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HIGHWAY TRANSPORTATION AGENCY
DEPARTMENT OF PUBLIC WORKS
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X-RAY ANALYSIS OF PORTLAND CEMENT

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M. & R. P.W.O. 645156

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Sacramento, California

Dear Mr. Womack:

Submitted for your consideration is a report on:

X-ray Analysis of

Portland Cement

Study made by: ---------- Concrete Section
Under direction of: ---------- D. L. Spellman
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Very truly yours,

JOHN L. BEATON
Materials and Research Engineer

cc: LRGillis
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X-RAY ANALYSIS OF PORTLAND CEMENT

I. Synopsis

The exposure of briquetted portland cement samples in General Electric XRD-5 X-ray equipment set for spectro-chemical emission makes it presently possible to analyze as many as 20 cements a week for oxides of silicon, aluminum, titanium, phosphorus, iron, calcium, strontium, magnesium, manganese, sulfur and chlorine. Conventional ASTM methods are used for the determination of ignition loss, insolubles, sodium and potassium. The precision of the determination of some minor elements by X-ray exceeds the precision obtained by routine wet chemical procedures, but for the other elements it is not as precise. A larger proportion of cement samples received may be analyzed by X-ray than is now possible using wet chemical procedures. The X-ray procedures used are the simplest ones considered practical for routine work. More refined procedures may increase precision but would defeat the purpose of the application of X-ray, that is, to provide for a rapid oxide analysis to replace conventional wet chemical methods.

II. Introduction

During the past several years, with an appreciable increase in the use of portland cement concrete by the California Division of Highways, the ratio of the number of cement samples received to the number of samples chemically analyzed has increased. This has been due, in part, to space and labor limitations in the Chemistry Laboratory.

With increasing instrumentation in chemical testing, speed is generally one of the prime factors involved. In view of this, in 1962, a General Electric XRD-5 Industrial X-ray was purchased and installed in the Chemical Laboratory of the Materials and Research Department.

One of the prime purposes of acquiring this equipment was to develop a faster method of analysis for portland cement, but it was also to be used in the study of clay minerals, metals and paint pigments.

Many details and problems in procedures for quantitative analysis have been discovered that were not apparent in 1963 when this equipment was first put into use. Communications with other organizations involved in similar studies indicate that many of the problems involved can be solved with varying degrees of success.

X-ray Diffraction is used for identifying many crystalline components of materials, and is particularly useful for clay and pigment identification. Diffraction appeared to be suitable for identifying the minerals in cement such as tri-calcium aluminate (C_3A), tri-calcium silicate (C_3S), di-calcium silicate (C_2S), tetra-calcium alumino-ferrite (C_4AF), etc., but so far exploratory tests have not been satisfactory. Available literature and private communications reveal that other investigators [1, 2, 3, 4, 5] have reservations concerning X-ray diffraction of portland cement and that many assumptions have been made in attempting to correlate results obtained with results desired. Generally, crystalline compounds present in less than 5% of the whole do not show up in diffraction.

X-ray Emission or Spectrochemical procedures are used to determine quantitatively the presence of many elements. Analysis by X-ray of a portion of the cements submitted to the Chemical Laboratory has been made since January of 1964 for oxides of silicon, aluminum, iron, calcium, magnesium and sulfur (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, and SO_3), and more recently for titanium, phosphorus (TiO_2, P_2O_5) and chloride reported as Cl. Generally, the results have been fairly satisfactory. The greatest difference between X-ray spectrochemical determinations and wet chemical determinations has been with CaO. This may be due to basing X-ray

results on wet analysis of certain local brands of portland cement that are not entirely suitable. Conventional ASTM procedures continue to be used for determining ignition loss, insolubles, sodium and potassium.

III. Summary

Conventional wet chemical methods of analysis of cement are time consuming, and an increase in the number of samples that can be tested is limited under existing conditions. The search for relatively quick but satisfactory methods of analysis should continue. This should include modifications for the X-ray procedure, wet chemical (but not present classical methods), and atomic absorption techniques.

The present X-ray equipment could be modified by the addition of a semi-automatic sample changer and a digital print-out device. This would greatly reduce the man-hours required per test.

The test method described in this report is not considered accurate enough to entirely replace some of the ASTM wet methods of chemical analysis. It is suitable for a "screening" test and can be used to identify with reasonable certainty samples which are considerably out of specification limits.

About 10 to 20% of the total samples to be analyzed should be tested by ASTM wet methods of chemical analysis. Samples which pass the "screening" test but are close to the specification limits should be selected.

IV. General

This research project was initiated in 1963 to determine the feasibility of determining the chemical analysis of portland cement by X-ray instead of by the more time consuming wet chemical methods.

Over the years, the now standard chemical methods of analysis such as those described by "Hillebrand and Lundell" or "Scott" have been accepted for finding all of the elements present in cement. Routine methods (frequently short cuts of the "standard" procedures) as accepted by ASTM are widely used by the industry. Manufacturing processes have been controlled by these analyses. Thus, for example, experience shows that certain physical characteristics are based on the tri-calcium aluminate (C_3A) content; the C_3A is calculated indirectly from the amount of Al_2O_3 and Fe_2O_3. By routine wet chemical procedures, the percent "R_2O_3" (a precipitate of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5) is determined, the percent Fe_2O_3 is determined separately and subtracted from this R_2O_3, and the balance is reported as Al_2O_3.

The determination of P_2O_5 and its deduction from the determination of ammonium hydroxide group are required only when a sample fails to meet a specification requirement (see ASTM designation C114-61).

V. Test Method Development

X-Ray Diffraction

By means of X-ray diffraction techniques, the presence of many crystalline substances can be measured. In addition to chemical specifications, certain hypothetical combinations exist in cement as crystalline compounds. e.g., C_3A, which may be expressed as tri-calcium aluminate ($3\ CaO\text{-}Al_2O_3$). Since the ratios of crystalline compounds to one another influence the properties of portland cement, they must meet certain specifications according to the type of cement desired.

The X-ray diffraction pattern is obtained by subjecting a flat surface of a prepared cement specimen to the X-ray beam. The sample, if crystalline, behaves like a diffraction grating and emits secondary radiation at precise angles for each crystalline component. The strength of this diffracted beam is measured by an electronic detector connected to a strip recorder and the result is a diffraction pattern. Peaks on the pattern curve indicate the presence of various compounds.

X-ray diffraction would appear to be an ideal means of measuring the crystalline compounds present. Experience has shown that this has not been very successful. An inkling of the difficulties may be gleaned by quoting a paragraph by P. K. Mehta[2]. "Selection of peaks for area measurement is complicated by the fact that most of the diffraction lines for alite overlap the lines due to beta C_2S, and the strongest ferrite phase reflections overlap the strongest C_3A peak." Thus, the ability to separate the whole into its parts is difficult, if not impossible, by this method.

An attempt was made to determine MgO quantitatively by diffraction, hoping that all of it might react in the beam as a crystalline MgO compound. This would be a very quick procedure, requiring 15 to 20 seconds per prepared sample. Unfortunately, this procedure was found to be unreliable and no further work has been done in this direction. A comparison between this and the more accepted emission procedure is shown in Figure 1.

X-Ray Spectrochemical Emission

This procedure measures the amounts of certain elements present. A strong X-ray beam is directed onto the flat surface of the prepared material held in a fixed position. Electrons in the elements are excited and emit secondary X-rays. Secondary X-rays are directed to an analyzing crystal which separates the characteristic wave lengths by diffraction. The diffracted beam is directed to a detector tube which amplifies and transmits the signal to a strip recorder or numerical counter.

To measure quantitatively certain elements present, the following are among many conditions which must be met:

1. The equipment must be electrically and thermally stable.

2. There must be uniform compaction and surface condition of the sample.

3. With some elements there must be no interference from the atmosphere in the total X-ray path (vacuum is most ideal, however helium, the second lightest gas is used as a compromise).

Beginning in February, 1965, it was recognized that various brands of cement have different percentages of minor elements which are grouped together and are reported as a group in wet chemical analysis. By X-ray they are determined separately, but previously were ignored.

Routine wet chemical analysis reports show:

Determined as:	Reported as:
SiO_2	SiO_2
R_2O_3-Fe_2O_3 (See Part IV)	Al_2O_3
Fe_2O_3	Fe_2O_3
CaO+SrO	CaO
MgO+Mn_2O_3	MgO
SO_3	SO_3
Chloride	Cl

X-ray analyses show that TiO_2 and P_2O_3 vary from 0.3 to 0.6% depending upon the brand, and this added to the Al_2O_3 can significantly affect the C3A value. SrO is usually low (maximum 0.14% approximately) compared to the amount of CaO present that it is ignored, as is Mn_2O_3 (0.07% max.). Cl has been found in significant amounts in only one local brand of cement but detecting and determining its presence is important because of its effect on cement shrinkage and possible effect on corrosion of embedded steel in concrete, if present.

Our cement sample preparation procedure for X-ray analysis consists of compressing 5 grams in a hydraulic press to about 12,000 psi, which takes about 5 minutes per sample. Alternate procedures described in the literature[3] are dissolving in acids

and X-raying the solution in a special cell, or fusing with borax or other fusion mixes followed by pulverizing the fused mass and compressing this pulverized material as above. These methods are time consuming and are objectionable for this reason. There is also a possibility of damage to the X-ray equipment. Any procedure which unduly increases the time to make the test tends to defeat its purpose.

VI. Test Method

After compressing the samples as above, our analytical practice is to determine aluminum, phosphorus, silicon, sulfur, and chlorine using a PET (pentaerythritol) analyzing crystal. It is necessary to exclude the presence of interferring oxygen and nitrogen molecules of the air by blanketing the entire beam path with an atmosphere of the lighter gas, helium. A vacuum system would be more desirable in this respect but it presents other difficulties that for our uses would not be practical. After the specimen is inserted into the sample chamber, 100 seconds is allowed to purge out air before calibrating or analyzing.

After the equipment has been on long enough to become electrically and thermally stabilized, the alignment for these elements is as follows:

A cement specimen is inserted into the chamber. The goniometer is set on the approximate angle sensitive to aluminum indicated by a deflection of the rate meter. The angle is very carefully adjusted to the nearest .01° to obtain a maximum count rate. Next, the detector circuit High Voltage Adjustment is made to obtain the maximum count rate. The angle and H.V.A. are recorded. This procedure is repeated for each of the subsequent elements mentioned above.

Next, high and low "standard" cements are run to determine the curves for each element. The cement samples under test can then be analyzed. Time consuming recalibration must be repeated for each element 2 or 3 times during a run, or every 3 hours.

The determination of magnesium is much the same except that the analyzing crystal used is ADP (ammonium di-hydrogen phosphate).

Iron, titanium and calcium are determined using a LiF (lithium floride) crystal. This crystal is more efficient than any other crystal available and an air atmosphere presents no problem. Each of these elements requires only 20 seconds exposure to the X-ray beam at the voltage and milliamperage used to obtain satisfactory analytical counts. For a group of twenty cements, generally only one calibration is necessary.

VII. Discussion

Analytical results obtained by X-ray have been compared with results from ASTM wet analysis, alternate method. A group of 29 samples were tested in duplicate by X-ray and ASTM methods. A comparison of the results is shown in Figure II. Further analysis of this data has shown the ratio of W/X is approximately 2 for Fe_2O_3 and SO_3, three for SiO_2, Al_2O_3, and CaO and four for MgO. (Where X is the difference between two X-ray tests; W is the difference between two wet chemical tests.)

Figure III gives a comparison for 51 cements which were tested on a routine basis, one analysis for each method. The shifting of the curve from the zero point is similar in both Figures II and III. This is probably due to the standards selected.

The length of time required for X-ray analysis of cement and especially the determination of Mg, Al, Si, P, S could be shortened appreciably by the use of a multiple sample holder in which all the prepared samples would be tested for one element before changing over to the next element. It would save much purge, X-ray tube and recalibration time.

In addition to the above, a great saving of operator's time could be effected by installing a digital printer. This device would print the count after each determination of a given element. The operator would set up the changer and digital printout, start it and leave it unattended until the determination of a particular element in all of the samples was completed. This type of arrangement would be far less expensive than a completely automatic changer. A digital printer is available for the XRD-5 ($1500). A sample "slide" changer will probably have to be our own design.

Between October 1, 1964 and May 31, 1965, a total of 193 cements were analyzed. This required 20 minutes exposure per sample in the X-ray beam. About two man hours per sample are required to prepare the sample, align the instrument and perform the X-ray portion of the analysis. The ignition loss, insoluble, and sodium and potassium tests should be performed by ASTM procedures and would be included in the time estimate of two hours per sample. On this basis, one operator could perform a "complete" chemical analysis of about 20 cements per week.

Some cement mills are using X-ray on a "routine" basis for production control testing of raw materials, clinker, and finished product. Here, calibration of the equipment is adjusted for a single "brand" of material, and sample preparation is under close control and the entire test procedure automated. In this laboratory,

however, a variety of brands and types are tested which necessitates frequent readjustments of the X-ray device.

The difference in particle size and matrix effects of different cements influence the analytical results, especially when all cements in California are compared with one set of standards for each element. As discussed previously, the analytical method for this study has been kept as simple as possible so as to increase the number of samples analyzed.

The analytical procedure given provides adequate control only when used as a "screening" test. Any sample in doubt must be further analyzed by ASTM methods.

References

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By Leonard Bean
National Bureau Standards Publication, May, 1964

Figure 1

COMPARISON BETWEEN X-RAY DIFFRACTION AND SPECTROCHEMICAL PROCEDURES OF MgO VALUES FOR A GROUP OF 35 CEMENTS

Notes: 1. Spectrochemical is considered to be the better method.
2. The + sign indicates Diffraction value higher than Spectrochemical.

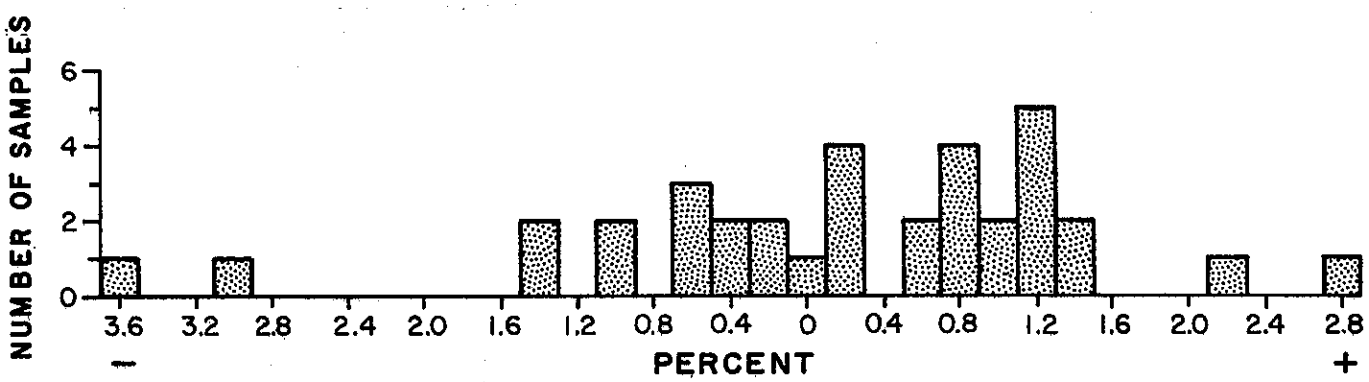
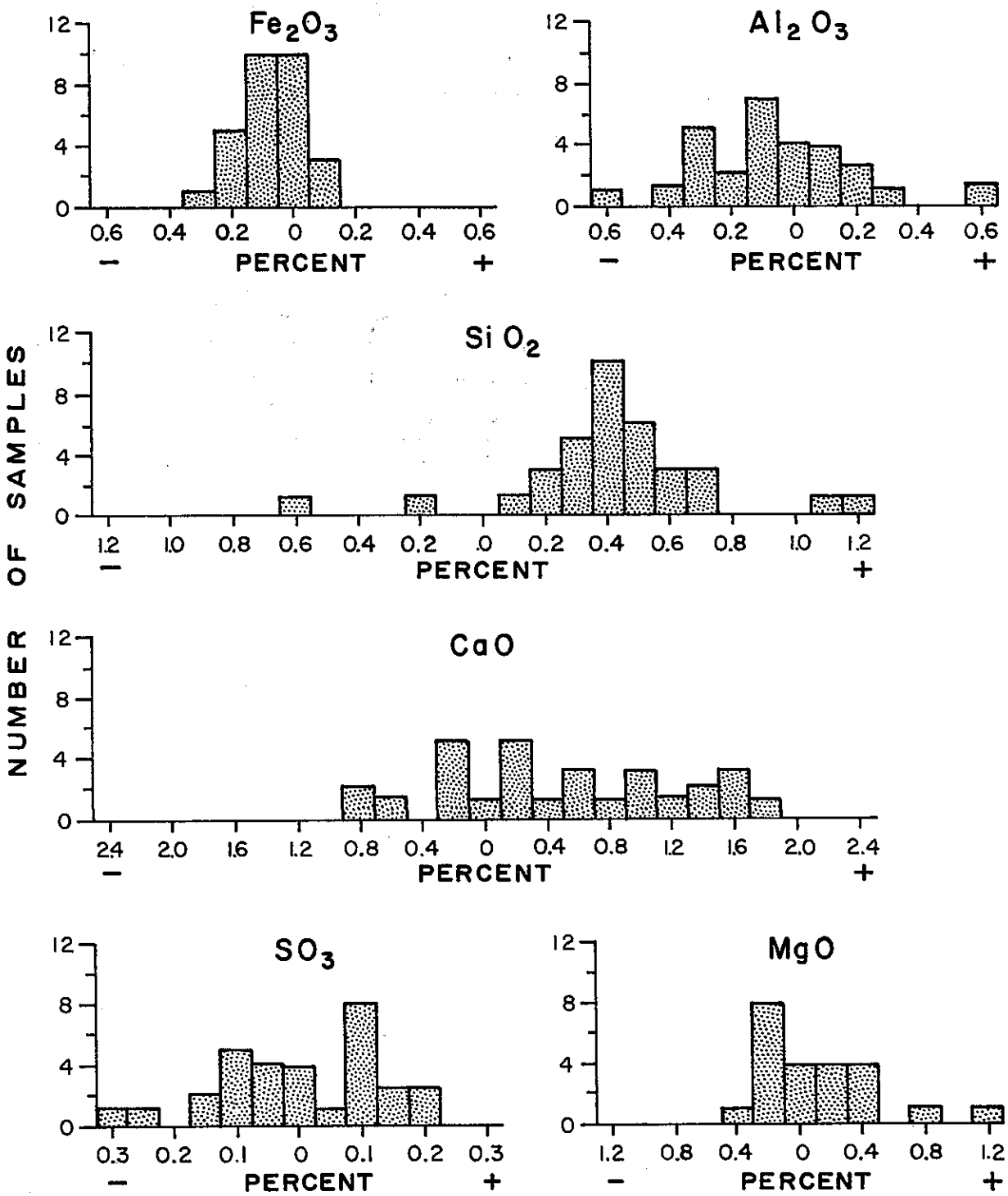


Figure 2

OXIDE ANALYSIS OF CEMENT. X-RAY VS WET CHEMICAL

Each value shown is the difference in the average of duplicate tests made by X-ray and ASTM alternate wet chemical methods. The + sign indicates the X-ray value to be higher than the wet value.



X-RAY ANALYSIS OF 51 CEMENTS COMPARED TO ROUTINE WET CHEMICAL ANALYSIS

The + sign indicates the X-ray value to be higher than the wet value.