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State of California
Transportation Agency
Department of Public Works
Division of Highways

Materials and Research Department

February 10, 1966
Laboratory Project
Work Order 440448

Mr. Lyman R. Gillis
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Dear Mr. Gillis:

Submitted for your consideration, is a final report on:

Chemical Analysis of Cement

and Cement in Concrete

Study made by ----------Concrete Section
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FINAL REPORT

Chemical Analysis of Cement and Cement in Concrete

Introduction

The analysis of portland cement for oxide content requires about 4 to 5 man hours per sample by conventional ASTM alternate wet chemical analysis. Analytical methods to shorten this time have been suggested by various investigators. The object of this project was to examine some of these potentially shorter methods to see if they could be used alone or with other analytical methods to determine the chemical composition of cements. Those tried were the flame photometric method for magnesium, being used by the Bureau of Standards Laboratory of the County of Los Angeles, and the methods for iron, aluminum and calcium used by the State of Nevada, Division of Highways, Materials and Research Laboratory. Only exploratory type tests were made because of the limited scope of the project. Any encouraging results were to be investigated in more detail under a new proposal in the planning stage.

Results

Generally results were not very satisfactory. The following comments are given for each element investigated.

1. Magnesium. The oxygen-acetylene burner on the Beckman D.U. spectrophotometer was used for this determination. The background was too high to hope for any results closer than roughly ± 0.5%. This is in the same range of accuracy as obtained with x-ray emission. The use of a hydrogen-oxygen burner would reduce this background somewhat and this method may be investigated further after review of any recent data available from other sources. See Figure 1.

2. Aluminum. This was determined by a colorimetric method using the ammonium salt of aurin tricarboxylic acid (Aluminon). A standard curve was drawn using National Bureau of Standard samples. (See Figure 2) Results on California cements using this curve were 0.2 to 0.5% low when compared with alternate ASTM wet chemical analysis.

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The reason for this difference proved to be the presence of phosphorous and titanium in the cement. Phosphorous and titanium are included in the results for aluminum obtained by the ASTM alternate method which is generally used for testing cements. In case of dispute, the referee ASTM method is required. This method corrects for the phosphorous and for the titanium if so required in the specification. The colorimetric method under investigation did not include the titanium and phosphorous but when the values for these elements were added to the colorimetric values, fair to good agreement was obtained with the ASTM alternate method. Figure 3 shows the correction made to the colorimetric method for titanium and phosphorous and the difference between this corrected value and the ASTM alternate method value. The results are somewhat better than obtained with x-ray emission and the agreement between the two methods listed in Figure 2 were essentially within the tolerance of $\pm$ 0.2% which ASTM gives as an acceptable value on duplicate values for aluminum expressed as the oxide.

This colorimetric method might be of occasional value when a direct determination for aluminum is desired but it is of little value in a rapid screening test for cements.

3. Calcium. The versenate titration for calcium was not consistent. While some fairly good ($\pm$ 0.3%) values were obtained, other values varied as much as 1.5 %. The determination of calcium was not of primary interest since it could be omitted from a rapid screening test. A reproducible answer for calcium, however, would have permitted a versenate titration for magnesium. Due to the unsatisfactory results for calcium, versenate titration for magnesium was not attempted. (See Figure 4)

Summary

Probably the most direct benefit from this project resulted from the values obtained for titanium and phosphorous in searching for an explanation for the low aluminum values by the colorimetric method. All brands of cement were tested for these 2 elements by x-ray diffraction. This was the first attempt by this Laboratory to analyze for these elements by this method and it proved to be a very simple operation.

The above information was used to alter the procedure for determining aluminum by x-ray emission.

The values for Tricalcium Aluminate (C_3A) as calculated from the aluminum and iron values determined by x-ray emission are not completely acceptable because of the inaccurate values for aluminum. Improved values for aluminum can be obtained by correcting each aluminum value fot titanium and phosphorous present.

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FIGURE 1

CURVE OBTAINED BY ADDING MAGNESIUM OXIDE IN 1% INCREMENTS TO PORTLAND CEMENT

Sample No. Pe 18929-0.90% MgO
MgO Beckman .3mm Slit
50% Methanol

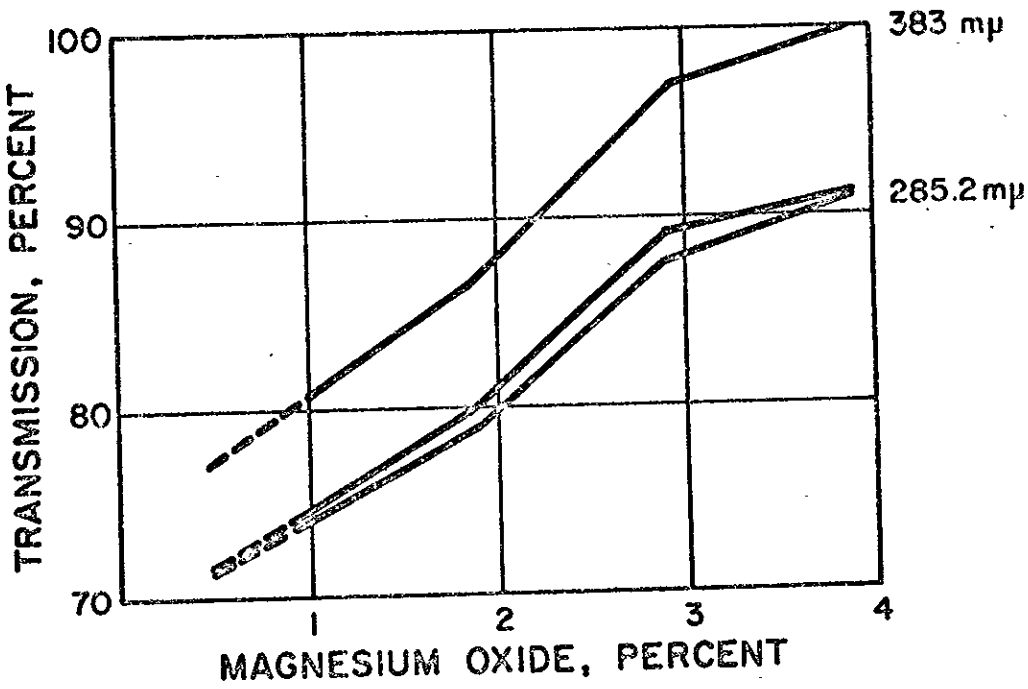

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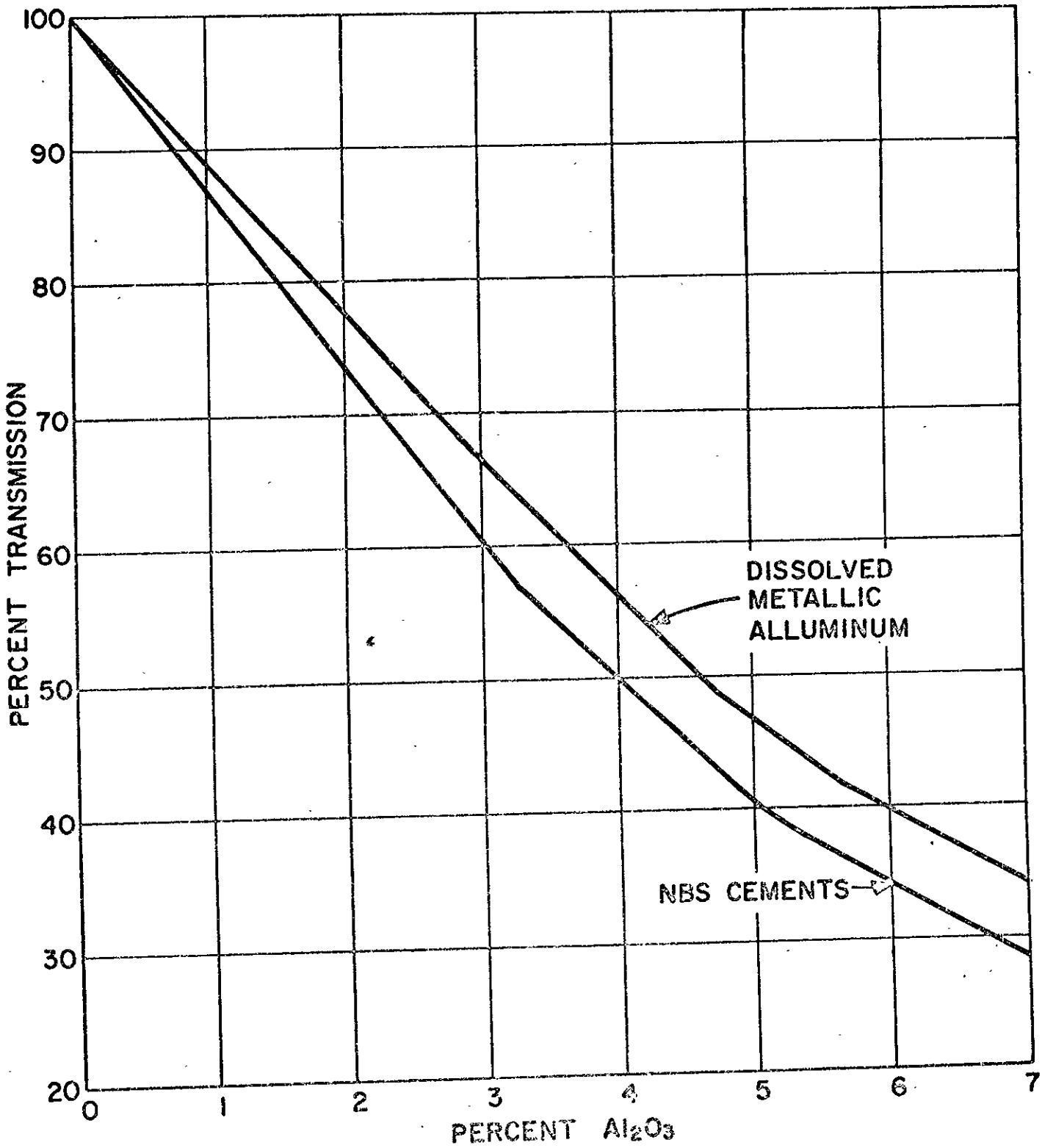
FIGURE 2

THIS GRAPH INDICATES THAT CEMENTS HAVE SOMEWHAT GREATER LIGHT ABSORPTION THAN THE EQUIVALENT AMOUNT OF ALUMINUM DISSOLVED IN HCl



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ALUMINUM IN CEMENTS BY NEVADA COLORIMETRIC METHOD

Sample Number	% Transmission	Al_2O_3 Using NBS Al_2O_3 Curve	Al_2O_3 Wet Analysis (ASTM Alternate)	Difference %	% Added for T_1O_2 and P_2O_5*	Net Difference
18900 Cal	49.2	4.10 %	4.64 %	−.54 %	.36 %	−.18 %
18929 Pe	70.2	2.28	3.62	−.34	.41	+.07
18932 Rv	48.0	4.24	4.60	−.36	.38	+.02
18933 Mo	51.0	3.90	4.36	−.46	.35	−.11
18955 Co	50.6	3.94	4.32	−.38	.35	−.03
18551 Id	40.4	5.00	5.10	−.10	.36	+.26
18807 SC	55.2	3.45	4.00	−.55	.35	−.20
19044 Vr	61.2	2.95	3.40	−.45	.23	−.22
19049 Be	51.2	2.88	4.10	−.22	.33	+.11
				−.38 av.		−.03 av.

* From memo of Mar. 4, 1965, Frank Norris. (Detn. by X Ray)

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FIGURE 4

CaO IN CEMENTS, NEVADA METHOD

Sample Number	% CaO by Wet Analysis	% CaO by Titration	Difference vs Wet Analysis	Repeat % CaO by Titration	Difference vs Wet Analysis
18900 Cal	64.38	63.69	−.69	64.82	+.44
18929 Pe	65.54	65.85	+.31	65.90	+.36
18932 Rv	62.30	61.92	−.38	63.80	+1.50
18933 Mo	64.00	63.96	−.04	64.28	+.28
18955 Co	63.40	—	—	64.01	+.60
18551 Id	63.40	63.01	−.40	62.39	−1.00
18807 SC	63.90	61.50	−2.40	64.01	+.10
19044 Vr	63.70	63.80	+.10	64.28	+.60
19049 Be	64.20	63.30	−.90	65.09	+.90

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