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ANALYSIS OF HIGHLY-HYDRATED DOLOMITIC LIME BY A GEIGER COUNTER X-RAY DIFFRACTOMETER

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Previous investigations of X-ray diffraction methods of analysis of highly-hydrated dolomitic lime have reported an accuracy no better than 10%, when compared with results of other chemical methods used for the quantitative determination of the constituents (Sprague, 1949). With the advent of more advanced instrumentation, the X-ray method is becoming more and more accurate. This report demonstrates that more reliability can, therefore, be placed in such improved instrumental techniques which have decided advantages in other respects.

The lime, building, fertilizer, and chemical industries have recently increased their demands for a more reliable, objective, and non-destructive method of analysis of limes containing mixtures of oxides, hydroxides, carbonates, sulfates, and impurities such as silicates. As an example of unsatisfactory analytical procedures, it should be mentioned that the chemical methods of analysis of hydrated dolomitic limes proposed by the National Bureau of Standards *assume* a distribution of total water between calcium and magnesium hydroxides without allowance for physically absorbed moisture. It has been claimed, in most cases unjustly, that residual MgO hydrates in plasters on walls with consequent volume change and failure. The result has been that the dolomitic lime industry has suffered serious losses, solely on the basis of a method of chemical analysis, even though X-ray patterns have demonstrated the presence of MgO in plasters up to several hundred years old.

The present investigation represents an extension of the work of Clark and Sprague (1952:688) and makes use of a new recording Geiger counter X-ray diffractometer, the *Spectron*, manufactured by the Ohio X-Ray, Inc. A series of synthetic lime samples of known concentrations of five constituents common to dolomitic limes was analyzed by X-ray diffraction to serve as standards for the preparation of working curves. Samples of the hydrates were then analyzed by similar techniques for determination of the percentage composition of each major constituent based on the previously prepared working curves.

Theory of the X-ray Method

The identification and quantitative determination of the actual crystalline constituents of highly-hydrated dolomitic limes offer a unique challenge to the field of X-ray diffraction analysis, since chemical

methods used in such an analysis are tedious and time consuming, as well as difficult, and of course yield information only on the elementary composition rather than the molecular species actually present in a complex mixture.

A diffraction pattern may serve for quantitative as well as qualitative analysis. The relative intensities of the lines in a pattern of a substance in a mixture are proportional (except for certain absorption effects) to the amount of the crystalline compound present. The advantages of the pattern obtained from the automatically recording Geiger counter X-ray diffractometer over the photographic film technique of recording diffraction patterns lie in greater speed of operation and ease of interpretation and in the direct evaluation of intensities from peak heights which for patterns on films requires the additional use of a microphotometer (Clark, *et al.*, 1954: 1413).

When more than one substance in the same sample is to be determined quantitatively by X-ray diffraction analysis, the use of a single internal standard, which involves comparison of the intensity of a standard and an unknown line very close together, is impractical; for the strongest lines of the compounds in these limes lie over an angular range of 25.65 to 50.85 degrees two theta. Therefore, it was necessary to prepare working curves which relate percentage composition of a substance to relative intensity of a diffracted X-ray beam (in arbitrary units) based on the analysis of specially prepared synthetic samples containing $Ca(OH)_2$, $CaCO_3$, $Mg(OH)_2$, MgO, and $CaSO_4$. Diffraction patterns of the samples of hydrated dolomitic lime were then similarly analyzed, and the diffraction intensities obtained were used to read off the working curves the percentage of each substance in the sample.

Experimental Methods and Results

Five samples of dolomitic lime hydrate were chemically analyzed by the methods previously described (Clark and Sprague, 1952). The results are given in Table 1. The compositions of seven synthetic mixtures made up for the preparation of working curves appear in Table 2.

X-ray analyses of the synthetic mixtures and hydrates were carried out under as nearly uniform conditions as possible. The work was done in an angular range of

Table 1.—Composition of Dolomitic Hydrates Calculated from the Chemical Analysis.

Hydrate	$Ca(OH)_2$	$CaCO_3$	$Mg(OH)_2$	MgO	$CaSO_4$
A	51.9%	5.5%	35.6%	5.8%	0.5%
B	52.1	5.2	36.4	5.2	0.5
C	49.6	7.5	38.4	3.3	0.7
D	51.9	3.6	40.2	1.3	2.7
E	51.2	5.0	39.1	3.3	0.8

15 to 70 degrees two theta and with a scan speed of two degrees per minute. A time constant of eight counts per second was used, and this, together with a finely collimated beam system, produced patterns that had a surprisingly low background count. All of the patterns were run with radiation from a copper target tube under excitation conditions of 30 pKv and 15 ma.

A special sample holder was designed for this work, patterned after one by Simonsen (Sept., 1954), in which it was possible, each time, to pack the sample fairly uniformly. The holder consists of two brass plates fitted together in a vise, with a carefully machined slot in which the sample could be inserted and packed with a brass tamping pin. The plates could then be separated from the molded sample. The apparent disadvantage is the possibility of destroying some of the random orientation of powder grains by this technique of packing a sample for analysis, and indeed, this proved to be the case in one or two instances.

As shown in Table 3, a diffraction peak was chosen for each constituent in the synthetic series for later relation of its corrected line intensity to percentage composition in unknowns.

TABLE 3.—Chosen Diffraction Line for Constituents in Synthetic Mixtures.

Substance	Angle (2θ)	d-spacing
$Ca(OH)_2$	34.25°	2.62A
$CaCO_3$	29.50°	3.03A
$Mg(OH)_2$	50.85°	1.80A
MgO	43.05°	2.10A
$CaSO_4$	22.65°	3.48A

The corrected intensity values (obtained by subtracting background count from the linear intensity value) when plotted versus composition, with one or two exceptions, gave excellent linear working curves. Figure 1 shows the working curve for $Mg(OH)_2$ obtained by this method. Similar working curves were plotted for $CaCO_3$, MgO, $CaSO_4$, and $Ca(OH)_2$.

It should be mentioned that planimeter methods for measuring relative intensity values from the areas under peaks on the chart gave no better results; they were abandoned as unnecessarily tedious.

Analyses of the hydrate samples were carried out by identical sample preparations and diffraction techniques, with subsequent relation of the intensity values for the same chosen maxima of five constituents to the working curves to determine

TABLE 2.—Composition of Synthetic Mixtures for Preparation of Working Curves.

Synthetic mixtures	$Ca(OH)_2$	$CaCO_3$	$Mg(OH)_2$	MgO	$CaSO_4$
50	49.0%	8.0%	35.0%	7.6%	none
51	49.5	7.0	36.0	6.0	1.1%
52	50.0	6.0	37.0	5.0	1.6
53	50.5	5.0	38.0	4.0	2.1
54	51.0	4.0	39.0	3.0	2.6
55	51.5	3.0	40.0	2.0	3.1
56	52.0	2.0	41.0	1.0	3.5

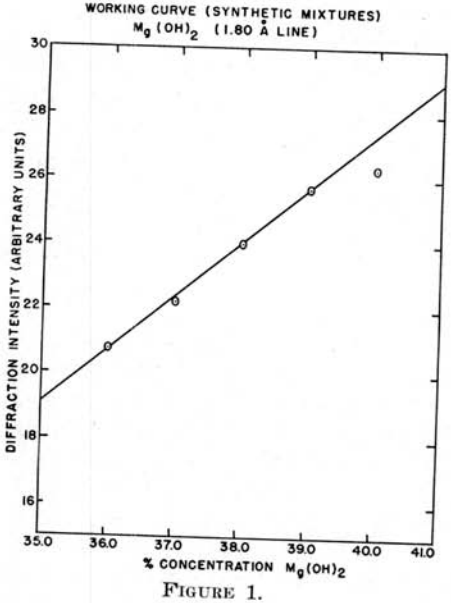

FIGURE 1.

the percentage composition of each constituent in the hydrate. A typical hydrate analysis appears in Table 4.

Although the chemical analysis listed 0.5% $CaSO_4$ in this particular sample of hydrate A, none was detected by X-rays. It is interesting to note that the only hydrate sample in which $CaSO_4$ was detected was one in which the calcium sulfate exceeded 2%. (All others contained less than 1% $CaSO_4$). However, in the standard series, $CaSO_4$ was detected in quantities as low as 1.6%. The deviation of the X-ray analysis of each sample from the chemical analysis is listed in Table 5.

For the five hydrates the average percentage concentrations were: $Ca(OH)_2$, 51.0%; $Mg(OH)_2$, 36.0%; MgO, 4.0%; $CaSO_4$, 2.0%; and $CaCO_3$, 5%. From consideration of the values listed in Table 5, it is obvious that the larger the relative percentage composition, the smaller the probability of percentage deviation. This is shown to be true for the analysis of the $Ca(OH)_2$ and $Mg(OH)_2$. There is no doubt that exposure to air will offer difficulty, as the samples are sensitive to carbon dioxide and moisture. This may account partially for the rather large deviations for the MgO and $CaCO_3$.

TABLE 4.—Comparisen of X-ray and Chemical Analyses of Hydrate A.

Substance and line	% conc. by X-ray	% conc. by chem. anal.	% difference
$Ca(OH)_2$ 2.62Å	50.5	51.9	2.3
$CaCO_3$ 3.03Å	4.1	5.5	25.0
$Mg(OH)_2$ 1.80Å	35.4	35.6	0.6
MgO 2.1Å	6.1	5.8	5.9
$CaSO_4$ 3.48Å	...	0.5	...

TABLE 5.—Percentage Deviation of Analysis by X-ray from Analysis by Chemical Methods.

Hydrate	$Ca(OH)_2$	$Mg(OH)_2$	MgO	$CaSO_4$	$CaCO_3$
A	2.3	0.6	5.9	....	25.0
B	5.0	1.6	7.6	....	7.6
C	0.4	6.5	15.1	....	22.6
D	1.9	5.4	....	14.9	22.2
E	2.3	...	9.2	....	10.0

It should be pointed out that, as the concentration exceeded 2%, the compound was readily detected by X-rays. Previous contentions had been that the compound had to be in excess of 5%. Sprague in earlier work (1949) was not able to detect below a 5% concentration in the sample.

A qualitative comparison of the results of the chemical analyses of the mixtures with the results by X-ray diffraction in this study is shown in Table 6. The table is read as follows: For the constituent $Ca(OH)_2$, the chemical analysis showed that the concentration of $Ca(OH)_2$ was greater in hydrate sample A than in D, E, B, or C, in the order of decreasing amounts. For the X-ray analysis of the same constituent, the percentage concentration was greater in B than in A, D, E, or C. From such a table it can be readily seen that agreement is, in general, good. There are only three discrepancies in the results of X-ray and chemical analyses. Of course, there is no assurance that the chemical analyses as reported are correct, since the analyses depend upon a Bureau of Standard's assumption of the distribution of water in the hydrates. It is felt that the X-ray method is a superior method, in that it is independent of any such assumption. There is also the possibility of the change in composition due to exposure to the atmosphere between the time of analysis by chemical and X-ray methods.

The results obtained appear to be in better agreement and far more precise than those earlier reported (Clark and Sprague, 1952). This is probably due to the use of a new X-ray diffraction unit and spectrometer, which was capable of more precise collimation, as well as the unique sampling procedure utilized.

TABLE 6.—Comparison of Results of Analyses by X-ray and by Chemical Methods.

		$Ca(OH)_2$			
Chem.	A	D	E	B	C
X-Ray	*B*	A	D	E	C
		$CaCO_3$			
Chem.	C	B	E	D	A
X-Ray	C	*A*	B	E	D
		$Mg(OH)_2$			
Chem.	D	C	B	A	E
X-Ray	D	*E*	C	B	A
		MgO			
Chem.	A	B	E	C	D
X-Ray	A	B	E	C	D
		$CaSO_4$			
Chem.	D	E	C	B	A
X-Ray	D	(others not detected)			

Further, it seems possible, and highly probable, that the method could be made more accurate, if sampling errors and orientation of the sample from packing could be reduced to a minimum. It might also prove valuable to work in an atmosphere of helium or nitrogen, since the samples are somewhat unstable in air.

Since all of the samples were determined by X-ray analysis with a reproducibility such that successive runs deviated less than 2% from each other and since most of the results deviated from chemical analysis less than 10%, and many less than 5%, more reliability may now be placed on X-ray methods of quantitative analysis, with its great compensating factors of speed and simplicity as compared with classical methods of chemical analysis.

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