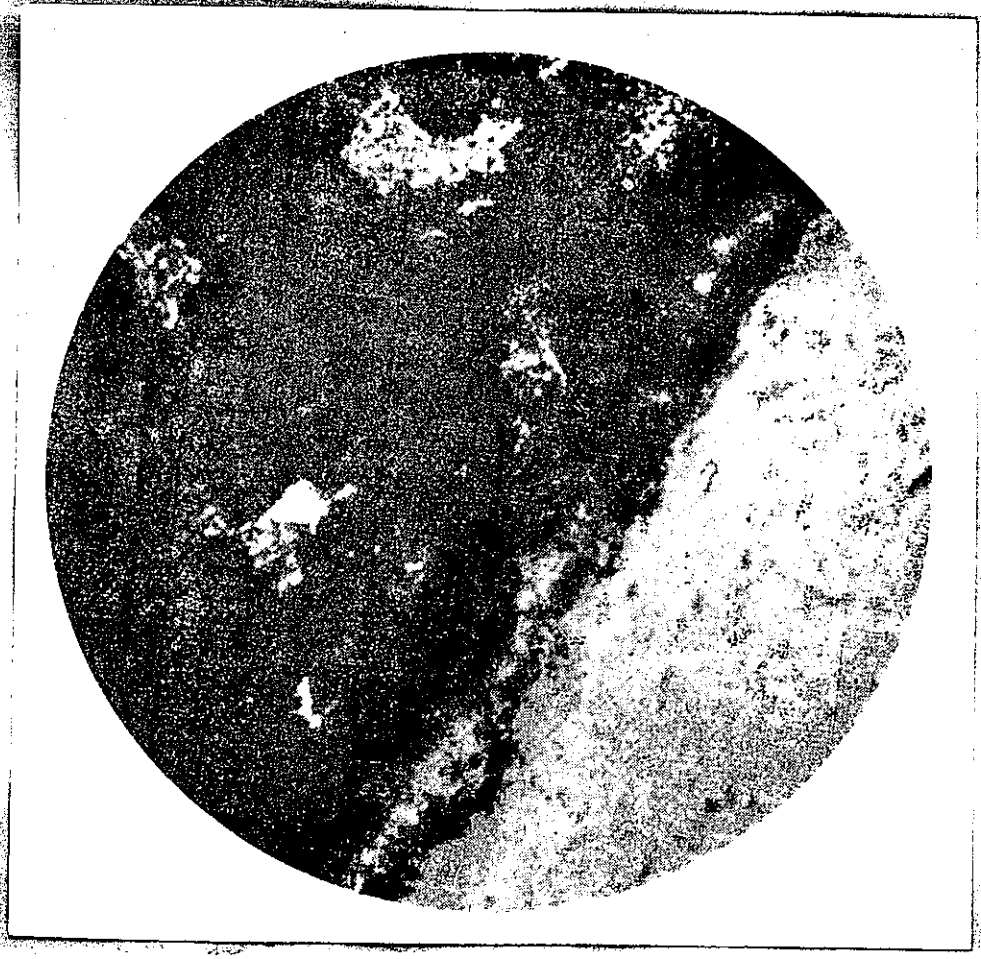
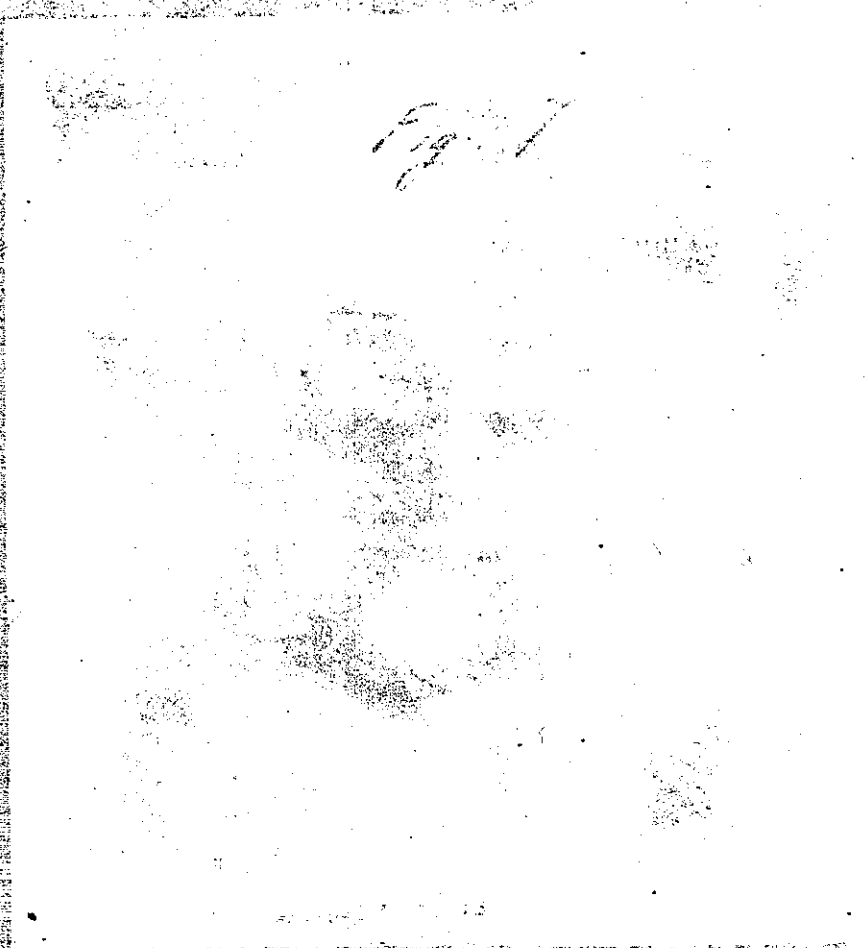


FIG. 7
BORDER OF CALCIUM CARBONATE
IN A POZZOLANA MORTAR



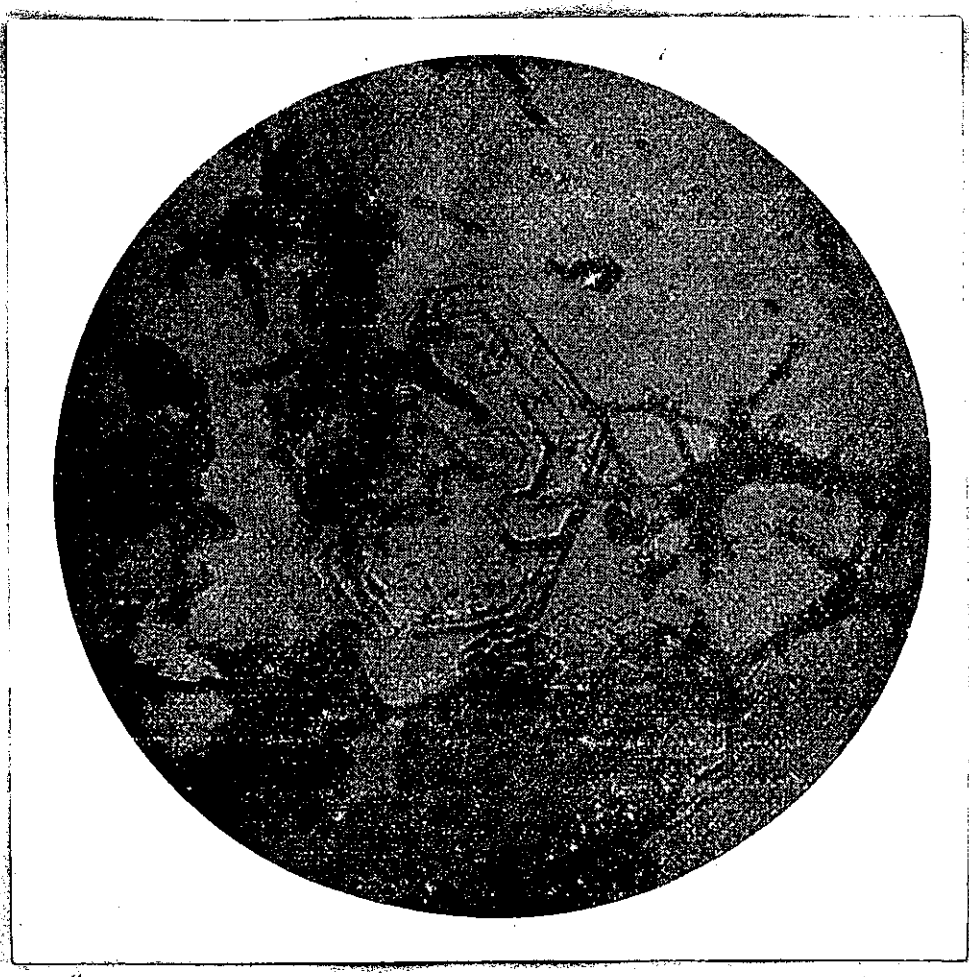


FIG. 8
CRYSTALS OF CALCIUM
ALUMINATE IN A POZZOLANA MORTAR.

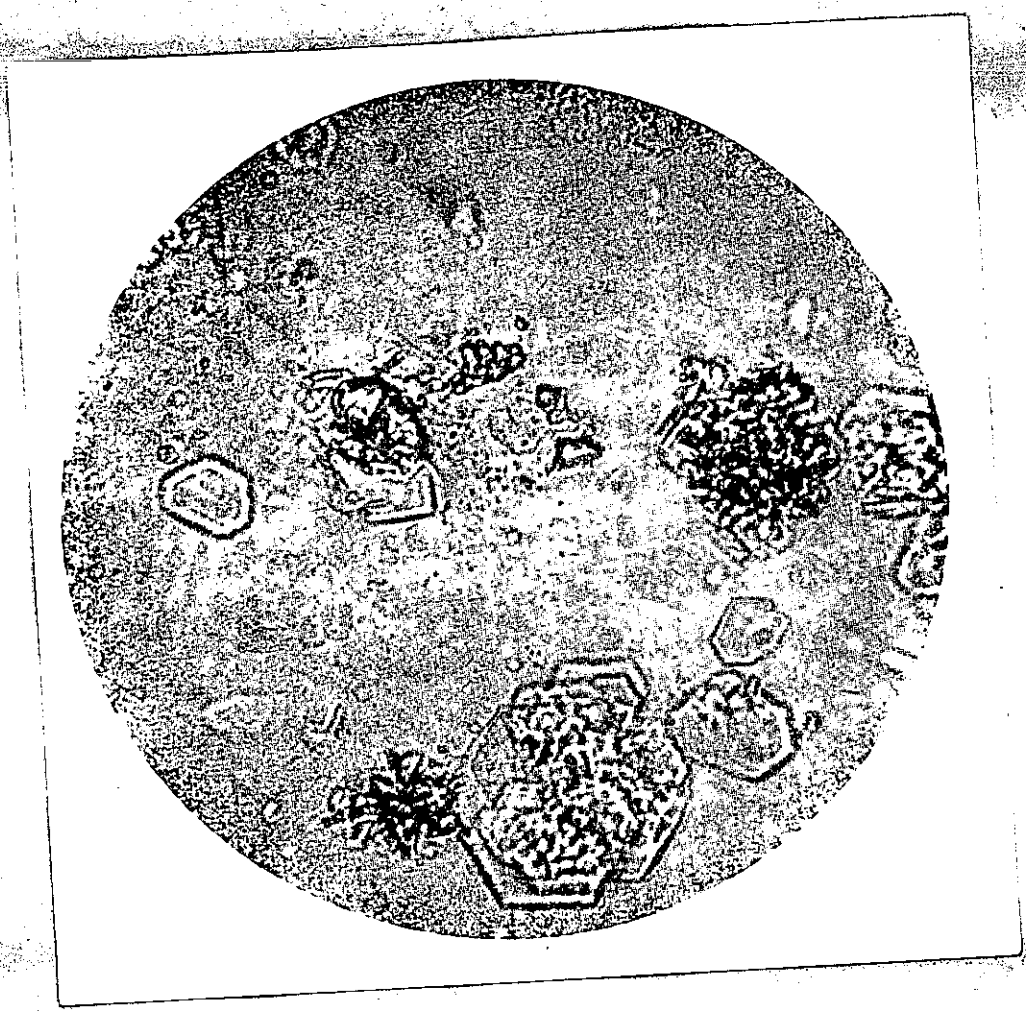


FIG. 9
CRYSTALS OF CALCIUM
ALUMINATE PREPARED ARTIFICIALLY

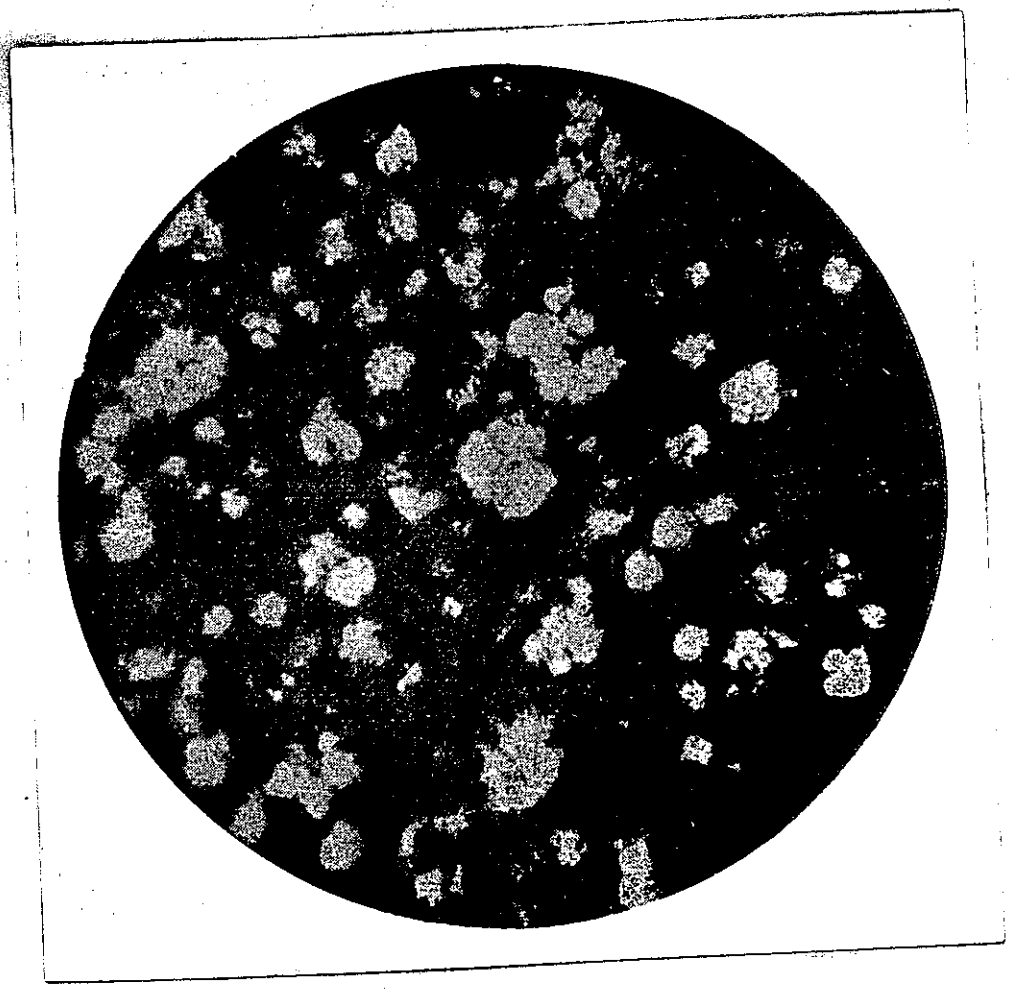


FIG. 10
CELLULAR STRUCTURE OF
A POZZOLANA MORTAR

Fig 10 - Bis

FIG. 10 - Bis
CELLULAR STRUCTURE
OF A PORZOLANA MORTAR

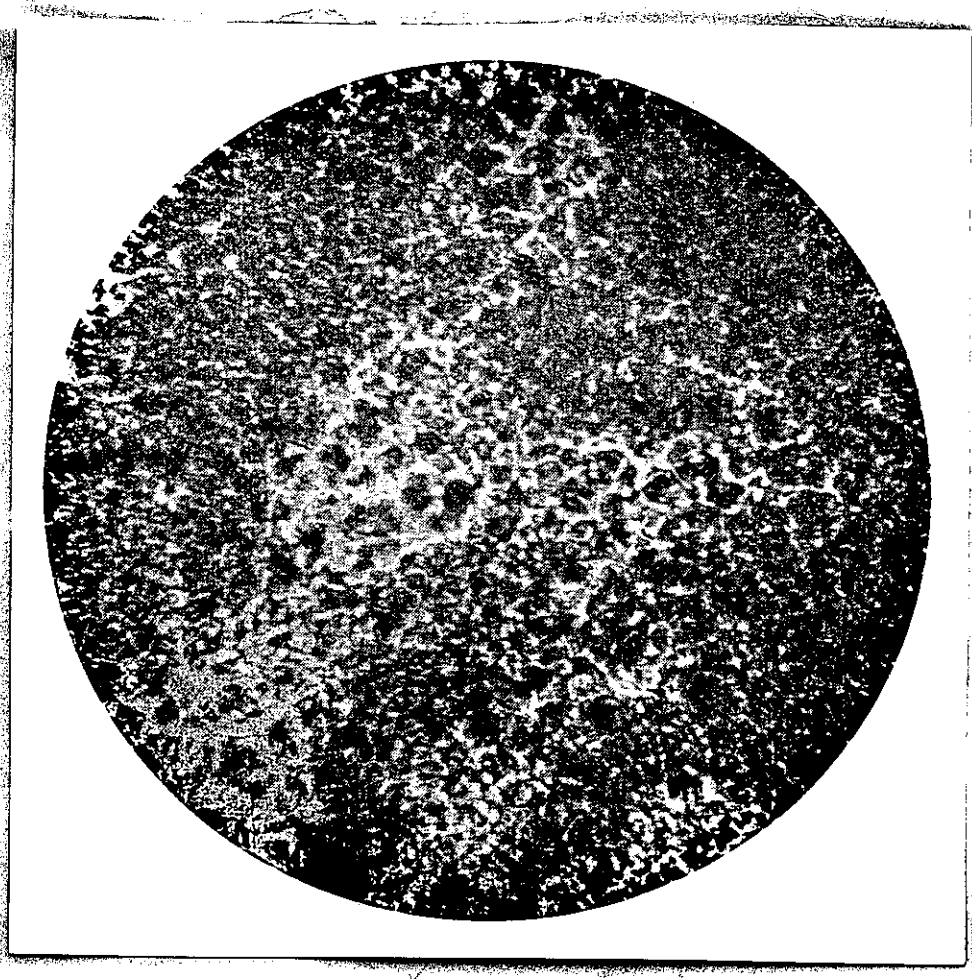


FIG. 11
STRUCTURE OF
GELATINOUS SILICA.

Fig. 11

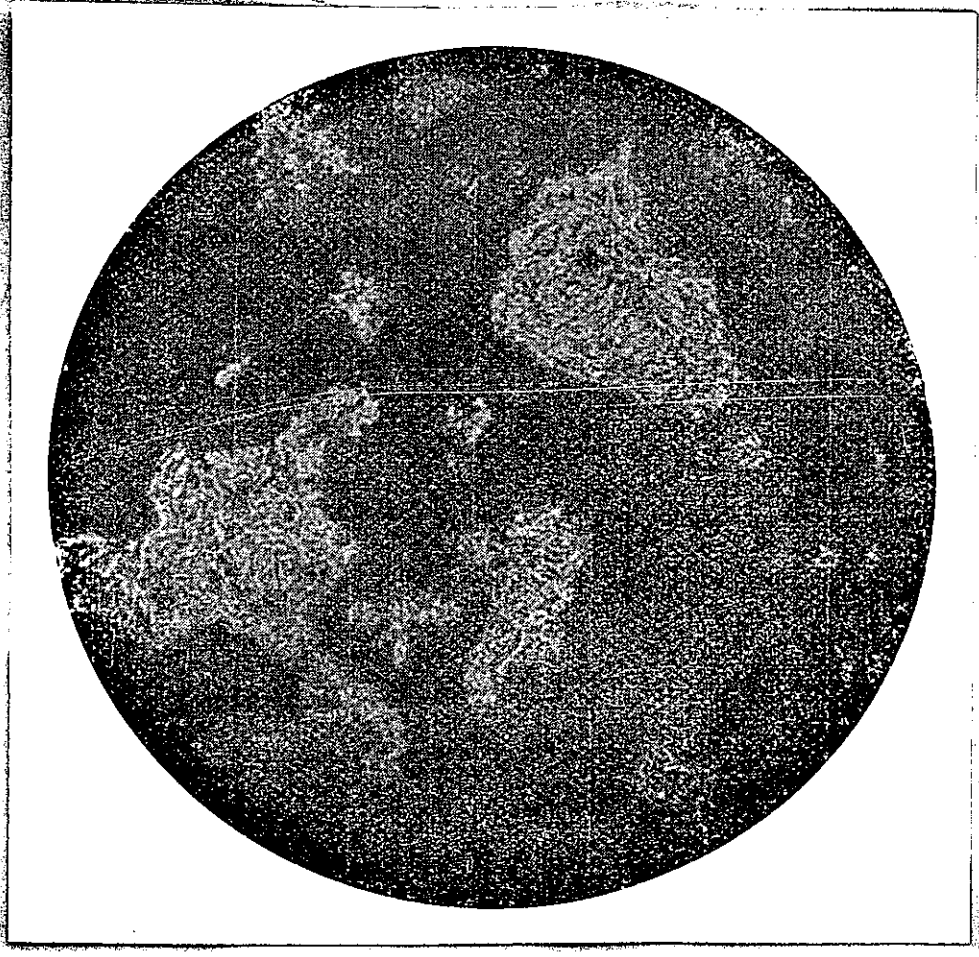


FIG. 12
CRYSTALS OF CALCIUM
HYDRATE WITHIN
A CELLULAR STRUCTURE.

Fig. 12

FIG. 13
DEPOSIT OF LIME AT THE SURFACE,
FROM A POZZOLANA IN A SOLUTION
DRIED WITH NO PRESENCE OF CARBONIC ANHYDRIDE.

Fig 13

FIG. 14
DEPOSIT OF LIME AT THE SURFACE,
FROM A POZZOLANA IN A SOLUTION
DRIED WITH NO PRESENCE OF CARBONIC ANHYDRIDE.

A RESUME OF

"The Microscopic Study of Pozzolana Mortars"

by

G. Gallo

in

Gazzetta Chimica, Ital. Vol. 38

The authors begins with the statement that pozzolanas are materials of very complex petrographic aspect, and that their mineralogic composition may vary between wide limits.

These statements are contrary to the widespread belief that pozzolanas are simply varieties of siliceous materials of almost universally uniform composition.

The fact however, that though they vary in composition, they manifest the common property of hydraulic setting and hardening, leads the author to state that there must be something which is common to all pozzolana, and which determines this hydraulic setting and hardening.

Passing to the investigation of what this something might be, the author states that:

"It is not possible to attribute in any way the hydraulic property of a pozzolana to its crystalline elements."

This statement leads to a ready way to classify and detect the hydraulic value of pozzolanas, through the analysis of their general composition of amorphous and crystalline parts - the larger the amount of amorphous material apparently the better is the hydraulic value of a pozzolana.

Passing next to a discussinn of the phenomena of ting and hardening, the author passes in review the various ries advanced for the exploration of these phenomena, rejecting them all.

It is interesting to notice though, how Le Chatelier ipating the researches of Lafuma, had discovered that the icium aluminate of ordinary Portland, in the process of ion, transforms itself into tetracalcium aluminate hydrate, tricalcium aluminate hydrate.

"From the chemical analysis of pozzolanas no conclusion can be derived regarding their hydraulic property", states the author.

This shows that the hydraulic value of pozzolana is not dependent upon the percentage of total silica present or the amount of soluble silica contained in the whole.

The author states further:

> "The active part of a pozzolana must be attributed uniquely to the granulous and amorphous part contained within the whole mass."

To determine what the chemical and mineralogic composition of this amorphous mass would be, the author develops a whole series of experiments out of which he draws the conclusion that:

> "If the particles of pozzolana, placed in presence of lime water show a tendency toward a diffusion in lumps, and a tendency toward an increase of volume, and if, furthermore, this swelling is manifested at once and reaches its peak in a short time"

all these characteristics constitute reliable criteria for passing judgment upon the hydraulic value of a pozzolana.

He also states:

> "A peculiar cellular structure is characteristic of all the good hydraulic pozzolanas".

which furnishes another basis for judging good hydraulically active pozzolanas.

Regarding the phenomenon of setting and hardening, the author advances a theory which appears to furnish a reasonable explanation.

Professor Rebuffat, however, has lately given in what appears to be a better explanation of the setting and hardening of pozzolana mortars, a complete refutation of Professor Gallo's theory. (See: "La Pozzolana di Bacoli" of which parts are translated in Chapter 5 of Report.)

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A P P E N D I X VII.

Natural and Artificial Pozzolanas.

By
G. Giorgis & U. Alvisi
in
Gazzetta Chimica Ital.
1899 - 1900

"Est etiam genus pulveris, quod efficit naturaliter res admirandas," Marcus Vitruvius Pollio. De Architectura, (liber 2°. caput 6°) "Puteolamus pulvis, si aquam attigit, saxum fit". Lucius Annaeus Seneca: (Quaestionum naturalium).

Natural and Artificial Pozzolanas

Our work is divided into four parts; first, natural volcanic and non-volcanic pozzolanas; second, artificial pozzolanas; third, technical tests upon pozzolana; fourth brief resume of the many theories upon the setting of hydraulic materials.

Finally, in the hope that the bibliographic work which we have done can be of some use to those who want to occupy themselves with this subject of pozzolanas, we report a summary of all the books and articles which we have consulted and to which we shall refer each time with the consecutive number according to their chronological disposition.

According to Plinius (Book 35, Page 13) pozzolana was called thus because it was found in the hills of Puteolis.

Filandro, instead, in his comment to Vitruvius was of the opinion that this name derived from the fact that pozzolana is excavated from wells (pozzi). Under the name pozzolana are comprised all those materials which mixed with fat lime can give what was once called, cement - that is, a material capable of

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setting under water (53). But not a long time ago, the word pozzolana was used in a much more restricted meaning: It is enough in fact to go back a few years, less than a century, when artificial pozzolanas were not yet known, or were very little known, as also was not known the pozzolanic property in some special rocks of non-volcanic origin. Under the name pozzolana was then meant (205) "Simply a volcanic tufa, soft and friable, composed essentially of silica, alumina and of ferric oxide to which are found accidently mixed some magnesium, calcium, potassium, and sodium oxides." These materials are always found in the neighborhood of volcanos, either dead or active, especially in Italy, around Naples and above all around Rome. Some have been found in other places as for instance in the Gravenaire Mountains, in the French districts of the Haute Loire (97), Haute Vienne and Herault (82), and also near the lake of Lauch.

To pozzolana are intimately connected two other varieties; trass, which is a trachitic tufa formed of earthen parts which adhere strongly one to another of a color variant from blue to yellow, which is found on the shores ot the Rhine especially at Brohl, at Plaidt near Andernach, etc. and Santorino which receives its name from an island of the Cyclades Group, which has the same volcanic origin and the same exterior aspect as Trass, but from which it differentiates on account of the fact that placed in contact with acids it disintegrates much less and can be, according to Feichtinger, considered as a mixture of cement and same (208). Later, it was discovered that these were not the only materials to be found which evinced pozzolanic properties, and that other rocks of non-volcanic origin partake of these properties. The family of natural pozzolanas was therefore, considerably enlarged, because almost at the same time, there was discovered, or to be more exact, there was largdy introduced into practice, the use of a so-called artificial pozzolana, which can be obtained through calcination of some special classes of schists, basalts, gres, etc.

Volcanic Pozzolanas

These pozzolanas are lavas or volcanic ejections, more or less ancient, modified through the action of time and atmospheric agents and composed essentially of silica, alumina, iron peroxide and lime, to which are accidently mixed magnesium, potassium and sodium oxides and probably other elements in very small quantities.

At this point we desire to call attention to the assumed accidentality of the presence of alkalis in pozzolana, because some have deduced the hydraulic value of a pozzolana from the presence of a larger or smaller quantity of them, assuming

that their absence indicates a too energetic and prolonged action of atmospheric agents, action which must have deprived the pozzolanas of a considerable quantity of active elements. This observation is not without foundation but we must not give to it a greater value than it really has, because it could lead us into erroneous deductions.

Thus it happens that of two Roman pozzolanas the one which has smaller quantities of leucite ($KAL(SiO_3)_2$ is of higher hydraulic value than the other, but if we take two different pozzolanas and from the quantity of potassium which is found in one of them draw a conclusion as to its superior or inferior hydraulic value we would be in error.

We believe it to be very difficult, therefore, to distinguish the essential and accidental constitutive elements of pozzolanas, because pozzolanas are highly complex, petrographic materials, which vary not only from one volcanic center to another but also from cave to cave and often from stratum to stratum of the same cave. Unfortunately petrographic researches on pozzolanas are still missing, and they remain as yet materials poorly defined and of vague meaning.

Throughout their mass, having in general a variable physical aspect and also a variable chemical composition, it is possible nevertheless to recognize macroscopically some recurring mineralogic elements, as for instance, leucite in the Roman pozzolanas and Sanidine in Neapolitan pozzolanas.

Marcus Porcius Cato (182) was the first to occupy himself with the useful proportions of lime and inert materials for the manufacture of mortars; indicating also which materials were supposed to be the best limestones, and even described a furnace for lime. Two hundred years before Vitruvius, in giving out the specifications for building a country house, he speaks frequently of cement and the mixtures of lime and sand. Whether or not under the name of sand were also included materials like pozzolanas cannot be determined although it remains highly improbable, owing to the location in which he lived and the chemical composition of the fragments of the constructions of those times.

According to Vitruvius, in the neighborhood of Vesuvius, there is a kind of powder "tophus", which mixed with lime and cement (meaning for cement, natural stone) not only can be used for buildings but also for sea water constructions as well. Vitruvius is also the first one to speak specifically of pozzolanas in his treatise "De Architectura" and with his ideas on the subject we shall occupy ourselves further. It is enough for the time being to mention that he says that pozzolanas are found in the Baja region and in the fields surrounding Vesuvius.

He also gives the proportions of the mixtures of lime and pozzolanas, proportions which were not substantially varied by authors which followed him like Plinius for instance, or like those of the fifteenth and sixteenth century; Leon Battista Alberti; Andrea Palladio and Scamozzi in Italy and Filiberto de Lorme in France, who do not add anything substantial to what Vitruvius had already said upon the subject of pozzolanas.

The fact is to be remarked that Vitruvius was completely silent upon the existence of deposits of pozzolanas in the Roman countryside; the explanation of this fact can be ascribed to his belief that the genesis of pozzolana was intimately connected with the action of internal heat, from which originated the hot springs found in the Baja region; now inasmuch as he had found none of these hot springs in the Roman countryside, he believed it opportune not to call the general attention to materials which he considered were not of the same nature as those of Naples. Even Strabo (186) after having said that the regions of Baja and Cumae called by the Greeks, "Dicarcee" were afterwards called Puteoli on account of their frequent wells, points to the fact that they are full of natural hot springs originating through the action of internal fire and heat. He adds then:

> "Quas ad res commodum conducit arenarum ingenium, quae calcis quam simmillimae compactae validissimum conglutinantur in modum. Unde commixta sabulo glarea, aggeres proiectantur in pelagus, ripasque sinuosas in recessus redigunt sic ingentes onerariae naves iactis ibi conquiescunt anchoris."

Other references to pozzolanas are found in Seneca (185) in Plinius (187): "Mersumque protinus fieri lapidem unum inexpugnabilem undis et fortiorem quotidie utique si Cumano Mesceatur caemento" and finally Palladio (189) in whose work are described the principal physical characteristics, of which even nowadays technicians make use to judge the quality of pozzolana, that is, "if pozzolana has good hydraulic value it is supposed to leave no mark on a linen cloth when compressed by hand." As we have already said, nothing of importance was added to what was known by Romans until the beginning of the 19th century. It was in the first half of the 19th century that Vicat began the study of these materials. With Vicat we must notice also Lepere Gay-Lussac; Treussart, Berthier, Girard; Racourt de Charleville; Minard, Noel, Chatoney and Rivot, of whose ideas we shall occupy ourselves in the next chapter. Even the National Association for the Testing of Materials has recently proposed a solution of the problem in:

"The way of testing pozzolanas from the point of view of their technical value for the manufacture of cements", (174-b). But so many researches had not the desired effect, because we are nowadays still very far from having the same knowledge of this material that we have of other materials of construction.

The most important deposits of pozzolana are found in Italy, and among them lead in importance those of Rome and Naples which are amply covered in the memoirs of L. Demarchi and O. Fodera (130-169) from which we report the following:

> "The Roman pozzolana is frequently met with in the volcanic zone of the Roman province and especially in the neighborhood of Rome. It can be divided into two distinct groups according to the condition of the deposits."

Regarding the genesis of the Roman pozzolana Professor Marchetti says:

> "Limiting ourselves exclusively upon their extreme characters and upon their geological formation we must hold that these Roman pozzolanas are derived from rocks of secondary formation constituted of very fine ash from the Tirrenean volcanos and found first upon the Apennines and then washed out or together with fragments of sedimentary rocks carried to lower levels by the rain waters."

The disposition of these materials in immediate contact with pleocenic rocks corresponds to that of the oldest tufas of the Roman countryside, which also rest directly upon pleocenic formation.

The technical value of Roman pozzolanas has always been considered as very high, the red one of S. Paolo above all being supposed to be the best and serving as a term of comparison in all technical tests upon pozzolanas. Even the black pozzolanas often give excellent results. As a matter of fact nowadays it is believed that they are not inferior to the red ones.

To Roman pozzolanas is usually assigned the density of 1.232. Following are analyses of some of the principal varieties of Roman pozzolanas which will give an idea of their composition, beginning with that of S. Paolo:

POZZOLANA OF S. PAOLO

	Analysis of Dufrenoy	Analysis of Ravier
Quarz	3.00	3.10
Silica	47.66	37.80
Alumina	14.33	19.40
Potassium Oxide	1.40	0.00
Sodium Oxide	3.73	3.40
Lime	7.66	9.80
Iron Perioxide	10.33	10.30
Magnesia	3.86	1.28
Water and Alkalies	8.03	12.74

POZZOLANA OF S. PAOLO

(Analysis of Professor Cavazzi (126)

	Elements Soluble in hydrochloric acid	Insoluble Residue	Total
Silica	0.525	44.975	45.500
Alumina	14.925	0.200	15.125
Lime	8.498	0.838	9.336
Magnesia	3.172	0.423	3.595
Ferric Oxide	11.200	0.850	12.050
Potassium Oxide	2.154	--	2.154
Sodium Oxide	3.782	--	3.782
Water & traces of other substances	8.458	--	8.458
	52.714	47.286	100.000

PULVERIZED POZZOLANA

Sugar Solution 1.99% of CaO

Pozzolana	DURATION OF IMMERSION	
	48 Hours	10 Days of 24 Hours
	CaO taken from 100 P. of Pozzolana	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo (Cave Mezzetti)	2.114	2.114
Pozzolana of the Pigno	1.094	1.094
Vegetable Soil	2.254	2.226

PULVERIZED POZZOLANA

Sugar Solution 1.54% of CaO

Pozzolana	DURATION OF IMMERSION
	Four days of 24 hours
	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo	1.68
" from the Cave Sette Camini..	1.51
" from the Pigno	0.97
" of S. Giovani	1.50
" " Coriano Sicoli.....	2.06
Clay of Bari	0.84
Vegetable Earth	2.27
Wollastonite (1)	0.04
Leucite (1)	0.00

(1) These are 2 natural silicates with which we thought to experiment at the same time we experimented with natural pozzolanas.

	Penetration to Vicat needles in mm.			Tensile Strength Kg. per sq. centimeter at 1 Yr.
	1 mo.	2 mo.	3 mo.	
1 lime - 2 Roman pozzolanas stored for 3 yrs. in contact with atmospheric agents.	7	5	2	4,500
1 lime - 2 Roman pozzolanas used soon after its excavation	5	-	-	7,200
1 lime - 2 Bacoli pozzolana stored for 3 years in closed containers	6	3	-	7,100
1 lime - 2 Bacoli pozzolana stored for 3 yrs. in contact of atmospheric agents.	8	4	3	3,100
1 lime - 2 Bacoli pozzolana used soon after its excavation	4	-	-	8,250

Table showing how the grinding of pozzolana affects the strength of a 1:2 mortar of lime - Roman pozzolana.

Type of Pozzolana	TENSILE STRENGTH Kg/cm.^{2}		
	3 m:	6 m:	18 m.
Commercial type mixed by hand	4.100	5.100	9.050
Ground to pass the sieve of 400 open:/cm.^{2}	5.200	9.000	12.050
Ground to pass the sieve of 121 open:/cm.^{2} and not 225 sieve	3.800	4.900	8.000
Ground to pass the sieve of 81 open:/cm.^{2} and not 121	3.800	4.200	6.100
Ground to pass the sieve of 16 open:/cm.^{2} and not 81	2.200	2.900	3.200
Commercial type mixed by machine	4.600	8.100	11.900

| | | |

Before writing of the Roman pozzolana we should have spoken of those of Naples which were known and employed in older times.

One of the best, and, as a matter of fact, judged indeed excellent, is that of the cave of Bacoli (130) near Pozzuoli, which extends for more than a Km. and whose stratum presents a thickness of about 40 m. constituted of a kind of volcanic ash of a clear grey color, resting on a sub-stratum of ashes, pumices and other volcanic ejections. This cave is near the coast line between baja and Bacoli. Of the analyses which were made we report the two following: The first from a memoir of L. Luiggi and V. Cardi (166-a) and the second from a note of O. Rebuffat (174-a).

A N A L Y S E S

	I.	II.
Silica	56.20	52.77
Alumina	19.30	17.90
Iron Sesauioxide	8.70	4.84
Magnesia	0.25	1.35
Sodium oxide	2.90	4.94
Potassium Oxide	3.45	7.65
Lime	2.90	3.28
Water	3.90	Loss by Ig. 7.25
Calcium, sulphate, chlorine, etc.	2.40	----
	100.00	99.08

Not far from bacoli is found the pozzolana of Baja, of which Professor Favilli of the University of Naples gives the following description and analysis:

"This pozzolana is a substance of a whitish color which adheres to the tongue and which has produced - through mechanical separation - almost 46% of a sand formed of small fragments of pumice and other substances of volcanic origin and almost 54% of clayey material. Its density is of 2.074, which is much greater than the density of Roman pozzolanas. (Regarding this value of the density, it is opportune to remember that it has to do with real density; in effect the number 2.074 is very near to that of the density of the Bacoli pozzolana:1.941).

Five grams of Baja pozzolana have liberated the lime from 10 cm.^{3} of lime water after two days of contact.

PERCENTAGE COMPOSITION

Water	3.50
Silica	55.10
Alumina	18.30
Ferric Oxides	7.60
Magnesia	0.40
Lime	6.55
Sodium Oxide	2.95
Potassium Oxide	2.80
Other elements Mg., Chl., etc.	2.80
	100.00

Another type of pozzolana is that of Vesuvius, found near Torre del Greco, at 13.3 Km. from Naples and about 70 m. from the shore. The cave is named: Cave of Bassano, and the pozzolana is found immediately under the vegetable earth, at a depth of about m. 0.40; it shows two distinct strata; the thickness of the first stratum is of about m. 2.80; the thickness of the second is of about m. 3.50. These two strata are separated by smaller alternate layers of sandy clay and black lapilli (fragments of pumice and slag). From an analysis of this pozzolana made by Professor Rebuffat, we obtain(174-a):

Water	5.10
Silica	50.10
Alumina	15.50
Ferric Oxide	1.60
Magnesia	0.10
Lime	0.55
Sodium Oxide	3.90
Potassium Oxide	3.90
Other elements	1.80
	100.00

Analyses of Pozzolana is that of resulting from the burning of pure limestone. The ashes are found in large quantities in the vicinity of Vesuvius, Rome, Italy. Pozzolana is found in many other places in the world.

Pozzolana is used by Professor Taylor as a substance of a dull brown color through admixture to the cement which has produced a strength equivalent to that of a neat Portland cement of a standard quality. Pozzolana is a substance of volcanic origin and almost pure silica and other substances that are peculiarly adapted to combine with lime at ordinary temperatures. Pozzolana is a substance of volcanic origin and almost pure silica and other substances that are peculiarly adapted to combine with lime at ordinary temperatures. Pozzolana is a substance of volcanic origin and almost pure silica and other substances that are peculiarly adapted to combine with lime at ordinary temperatures.

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Loss by Ignition	2.21
SiO_2	47.10
Al_2O_3	21.90
Fe_2O_3	8.01
CaO	9.91
MgO	1.56
K_2O	6.01
Na_2O	2.56
	99.35

It is worthy of notice that the Neapolitan pozzolanas possess in general a much larger content of lime than that of the Roman pozzolanas, or of Trass and of Santorino.

FRENCH POZZOLANAS

In a report of Chaptal (17) to the Institute of France upon two memoirs of Gratien Lepere upon natural and artificial pozzolanas we read:

> "M. Desmaret et Faujas de Saint-Fond have made known some deposits of pozzolana in the volcanos of the Department of L'Auvergne and of Vivarais. I have myself found it in the volcanos which separate Lodeve and Bedarieux in the Department of L'Herault and this pozzolana has been used to advantage for the construction of many bridges and other hydraulic works."

Vicat in a memoir of 1849 (82) gives a more detailed notice to the pozzolanas discovered by the French naturalist Faujas de St. Fond upon the summit of the Chevanary.

> "In them", he says, "are found volcanic lavas, altered by atmospheric agents, and also (like in Italy) considerable homogeneous masses of red, black and gray pozzolanas."

They were in 1777, by order of Sartines, Minister of the Navy, investigated by Faujas at Toulon in comparison with the Italian pozzolanas, but Vicat remarks that the results must have been unfavorable, because they were not published.

Chaptal in 1786 resumed the studies, always as a comparison with an Italian and an artificial pozzolana. The results were very poor, because after five months of immersion in sea water, it was found that the mortars manufactured with the pozzolanas of Vivarais were very much deteriorated, while those manufactured with Italian or with artificial pozzolana were not.

Vicat, attributing such results to mistaken proportions, wanted to experiment personally largely extending his researches and his studies to all the varieties of pozzolanas of the various localities of the Vivarais region.

The pozzolanas experimented on had the following composition:

Locality	Sand	Silica	Alumina	Iron Peroxide	Lime	Magnesia	Soluble and Volatile elements
Mountain of Chastellas	--	60.59	14.15	7.96	2.21	1.34	13.75
	3.95	35.09	17.65	16.82	4.26	3.17	19.06
	6.17	36.55	10.41	23.74	4.27	3.80	15.02
Mountain of Chenavary	7.48	30.73	11.63	24.92	3.73	2.49	19.02
	1.50	40.97	15.92	18.70	0.47	0.34	22.01
	3.70	34.22	12.02	25.90	4.14	4.12	15.90
Mountain of Charay	3.63	33.60	20.89	18.16	4.58	3.63	15.51
	5.11	38.34	15.76	20.44	1.70	1.14	17.51
Coirans	4.76	35.81	25.58	11.08	2.56	1.70	19.01

Note that for each locality there are various types of pozzolana, differing in the content of one single material or several. These various types can be distinguished externally by their different color. We find thus, that these colors may range all the way from gray to white.

Even at this time, the results, although rather good for tests in fresh water, result instead very poorly for tests in sea water, so much so, that specimems made with one part lime and two parts pozzolana or with one part lime and four parts pozzolana immersed afterwards in sea water were destroyed after 24 hours.

ARTIFICIAL POZZOLANAS

For all mortars for construction purposes which were supposed to remain in contact with water, the ancient Romans used mixtures different from those for construction in open air. Vitruvius prescribed for the lower and the damp parts of buildings, mortar made not with lime and sand, but with lime and powdered bricks or tiles.

It is in such a prescription that we find in embroyo the principle of the manufacture of artificial pozzolanas.

In a report of Chaptal to the Institute of France (17) upon two memoirs of Graziano Lepere, we read as follows:

> "It is difficult to assign the epoch in which the substitution of pulverized bricks for volcanic pozzolanas began. These bricks do not give in general, a good cement except when they are highly calcined and made with clays highly ferrous."

In the same report Chaptal passes in rapid review whatever was known in regard to the memoirs of Lepere and he mentions that 20 years before he had proposed the use of some special schists as a substitute for pozzolana when subjected to previous calcination. The process of manufacture consists in calcining to a dark red some quantities of this material made in spheres of a diameter of 10 centimeters.

Contemporaneously with Chaptal, Cessart occupied himself with the same argument and Guyton refers to the authority and experience of Cessart to back up his proposal of substituting artificial pozzolana for natural and he adds that the results obtained by Cessart (as seemed to be shown by a report of the same) had been excellent and such as to lead toward a preference of the concrete made with these materials to that made with Italian pozzolana. He comes to the conclusion that although the tests have been made upon too small a scale, it is possible to affirm that this artificial pozzolana made with basalt of a dead volcano of Drevin (Department of Saone and Loize) calcined first and then thrown into hot water and sieved in such a way as

to reject all the particles larger than a small pea, is almost as good as that of Italy. In the same memoir, Guyton proposes to substitute the ashes of coke to pozzolana and he mentions Smeaton, who indicated that all ferrous matter and especially furnace slags would set in the presencence of lime.

The work of Cessart was continued by Lepere, who succeeded him in charge of the works in the military harbor of Cherbourg. From one of his reports, we find that Lepere procured the pozzolana which he needed by calcining the rock of the shores of Cherbourg. He got quite good results and still better ones when he used some schists from the neighborhood of Cherbourg and inferior ones, although not absolutely bad, with some ferrous material from Hainerville.

The results of Lepere were confirmed by the examination of a commission composed of Guyton, Dillon, Lamande and Lepere. The report of the commission was favorable providing that the calcination of the material was made in a reverberating furnace. We find, therefore, that up to the beginning of the 20th Century the development of artificial pozzolana was as follows:

It was known that the ancient Romans had used for the manufacture of hydraulic mortars, calcined clayey materials (pulverized bricks and tiles). Then a notable step was made when was begun the calcination of special natural materials, with the aim of employing them as substitutes for pozzolanas. Great stress was placed upon the temperature at which these materials had to be calcined when for the rocks of Cherbourg it was established that the calcination should have been made with a reverberating furnace. It is enough though to go over the referred memoirs to see that all these tentatives were isolated as they were made in a very restricted field without any connection between them, and (what mattered the most) made empirically inasmuch as nobody had ever occupied himself with discovering the chemical composition of those materials which were subjected to calcination, or to clarify the transformation which they underwent under the action of heat.

It is at this point that Vicat begins to study the question of artificial pozzolanas with the scientific criterions, to which we have already made reference.

The first discovery of Vicat goes back to the year 1812. Near the bridge of the town of Souillac he found some reddish clay which he tested for use as pozzolana. He calcined it and because of the fact that the clay contained some calcium carbonate he was successful in obtaining a hydraulic mortar. In his work of 1818 (20) and in a memoir published two years afterward (21) Vicat says that the general ideas about materials able to furnish hydraulic cement were at that time very vague, apart from the knowledge of the use of pozzolana and trass, inas-

much as pulverized brick or furnace slags according to some, gave good results, while according to others they did not. This was the reason why he proposed to make a series of experiments following a rational program.

Regarding artificial pozzolanas he observed that by mixing lime and clay and clinkering the mixture, it is possible to produce hydraulic limes, and because the analysis showed that pozzolanas have an oxide composition analogous to clays it was natural to believe that by calcining clays these materials could be easily transformed into pozzolanas. This idea is very old, but nobody up to that time had been able to apply it on a large scale or to find out the conditions according to which it could be easily transformed into pozzolanas. This idea is very old, but nobody up to that time had been able to apply it on a large scale or to find out the conditions according to which it could be put to practical use. For instance, it was thought at first that the percentage of iron had a great influence and on account of that a particular type of clay very rich in iron was used; than it was believed that it was necessary to reach a very high temperature to approximate those conditions according to which it was supposed the formation of natural pozzolanas had taken place. This supposition however, is erroneous because as Vicat noticed, if it is true that pozzolana has been ejected by volcanic action in the state of lava, it has been also transformed by other actions, therefore it can be demonstrated that it is possible to have some good artificial pozzolanas with a very low temperature of calcination.

In effect, Dufrenoy in his treatise on mineralogy says,

> "The combination of alumina and silica into the alumino silicate of clays becomes less and less stable under the action of heat, and lime can in this way exercise upon the components of clay an action much more effective than the action it can exercise before calcination. But the temperature must be moderate because bringing it to a very high temperature, clay becomes insoluble in acids just as happens for artificial pozzolanas, which calcined at too high a temperature become hydraulically inert."

Also, Tenore (215) speaking of the Neapolitan pozzolanas refers to the opinion of Dufrenoy and adds that when he heats artificial pozzolanas to a very high temperature there takes place the formation of magnetite which is inert. Vicat also noticed that the degree of calcination must vary according to the composition of the material and upon which degree lime and iron have no in-

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fluence but only have influence upon alumina and silica, or better yet, a particular state of combination of alumina and silica.

It was thus that the problem was finally placed on a rational and scientific basis.

The invitation extended by Vicat to study the question was accepted by other scientists. In a memoir of 1824 (29) we find a report of work done by Bruyere and Saint-Leger. Bruyere had obtained good results by calcining three parts of clay and one part of lime to a light red for a few hours. Saint Leger in his note confirms the results of Bruyere, pointing out furthermore that any additional sand to the mortar, lime-pozzolana, is deleterious. That, further, the mortars made with these pozzolanas gave some good results when tested with a Vicat needle, as well as in practice. Before that time, an engineer, Racourt de Charleville, in a treatise published in 1822, expounded the idea that contact with the atmosphere was necessary to transform clays into pozzolanas through calcination and that calcined magnesia and all metallic oxides would set up when mixed with lime. Treussart (30) also occupied himself with the question and sets forth the theory that the setting of artificial pozzolanas is due to the fact that the alumina absorbs oxygen during calcination. He bases this theory on the fact that alumina heated in a current of air sets with lime much sooner than alumina calcined without the contact of air.

The idea of Treussart of the absorption of oxygen by alumina was opposed in a study of Girard (36) in which he says that he weighed the clay before and after calcination to find out if it had lost any weight on account of the elimination of water. Vicat also in the following year published a study (37) in which he rejected the ideas of Racourt and of Treussart in regard to the absorption of oxygen by alumina during the heating. He observed that by calcining the alumina out of contact with air, he always obtained equal weights of material, furthermore, he noticed that when the material was calcined in an open vat, it made a quicker set, and was more easily attacked by hydrochloric acid, than material calcined in a closed vat. He held that this confirmed his theory expounded in a note to the Institute of France of February 1, 1819, to the effect that the hydraulic qualities of both natural and artificial pozzolanas are measured by the degree of action which chemical agents have upon them.

Girard (38) subsequently experimented upon three kinds of sand, the first being very energetic, the second moderately so, and the third completely inert. From them he separated the clayey part to which he held should be attributed the properties

of setting. No explanation of their difference of behavior could be obtained from the analysis of their chemical composition due to the fact that the last ones differed from the first in the quantity of silica only. He did not believe it proper to attribute the pozzolanic properties to the content of alumina - inasmuch as Vicat with his experiments had demonstrated this assumption to be erroneous and he noticed that during the treatment of these materials with hydrochloric acid, the cements made with the first part set up while those made of the second hardly underwent any set and the cement produced with the third part did not set at all. Girard therefore deduced that the silica present was in those three parts in two different allotropic states:

1. A state of combination with the oxides, such that it could easily combine with lime.

2. In a free state in the first place and then in a state of combination.

From this observation, Girard deduced that the sand under question varied in its setting properties according to the relative amount of silica in the first or second state.

Having calcined the three kinds of clay he found from calcination there was development of water and that the first were highly hydrated, and furthermore that after calcination upon treating with hydrochloric acid, silica separated out and that as a product of calcination even the clay of the third kind became very apt to set.

A final deduction was that during the calcination, due to the decomposition of the hydrates, the silica became separated, therefore the condition according to which clay may evince pozzolanic properties is that the silica be found isolated from other oxides and in a state such as to be ready to form new combinations. Consequently in natural clays the separation of the silica does not take place entirely as in calcined clays, the setting takes place slowly and the hardening is also much less rapid.

Up to this stage, the general ideas on the subject were somewhat confused, but in comparison with the empirical beliefs commonly held up to this time, a great step had been made.

In two successive notes, one of the year 1834 (55) the other of the year 1836 (58), first Julian and then Vicat describe the manufacture of two artificial pozzolanas and the details of the manufacture. In the first place, the authors insist that the material must be finely ground (passed through a sieve of 64 openings per square centimeter) and that the calcination must vary from a low temperature for calcarious clays to a very high temperature for pure clays.

In 1836 Dumesnil-Adelee advanced the theory that the addition of artificial pozzolana passed through a sieve of 80 openings per square centimeter to a cement made with hydraulic lime and sand increases its resistance.

Five years later, we find a resume of Petzold on the researches made for the manufacture of artificial pozzolana with the type of clay used to make bricks in the neighborhood of Algiers. Petzold was concerned with the best degree of temperature for calcination. He therefore calcined six specimens at successively higher temperature until the material assumed the following colors:

1 - Dark gray

2 - Bluish gray

3 - Blue

4 - Purple

5 - Pink

6 - Yellow

From these experiments it appears that the fifth material presented the best hydraulic energy and that immediately after came the second, while the others were worthless. Vicat who by this time considered the manufacture of artificial pozzolanas with clay his own patrimony, with the authority that was generally granted to him, answered Petzold (67) calling attention to the fact that in his opinion the assumption that the pink color of the calcination of the materials is an index of pozzolanic property was erroneous. Vicat contended that the color of Italian pozzolana could vary within quite a great range (this color being deemed, above all, due to the lesser or greater quantity of iron present) without any relationship whatsoever to the chemical composition upon which the hydraulic quality of calcined clay depends. Further, he states that the pozzolanic property is essentially inherent in the silicate of alumina and that the coloration of the pozzolana has influenced the carbonization of organic matter which gives origin to the various colors found during calcination. According to Vicat it is possible to have excellent pozzolanas of all colors beginning with gray amd ending with red, passing through all gradations. He mentions finally that the best clays are those of the strata of transition from the primary to the secondary, which, with the best process of calcination, regulating the effect and the intensity of the heat so as to evaporate, or almost entirely evaporate the water of the hydro-silicate of alumina, it is possible to obtain pozzolanas equal and often superior to the Italian pozzolanas.

Thus, up to this time, artificial pozzolanas had followed a triumphant march in the opinion of the French engineers and chemists, leaving behind the natural pozzolanas, when Noel, an engineer of the Harbor of Toulon made known that experiments made in the Harbor of Toulon with blocks manufactured with artificial pozzolanas after a few days of immersion in sea water disintegrated into pieces opening from the surface toward the center.

Vicat (71) from a comparison of analyses of the disintegrated parts and of the inner-decomposed core, believed that he could furnish an explanation of the phenomenon on the assumption that the magnesium salts of sea water had replaced the lime of the mortar. He then attempted to explain the difference between the results obtained in Algiers with those obtained in Toulon through the different composition of the water of the ocean and that of the Mediterranean Sea, so far as it concerns the quantity of magnesium sulfate. We find thus, that the magnesium sulfate of the ocean is only about 7.02% of the solids. Vicat however, does not limit himself to this theory but sets himself the task of thoroughly studying the question and next year he sets forth in a note (73) the conditions which must be satisfied in a pozzolana which is to be used in sea water. These conditions are:

1. Pozzolana must contain a certain quantity of calcium carbonate, about one tenth of the clay present.

2. Calcination must be made at a relatively low temperature (the temperature necessary to the decomposition of calcium carbonate).

3. Calcination must not be prolonged beyond the time necessary to accomplish this decomposition. Potassium hydrate can be added in the proportion of 5% to replace calcium carbonate.

In spite of the results accomplished, the experiments were not successful and the disasters which followed in time, did not increase the general faith in artificial pozzolana.*

Vicat in another study (82) asks the question: "Are natural or artificial pozzolanas best adapted for maritime works?" And his answer was, that while it is true that there are some artificial pozzolanas which disintegrate in sea water there are also some natural ones which follow the same course. Furthermore while the natural pozzolanas cannot be scientifically classified

*These disasters referred to are those in some harbor of Southern France. Reference to same can be found in Annales des Ponts et Chaussees.

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owing to the hydrated state in which they are found, and due to the variable percentages of ferric oxide and of other components present, artificial pozzolanas can instead be naturally divided into two classes: Those adapted to maritime works and those not adapted.

The question seems to have rested here for a while because we do not find any other work regarding artificial pozzolanas until 1853. While Vicat and his followers kept their faith in artificial pozzolanas, even for maritime works, we find others who take the opposite stand. We find thus, Minard, who begins a study in this way (89):

> "It is a few years since some new elements have been introduced into the composition of hydraulic mortars. These innovations which have produced some great economy have been successful for fresh water works but for mortars exposed to sea water have given place to the alteration of the same and to final disintegration. Artificial pozzolanas which promised a good result through first hardening of the mortars which contained them, have after two or three years of immersion in the water of the ocean become subjected to a softening quite remarkable and finally to complete destruction."

Owing to this, he maintains that in the maritime works it is necessary to use natural pozzolanas.

Vicat defends himself in a letter, but while he mentions the good results obtained with hydraulic limes and with cements, he does not report any for the artificial pozzolanas and he limits himself to the hope that further studies can adequately solve the problem of the right calcination of clays.

Noel remarks (90) that regarding the works in Genoa Harbor where such splendid results were obtained, those results were to be foreseen because fat lime and natural pozzolana had been used as had been done in the Harbor of Toulon, and he maintains this attitude in a later study (91) in which he points to the resistance of the old Roman works made with natural pozzolana.

At this time, Ravier (94) Director of the Maritime Works of the Harbor of Algiers, noticed some very serious damage in the construction of that Harbor, construction made with fat lime and Roman pozzolana, which mortar, according to him, did not withstand the action of sea water. At the same time not even Neapolitan pozzolana or that of Rochgoun from the Island of Rouchgoun had made any better showing, but he does not mention at all artificial pozzolana.

Rivot and Chatoney (102) then occupy themselves in a very thorough work, passing in review all the materials employed in sea water construction. They express themselves in this regard as follows:

> "For quite a few years, clays more or less pure either before or after calcination had been used under the name of artificial pozzolana. But in a number of cases, the results have not been very favorable and the explanation of their failure is easy to give. Clays not calcined are in general much less subject to attacks by acids and alkalis than natural pozzolanas, and consequently the action exercised upon them by lime in presence of water must be very slow and only a very partial one. We therefore encounter difficulties when we use mixtures of lime and clay in sea water construction because the partial initial setting is followed by the relentless action of the still free lime upon the clay. The result is a molecular movement which causes the slow disintegration of the mortar."

The pure clays, used after calcination like pozzolanas, are analogous and consequently cannot leave any hope of good results except in rare cases and under special conditions.

Ferruginous and calcareous clays subjected to a prolonged calcination cannot be considered as pozzolanas because they already contain combinations of lime with silica and with alumina, although they contain at the same time clay with which lime can react.

In the use of substances mixed with a certain proportion of lime, the reactions are necessarily very complex. It is possible to draw some good out of calcined clays whether pure, calcareous or ferrouginous, by mixing them with an excess of hydrated lime and leaving the mixture to react undisturbed through many months or even many years. The action of the lime upon the clay having been completed before immersion, the setting will take place through reactions very simple and simultaneous. But the artificial pozzolanas seldom give favorable results.

The memoir of Chatoney-Rivot was presented to the Academy of Science in a meeting of June 9, 1856 and their theory was approved by a special commission. As set forth in two successive reports of Vaillant, Secretary of this Commission, the other members of which were Chevreul, Poncelet and Dufrenoy. The commission proposed to send this report to the Department of Public works for the information of the mixed commission of the

-8-

Departments of the Navy, War and Public Works, named to investigate the disaster which had happened in the Harbors of Havre and La Rochelle.

Vicat did not lose any time in answering with a note (99) in which he treats of all of the materials employed in maritime works. In this note he affirms that regarding artificial pozzolanas he, having investigated all the hydraulic materials, has come to the conclusion, on the basis of his experiments, that only the mortar made with 15 or 20 parts of lime to 100 parts of artificial pozzolana lightly calcined is capable of withstanding the action of sea water. He then rejects the statements of Chatoney and Rivot adding that he had kept in sea water, in a most aggressive condition for ten years, some specimens of mortars made with artificial pozzolana and that their remarkable state of preservation was due to a natural property of the silicates made of white clay, lightly calcined. Basing his opinion upon this last observation, he established the solution of the problem of the resistance of hydraulic material through the selection of the light pozzolana and the low temperature of calcination.

In another study however (101), having perhaps examined a little deeper into the arguments of Chatoney, Rivot and Vaillant he modifies his conclusions somewhat, approaching in a large part their ideas. As a matter of fact, he claims for himself the priority of these same ideas, but as far as artificial pozzolanas are concerned he does not say a word. This leads us to believe that he has come to full agreement with his opponents regarding them. Nevertheless, he reversed himself once more upon this argument (105) recalling all his studies and all his detailed experiments made in 1846 and continued up to that time, which, according to him had demonstrated the superiority of artificial pozzolanas, manufactured through light calcination of clays, over all natural pozzolanas.

Rivot then replied that he had misunderstood the findings of the Commission and that he had made them say what they had never intended. Their only statement relative to artificial pozzolanas was that they must be used with small quantities of lime and must be made to undergo a previous mixing (this was confirmed a little later by Chatoney (113).

Vicat returned to the question insisting upon the truth of what he had previously said and remarking that he had not been the one to propose the use of artificial pozzolanas, which proposal goes back to 1796. All he did was to demonstrate in 1819 and 1828 that the hydraulic energy of artificial pozzolanas depends upon the appropriate calcination of the clay and that he had remained completely apart from the application of his principle from 1830 to 1845, in which intervening time, mari-

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time works had been built which had been attacked by sea water. Later, however, perhaps regretting the fact that he had somewhat declined the paternity of artificial pozzolanas of which he had been the strongest champion, and regretting to see them banished from maritime works, he began a new investigation going much deeper with his research and publishing a new study (110). The aim of this work, he says frankly, is that of introducing the use of artificial pozzolanas for maritime works. To accomplish this result the clays which can furnish these pozzolanas must contain in one hundred anhydrous parts from 20 to 45 parts of alumina and from 80 to 55 parts of silica; they can contain also some quarz and some small quantities of iron oxides and they must be mixed with lime in the proportion of 15 to 18 parts of lime for each 100 parts of pozzolana. In fresh water these materials set in three or four days and in 12 months they have attained their final strength. In sea water if they are in small pieces, they are attacked and destroyed unless pozzolana contains an excess of silica, for instance, 76 parts of silica to 24 of alumina. But these same pieces hardened first for 15 days, in fresh water, or under wet sand are no longer attacked. All large blocks are attacked but disintegration stops at a certain depth and does not go any further. Rapid drying in the atmosphere or under the sun seems to exercise a favorable influence upon setting, but if mortar is cured in this way, and immersed afterwards, either in fresh water or salt water, an absorption of water takes place of such magnitude as to give rise to cracks. This can be obviated by the addition of sand, but then the concrete loses its strength, especially if these proportions are exceeded: 1-1/3 volume of sand for 1 volume of mortar.

From the tests and the analysis made by Vicat, it is realized that the action of sea water upon mortars has for effect a substitution of magnesia for lime. He says that this continuous action does not impair the cohesion, therefore, he claims that these mortars are superior to others which must be protected to avoid the penetration of magnesium salts. Finally, he gives a few hints on how to form the blocks, warning against their alternate exposure to water and dry air and finally he occupies himself with the matter of calcination, which must be made at 800 degrees and according to the specifications of Raffenau(63).

This was the last study upon the subject written by Vicat.

Nobody else occupied himself with it except Chatoney in his answer to Vicat (113).

Attempts to put back in use pozzolanas made of clay are very rare and we will not mention any of them other than that of Nicholson who in 1875 obtained a patent in France for

SANTORINO AND TRASS

Elsner was the first to occupy himself with Santorino in 1849 and he refers to it in a mrmoir of the same year (84). In a more detailed way, L. Montant, referring to his own ideas and those of E. F. Heider, treats of this material in a very interesting study. He says that Santorino is in Greek called "Aspus" and is a product of the Island of Santorino of the group of Cyclades Islands in the Aegian Sea, where it is found at the foot of a cliff, which forms the central part of the island in a bank of an average of 10 meters of thickness, homogeneous and pure.

Santorino is a gray powder, almost like ash, found mixed more or less with sand. This sand is nothing more or less than a mixture of pumice and oxidian with fragments of crystals of feldspar, of quarz, pyroxene, augite and lava. At a very high temperature Santorino fuses, giving as a result of the fusinn a green glass, whose composition differs very little from that of the glass of bottles. In the following tables, we give the various analyses of Santorino:

CONTRIBUTING AND PRESS

Elsner was the first to occupy himself with Santorino in 1849 and he refers to it in a memoir of the same year (34). In a more detailed way, L. Montant, referring to his own ideas and those of G. R. Neider, treats of this material in a very interesting study. He says that Santorino is in Greek called "Aspua" and is a product of the Island of Santorino on the group of Cyclades Islands in the Legion Sea, where it is found at the foot of a cliff, which forms the central part of the island in a bank of an average of 10 meters of thickness, homogeneous and pure.

Santorino is a gray powder, almost like ash, found mixed more or less with sand. This sand is nothing more or less than a mixture of pumice and oxidian with fragments of crystals of feldspar, of quartz, pyroxene, augite and lava. At a very high temperature Santorino fuses, giving as a result of the fusion a green glass, whose composition differs very little from that of the glass of bottles. In the following tables, we give the various analyses of Santorino:

ANALYSIS, SANTORINO

Components	ANALYSIS OF FEICHTINGER (208)				ANALYSIS OF MARGUILES of Trieste			ANALYSIS OF THEIL Polytech. of Vienna		
	Part Soluble in Water	Part Soluble in HCl	Part Insoluble in HCl	Total	Part Soluble in HCl	Part Insoluble in HCl	Total	Part Soluble in HCl	Part Insoluble in HCl	Total
Silica	----	Trace	66.37	66.37	----	66.96	66.96	----	64.34	64.34
Alumina	----	1.36	12.36	13.72	5.91	7.20	13.11	5.83	5.05	10.88
Pot. Oxide	----	----	2.83	2.83	----	3.23	3.23	----	4.83	4.83
Sodium Oxide	----	----	4.22	4.22	----	4.81	4.81	----	6.05	6.05
Lime	----	0.40	2.58	2.98	2.46	----	2.46	3.62	----	3.62
Ferric Oxide	----	1.41	2.90	4.31	3.30	2.12	5.42	4.83	1.61	6.44
Manganese Oxide	----	----	----	----	----	0.83	0.83	----)	2.77	2.77
Magnesia	----	0.23	1.06	1.29	----	1.03	1.03	----)		
Water	----	----	4.06	4.06	1.55	----	1.55	1.50	----	1.50

According to Montant its chemical composition is not sufficient to furnish the explanation of its hydraulicity with lime because analogous substances, such for instance as feldspar, do not set. Santorino itself loses this property when it is fused and pulverized.

From the works of Heider and those of Feichtinger it results that Santorino can be separated through a thorough washing into three parts.

1. Pumice which is lighter than water and floats at the surface.

2. Powder much finer of a clear brilliant gray.

3. Very fine sand usually black, although sometimes red, yellow or differently colored, which is composed of oxidian in its various forms.

These three parts into which it is possible to separate Santorino are not only different as to their general aspect and their behavior with lime, but also as to their chemical composition inasmuch as they contain different quantities of amorphous silica, soluble in a solution of potassium carbonate.

According to Feichtinger, they have the following percentage composition after grinding and drying at 100°C.

According to textbooks, they have the following percentage composition after grinding and drying at 100°C:

	PUMICE			FINE PART			COARSER PART		
	Part Soluble in HCl	Part Insoluble in HCl	Total	Part Soluble in HCl	Part Insoluble in HCl	Total	Part Soluble in HCl	Part Insoluble in HCl	Total
Silica	Trace	72.84	72.84	Trace	71.44	71.44	Trace	63.07	63.07
Lime	0.40	2.15	2.55	0.84	1.80	2.64	0.68	3.15	3.83
Magnesia	0.25	1.33	1.58	0.48	1.36	1.84	0.35	1.58	1.93
Alumina	0.75	11.51	12.26	1.31	8.56	9.87	1.64	14.03	24.67
Ferric Oxide	0.28	4.07	4.35	0.54	3.30	3.84	1.86	6.87	8.73
Pot. Oxide	----	1.28	1.28	----	1.86	1.86	----	1.87	1.87
Sodium Oxide	----	2.65	2.65	----	3.74	3.74	----	3.86	3.86
Water	----	2.25	2.25	----	4.61	4.61	----	1.14	1.14
			99.76			99.84			100.00

Santorino is therefore, a mixture of cementitious material and sand. The cement is the fine part and the sand consists of pumice which floats on the water and of oxidian which is heavier than water.

Santorino owes its hydraulic properties to its fine particles - that is, to the amorphous silica, of which it contains a considerable percentage. The demonstration that amorphous silica is the material which confers hydraulicity to Santorino was obtained by mixing its residue after treatment with a solution of potassium hydrate and calcium hydrate; this mixture had not hardened after a year while the natural Santorino treated with the same calcium hydrate, after a day under water, could not be readily broken, and after a month acquired the strength of Portland cement. The fact that one of the three parts in which Santorino can be separated is the one which determines the setting does not imply that the other two parts are perfectly inert. As a matter of fact, if a piece made of recently mixed mortar is broken, it is possible to see small particles of pumice and small grains of sand with their contours well-defined, and their forms distinct. If the mortar instead is rather old, the contours are less defined and after some time from the immersion, the mortar seems quite homogeneous and under the microscope it is possible to notice that the pumice and the sand are integrally united entering into a perfect chemical composition.

The results obtained with the use of Santorino are excellent. The preparation of the mortars does not differ from that of other hydraulic materials. The mortar must be prepared for some time before being used (at least 24 hours - or, better yet, five or six days) must have an appropriate consistency, because in this way only, is it possible to avoid a milky effect of the magnesia, thus bringing about the chemical reaction which paves the way to hardening. (See Rivot and Chatoney).

The mortar, owing to the composition of Santorino must be made with three volumes of lime and seven of Santorino. After the tests of Colonel Koerber at Fiume, it has been found that a better mortar is obtained by adding a slight amount of sand. This fact was observed by Minard for the mortars made with gres, contrary to what takes place with volcanic pozzolanas, in which any addition of sand seems to weaken the pozzolanic action.

Koerber proposes to have the mortar proportioned in the following way:

Santorino	6 Volumes
Lime	2 "
Fine Sand	1 "

Santorino must be kept free of the action of atmospheric agents to obviate the possibility that the finer particles may be carried away with consequent loss of pozzolanic energy.

They may be compared to ramifications of trees from the root and are formed especially if lime is present in excess. Their physical strength grows rapidly until after nine months of immersion in sea water, then a period of arrest of the growth of the physical strength appears to intervene until the end of the second year, finally the hardening grows until the 13th year and the resistance appears equal then to that of the calcareous materials. Elsner refers to the fact that according to what was said by Beuth, Santorino differs as construction material from the Roman cement owing to the property which it presents of remaining hard when kept under water, while it crumbles when kept out in the open.

> "It is very probable," he says, "that this property finds an explanation in the various allotropic states of silica, which, while in trass it is transformed by hydrochloric acid almost exclusively into a hydrated compound (and therefore shows a great facility in entering into chemical composition with water) in Santorino instead, according to chemical analysis, is not found in this favorable state of hydration. It appears clear then that Santorino must always remain in contact with water to be able to form the hydration necessary for a hydraulic mortar."

Works executed with Santorino can be found in Trieste, Pola, Fiume (131) or on the shores of the Adriatic Sea and in Egypt in the Harbor of Alexandria.

T R A S S

Trass very much resembles artificial pozzolanas. The Romans found in the neighborhood of Bonn, upon the River Rhine a tufa almost similar to pozzolana. That this tufa was used at that time for hydraulic works is not very well ascertained, nevertheless, it is a fact that toward the end of the seventeenth century it was used for this purpose. It is said that Van Santan, Holland Dutch, in 1862 built the first windmill to be used to grind the trass. It is from this time that it is known for certain that trass was used for hydraulic mortars to a very great extent in France, England, and Germany.

Trass seems to be derived from the Holland word "Tyrass" which means cement. In the Middle Ages, trass was used on a large scale as a material of construction all along the Rhine. It is, in effect, a material very useful for fulfilling the purpose of hydraulic cement for river works, owing to its great physical strength, its easy workability and hardening properties.

DEPOSITS

Trass is found in the neighborhood of the Eifel, particularly in the neighborhood of the Laacher Lake near the Rhine (where it is still called "Tufa","Dukstein") in the valleys of Nette and of Bruhl near Neuwied and Andernach. In many villages around these places we find developed the industry of grinding tufaceous stones. A tufaceous stone is a product of ejections of ancient volcanos, which ejections, owing to the action of steam and pressure were solidified in strata, so that in the lower part it is found in a state of solid stone and in the upper part as a material which is much more friable, made of volcanic ash covered by the vegetable soil. The thickness of the various strata is varied. In the Valley of Bruhl, it is said to be about 10 m. The oldest tufaceous stone which constitutes the true trass is as hard as a well burned brick. It is porous, of a gray, yellowish color, with a tendency at times towards blue (the color blue being an index of a good quality) and after grinding is a gray rather harsh powder.

The tufaceous stone more recently called at Bruhl "Knuppen" and in Andernach "Tanch" has the hardness of creta, is not porous and is often found mixed with pumice and schists. The upper stratum which is of more recent formation is made of volcanic ash and is called bastard trass and in German welder trass. It is very soft, of a whitish gray and very slightly hydraulic.

In the Valley of Bruhl, the tufaceous stone lies almost exclusively above the level of the streams upon the side of the mountains; in fact the deposit extends in the south direction through some six to nine meters below the surface. The tufaceous stone is handled in commerce partly in chunks of a weight of about 10 kilograms and partly ground like trass.

The property of being found in large chunks and the blue color constitute two favorable conditions against falsification. Trass loses, like pozzolana, its water through heating and in a large part appears to be soluble in a concentrated solution of hydrochloric acid. Beside the materials which are reported in the following tables, Vohl found in trass about 0.62% of sodium, potassium and magnesium chlorides.

From the locality of Ries near Nordinger in Bavaria there derives a tufaceous stone, which is also employed either as a material of construction for ordinary works or as a hydraulic material. But this stone differs greatly from pozzolana, from trass of the Rhine and from volcanic tufas. This material does not form any gelatinous solution with hydrochloric acid. As a matter of fact it dissolves readily even in a dilute solution. It appears to be of variable color and presents variations of composition which are very noticeable even to the naked eye.

Feichtinger (208) found for the trass of Ries two different deposits; the deposits of Mauern and Christgarten, which have the following composition:

		Trass of Mauern	Trass of Christgarten
Silica soluble in diluted potassium hydrate		2.18	2.57
Soluble in Hydrochloric Acid.	(Lime	2.98	2.16
	(Magnesia	1.20	1.32
	(Alumina	5.95	5.48
	(Oxide of iron with (trace of manganese	4.66	3.55
	(Silica	0.12	0.18
Silica after decomposition with HCl, soluble in diluted Potassium Hydrate.		13.22	6.13
	(Silica	49.54	59.85
	(Alumina	7.46	8.45
	(Iron Oxide	1.10	2.95
	(Lime	1.71	1.78
	(Magnesia	0.88	0.95
	(Potassium Oxide	2.91	1.82
	(Sodium Oxide	0.35	0.34
	(Water	5.66	2.59

Knapp (205) concerning himself with the composition of this rock, adds that it is of a very complex nature and that it generally contains decomposed pumice which disintegrates into a yellowish powder, also fragments of basalt, volcanic rocks, grains of quarz, schists and iron oxide, and noticed that it seems to originate from new ejections because it contains carbonized timber, shells, bones, etc.

There are three distinct varieties of trass which are used in constructions; the bluish trass, the yellowish and the dark, the first two varieties of which constitute the "Tufstein" or trass properly called. Following are the characters which Knapp assigns to them.

The bluish trass constitutes the best quality. It is tenacious, sonorous, capable of being cut in sharp sections; its pores are small and it is much more prized; is more compact and resistant.

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	Trass of Mauern	Trass of Christgarten
Silica soluble in diluted Potassium hydrate	3.18	2.57
Soluble in Hydrochloric acid. (Lime	2.98	2.16
(Magnesia	1.20	1.32
(Alumina	5.95	5.48
(Oxide of iron with trace of manganese	4.66	5.[illegible]
(Silica	0.3[illegible]	0.12
Silica after decomposition with HCl, soluble in diluted Potassium hydrate.	13.22	6.13
(Silica	49.[illegible]	59.[illegible]
(Alumina	7.[illegible]	8.[illegible]
(Iron Oxide	1.10	2.[illegible]
(Lime	1.71	1.[illegible]
(Magnesia	0.88	0.[illegible]
(Potassium Oxide	2.[illegible]	1.82
(Sodium Oxide	0.[illegible]	0.34
(Water	5.68	2.59

Kampf (205) concerning himself with the composition of this rock, adds that it is of a very complex nature and that it generally contains decomposed pumice which disintegrates into a yellowish powder, also fragments of basalt, volcanic rocks, grains of quartz, schists and iron oxide, and noticed that it seems to originate from new ejections because it contains carbonized timber, shells, bones, etc.

There are three distinct varieties of trass which are used in constructions; the bluish trass, the yellowish and the dark, the first two varieties of which constitute the "Ministein" or trass properly called. Following are the characters which Kampf assigns to them.

The bluish trass constitutes the best quality. It is tenacious, sonorous, capable of being cut in sharp sections; its pores are small and it is much more prized, as more compact and resistant.

The yellowish trass presents unequal hydraulic qualities and often becomes disintegrated by atmospheric action.

The third variety of trass, called in German (Wilde Trass) is much less hydraulic than the other two; this trass is much less porous and disintegrates easily under the action of atmosphere. Various analyses of trass are reported in the following table:

Components	1	2	3	4			5			6			7		
	Analysis of Berthier			Trass of Holland — Analysis of Rivot			Trass of Holland — Analysis of Rivot			Trass of Havre furnished by Chevalier — Analysis of Rivot			Trass of Havre furnished by Chatoney — Analysis of Rivot		
	Trass of Holland	Trass of the Shores of the River Rhine		P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total
Mixed Sand	--	--	8.75	--	--	--	--	--	--	--	--	--	--	--	--
Silica	57.00	46.60	46.25	28.00	29.5	57.5	23.0	31.0	54.0	17.0	37.4	54.4	31.0	23.0	54.0
Alumina	16.00	20.60	20.71	5.0	5.1	10.1	6.0	10.5	16.5	11.15	7.0	18.5	17.0	6.0	17.0
Lime	2.6	3.00	2.15	1.2	6.5	7.7	1.0	3.0	4.0	1.4	0.6	2.0	1.6	1.0	2.6
Magnesia	1.0	--	1.00	--	1.1	1.1	--	0.7	0.7	3.0	--	3.0	1.0	--	1.0
Iron Oxide	5.0	12.00	5.48	--	3.9	3.9	--	6.1	6.1	4.5	--	4.5	6.0	--	6.0
Pot. Oxide	7.0	5.00	6.30		6.4	6.4		10.0	10.0	7.0		7.0	10.0		10.0
Sodium Oxide	1.0														
Volatile Substs.	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Water	9.6	12.80	9.25			12.6			7.7			10.2			8.0
Total	98.2	100.00	99.19			99.3			99.0			99.6			98.6

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8			9			10			11			12			13		
Trass of Flessing furnished by Minard Analysis of Rivot			Trass of Andernach (Prussia) Analysis of Elsner			Blue Trass of the Herfeldt in the Valley of Bruhl			Yellow Trass of the excavation of Herfeldt.			Gray Trass of Kill			Blue Trass of Kill		
P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total	P. Soluble in HCl	P. Insoluble in HCl	Total
22.5	33.0	55.5	11.50	37.44	48.94	5.15	47.93	53.08	14.5	42.3	56.8	10.6	48.7	59.3	8.2	44.0	52.2
11.0	5.0	16.0	17.70	1.25	18.95	16.02	2.26	18.28	8.3	8.3	16.6	6.1	6.1	12.2	5.2	10.0	15.2
1.6	1.0	2.6	3.16	2.25	5.41	1.25	--	1.25	3.5	4.8	8.3	3.6	2.6	6.2	2.2	4.5	6.7
3.4	--	3.4	2.15	0.27	2.42	0.81	0.50	1.31	0.9	1.3	2.2	0.9	1.0	1.9	0.9	1.6	2.5
4.5	--	4.5	11.77	0.57	12.34	3.33	0.48	3.81	4.8	4.6	9.4	3.6	4.9	8.5	4.3	7.1	11.4
	--		0.29	0.08	0.37	3.52	0.65	4.17	1.8	0.3	2.1	1.2	2.3	3.6	1.3	2.8	4.1
6.6	--	6.6	2.44	1.12	3.56	2.17	1.27	3.44	0.6	0.5	1.1	1.5	1.8	3.3	1.5	1.1	2.6
--	--	--	--	--	--	--	--	--	--	--	--	--					
--	--	10.5	7.65	--	7.65	12.65	--	12.65	2.8	--	2.8	5.5		5.5	6.1		6.1
		99.1			99.64			97.99			99.3			100.4			100.8

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NATURAL NON-VOLCANIC POZZOLANAS

These are some rocks of non-volcanic origin which were referred to for the first time by Vicat (32) who said that some good cements had been made of fat lime with substances not calcined, not porous, and not absorbent, composed of rather weak elements, that is, first, some feldspatic sands and some disintegrated granites, second, some psammites dark and soft from the lower part of England. Another reference on the same subject was made by Girard(36), who refers to having found in the Valley of the Isle the Department of the Gironde, some fossil clayey sands of a color variable from dark red to yellow red, called "Arène", which, when mixed with lime in the proportion of three to one, or better yet, five to one, set under water. The same Girard in another note (38) upon the same subject, mentions Meril and payen who are supposed to have found such materials in England.

Minard speaks of a substance which presents pozzolanic properties, found in the Department of the Aisne to which he gives the name of pozzolanic gres. He found this material in banks of thickness of two to five meters, deposited immediately upon gray or yellow clay. Its consistency varies from the friable sand to the moderately hard gres. The sand having black and white grains is very fine and is mixed with gres by means of a clayey gang which is the main agent of the pozzolanic characters. This material contains at times small fragments of black silica, of quarz and veins of ocrean clay. The pozzolanic property seems to grow in direct ratio with the adherence of the parts owing to which the friable gres appears to be more energetic than sand, although it is less so than moderately hard gres, which the author considers to be the rival of the Italian pozzolana. Vicat mentions that a certain rock of the Mountains of the Ardennes, called gaize (77) also presents pozzolanic properties. This stone has the following composition:

Fine sand	17%
Green fine sand	12%
Clay	7%
Gelatinous Silica	56%
Water	8%

The presence of a greater quantity of gelatinous silica led him to believe that this material mixed with lime could act like pozzolana, and this was in effect confirmed by practice.

Saint-Claire Deville from a great number of analyses made upon samples taken during the construction of the railroad from Chalon to Verdun found:

			Average
Hygrometric water (loss at 100°)	2.7	to 4.2	3.50
Water of Comb. (loss at red Temp)	2.3	to 23.5	6.33(?)
Soluble Silica (1/10 Pot. Hydrate)	29.2	to 47	28.85
Insoluble Silica	24.7	to 42	38.86
Alumina	3.7	to 8.3	5.56
Iron Perioxide	2.0	to 4.4	3.27
Lime	Trace	to 9.5	2.60(?)
Magnesia	0.0	to 1.6	0.46(?)
Alkalis (and other elements)			0.67
			100.00

	Mixed Sand	Silica	Alumina	Magnesia	Lime	Fe_2O_3	$CaCO_3$	Water	Alkaline and Volatile Substs	Total
Rocks of Chateaulin after clinkering	--	60.30	23.70	2.50	traces	10.30	--	--	3.20	100.-
The same of St. Servan	10.50	38.50	29.40	--	2.00	18.40	--	--	1.50	100.-
Reddish White rocks	10.50	42.10	23.65	--	trace	22.47	--	--	1.28	100.-
Sands of Brittany after calcination	4.13	60.33	21.43	6.69		8.57	--	--	2.75	99.-
Sand of St. Astier not calcined	--	38.54	20.00	--	--	12.00	8.00	17.00	--	99.-

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TECHNICAL TESTS UPON NATURAL POZZOLANAS

To the builder who must avail himself of pozzolana, the problem of the valuation of its technical qualities presents itself under a dual aspect, first, he must see if the pozzolana has been artificially or naturally adulterated; second he must determine the hydraulic value.

ADULTERATION OF POZZOLANAS.

The material which is most commonly used in the adulteration of pozzolanas is clay, therefore red pozzolanas are most difficult to adulterate because it is less easy to find a clay of the same color, while the black and the gray pozzolanas lend themselves to such an adulteration.

Since very remote time, builders were careful about adulterations of pozzolana. The prescription of Palladio that a pozzolana can be judged favorably if it does not leave any spot upon a linen cloth is a testimonial of this.

Mr. Luigi Luiggi who occupied himself with the study of pozzolanas in connection with the works of Genoa Harbor (166) regarding adulteration with clay, proposes to subject pozzolana to a test of calcination, a test which is also among those proposed by Dardenne (215) for natural pozzolanas for trass.

When we think that whatever the nature of the soil which may be ground or mixed with pozzolana it must contain in general organic matters, it appears natural to try a test which will reveal their presence. The quantative determination of organic matter has for us no value whatsoever, all we are interested in is the qualitative value.

Besides tests of qualification there are to be noticed sieve analyses and the determination of the fineness, the specific gravity, the apparent density and the water of combination. Chemical analysis does not furnish other than very ambiguous results. Nevertheless, it is rather interesting to determine on one hand the proportion of silica and alumina soluble in acids and alkalis and on the other hand the proportion of insoluble matter.

Regarding the sieve analysis and surface fineness in relation to pozzolana this test has no very great importance inasmuch as pozzolana is a material which is ordinarily used in the state in which it is found in nature. Sometimes, it is used after having been sieved through large screens to free it of those parts of larger dimensions. The smallest openings of these screens are about 5 mm. and the largest 20 mm., meaning that with these dimensions are denoted the lineal dimensions of the particles which can pass through the screen.

TECHNICAL TESTS FOR QUALITY

TECHNICAL TESTS

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We must always remember though that pozzolanas are very complex materials which are constituted ultimately of various mineralogic parts which can even be rendered more complex by possible alterations, therefore, to pozzolanas can never be applied the criterions and the determinations which characterize cement in general and Portland in particular, which can in a certain way be regarded as a well defined compound, at least technically speaking.

But even if these tests could furnish a useful criterion to judge the hydraulic value of a pozzolana, it would still be necessary to establish the conditions according to which it is necessary to proceed to the various determinations, especially insofar as it has to do with the apparent specific weight.

For our tests we have chosen a series of pozzolanas of known technical value, the best being the pozzolana of S. Paolo. Regarding the apparent specific weight, we have determined it in two conditions, that is, first, in the grade of fineness in which it is practically used, and, second, when reduced to a very fine powder which leaves no residue larger than 25 or 30% when passed through the sieve of 5,000 openings per square cm. Of the same pozzolana we have determined the water of combination, which in trass, according to Dordenne is in direct ratio with its hydraulic particles, by operating upon the pozzolanas briefly dried to a temperature variable between 100° and 110° and then determining their loss of weight due to the furnace. We report in the following table the results of the various tests:

We must always remember though that pozzolanas are very complex materials which are sometimes mixed or various mineralogic parts which can even be rendered more complex by possible alterations. Therefore, to pozzolanas can never be applied the criterions and the determinations which characterize in general and Portland in particular, which can in a certain way be regarded as a well defined compound, at least technically speaking.

But even if these tests could furnish a useful criterion to judge the hydraulic value of a pozzolana, it would still be necessary to establish the conditions according to which it is necessary to proceed to the various determinations especially insofar as it has to do with the apparent specific weight.

For our tests we have chosen a series of pozzolanas of known technical value, the best being the pozzolana of Pesolo. Regarding the apparent specific weight, we have determined it in two conditions, that is, first, in the grade of fineness in which it is practically used, and second, when reduced to a very fine powder which leaves no residue larger than 25 or 30 when passed through the sieve of 5,000 openings per square cm. Of the same pozzolana we have determined the water of combination, which in these according to porderone is in direct ratio with its hydraulic properties, by operating upon the pozzolanas briefly dried to a temperature variable between 130° and 140° and then determining their loss of weight due to the furnace. We report in the following table the results of the various tests:

Pozzolana	Treatment with Potassium Hydrate	Apparent Density Pozzolana		Specific Weight	Water of Combination Loss through Ignition %	Carbonic Anhydride
		Natural State	Ground			
1	Limpid Liquid	1.164	1.044	2.352	5.92	---
2	Id.	1.113	0.943	---	5.88	---
3	Id.	0.997	0.9936	---	5.59	---
4	Id.	1.149	1.006	2.439	5.88	
5	Id.	1.129	1.006	---	5.23	---
6	Id.	1.187	1.0506	---	5.15	---
7	---	---	---	---	3.13	
8	Limpid Liquid	---	---	---	5.50	---
9	Id.	1.124	1.057	---	4.65	---
10	Gray	0.942	---	2.174	12.50	6.70
11	Yellow	0.957	---	---	8.13	2.19
12 (Veg. Soil)	Id.	---	---	---	9.30	---
13 (Veg. Soil)	Gray	---	---	---	17.26	4.98
14 (Clay)	Yellow	---	---	---	15.90	10.20

Pozzolana	Hydrate assimilation with Pozzolana	Grade	Ground	Metals Specific	Ignition & Moisture Loss	Carbonic
	Treatment	Hydrate Density	Pozzolana		Combination Water of	
1	Limpid	1.154	1.044	2.552	2.62	---
2	Limpid	1.112	0.942	---	2.88	---
3	Limpid	0.966	0.9326	---	2.62	---
4	Limpid	1.146	1.009	2.426	2.88	
5	Limpid	1.152	1.009	---	2.52	---
6	Limpid	1.184	1.0209	---	2.12	---
7	---	---	---	---	2.12	
8	Limpid	---	---	---	2.20	
9	Limpid	1.124	1.024	---	4.62	---
10	Grey	0.942	1.4142	2.20	2.40	
11	Yellow	0.924	---	---	2.12	2.16
12	Grey	0.942	---	---	2.20	---
13	Grey	1.12	---	---	2.12	2.16
14	Yellow	---	---	---	2.12	2.16

From the above it is readily seen that the treatment of pozzolana with a dilute solution of potassium hydrate and the test of clarification are sufficient data to differentiate the true pozzolanas from those which were adulterated with earthen materials.

The same thing cannot be said with regard to the density be it real or apparent, because these densities do not vary much in the various pozzolanas although they have technical value different in various cases, and this cannot be otherwise because if it is true that pure clay has an apparent density of about two and therefore whenever it is mixed with pozzolana is supposed to increase its density, it is nevertheless a fact that in all adulterations it is never a question of pure clay, it is always a case of clayey earth which contains in turn many impurities which can lower its density so as to render it very close to that of pozzolanas. It is also worth while to notice that those pozzolanic deposits like that of the cave of S. Giovanni, of Goriano Sicoli and others to which we made reference in the first part of our work, were transported by winds rather far from the crater of ejection. They are constituted in general of very fine and light elements, owing to which their density is diminished.

Regarding the apparent density, we notice that we have found it always larger for pozzolanas in their natural state than for pozzolanas finely ground. In other words, it appears that for them the same thing happens as in cements, above all in Portland cements in which their apparent density diminishes with the fineness of grinding, which is explained by the contraction which has taken place on account of their high temperature of clinkering.

Concerning the determination of the water of combination while this determination reveals quite well the presence of vegetable matter or of clay, it does not present any interest for what has to do with the technical value of the various pozzolanas, first of all because the percentage is too small to offer characteristic gradations and in the second place, in all pozzolanas studied, although they were quite different as regards the technical value, this percentage varied little with the exception of the pozzolana of Di Paliano or better yet that of Vicovaro, which differentiates from the Romans on account of the larger quantity of base soluble in acids.

Next we want to call to general attention that in the true pozzolanas, carbonate anhydride is seldom found and then only in small quantities, while it can be found in remarkably large quantities in all adulterated pozzolanas, in clays, etc. The proposed test to determine the value of pozzolanas are those of Vicat and Chatoney-Rivot, which appear to be the only ones of their kind.

From the above it is readily seen that the treatment of porcelains with a future solution of porcelain bodies and the true porcelains from those which were adulterated with earthen material.

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Regarding the apparent density, we notice that we have found it always larger for porcelains in their natural state than for porcelains finely ground. In other words, it appears that for them the same thing happens as in cements: above all in Portland cements in which their apparent density is almost the thickness of putting, which is explained by the suppression which has taken place on account of their high sampore- ture of clinkering.

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VICAT TEST

The principle upon which this test is stated by Vicat is as follows (35):

"The energy of a pozzolana is directly proportioned to the quantity of lime water which it is capable of fixing during a determinate time. (Vicat used a solution of lime in water but inasmuch as the solubility of lime in water is rather small (128) he afterward substitutes for it a solution of sugared water which has a much larger dissolving power for the calcium hydrate. This test must necessarily be made in comparison with a pozzolana of which the technical value is practically known and is conducted in the following manner.

"A determinate weight (20 gr.) of the pozzolana to be examined and an equal weight of the comparative one are each placed in contact with an equal and determinate value (100 cm.) of a solution of calcium hydrate in sugared water, a solution which is tested with hydrochloric acid. The calcium oxide which we have used to prepare all the tests which we have described was a very pure substance, which at the furnace gave a loss of only 3.76% of which 0.74% was carbonic anhydride (CO_2). This lime in the sugared solution left an insoluble residue of 1.18%. It contained very little traces of magnesia and was also entirely exempt from the presence of alkalis. We would perhaps have found some calcium oxide purer than that or we could have prepared one with precautions which must be followed for a technical product instead of a product of a laboratory. Though the laboratory preparation is purer it does not present those qualities which render it so well adapted for technical tests.

"Regarding the quantity of sugar to be used for the solutions, from our tests we have found that the maximum solubility of calcium oxide (CaO= 2.5%) in sugared water is obtained by the dissolving of a kilogram of sugar in about 10 liters of water. This solution can be further diluted, but to see that this happens in the right way, it is necessary to take precautions to first hydrate the lime and after the hydration has taken place it must be placed in contact with sugared water and filtered after being left in it ten or twelve hours, being careful to shake it from time to time.

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The whole is filtered upon a dry filter and an aliquot part is brought again in contact with a normal solution of hydrochloric acid. It is thus possible to calculate all the lime which is liberated from the pozzolana by the solution.

"We have made a test upon pozzolanas of the degree of fineness with which they are used in practice and also upon the same pozzolanas when reduced in a very fine powder, using always as a means of comparison the pozzolanas of S. Paolo. We have also seen the behavior of earth, clay and some natural silicates.

NATURAL POZZOLANA

Sugar Solution 1.53% of CaO

POZZOLANA	DURATION OF IMMERSION	
	48 Hours	10 days of 24 hours.
	CaO taken from 100 P. of Pozzolana	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo (Cave Mezzetti)	1.71	1.88
Pozzolana of S. Sebastiano	1.18	1.60
" " Porta Maggiore	1.29	1.20
" " the Pigno	1.04	1.20
" " Vicovaro	1.05	1.26
" " Anzio	1.18	1.54
" " Pagliano	1.32	1.48
" " S. Giovanni	1.64	1.48
" " Goriano Sicoli	2.17	2.07
Vegetable Soil	3.16	3.44
Pozzolana of S. Paolo (Tre Fontane)	1.65	1.90

Pozzolana of S. Paolo (The Fontane)	1.93	1.90
Vegetable Soil	2.19	2.44
" " Coriano Sicoli	2.14	2.04
" " S. Giovanni	1.94	1.78
" " Pagliano	1.22	1.48
" " Anzio	1.18	1.34
" " Vicovaro	1.02	1.29
" " Tre Pigno	1.04	1.20
" " Porta Maggiore	1.26	1.20
Pozzolana of S. Sebastiano	1.18	1.90
Pozzolana of S. Paolo (Cave Mezzetti)	1.41	1.88

	Duration of Immersion	
	48 Hours	10 days
	Cao taken from 100 P.	Cao taken from 100 P.
Pozzolana	of Pozzolana	of Pozzolana

Sugar Solution 1.22 of Cao

NATURAL POZZOLANA

The whole is filtered upon a dry filter and
the filtered part is brought again in contact
with a normal solution of hydrocarbonic acid.
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the Vegas of Ilmenesse with which they are
used in Bergen and also upon the same pozzo-
lanas when reduced in a very fine powder, using
always as a means of comparison the pozzolanas
of S. Paolo. We have also seen the behavior of
early, clay and some natural silicates.

PULVERIZED POZZOLANA

Sugar Solution 1.99% of CaO

Pozzolana	DURATION OF IMMERSION	
	48 Hours	10 Days of 24 Hours
	CaO taken from 100 P. of Pozzolana	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo (Cave Mezzetti).....	2.114	2.114
Pozzolana of the Pigno	1.094	1.094
Vegetable Soil	2.254	2.226

PULVERIZED POZZOLANA

Sugar Solution 1.54% of CaO

Pozzolana	DURATION OF IMMERSION
	Four days of 24 hours
	CaO taken from 100 P. of Pozzolana
Pozzolana of S. Paolo	1.68
" from the Cave Sette Camini..	1.51
" from the Pigno	0.97
" of S. Giovani	1.50
" " Goriano Sicoli.....	2.06
Clay of Bari	0.84
Vegetable Earth	2.27
Wollastonite (1)	0.04
Leucite (1)	0.00

(1) These are 2 natural silicates with which we thought to experiment at the same time we experimented with natural pozzolanas.

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"As we notice from the table which represents the results of the third test, we have experimented with the action of a sugared solution upon two natural silicates, Wollastonite and Leucite. Wollastonite does not set with lime. Leucite is found frequently but always kaolinized in pozzolanas, especially those of the Roman type, but very seldom found unaltered like the pozzolana of Pino. Making a mortar in the proportion of one part of Leucite to two parts of lime in volume and making an analogous type of mortar with the pozzolana of S. Paolo we placed both mortar specimens under water. After a few days, the pozzolana had set while the Leucite had not. After about three months we noticed a certain superficial set even in the Leucite mortars. This set is easily explained if account is taken of the action of water and carbonic acid of the air upon the lime and the Leucite. The final result of these actions is the Kaolinization of the Leucite followed by its setting. But these actions are very slow and this explains the behavior of Leucite at the Vicat test.

"From the three tests made, it is noticed that the length of immersion beyond a certain time has little influence, although such a statement deserves to be verified by a greater number of tests than those which we have made.

"Also, it is certain that the quantity of lime which is fixed by the pozzolanas is always very small, even if to be able to get any kind of index the test is prolonged for many hours.

"To this there must be added another objectionable feature of greater entity which can lead to many mistakes and which is rendered manifest by the observations of the percentage of lime absorbed by the common earth which is so much larger than that of the pozzolana of S. Paolo. Of this on the other hand we can very easily find an explanation, when we consider that lime combines itself to what is humic matter (65) giving rise to insoluble compounds. From this it follows that considerable quantities of this substance can materially alter the results of the test and lead to mistakes. This is confirmed by the percentage of the pozzolanas of S. Giovanni and of Voriano Sicoli as well as from that of the

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clay of Bari which is much less than that of the earth containing smaller quantities of humic matter.

"One thing seems noticeable though, whenever the humic substances are lacking altogether the test gives results that do not always conform to the truth. In effect, the pozzolana of S. Paolo in all the tests made, is always above any other which follow it in the order of their technical value as known in practice. From this we are brought to agreement with Professor Rebuffat (174-c) who says in a study upon the technical analysis of pozzolana: "To have a good method of technical analysis of pozzolanas it is convenient simply to accelerate the action of lime upon pozzolana in such a way as to be able to determine its effect in a practically short time.

TESTS OF RIVOT

This test is described by Rivot himself (203) as follows:

"Take 5 gr. of the substance ground to the degree of fineness adopted in practice for the manufacture of mortars, and submit to the action of the nitric acid, pure and concentrated. Leave the acid to react upon the silicate for about 24 hours at a temperature of 50° to 60°. Evaporate the solution and treat again by a diluted solution of nitric acid. From the liquid part, there is obtained the alumina, the iron oxide, the lime, the magnesia, and the alkalis. The insoluble part is first calcined, then weighed, then placed in a weak solution of potassium hydrate brought to a temperature of about 40°C. and left in this solution for 12 hours. The insoluble part in this alkaline solution is washed out with great care, dried, calcined and then weighed. The difference between the two weights is considered as representing the silica which became soluble through the successive action of acids and alkalis. In this determination of soluble silica rests the important result of the analysis because it is the best term of comparison of values of pozzolanas. It is useful to complete the analysis by determining the composition of that part of silicate which has not been a part of the two reagents in the wet process, therefore, it is mixed intermittently with an equal weight of

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lime perfectly pure and brought to a bright red temperature. After cooling, it is subjected to the action of nitric acid and then the determination is made of the silica and the bases. One must take care in this test to add to the weight of the lime, the weight of that particular base which has been added to render the silica of easy attack. As we have done for the test of Vicat we report in the following table also for the test of Rivot, the results obtained with various pozzolanas, with earth, with clay and some silicates.

Pozzolana	Water Hygroscopic	Water of Combination: Loss thru Ignition	Soluble in HNO_3	Part Soluble in Potassium Hydrate	Part Insoluble
Pozzolana of S.Paolo	4.60	5.92	40.03	31.42	28.55
Pozzolana from the Cave of the Sette Camini.....	5.88	5.88	39.39	31.37	29.24
Pozzolana of S. Giovanni.....	6.85	12.50	38.07	22.55	39.38
Pozzolana of Goriano Sicoli	6.31	8.13	47.42	24.90	27.68
Clay of Bari	4.52	17.26	44.58	12.43	42.99
Vegetable Earth	11.77	9.30	57.16	25.81	17.03
Wollastonite	0.17	4.26	51.47	46.40	2.13
Leucite	0.12	0.13	39.60	24.71	35.69

The principle upon which this matter is based seems to somewhat beg the question, because it consists in examining the action which strong reagents exercise upon pozzolanas, reagents like nitric acid and potassium hydrate. Now to obtain some degree of comparison between the results, it is necessary to operate the same way with reagents always in the same degree of concentration and within limits almost rigorously equal in time and temperature."

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The principle upon which this matter is based seems to somewhat beg the question, because it consists in examining the action which strong reagents exercise upon pozzolanas, reagents like nitric acid and potassium hydrate. Now to obtain some degree of comparison between the results, it is necessary to operate the same way with reagents always in the same degree of concentration and within limits almost rigorously equal in time and temperature.

"Within these limits", says Rivot, "it is possible to admit that the various silicates are slowly decomposed by lime and during the decomposition liberate silica and alumina with a facility comparable to that which can be detected through the action of nitric acid or a solution of potassium hydrate."

Rivot himself never nourished many illusions regarding the effectiveneness of the method which he proposed. In fact in his report written in collaboration with Chatoney (102) he expressed himself in these terms:

"This method has the objectionable feature of not determining the proportions of silica and alumina which can be combined with lime as well as that of only giving an indication of the facility with which the pozzolanic matter is attacked by the ordinary reagents of analysis in the wet process. There cannot exist anything else but a very uncertain relationship between the action of the nitric acid and potassium hydrate in the laboratory and that of the lime in its practical application, and they cannot be considered by any means to be proportional. At most, it can be admitted that the pozzolanas which are more easily attacked by acids and alkalis will be also those which will react the most easily with lime."

On our side we must add that there are other considerations which can be easily derived comparing the results obtained with pozzolanas with those obtained instead with soils - Wollastonite or Leucite. In effect, if we should draw any conclusion whatsoever from these results they would indicate Wollastonite as being a product containing a quantity of silica apt to set much stronger than the best pozzolanas, while instead we know very well that Wollastonite does not make any kind of set and the same can be said of Leucite, if it has not undergone, first, a process of kaolinization. Furthermore, it is necessary to notice that there is something else which plays a tremendous part in the falsification of the results - a question which has been noticed by Fresenius and also by Rebuffat (174-c), and that has to do with the capacity which the insoluble residue of the attack of a pozzolana with acid has for fixing a certain quantity of alkalis, even after the water has become perfectly neutral, which in turn, brings about the necessity of washing this residue with a very dilute acid.

"Within these limits," says Hayes, "it is possible to admit that the various silicates are slowly decomposed by time and during the decomposition liberate silica and alumina with a facility comparable to that which can be detected through the action of nitric acid or a solution of potassium hydrate."

Hayes himself never mourned many illusions regarding the effectiveness of the method which he proposed. In fact in his report written in collaboration with Chauvenet (1859) he expressed himself in these terms:

"This method has the objectionable feature of not determining the proportions of silica and alumina which can be combined with lime as well as that of only giving an indication of the facility with which the possible mortar is attacked by the ordinary reagents of analysis in the wet process. There cannot exist anything else but a very uncertain relationship between the action of the nitric acid and potassium hydrate in the laboratory and that of the lime in its practical application, and they cannot be considered by any means to be proportional. At most, it can be admitted that the pozzolanas which are more easily attacked by acids and alkalis will be also those which will resist the most easily with time."

On our side we must add that there are other considerations which can be easily derived comparing the results obtained with pozzolanas with those obtained treating with acids - sulfates or Lenotte. In effect, if we should draw any conclusion whatsoever from these results they would indicate Vitaston te as being a product containing a quantity of silica apt to set much stronger than the best pozzolanas, while instead we know very well that Vitaston te does not make any kind of set and the same can be said of Lenotte, if it has not undergone, first, a process of calcination. Furthermore, it is necessary to notice that there is something else which plays a tremendous part in the satisfaction of the results - a question which has been noticed by Tessenius and also by Rebuffat (1874-c), and that has to do with the capacity which the insoluble residue of the attack of a pozzolana with acid has for fixing a certain quantity of alkalis, even after the water has become perfectly neutral, which in turns brings about the necessity of washing this residue with a very dilute acid.

E. Landrin (141) proposed a modification of the method of Rivot, which modification consists in substituting hydrochloric acid for nitric acid and lime or water to a solution of potassium hydrate. The method of Landrin therefore can be held to be a combination of the methods of Rivot and Vicat, and on account of that in its first part - that is, the part which has to do with the action of the acid upon pozzolana - it lends itself to all the criticism that we have already made of the method of Rivot, although it represents some progress. In other words, it is a method which at least partially can be considered as a direct method while the one of Rivot, as we have said, is altogether an indirect method.

G. Signorile (160) proposed another modification of the method of Rivot as it seemed to him impossible to recognize the hydraulic energy of a pozzolana with two reactions only, one acid and the other alkali.

According to him:

> "A third reaction is necessary which requires time and labor but which need not be made more than once for all pozzolanas of the same volcanic ejection, provided that the materials be homogeneous and furnish pozzolanas of the same type, either basaltic or trachytic. This third reaction will provide a knowledge of the quantity of silica and of the bases that calcium hydrate fixes in the pozzolana during the hardening of the mortar. This third reaction consists practically in making a mortar with one volume of fat lime and two volumes of pozzolana, and then leaving it under water until the final hardening (which takes place about one year later for the pozzolana of Rome) and then treating it with hydrochloric acid and determining the percentage of silica liberated in relation to the composition of the mortar ....."

Having established these general ideas Signorile chooses as a pozzolana of comparison that of Rome which in the first reaction of the hydrochloric acid diluted with two volumes of water liberates about one tenth of the bases contained in pozzolana and about one tenth of silica. The second reaction with an alkaline solution containing ten parts of potassium oxide in 100 parts of water gives about 5% for the quantity of silica dissolved. From the test then made with the hydrochloric acid and the potassium hydrate after one year of curing under water he obtained instead about 8% of silica soluble in sodium hydrate for each 100 parts of pozzolana.

8. Tandrup (1911) proposed a modification of the method of Tivot, which modification consists in substituting hydrochloric acid for nitric acid and lime or water to a solution of potassium hydrate. The method of Tandrup therefore can be held to be a combination of the methods of Tivot and Tivot, and on account of that in its first part - that is, the part which has to do with the action of the acid upon pozzolans - it lends itself to all the criticism that we have already made of the method of Tivot, although it represents some progress. In other words, it is a method which at least partially can be considered as a direct method while the one of Tivot, as we have said, is altogether an indirect method.

9. Stamovile (1920) proposed another modification of the method of Tivot as it seemed to him impossible to recognize the hydraulic energy of a pozzolana with two reactions only, one acid and the other alkali.

According to him:

> "A third reaction is necessary which requires time and labor but which need not be made more than once for all pozzolanas of the same volcanic eruption, provided that the materials be homogeneous and furnish pozzolanas of the same type, either reactive or inactive. This third reaction will provide a knowledge of the quantity of silica and of the basis that calcium hydrate fixes in the pozzolane during the hardening of the mortar. This third reaction consists briefly in making two mortars with one volume of fat lime and two volumes of pozzolana, and then leaving it under water until the final hardening (which takes place about one year for the pozzolanas of Rome) and then treating it with hydrochloric acid and determining the percentage of silica liberated in relation to the composition of the mortar ....."

Having established these general ideas Stamovile chooses as a pozzolana of comparison that of Rome which in the first reaction of the hydrochloric acid diluted with two volumes of water liberates about two tenth of the bases contained in pozzolana and about one tenth of silica. The second reaction with an alkaline solution corresponding ten parts of potassium oxide in 100 parts of water gives about 5% for the quantity of silica dissolved. From the test then made with the hydrochloric acid and the potassium hydrate after one year of curing indeed we be obtained inclosed about 8% of silica soluble in sodium hydrate for each 100 parts of pozzolana.

From this he derives that leaving aside the consideration of the bases which do not influence the hardening of mortar under water, it is well to direct attention to the silica which appears to be the principal agent involved in the reaction. It results thus that the actions of acids and alkalis upon pozzolanas give no more than 5/8 of the action exercised by the hydrated lime, consequently, knowing the value of the acid and alkaline reactions upon Roman pozzolana it is enough to multiply by 1.6 to obtain the action of lime.

It is unnecessary that we extend our consideration at length to be able to notice the weakness in this method of reasoning of Signorile. First of all the assumption that the pozzolanas of a certain volcanic center are all equal is never verified in practice. Then it is necessary to take into account the very little reliability of the respective actions of acid, alkaline solution and lime upon pozzolana, inasmuch as this method rests essentially upon such a comparison. Once the homogeneous character of pozzolanas is excluded, it is necessary to repeat the entire test for each specimen of pozzolana, which means that it will take a year to get adequate results, and therefore, the test becomes practically worthless.

Professor Rebuffat (174-c) also attempted upon the basis of the method of Rivot, the study of pozzolana, modifying the method according to the conception of Signorile, that is, studying the behavior toward determinate reagents of a determinate pozzolana either in combination with sand or in a free state. From his tests the scission of mortars through the action of the normal solutions of hydrochloric acid takes place in a very neat way and practically in its entirety. Therefore, it is possible to obtain an idea of the technical value of a certain pozzolana from the analysis of the soluble and insoluble parts which differ in a certain relationship with the action of the lime upon the mortar.

But this test, owing to the reasons to which we have already referred was not practicable and of this Rebuffat himself was the first one to be aware. In the same note, studying the action of the hydrochloric acid acting directly upon pozzolana, he comes to the conclusion that it is not possible to obtain a separation of the active part of a pozzolana through a normal solution of hydrochloric acid. It does not matter whether the pozzolana is in its natural state or in a fine powder nor is it possible to obtain the separation by using a more concentrated acid solution although in such case, the attack of the acid is much larger.

In his study, Rebuffat used two types of pozzolana, that of the Vesuvius and that of Bacoli and from the comparison of the results of the attack with hydrochloric acid of heavier concentration upon mortars and upon pozzolanas, he noticed that

From this he derives that leaving aside the concentration of the bases which do not influence the hardening on mortar under water, it is well to direct attention to the silica which appears to be the principal agent involved in the reaction. It results thus that the actions of acids and alkalis upon pozzolanas give no more than 1/3 of the action exerted by the pozzolana mixed with lime, considering the value of the acid and alkaline reactions upon Roman pozzolana it is enough to multiply by 1.6 to obtain the action of time.

It is unnecessary that we extend our consideration at length to be able to notice the weakness in this method of testing of Signorile. Fifty of all the assumption that the pozzolanas of a certain volcanic center are all equal is never verified in practice. Then it is necessary to take into account the very little reliability of the respective actions of acid, alkaline solution and lime upon pozzolana, inasmuch as this method tests examplically upon such a comparison. Once the homogeneous charge ter of pozzolanas is excluded, it is necessary to repeat the entire test for each specimen of pozzolana, which means that it will take a year to get adequate results, and therefore, the test becomes practically worthless.

Professor Rebuffat (Liv-d) also attempted upon the basis of the method of Rivot, the study of pozzolana, modifying the method according to the conception of Signorile, that is, studying the behavior toward determinate reagents of a determinate pozzolana either in combination with sand or in a free state. From his tests the solubility of mortars through the action of time, normal solutions of hydrochloric acid taken place in a very neat way and practically in its entirety. Therefore, it is possible to obtain an idea of the technical value of a certain pozzolana from the analysis of the soluble and insoluble parts which differ in a certain relationship with the action of the lime upon the mortar.

But this test, owing to the reasons to which we have already referred was not practicable and of this Rebuffat himself was the first one to be aware. In the same note, adopting the action of the hydrochloric acid acting directly upon pozzolana, he comes to the conclusion that it is not possible to obtain a separation of the active part of a pozzolana through a normal solution of hydrochloric acid. It does not matter whether the pozzolana is in its natural state or in a fine powder nor is it possible to obtain the separation by using a more concentrated acid solution although in such case, the attack of the acid is much larger.

In his study Rebuffat used two types of pozzolana, that of the Vesuvius and that of Bacoli and from the comparison of the results of the attack with hydrochloric acid at various concentration upon mortars are upon pozzolana, he noticed that

this acid reacts with the pozzolana of Vesuvius much more energetically than the lime, while it acts less energetically than lime upon the pozzolana of Bacoli. This clearly indicates that the action of the acid cannot be compared with that of the lime and leads him to experiment upon the reaction of pozzolana with the concentrated solution of sodium hydrate. Even these results, though, are not satisfactory because this reagent acts in a very weak manner. The final conclusion of his work is therefore, that:

> ".....it is not possible to reach with other reagents the same effect of lime and that to have a good method of technical analysis of pozzolana there is nothing left but to accelerate the action of lime upon pozzolana in such a way that it is possible to determine its effect during a comparatively short time."

This was the state of the problem when we began to occupy ourselves with it. We had had occasion to make some industrial tests upon pozzolanas, and during the course of these tests we had seen that these pozzolanas treated with sulphuric acid diluted with 60% of water, while the mixture was still warm, were profoundly attacked without need of further help from heat. As a matter of fact, the reaction took place with great violence. (This happened whenever the quantity of pozzolana was not too small, not less for instance than 50 gr.). That the attacks were rather remarkable can be easily judged from the results obtained with the pozzolana of San Paolo of which we know the average composition. In this pozzolana in fact the insoluble residue was only about 60%. This insoluble residue well washed out and deprived completely of sulphuric acid underwent a good set whenever mixed with fat lime.

This information was not entirely new because of them Landrin had occupied himself (131) and upon these criterions he had found his method of testing pozzolanas to which we have already made reference.

The consideration that he had used hydrochloric acid whose action upon pozzolana was much less profound even with the help of the heat than the action of sulphuric acid led me to try out whether with this substitution of one acid for another the test would have given better results. Following are the results obtained, leaving the insoluble residue for six days in a sugar solution of lime.

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> "..... it is not possible to reach with other reagents the same effect of time and that to have a good method of technical analysis of pozzolana there is nothing left but to accelerate the action of time upon pozzolana in such a way that it is possible to determine its effect during a comparatively short time."

This was the state of the problem when we began to occupy ourselves with it. We had had occasion to make some industrial tests upon pozzolanas, and during the course of these tests we had seen that these pozzolanas treated with sulphuric acid diluted with 80% of water, while the mixture was still warm, were profoundly attacked, without need of further help from heat. As a matter of fact, the reaction took place with great violence. (This happened whenever the quantity of pozzolana was not too small, not less for instance than 50 gr.). That the attacks were rather remarkable can be easily judged from the results obtained with the pozzolana of San Paolo of which we know the average composition. In this pozzolana in fact the insoluble residue was only about 60%. This insoluble residue well washed out and deprived completely of sulphuric acid underwent a good set whenever mixed with fat lime.

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Pozzolana	DURATION OF IMMERSION Day of 24 hours CaO liberated from 100 parts of Pozzolana
Pozzolana of S. Paolo	8.3670
Pozzolana of Pigno	9.1656
Pozzolana of S. Giovanni	16.2725
Pozzolana of the Cave Sette Camini..	7.1392
Leucite	13.6618

These results have nothing interesting which would make it worth while to mention them, the method used lending itself to all the criticism made of the method of Landrin. One thing, though, stands out in a very definite and absolute way and that is that the action of mineral acid upon pozzolanas although quite profound is never to be compared to the action of the lime.

When we spoke of the action of Potassium hydrate, upon pozzolanas, as studied by Rebuffat, we said that pozzolanas always retain a certain quantity of potassium, which they lose only when they are washed out with hydrochloric acid. On this subject Rebuffat believes that it is a question of a true chemical combination, that is, of the formation of insoluble potassium silica aluminates and we are rather inclined to agree with him, and for that matter even without giving to the test of potassium hydrate a great importance we have repeated it to see whether it was possible to obtain some useful knowledge from it. Consequently we treated a determinate weight, 10 gr., of various pozzolanas, silicates, etc. with a determinate number of cubic centimeters of potassium hydrate, 1/10 normal solution (200 cu.-cm.). After four days we filtered an aliquot part of it and we treated again with the 1/10 normal solution of hydrochloric acid. In this way it was possible to immediately calculate the quantity of potassium retained. The percentages are set forth in the following table:

Pozzolana	DURATION OF IMMERSION Day or 24 hours CaO liberated from 100 parts of Pozzolana
Pozzolana of S. Paolo	8.3670
Pozzolana of Pigno	9.1656
Pozzolana of S. Giovanni	16.2725
Pozzolana of the Cave Sette Camini..	7.1392
Leucite	13.6618

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Pozzolana	1st TEST Potassium absorbed from 100 P. of Pozzolana	2nd TEST Potassium absorbed from 100 P. of Pozzolana
Pozzolana of S. Paolo	2.49	---
Pozzolana of S. Paolo	2.21	1.96
Pozzolana from the Cave Sette Camini	2.15	---
Pozzolana of Pigno	1.42	1.38
Pozzolana of S. Giovanni	1.88	---
Pozzolana of Goriano Sicoli	2.44	2.04
Clay of Bari	1.14	0.96
Vegetable Soil	2.37	2.31
Wollastonite	0.25	---
Leucite	0.02	---

In his memoir already mentioned (102) Rivot expresses himself in this way:

"It is possible to consider as almost certain that in mortars of pozzolana and lime the setting is due to the slow action of the lime upon the silica and upon the alumina of the pozzolana, as well as to the formation of hydrated silicate and aluminate of lime."

Regarding the method of Vicat he says:

"The method is too long to be of particular advantage, on the other hand it would be difficult to distinguish through analysis the hydrosilicate produced in presence of a part of pozzo-

Pozzolana	2.45	---
Pozzolana of S. Paolo	2.21	1.66
Pozzolana of S. Paolo	2.12	---
Pozzolana from the Cave	2.13	---
Pozzolana of Pigno	1.72	1.38
Pozzolana of S. Giovanni	1.88	---
Pozzolana of Coriano Nicoli	2.44	2.07
Pozzolana of Bari	1.17	0.96
Clay of Bari	2.24	2.21
Vegetable Soil	3.24	3.21
Mollasconite	0.32	---
Tenerife	0.02	---

There remained, therefore, only the necessity of remedying the other difficulty, that is, the time which had to elapse to be able to obtain reliable results. We have consequently brought our attention naturally upon the second phase of the problem. The first thought was to accelerate the action of lime upon pozzolana by placing the mixture of slaked lime and ground pozzolana into a closed tube with very little water and keeping the mixture at a temperature of 100°C. or even at a higher temperature. We followed this experimental process in the following way. In a closed glass tube we introduced three grams of lime not powdered which was afterwards slaked with water, and after 24 hours, to make sure that the hydration was completed we added 10 gr. of powdered pozzolana and very little water (assuming as apparent density of pozzolana 1.232 and knowing that 100 kg. of fat lime give 0.240 cu. meters of slaked lime, the proportion in weight - 3 to 10 - of lime and pozzolana upon which we operated, translated in volume become 7.2 to 8.12). We had therefore, a large excess of lime over the amount that is usually used in construction: a proportion of one lime for two of pozzolana.

The tube was then hermetically sealed and shaken well to mix the lime and pozzolana, and then placed in a special furnace. After remaining in the tube a certain time the tube was broken and the material was gathered and treated with a quantity of sugared water capable of dissolving a quantity larger than two times the quantity of lime contained in each tube. The container was closed so that there was no possibility of access of carbonic anhydride of the atmosphere and was agitated from time to time during the first 24 hours. Then, brought to a fixed volume with boiled and distilled water, a liquid part of it was filtered, and the contained lime was determined with a normal acid solution. The percentage of lime fixed respectively by the various pozzolanas we report in the following table, taking as a term of comparison in every test the pozzolana of San Paolo of Rome.

There remained, therefore, only the necessity of removing the other difficulty, that is, the time which had to elapse to be able to obtain reliable results. We have consequently brought our attention naturally upon the second phase of the problem. The first thought was to accelerate the solution of time upon pozzolans by placing the mixture of ashed lime and ground pozzolana into a closed tube with very little water and keeping the mixture at a temperature of 100°C. or even at higher temperature. We followed this experimental process in the following way. In a closed glass tube we introduced three grams of lime not powdered which was afterwards slaked with water, and after 24 hours, to make sure that the hydration was completed we added 10 gr. of powdered pozzolana and very little water (assuming as apparent density of pozzolana 1.505 and leaving that 100 Fe. of fat lime give 0.240 cm. meters of slaked lime, the proportion in weight - 3 to 10 - of lime and pozzolana upon which we operated, translated in volume become 7.5 to 8.15); we had therefore, a large excess of lime over the amount that is usually used in operation: a proportion of one lime for two or pozzolanas.

The tube was then hermetically sealed and shaken well to mix the lime and pozzolana, and then placed in a special cage. After remaining in the tube a certain time the tube was broken and the material was pestered and dressed with a quantity of sugared water capable of dissolving a quantity larger than two times the quantity of lime contained in each tube. The container was closed so that there was no possibility of access of carbonic anhydride of the atmosphere and was agitated from time to time during the first 24 hours. Then, brought to a fixed volume with boiled and distilled water, a liquid part of it was filtered, and the contained lime was determined with a normal acid solution. The percentages of lime fixed respectively by the various pozzolanas we report in the following table, taking as a term of comparison in every test the pozzolana of San Paolo of Rome.

	Indirect Heating for 24 Hours			Calcination 170° to 200° for 12 Hours	Indirect Heating for 24 Hours
	Time passed before breaking of Tube 2 days of 24 hours			Time elapsed before breaking of tubes - Two Days	Time elapsed before breaking of tube 15 days
	1st Test CaO Liberated from 100 Parts of Pozzolana	2nd Test CaO Liberated from 100 Parts of Pozzolana	3rd Test CaO Liberated from 100 Parts of Pozzolana	4th Test CaO Liberated from 100 Parts of Pozzolana	5th Test CaO Liberated from 100 Parts of Pozzolana
Pozzolana of S. Paolo	15.434	18.42	17.42	19.27	20.30
Pozzolana of Sette Camini	----	---	---	---	19.32
Pozzolana of Pigno	14.195	17.554	15.88	---	18.30
Pozzolana of S. Giovanni	----	---	---	---	26.92
Pozzolana of Goriano-Sicoli	----	---	---	---	26.15
Vegetable Earth	9.140	12.509	11.33	16.58	---

Partial Weather Report

Observed at 0700 GMT 02 Oct 01

Station	Sky & Weather	Temp (°C)	Dew Point (°C)	Wind (kts)	Visibility	Altimeter
Bagram AB	Clear	12	2	090 @ 5	10+	29.92
Kandahar Intl	Clear	14	3	110 @ 7	10+	29.90
Herat Intl	Few 250	15	4	080 @ 6	10+	29.91
Mazar-e-Sharif	Clear	13	1	100 @ 4	10+	29.93
Kabul Intl	Clear	11	0	070 @ 8	10+	29.94
Jalalabad	Clear	16	5	120 @ 3	10+	29.89
Shindand	Few 250	17	4	090 @ 9	10+	29.88
Tarin Kowt	Clear	12	2	060 @ 5	10+	29.92
Gardez	Clear	10	-1	050 @ 4	10+	29.95
Khost	Clear	15	3	130 @ 6	10+	29.90
Kunduz	Clear	14	2	080 @ 5	10+	29.91
Farah	Few 250	18	5	100 @ 10	10+	29.87
Lashkar Gah	Clear	19	6	110 @ 8	10+	29.86
Zaranj	Clear	21	7	120 @ 12	10+	29.84
Qalat	Clear	13	1	070 @ 4	10+	29.93
Ghazni	Clear	9	-2	040 @ 3	10+	29.96
Bamiyan	Clear	8	-3	030 @ 2	10+	29.97
Pul-e-Khumri	Clear	12	2	090 @ 5	10+	29.92
Sharana	Clear	14	3	100 @ 6	10+	29.91
Asadabad	Clear	15	4	110 @ 4	10+	29.90
Chaghcharan	Clear	7	-4	020 @ 3	10+	29.98
Maymana	Clear	16	4	090 @ 7	10+	29.89
Sheberghan	Clear	17	5	100 @ 8	10+	29.88
Kandahar Intl	Clear	14	3	110 @ 7	10+	29.90
Herat Intl	Few 250	15	4	080 @ 6	10+	29.91
Mazar-e-Sharif	Clear	13	1	100 @ 4	10+	29.93
Kabul Intl	Clear	11	0	070 @ 8	10+	29.94
Jalalabad	Clear	16	5	120 @ 3	10+	29.89
Shindand	Few 250	17	4	090 @ 9	10+	29.88
Tarin Kowt	Clear	12	2	060 @ 5	10+	29.92
Gardez	Clear	10	-1	050 @ 4	10+	29.95
Khost	Clear	15	3	130 @ 6	10+	29.90
Kunduz	Clear	14	2	080 @ 5	10+	29.91
Farah	Few 250	18	5	100 @ 10	10+	29.87
Lashkar Gah	Clear	19	6	110 @ 8	10+	29.86
Zaranj	Clear	21	7	120 @ 12	10+	29.84
Qalat	Clear	13	1	070 @ 4	10+	29.93
Ghazni	Clear	9	-2	040 @ 3	10+	29.96
Bamiyan	Clear	8	-3	030 @ 2	10+	29.97
Pul-e-Khumri	Clear	12	2	090 @ 5	10+	29.92
Sharana	Clear	14	3	100 @ 6	10+	29.91
Asadabad	Clear	15	4	110 @ 4	10+	29.90
Chaghcharan	Clear	7	-4	020 @ 3	10+	29.98
Maymana	Clear	16	4	090 @ 7	10+	29.89
Sheberghan	Clear	17	5	100 @ 8	10+	29.88

The test made in the described way presented various practical difficulties. The tubes broke easily, not only when they were brought to a temperature higher than 100°C. but even when they were heated indirectly so that the determinations that we have reported are not even the fourth part of those begun, the others having been lost through the breaking of the tubes. It was on account of this that we modified the method of operation. What we did was to use a bowl or glass very resistant in which there was placed lime first and then pozzolana with a little water. This bowl could be closed by a rubber lid having only one opening through which entered a tube bent at right angles at one extremity. At the other end this tube was bent and terminated in a cylindrical base of about one meter high, almost full of mercury. In this way placing the bowl in a container with water and heating the whole thing, it was possible to obtain quite a high pressure in the interior of the apparatus which lent itself very well to the use for which it had been selected. We never tried to reach the pressure that could be obtained with closed tubes and furthermore we have placed the lime to react upon pozzolana for a rather short time (12 hours) obtaining therefore some percentages of lime liberated from pozzolana slightly smaller than those obtained with closed tubes, however, always high in relation to those which are obtained with the method of Vicat. The tests were always made in duplicate using for comparison the pozzolana of S. Paolo.

	1st Test	2nd Test	3rd Test	4th Test	5th Test
Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana	CaO Liberated from 100 Parts of Pozzolana
Pozzolana of S. Paolo	12.22	12.78	12.78	8.44	3.90
Pozzolana of Anzio	10.54	11.10	---	9.98	4.10
Pozzolana of S. Giovanni	---	---	12.92	---	---

From the above tests, we can derive that under pressure the quantity of lime liberated from pozzolana is much larger than that liberated in the test of Vicat, and therefore, it is our belief that we have reached the desired goal, namely of accelerating the action of lime upon pozzolana in such a way as to be possible to determine its effect during comparatively short time.

The test made in the described way presented various practical difficulties. The tubes broke easily, not only when they were brought to a temperature higher than 100°C. but even when they were heated indirectly so that the determinations that we have reported are not even the fourth part of those begun, the others having been lost through the breaking of the tubes. It was on account of this that we modified the method of operation. What we did was to use a bowl or glass very resistant in which there was placed lime first and then pozzolana with a little water. This bowl could be closed by a rubber lid having only one opening through which entered a tube bent at right angles at one extremity. At the other end this tube was bent and terminated in a cylindrical base of about one meter high, almost full of mercury. In this way placing the bowl in a container with water and heating the whole thing, it was possible to obtain quite a high pressure in the interior of the apparatus which lent itself very well to the use for which it had been selected. We never tried to reach the pressure that could be obtained with closed tubes and furthermore we have placed the lime to react upon pozzolana for a rather short time (12 hours) obtaining therefore some percentages of lime liberated from pozzolana slightly smaller than those obtained with closed tubes, however, always high in relation to those which are obtained with the method of Vicat. The tests were always made in duplicate using for comparison the pozzolana of S. Paolo.

Pozzolana	1st Test CaO Liberated from 100 Parts of Pozzolana	2nd Test CaO Liberated from 100 Parts of Pozzolana	3rd Test CaO Liberated from 100 Parts of Pozzolana	4th Test CaO Liberated from 100 Parts of Pozzolana	5th Test CaO Liberated from 100 Parts of Pozzolana
Pozzolana of S. Paolo	12.22	12.78	12.78	8.44	8.90
Pozzolana of Anzio	10.64	11.10	---	9.93	4.10
Pozzolana of S. Giovanni	---	---	12.92	---	

From the above tests, we can derive that under pressure the quantity of lime liberated from pozzolana is much larger than that liberated in the test of Vicat, and therefore, it is our belief that we have reached the desired goal, namely of accelerating the action of lime upon pozzolana in such a way as to be possible to determine its effect during comparatively short time.

Regarding organic matter, we have tried to eliminate their ill effect; first of all we tried calcining the pozzolana although we had very little faith in this method, because during calcination pozzolanas as well as the other materials upon which we have experimented were altered. Upon the calcined material we placed the solution of sugar, lime or water to react for about 12 hours, and the following are the results obtained (123). The quantity of lime fixed from the pozzolana in this test is too small to permit us to draw conclusions, even in comparison with the quantity of the test of Vicat. At any rate it would be necessary to make quite a great number of tests and also make some under pressure. We are therefore, quite sure that with the above test we have not succeeded in solving the problem of finding the technical value of a pozzolana, but we have however reported the tests made in the hope that they may be of some value to those who will in the future occupy themselves with this argument. We do not want to end this study without calling the attention of those who want to study such a complex material as pozzolana, the fact that the petrographic study is of capital importance which would show the way how to study separately the essential components of pozzolanas thus greatly simplifying the problem.

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B I B L I O G R A P H Y

Abbreviations:

Ann. d. Chim. - Annales de Chimie

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Ann. Ponts et Ch. - Annales des Ponts et Chaussees

C.R. - Comptes rendus de L'Academie

Ann. d. min. - Annales des Mines

Dingl. J. - Dingler's Polytechnisches Journal

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Wagner's Iahresber - Wagner-Iahres, bericht der chemischen Technologie.

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1916	Effect of Salt Water on Concrete - In Trans. Amer. Soc. Civ. Eng. Vol. 80	H. S. Taft
1917	Tests of Concrete Specimens in Sea Water at Boston Navy Yard - In Trans. A.S.C.E. #81	
1917	Concrete and Reinforced Concrete in Fresh and Saline Waters - In Proceed. 2nd Pan-American Science Congress.	C. Davis
1917	Action de l'eau de mer sur les Ciments In - Annales des Ponts et Chaussees. Ser. 9 - Vol. 37 - pg. 253-4	
1917	Investigation of concrete structures in Sea Water - Public Works of the Navy Bul. #27 and 28	
1917	Concrete Structures in Sea Water - In Eng. N.R. - Vol. 79	R. J. Wig & L. R. Ferguson

Year	Title	Author
1915	Probable and presumtive life of Concrete Structures made from Modern Cement - In Report of Inter. Eng. Congress, San Francisco.	B. Blount
1915	High Silica Cements for Maritime Works In Giornale del Genio Civile	L. Luiggi
1915	Sui Calustruzzi pozzolanici - In Annali di Chemica Applicata	G. Cenni
1915	Use of Concrete in Sea Water - In Western Engineer - Vol. 6	[illegible] Hood
1915	Composition of Mortars in Sea Water - In Annali di Chimica Applicata - Vol. 5	G. Giorgis & A. Cenni
1916	The ternary System CaO, Al_2O_3, SiO_2, In American Journal of Science - Vol. 39	Rankin
1916	Chemical Destruction of Concrete Structures - In Concrete - Vol. 9	W. D'Echan
1916	Deterioration of Concrete in Sea Water In - Trans. Amer. Soc. of C.E. - Vol. LXXX	Hanford
1916	Destructive action of Sea Water on Concrete - In Eng. & Contr. Vol. 45	W. W. Page
1916	Effect of Salt Water on Concrete - In Trans. Amer. Soc. Civ. Eng. Vol. 80	H. S. Staff
1917	Tests of Concrete Specimens in Sea Water at Boston Navy Yard - In Trans. A.S.C.E. #61	
1917	Concrete and Reinforced Concrete in Fresh and Saline Waters - In Proceed. 2nd Pan-American Science Congress.	[illegible] Davis
1917	Action de l'eau de mer sur les Ciments In - Annales des Ponts et Chaussees. Ser. 9 - Vol. 37 - pg. 253-4	
1917	Investigation of concrete structures in Sea Water - Public Works of the Navy Bul. 27 and 28	
1917	Concrete Structures in Sea Water - In Eng. N.R. - Vol. 79	R. W. Wig & L. B. Ferguson

Year	Title	Author
1917	Effect of alkali upon P.C. - In Wyo. Agr. Expt. Sta. Bul. 69	K. Steik
1918	Formation of the Double Sulphates of Ca and Al in Cements - In Chem. Abstr. V. 13, p. 1006	Nitzsche
1918	Effect of Sea Water on Concrete - In "Concrete" - Vol. 13	
1918	Study of Failures of Concrete Structures Bul. Am. Ry. Eng. Ass. - Vol. 20	
1919	L'impiego delle pozzolane nelle opere marittime Italiane - In Giornale del Genio Civile	L. Luiggi
1919	The Economy of Mortars of Cement Pozzolana In - Annali della Societa degli Ingegneri Roma	L. Luiggi
1919	Pozzolana and Sea Water Resistant Cement In - Le Industrie Costruttive	O. Rebuffat
1919	Behavior of Different Cements in Solution of Sodium and Magnesium Sulphates - In J. Soc. Chem. Ind. Vol. 38	Nitzsche
1919	Concrete in Sea Water - In Concrete - Volume 15	J. L. Harrison
1919	Cement in Sea Water - In Le Industrie Costruttive	O. Rebuffat
1920	Dei Seganti Calcarei in Contatto di acque marine o Solfatate in genere. In Annali del Genio Civile	F. Ferrari & L. Marino
1920	La Miscela Portland Pozzolana - In Giornale di Chimica Industriale e Applicata - Vol. 14	F. Ferrari
1920	Deterioration of structures in sea Water - in Concrete and Constr. Eng. Vol. 13	E. R. Matthews
1920	Aberthaw Tests of Concrete in Sea Water	Aberthaw Const Co., Boston
1920	Report of Santa Monica Pier Failure Eng. & Constr. - Vol. 53	

Year	Title	Author
1920	Effect of sea water on concrete - In Concrete	[illegible]
1920	Deterioration of structures in sea water - In Concrete and Constr. Eng. Vol. 15	E. R. [illegible]
1920	Al Mission Portland Pozzolana - In Giornale di Chimica Industriale e Applicata Vol. 2	E. Terni
1920	Del Segnali Galleria in Concreto di Cemento Pozzolanico in Genere - In Annali del Genio Civile	[illegible]
1921	Cement in Sea Water - In The Industrial Constructive	C. Hendrick
1922	Concrete in Sea Water - In Concrete Volume 19	[illegible]
1922	Behavior of Different Cements in Solution to Various Chemical Substances - In Proc. Amer. Soc. Civil Eng. Vol. 48	Mitzscherling
1922	Portland and Sea Water Resistant Cement - In The Industrial Constructive	C. Hendrick
1922	The Economy of Mortars of Cement Pozzolana - In Annali della Società degli Ingegneri Roma	[illegible]
1922	Trimbiere delle Pozzolane nelle opere marittime - In Giornale del Genio Civile	[illegible]
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1923	Formation of the Calcium Silicates of the Concrete Aggregate - In Chem. Metall. Engineering Vol. 30	Mitzscherling
1924	Effect of Sea Water on Concrete - In Concrete Vol. 24	[illegible]
1924	Effect of Alkali upon S.O.3 - In Proc. Amer. Soc. Civil Eng. Vol. 50	E. Stern

Year	Title	Author
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1920	L'Analisi del Cemento Portland - In Giornale di Chimica Industriale e Applicata - No. 8, year 1920	F. Ferrari
1920	Behavior of Cement Mortars in Sulphate Bearing Waters - In Chem. Absts. Vol. 15, P. 3190	Nitzsche
1920	Dei Leganti calcaris in Contatto di Acqua marine o Solfatate in Genere. In Annali del Genio Civile	F. Ferrari & L. Marino
1921	Report of Concrete - Alkali Investigation in Minnesota - In Minn. Dept. Drainage and Water Dept.	
1921	Behavior of Cement in Solution of Calcium Sulphate. - In J. Soc. Chem. Ind. Of Vol. 40	Strebel
1921	Observations of Effect of Sea Water on Concrete - In Eng. News Rec. - Vol. 86	
1921	Use of Reinforced Concrete in or near Sea Water - In Municipal Engineer Journal - Vol. 7	K. Allen
1921	Pozzolana & Ferro Portland - In Giornale di Chimica Industriale e Applicata - No. 2	F. Ferrari
1921	Three Lines of Attack - High Silica, High Iron, High Alumina; isolated, worthless. See: Tests of Boston Eng. N.R. Vol. 86, N. 3	
1922	Los Cementos para las obras en el mar In - Revestade Obras Publicas, Madrid	E. De Castro
1922	Aluminous Cement - In Revue Universelle des Mines	J. Bied.
1923	Report on the Action of Sea Water on Concrete - In Proceed. XIII - Int. Cong. of Navigation - London	K. Aki and S. Oaklee
1923	Disintegration of Cement in Sea Water In - Proceed. Am. Soc. C.E. - Vol. 49	W.G. Atwood & A.A. Johnson
1923	Studies on Portland Cement. In X. Congresso dell'Associazione per gli studi dei materiali di costruzione	F. Ferrari

Year	Title	Author
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1920	In Canadian Eng. - Vol. 39	C.E.A. Dodge
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1920	Lightning Protection - In Cleveland	
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1920	Del Genio Civile	F. Marino
1921	Report of Concrete - Alkali Investigation	
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1921	Behavior of Cement in Solution of Calcium	
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1921	Tubes Lines of Attack - High Silica, High	
1921	Iron, High Alumina, Isolated, Low Silica.	
1921	See: Tests of Boston Eng. M.B. Vol. 38,	
1922	Los Cementos para las obras en el mar	
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1922	Aluminous Cement - In Revue Universelle	
1922	des Mines	
1922	Report on the Action of Sea Water on Con-	
1922	Crete - In Proceed. XIII - Int. Cong. of	K. Axi and S.
1922	Navigation - London	Oakley
1922	Disintegration of Cement in Sea Water	
1922	In - Proceed. Am. Soc. C.E. - Vol. 49	F.A. Johnson
1922	Supplies on Portland Cement. In X. Con-	
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1922	Del Materiali di costruzione	F. Ferrari

Year	Title	Author
1923	Behavior of Concrete Exposed to Sea Water In Proceed. Amer. Soc. Test. Mater.	S.C. Hollister
1923	I Cementi Alluminosi - In Giornale di Chimica Industriale ed Applicata - Page 610	J. Bied
1923	Report of the XIII. International Congress of Navigation - London	
1923	Tests of Concrete in Sea Water In - Trans. Am. Soc. C.E.	L. C. Wason
1923	Tests of Concrete in Sea Water In Trans. A.S.C.E. - Vol. LXXXVI.	L. C. Wason
1925	Recherches sur les aluminates de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium - Paris 1925	H. Lafuma
1925	The Chemical Action of Alkali in Hydraulic Cements - In Towa Eng. Expt. Sta. Bul. 74	G. W. Burke
1926	Recherches Industrielles sur les Chaux, Ciments et Mortiers - Paris	J. Bied
1926	Sulle trasformazioni finihe del Cemento In - Giornale di Chimica Industriale ed Applicata - No. 9	C. Zamboni
1926	Durability of Cement Drain Tiles and Concrete in Alkali Soils - In Bureau of Standard Techn. Paper #307	G. M. Williams & I. Furlony
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1927	Studies of the System - Lime, alumina, silica - In Journ. Phys. Chem. Vol. 31	Hansen, Dy[illegible] Ashton & Bogue
1927	The Decomposition of Mortars - In Le Genie Civil - Ag. 13, 1927	Maynard
1927	The Action of Sulfates on the Components of Portland Cement - In Trans. of the Royal Society of Canada - Ser. 3 - Vol. 21	Thorvaldson

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1922	I Cement Alliance - In Chemical Ind. Bases of Agriculture. Page 910	F. Bird
1922	Chemical Industries be Applied - Page 910	
1922	Tests of Concrete in Sea Water. In Trans. Am. Soc. C. E.	F. C. Mason
1922	Tests of Concrete in Sea Water. In Trans. A.S.C.E. - Vol. LXXXVI	F. C. Mason
1922	Report of the XIII. International Congress of Navigation - London	
1922	Recherches sur les stalactites de calcium. Recherches sur les combinaisons avec le calcaire et sur leurs compositions. Paris 1922	H. Lajoux
1922	The Chemical Action of Alkali in Hydraulic Cement - In Journ. Phys. Chem. Vol. 26	G. A. Rankin
1922	Cements de Mortiers - Paris	T. Bied
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1922	The Chemical Action of Alkali in Hydraulic Cement - In Journ. Phys. Chem. Vol. 26	
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1922	Studies in the Hydrolysis of Compounds which may occur in Portland Cement. Trans. Amer. Electr. Chem. Soc. Vol. 42	
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1922	Durability of Cement Drain Tiles and Concrete in Alkali Soils. Amer. Tech. Paper 202	F. L. Ransome
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1922	Cements de Mortiers - Paris	T. Bied
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1922	Tests of Concrete in Sea Water. In Trans. A.S.C.E. - Vol. LXXXVI	F. C. Mason
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1922	I Cements Alliminoses - In Chimie et Industrie de Applicata - Page 910	F. Bied
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1922	Behavior of Concrete Exposed to Sea Water. In Proceed. Amer. Soc. Test. Mater.	S. S. Hollister

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1927	Studies of the hydrolysis of Compounds which may occur in Portland Cement. In Jour. Phys. Chem. - Vol. 31	
1927	Les Ciments Alumineux - Communication of H. Le Chatelier to the Association Franco-Belge pour l'essai des materiaux	Lerch & Bogue
1927	Corrosion of Concrete - In Trans. A.S. C.E. - Vol. 90	
1928	Dei Cementi Razionali - In Le Industrie del Cemento No. 1	
1928	Equilibrium Studies in Alumina and Ferric Oxide and Combinations of these with Magnesia and Calcium Oxide. Paper #14 of the P.C.A.F. in Amer. Jour. Si. #15.	F. Ferrari
1928	Studies on the System Calcium Oxide-Alumina Ferric Oxide - Paper #13 of the P.C.A.F. - Journ Amer. Chem. Soc. #50	
1928	The effect of steam treatment of Portland Cement Mortars on their resistance to sulphate action. - In Engin. Journ. Canada Of Fol. 11	T. Thorvaldson & V.A. Vigfusson
1928	Resistance of Portland Cement Concrete to the Action of Sulphate Waters as influenced by the Cement. Amer. Soc. Testing Mater. Proc. #28	
1928	Notes on the Relative Resistance of Various Cements to the action of Sulfate Waters. In - Engineering Journal, 1928.	Thorvaldson
1929	The Sulpho-Aluminates of Calcium-Bureau of Standards Journal of Research #4	W. Lerch & F.W. Ashton & R.H. Bogue
1929	Il Processo d'indurismento del Cemento Portland - In Giornale di Chimica Industriali & Applicata No. 5	D. Advalian & E. N. Gapon
1929	Les Defauts des Mortiers et des Betons Paris	
1929	The Chemical Basis for Durable Concrete Special Report of the P.C.A.F.	J. Malette

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1927	Studies of the hydrolysis of Compounds which may occur in Portland Cement. In Jour. Phys. Chem. - Vol. 31	Lerch & [illegible]
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1928	Studies on the System Calcium Oxide-Alumina Ferric Oxide - Paper #13 of the P.C.A.E. - Journ Amer. Chem. Soc. #50	
1928	The effect of steam treatment of Portland Cement Mortars on their resistance to sulphate action. - In Engin. Journ. Canada Of Vol. 11	T. [illegible] & V.A. Vicinsson
1928	Resistance of Portland Cement Concrete to the Action of Sulphate Waters as influenced by the Cement. Amer. Soc. Testing Mater. Proc. #28	
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1929	The Hydration of Portland Cement - Studies to the P.C.A. Fellowship under the direction of R. H. Bogue (Papers published in 1928-29-30-31-32)	
1930	Dei Cementi Speciali in Presenza di acqua aggressive - In Le Industrie del Cemento Milano	F. Ferrari
1930	The X-Ray Method Applied to a Study of the Constitution of Portland Cement. Bureau of Standards - Journal of Research R.P. #233	L.T. Brown-miller and R. H. Bogue
1931	Portland Cement and Sea Water - In Columbia University C.E. Testing Laboratory - Bul. #4	R. J. Colony
1932	The effect of Sea Water on Cement in l'age du Ciment - October	H. Le Chatelier
1932	Studies on the Action of Sulphates on Portland Cement - In Canadian Journal of Research - Vol. 6	T. Thorvaldson V.A. Vigfusson
1932	Sui Calcestruzzi pozzolanici Impliegati nella costruzione di opere marittime - In Annali dei Lavori Pubblico - Vol. 70 N. 2	L. Levi
1932	The Decomposition des Mortiers de Ciment In Le Genie Civil	E. Marcotte
1932	La Pozzolana di Bacoli nei lavori Marittimi in Annali d'ingegneria - Anno V., N. 10	C. Rebuffat
1933	Laboratory and Field Tests of Concrete Exposed to the Action of Sulphate Waters. Techn. Bull. #358 - U.S. Dept. of Agriculture	D.G. Miller & P. W. Manson
1933	Die Chemie des Portland zementes in Komplex Chemischer - In Darstillung Zement February	Dr. Ing. Hemart Torsin
1933	Recherches sur la nature et la progression de l'action pouzzolanique	R. Feret

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1931	Portland Cement and Sea Water - In Columbia University C.E. Testing Laboratory - Bul. #4	H. [illegible]
1932	The effect of Sea Water on Cement in l'age du Ciment - October	H. Le Chat[illegible]
1932	Studies on the Action of Sulphates on Portland Cement - In Canadian Journal of Research - Vol. 6	T. Thorvaldson V.A. [illegible]
1932	Sui Calcestruzzi pozzolanici impiegati nella costruzione di opere marittime - In Annali dei Lavori Pubblici - Vol. 70 N. 2	L. Devi
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A P P E N D I X IX.

B I O G R A P H I C A L N O T E S

R. Feret - Chief of the Laboratory of Bridges and Roads, Boulogne-sur-Mer, France.

One of the foremost cement experts of France, Feret has made a special study of the action of sea water upon concrete, this study extending through almost half a century.

One of his earliest publications on the subject can be found in "Annales des Ponts et Chaussees" of the year 1892, Vol. 11, Page 93. Note also the important study forming the XVI. Chapter of the book "A Treatise on Concrete, Plain and Reinforced" by F.W. Taylor and S. E. Thompson.

His latest important contribution is "Recherches sur la Nature et la Progression de l'action Pouzzolanique", published in "Revue des Materiaux de Construction", No. 281-82-1933.

F. Ferrari - Professor of Chemistry at the Royal University of Pisa, Italy.

He is especially noted for his advocacy of the mixture Portland-pozzolana and Ferro-Portland-Pozzolana. His series of studies upon the characteristics of these materials published in "Giornale di Chimica Industriale e Applicata" during the year 1920 and 1921 are ~~to be considered as epoch making~~ - marking ~~in fact~~ the beginning of the manufacture of modern pozzolanic cement.

G. Gallo, G. Giorgis and U. Alvisi - Professors at the Royal University of Rome and the Royal School for Engineers in Italy.

Especially noted for studies on pozzolana which have paved the road to microscopic and petrographic observations and also for their contribution to the study of artificial pozzolana.

H. Le Chatelier - Celebrated French Chemical Engineer.

He is the father of cement chemistry. His book on the constitution of hydraulic cements, his book on the silica and silicates, and his studies on the decomposition of cement in sea water, places him in the front rank of cement experts.

Luigi Luiggi - The most famous modern Italiam Engineer (Died in 1932)

Especially known for his contribution to the knowledge of the effects deriving from the addition of pozzolana or other siliceous substance to Portland.

BIOGRAPHICAL NOTES

A. Teret - Chief of the laboratory of Bridges and Roads, Boulogne-sur-Mer, France.

One of the foremost cement experts of France, Teret has made a special study of the action of sea water upon concrete, this study extending through almost half a century.

One of his earliest publications on the subject can be found in "Annales des Ponts et Chaussees" of the year 1892, Vol. II. Page 93. Note also the important study forming the XVI. Chapter of the book "A Treatise on Concrete, Plain and Reinforced" by F. W. Taylor and S. E. Thompson.

His latest important contribution is "Recherches sur la Nature et la Progression de l'Action Pouzzolanique", published in "Revue des Materiaux de Construction", Ire. Sol-Sep-1923.

E. Morisi - Professor of Chemistry at the Royal University of Pisa, Italy.

He is especially noted for his advocacy of the mixture Portland-pozzolana and Porto-Portland-Pozzolana. His series of studies upon the character [illegible] of these mixtures is published in "Giornale di Chimica Industriale e Applicata" during the year 1920 and 1921 are to be considered as epoch making - marking the beginning of the manufacture of modern pozzolanic cement.

G. Bellio, G. Giorgis and V. Alyrai - Professors at the Royal University of Rome and the Royal School for Engineers in Italy.

Especially noted for studies on pozzolana which have paved the road to microscopic and petrographic observations and also for their contribution to the study of artificial pozzolanas.

F. Le Chatelier - Celebrated French Chemical Engineer.

He is the father of cement chemistry. His book on the constitution of hydraulic cements, his book on the setting and [illegible] cretes, and his studies on the decomposition of cement in sea water, places him in the front rank of cements experts.

Luigi Luiani - The most famous modern Italian Engineer. Died in 1893.

Especially known for his contribution to the knowledge of the effects deriving from the addition of pozzolana or other siliceous substances to Portland.

H. Maynard - French Chemical Engineer.

His studies upon the liberation of lime and its diffusion from the interior of the mass of a mortar or a Portland cement concrete awoke cement chemists to the realization of the danger connected with this free lime.

W. Michaelis - Celebrated German Chemical Engineer.

~~He was~~ One of the first to advocate the addition of siliceous material to Portland cements to take care of the free lime liberated during the process of hydrolysis of the calcium silicates.

O. Rebuffat - Professor of Chemistry at the Royal School for Engineers in Naples, Italy.

~~Foremost~~ The dean of Italian chemists and ~~foremost~~ expert on natural and artificial pozzolanas.

His earliest publication on the subject dates from 1896 and his latest from July 1932. During these 36 years he has published one of the most comprehensive series of studies on pozzolana and hydraulic cements in general, advancing the ~~best available~~ theory of the nature of pozzolanic reactions.

L. J. Vicat - Celebrated French Engineer. (Deceased)

He ~~must~~ may be considered as the father of artificial pozzolana. Throughout 50 years or more he studied and experimented upon this material, bringing about a quite important contribution to the solution of the problem of substituting artificial pozzolana for natural pozzolana.

C. Vittori - Chemical Engineer of the Di Segni Cement Plant of Italy.

Especially known for his contribution toward the development of a rational type of pozzolanic cement and toward the advocacy of such a type in all construction works subjected to the action of chemically aggressive waters.

H. Lafuma - The most celebrated modern French Chemist.

His studies on the Aluminates of Calcium are ~~the last word ever said~~ a excellent contribution on the subject.

[illegible]

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H. Lafuma - The most celebrated modern French Chemist.

Especially [illegible] for his contribution towards the development of a rational type of [illegible] cement and towards the advocacy of such a type in all construction works subjected to the action of chemically aggressive waters.

G. Alfano - Chemical Engineer of the Di Segni Cement Plant of Italy.

Has for natural pozzolana.

To the solution of the problem of substituting artificial pozzolana for natural pozzolana.

Is the material, [illegible] about a [illegible] important contribution [illegible] pozzolana.

He must be considered as the [illegible] of artificial.

T. T. Vicat - Celebrated French Engineer. (Deceased)

[illegible] of the nature of pozzolanic reactions.

Has [illegible] in General, advancing the [illegible] and [illegible] of the most comprehensive series of studies on pozzolana [illegible] from July 1922. During these 20 years he has [illegible] his earliest publication on the subject dated from 1930.

Has [illegible] and artificial pozzolanas.

The [illegible] of Italian chemists and foremost expert on [illegible] Engineers in Naples, Italy.

O. Hoffman - Professor of Chemistry at the Royal School for [illegible] during the process of hydrolysis of the calcium silicates [illegible] to Portland cements to take care of the free lime [illegible]

He was the first to advocate the addition of siliceous [illegible]

F. Michaelis - Celebrated German Chemical Engineer.

[illegible] connected with this free lime.

[illegible] concrete smoke cement chemists to the realization of the [illegible] from the interior of the mass of a mortar or a Portland cement [illegible]

His studies upon the liberation of lime and its [illegible]

E. Maynard - French Chemical Engineer.

A P P E N D I X X.

German Standard Trass

Definition and Properties

Contents

Definition
Content of Water Hydration
Fineness
Mortar Strength

Definition:

1. Trass in the sense of building practice is a finely ground tuffa, volcanic ejecta. On mixing with slacked lime it forms a binding material which hardens in air and under water to give the properties in parts 2 to 4. The specific gravity is 2.32 to 2.5.

Content of Water Hydration:

2. Trass must yield on the average not under seven percent of water hydration (chemically bound water). An inferior content (up to six percent) will not be objected to when the trass will attain the standard prescribed strength.

Fineness:

3. Trass must be ground so fine that by the standard method of sieving on sieve #30 DVN 1171 (900 mesh per square centimeter) there is not over 20% residue.*

Mortar Strength:

4. Trass must in the mortar mixture of following composition one part by weight of trass, 8/10ths part by weight of standard-trass-pulverized-lime (DIN-DVN 1043 Part 3, Paragraphs 1 to 4), 1-1/2 parts by weight standard sand (DIN DVN 1043, Part 3, Paragraphs 5 to 8); must achieve the following strengths:

Mortar Strength	7 Days Water Storage as in Par. 5.	28 Days
Tensile Kg./cm.^{2}	5	16
Comprsn Kg./cm.^{2}	45	140

APPENDIX X.

German Standard Trass

Definition and Properties

Contents

Definition
Content of Water Hydration
Fineness
Mortar Strength

Definition:

1. Trass in the sense of building practice is a finely ground tuffa, volcanic ejecta. On mixing with slacked lime it forms a binding material which hardens in air and under water to give the properties in parts 2 to 4. The specific gravity is 2.52 to 2.5.

Content of Water Hydration:

2. Trass must yield on the average not under seven percent of water hydration (chemically bound water). An inferior content (up to six percent) will not be objected to when the trass will attain the standard prescribed strength.

Fineness:

3. Trass must be ground so fine that by the standard method of sieving on sieve #30 DVN 1171 (900 mesh per square centimeter) there is not over 20% residue.*

Mortar Strength:

4. Trass must in the mortar mixture of following composition one part by weight of trass, 8/10ths part by weight of standard trass-pulverized-lime (DIN-DVN 1043 Part 3, Paragraphs 1 to 4), 1-1/2 parts by weight standard sand (DIN DVN 1043, Part 3, Paragraphs 5 to 8), must achieve the following strengths:

	7 Days	28 Days
	Water Storage as in Par. 5.	
Mortar Strength		
Tensile Kg./cm.^{2}	5	16
Compran Kg./cm.^{2}	45	140

5. Underwater storage is to be understood: The test sample lies in a dampness saturated space of temperature 17 to 20° C. The rest of the time (4 to 25 days) under water at a temperature of 17 to 20° C.

Test:

The properties will be tested according to DIN DVM 1043 Part 2, Trass Test Method and Din DVM 1043 Part 3, Trass, Standard Trass Lime Powder, Standard Sand, Test Apparatus.

NOTE: *The fineness of Trass is of influence on the stremgth of the mortar. From the fineness only man cannot conclude of the value of the Trass.

5. Underwater storage is to be understood: The test sample dries in a dampness saturated space at temperatures 17 to 20° C. The test of one time (4 to 28 days) under water at a temperature of 17 to 20° C.

Test:

The properties will be tested according to DIN 1045 Part 3, Trass Test Method and DIN DVM 1045 Part 3, Trass Standard Trass Lime Powder, Standard Sand, Test Apparatus,

NOTE: The fineness of Trass is of influence on the strength of the mortar. From the fineness only must cannot conclude of the value of the Trass.

Naples, August 29, 1933

Dear Sir:

In answer to your letter of August the 10th, I wish to state that the technique followed at present in Italy for the rapid construction of piers, quays, etc., to be built in sea water even at notable depths, is that of casting on the grounds cement caissons which will serve as shells to a mass of mortar made of fat lime and pozzolana.

These floating caissons are launched and brought to the place of their immersion, where they are gradually filled with the pozzolana mortar. In this way the mortar is well compacted and is protected from the mechanical action of the waves during the process of setting and hardening. In case there is plenty of time to spare it is suggested to prepare the blocks of pozzolana mortars on the ground, and, after their hardening, sink them in place with the help of a floating derrick.

Yours very truly,

O. REBUFFAT (Signed)

Naples, August 20, 1923

Dear Sir:

In answer to your letter of August the 10th, I wish to state that the technique followed at present in Italy for the rapid construction of piers, quays, etc., to be built in sea water even at notable depths, is that of casting on the ground cement caissons which will serve as shells to a mass of mortar made of fat lime and pozzolana.

These floating caissons are launched and brought to the place of their immersion, where they are gradually filled with the pozzolana mortar. In this way the mortar is well compacted and is protected from the mechanical action of the waves during the process of setting and hardening. In case there is plenty of time to spare it is suggested to prepare the blocks of pozzolana mortars on the ground, and, after their hardening, sink them in place with the help of a floating derrick.

Yours very truly,

C. FERRETTI (Signed)