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# Some Plastic Properties of Pastes Made from Hydrated Dolomitic and High-Calcium Limes

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# SOME PLASTIC PROPERTIES OF PASTES MADE FROM HYDRATED DOLOMITIC AND HIGH-CALCIUM LIMES

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## ABSTRACT

Four commercial hydrated limes were studied. Two from northwestern Ohio were partially hydrated dolomitic varieties that gave instantaneous Emley plasticity values of about 120. After soaking, the Emley values increased to about 310. One Illinois hydrate was a high-calcium hydrate and had a plasticity of about 100, both immediately before and after soaking. The other Illinois hydrate was a highly hydrated dolomitic type. Its immediate plasticity was 274 and, after soaking, the value rose to 340.

A study of particle-size distribution data and X-ray diffraction analysis show that the differences in the observed plasticities are correlated with high  $Mg(OH)_2$  content and high relative amounts of fine particles.

## INTRODUCTION

In connection with a study of the plastic properties of lime hydrate derived from Illinois dolomites, some measurements of plasticity of pastes made from commercial hydrates marketed in Illinois are presented in this communication.

Four commercially prepared dry hydrates were purchased in the open market and are referred to as hydrates H, G, R, and M. The hydrates were received in 50-pound paper bags. All samples used in the tests reported below were immediately transferred to glass containers with tight screw-cap lids in order to preserve their as-received compositions.

Samples R and G were dolomitic hydrates from Ohio, M a dolomitic hydrate from Illinois, and H, also from Illinois, was a high-calcium hydrate. The labels on the bags described H as "chemically pure" lime, M and R as "mason's lime," and G as "finish lime."

## EXPERIMENTAL PROCEDURES

### Plasticity Determinations

The visco-plastic properties of the four hydrate pastes or suspensions were explored by two methods - the conventional Emley plasticimeter and a Stormer rotational viscometer.

A number of measurements of torque versus rate of shear were made on each hydrate at various water contents using a calibrated Stormer viscometer. The pro-

cedure used was as follows: 100 grams of hydrate was placed in a beaker, the desired amount of water was added, and the mixture was stirred mechanically for five minutes to insure a uniform paste. The paste was transferred to the viscometer cup and the torque was measured at various uniformly increasing rates of shear. No measurements were made at decreasing rates of shear.

Because the Emley plasticimeter is so widely used in the lime industry, Emley plasticity figures were also determined for each hydrate. The apparatus was constructed at the Illinois Geological Survey after the A.S.T.M. (1949) specifications. Porcelain base plates were used. They were made at the University of Illinois in the Ceramic Engineering Department to conform to the prescribed absorption rates specified by A.S.T.M. (1949). The plasticity determinations were made in accordance with the standard procedure described by the A.S.T.M. method C-110-49. The plasticity of each hydrate was measured immediately after tempering with water to the standard consistency and again after soaking for 24 hours. The water at standard consistency, as given in the text, is the weight percent of water in the total water-solid mixture necessary to produce a paste of standard penetration on the penetrometer (or standard consistency).

Duplicate runs were made and the reproducibility was within  $\pm 15$  percent of the average value of the two runs.

#### Drying of Soaked Hydrates

In order to study the hydrates after they had been soaked to see what alterations had taken place during soaking, it was necessary to dry the samples in such a way as to minimize any alteration caused by the drying itself. The drying method used is similar to that given by Wells and Taylor (1937). Seventy-five grams of the soaked sample were placed in 150 milliliters of absolute ethanol and shaken for several minutes. The slurry was placed on a Büchner vacuum filter and the liquid removed by suction. The cake was then washed with ethanol and ether. The nearly dry cake was placed in a vacuum desiccator, at room temperature, which was continuously pumped for a period of 24 to 48 hours to remove the last ethanol and ether.

#### Ignition Loss

The ignition loss was determined by heating weighed samples in platinum crucibles to 975° C. for two hours.

#### X-ray Identification

The components of the hydrates were identified from X-ray powder diffraction patterns made on a G.E. XRD-3 recording spectrometer, using  $\text{CuK}\alpha$  radiation. A shallow aluminum sample holder was used.

#### Particle Size Analysis

The size distribution of these hydrates was determined by the usual sedimentation method using n-butanol as the dispersing agent, as suggested by Bishop (1939).

Electron Micrographs

The electron micrographs were made by Dr. A. E. Vatter in the Chemistry Department of the University of Illinois. The carbon replica technique as first described by Bradley (1954) was used.

Surface Areas

Surface areas were determined by low-temperature—low-pressure adsorption of nitrogen, using the method of Brunauer, Emmett, and Teller (1938). The value of the surface area measured is reproducible to about ± 5 percent when the area is more than one square meter per gram.

EXPERIMENTAL RESULTS

Visco-Plastic Character

The visco-plastic properties of the commercially prepared hydrates were investigated by means of two different instruments, the Emley plasticimeter and the Stormer viscometer mentioned previously.

Figure 1 shows the rate of shear versus the shearing stress for hydrate G from Ohio as an illustration of the influence of water on the viscous properties of the lime slurry as determined by the Stormer viscometer. The yield points for each water content were found by extrapolating the linear portion of each curve until it intersected the zero rate of shear axis. The water content is expressed as the percentage of the total weight of the water-solid slurry.

The yield points and water contents of each hydrate are given in table 1 and shown graphically in figure 2.

Table 2. - Emley Plasticity Values for the Commercial Hydrates

Hydrate	Emley value		Water at standard consistency (percent)	Yield point at water of standard consistency* (dynes/cm <sup>2</sup> )
	Unsoaked	Soaked		
H	91.	103.	51.5	1900.
M	274.	340.	47.0	1150.
R	111.	320.	45.5	1350.
G	120.	305.	46.0	1400.

\* Yield point is obtained from figure 2 by extrapolation to the content of water at standard consistency.

Table 1. - Yield Points and Water Contents of Commercially Hydrated Limes (Stormer)

Water content (percent)		Yield point (dynes/cm <sup>2</sup> )
56.5	Hydrate H	600
58.3		500
60.0		325
63.6	Hydrate M	125
66.7		70
50.0		710
53.5		380
56.5		225
58.3	Hydrate R	180
60.0		140
48.7		820
50.0		515
52.4		390
53.5		280
55.6		180
60.0	80	
48.7	Hydrate G	840
50.0		665
53.5		320
55.6		210
60.0		80

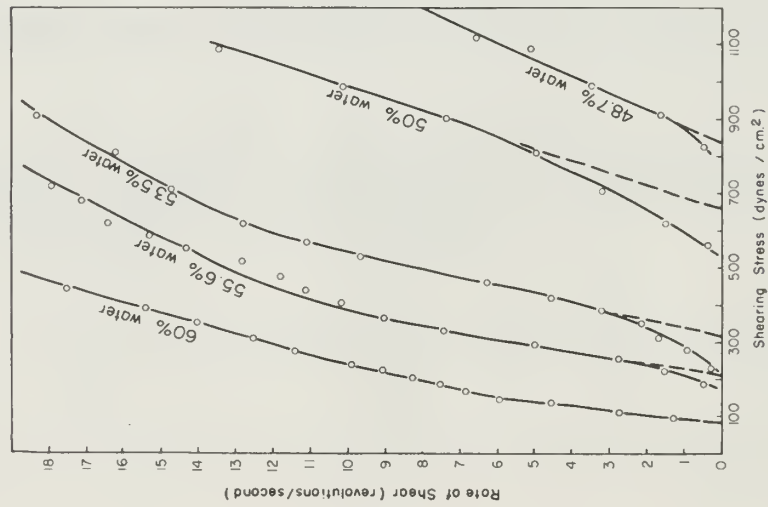


Fig. 1. - Shearing stress vs. rate of shear for hydrate G.

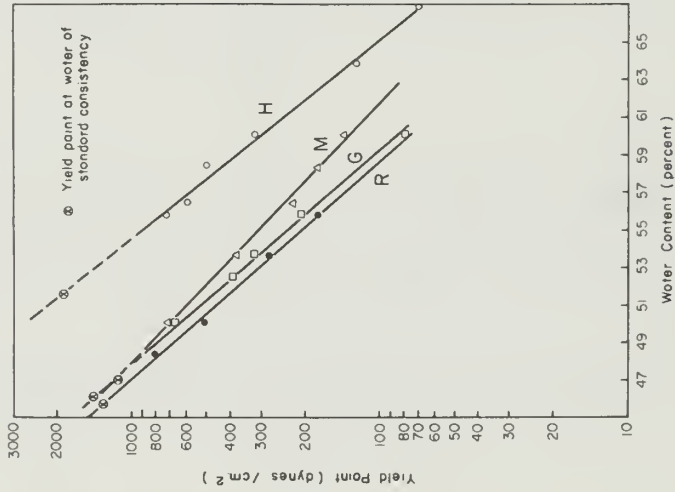


Fig. 2. - Yield point vs. water content for hydrates H, R, G, and M.

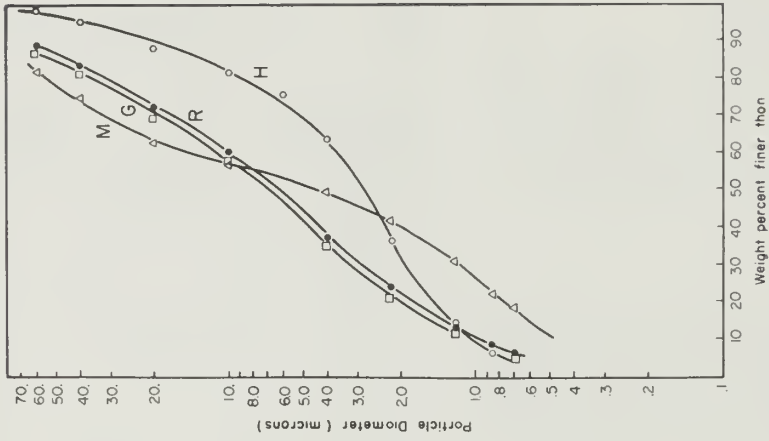


Fig. 3. - Particle size distribution of hydrates H, R, G, and M, as received.

Table 3. - Particle-Size Distribution of the Hydrates  
(as received)

Particle diameter (microns)	Weight percent finer than			
	H	M	R	G
60	98.7	82.1	89.5	87.6
40	96.0	75.4	84.1	82.0
20	88.5	63.1	72.6	70.1
10	82.0	57.4	60.4	58.5
6	76.0	-	-	-
4	64.0	49.7	37.8	35.6
2.2	37.0	42.6	24.1	21.8
1.2	14.3	31.0	13.6	11.8
0.86	6.8	22.7	8.5	7.0
0.70	-	19.2	6.7	5.8
0.46	-	9.1	-	-

Emley plasticity values for the four hydrates, before and after soaking in water, are given in table 2. The yield point given is that for a water content equal to the water at standard consistency used in the Emley measurement.

From table 2 one can see that the Emley value of plasticity for hydrate H shows no significant increase after soaking. However, hydrates M, R, and G show significant increases on soaking, particularly R and G. Hydrates R and G have rather low Emley values in the unsoaked condition, but hydrate M has a very high Emley value in this state. If one compares the yield point values with the unsoaked Emley values it appears that the yield points tend to be smaller for the more plastic hydrates.

Table 4. - Surface Areas of the Hydrates  
Size, Area, and Shape of Hydrate Particles

The particle size distribution of the hydrates was determined by sedimentation in n-butyl alcohol. The results are given in table 3 and shown graphically in figure 3. The surface areas of both the unsoaked and soaked hydrates were measured and the results are given in table 4.	Hydrate	Unsoaked	Soaked
		H	18.46
	M	17.91	17.81
	R	14.14	14.85
	G	11.59	15.16

Electron micrographs of the unsoaked hydrates are shown in plates 1 and 2. Plate 1 shows, magnified 7,000 times, the shape and relative size distribution of the hydrate particles of less than 2.2 microns separated by butanol sedimentation. Hydrate M appears to have a slightly greater proportion of very fine and rather flat particles. Hydrates R, H, and G, particularly H and G, seem to have more massive, coke-like particles or aggregates.

Plate 2 shows the shape of the particles of the unsoaked hydrates of less than 0.86 microns magnified 7,000 times. Hydrate H shows many well formed hexagonal platelets. Hydrates M, R, and G show fewer particles with well formed hexagonal outlines. The surfaces of the particles in hydrates M, R, and G appear to be rather uneven or rough compared to those of hydrate H.

By measuring the particles in plate 1, it was found that all of them are less than 2.2 microns, the maximum size that is supposed to be present from sedimentation calculations. This is a fairly good check that the sedimentation determination of particle size is valid. A number of particles smaller than 0.1 micron are also present. Measurement of particles in plate 2 show that all of the particles are actually less than  $0.86\mu$  as required by the sedimentation calculations. This further substantiates the sedimentation determination of particle size.

#### Composition of the Hydrates

The composition of the hydrates in terms of  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ , and  $\text{MgO}$  was estimated from ignition-loss data on the assumption that all the  $\text{CaO}$  is hydrated, that there is no carbonate present, and that the stone used in making the hydrate was pure dolomite. The results, given in table 5, must be accepted with caution, because during the time from their manufacture until they were purchased from a supply dealer, the hydrates were stored in paper bags and therefore had carbonated to some extent. No correction for this carbonation was made in calculating the compositions. Also, the purity of the original stone is unknown.

Table 5. - Composition of the Hydrates Estimated from Ignition Loss

Hydrate	Ignition loss (percent)		Composition (percent)					
	Unsoaked	Soaked	Unsoaked			Soaked		
			$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{MgO}$	$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{MgO}$
H	24.8	25.4	100	0	0	100	0	0
M	27.4	27.9	56.0	44.0	0	56.0	44.0	0
R	20.7	23.1	60.7	19.2	20.1	58.9	28.1	13.0
G	22.6	24.1	59.3	26.2	14.5	58.2	32.0	9.8

X-ray powder diffraction patterns of the unsoaked hydrates were made. Table 6 shows the composition of the hydrates based on the diffraction patterns of the dry hydrates as received. These results agree with those given in table 5 qualitatively.

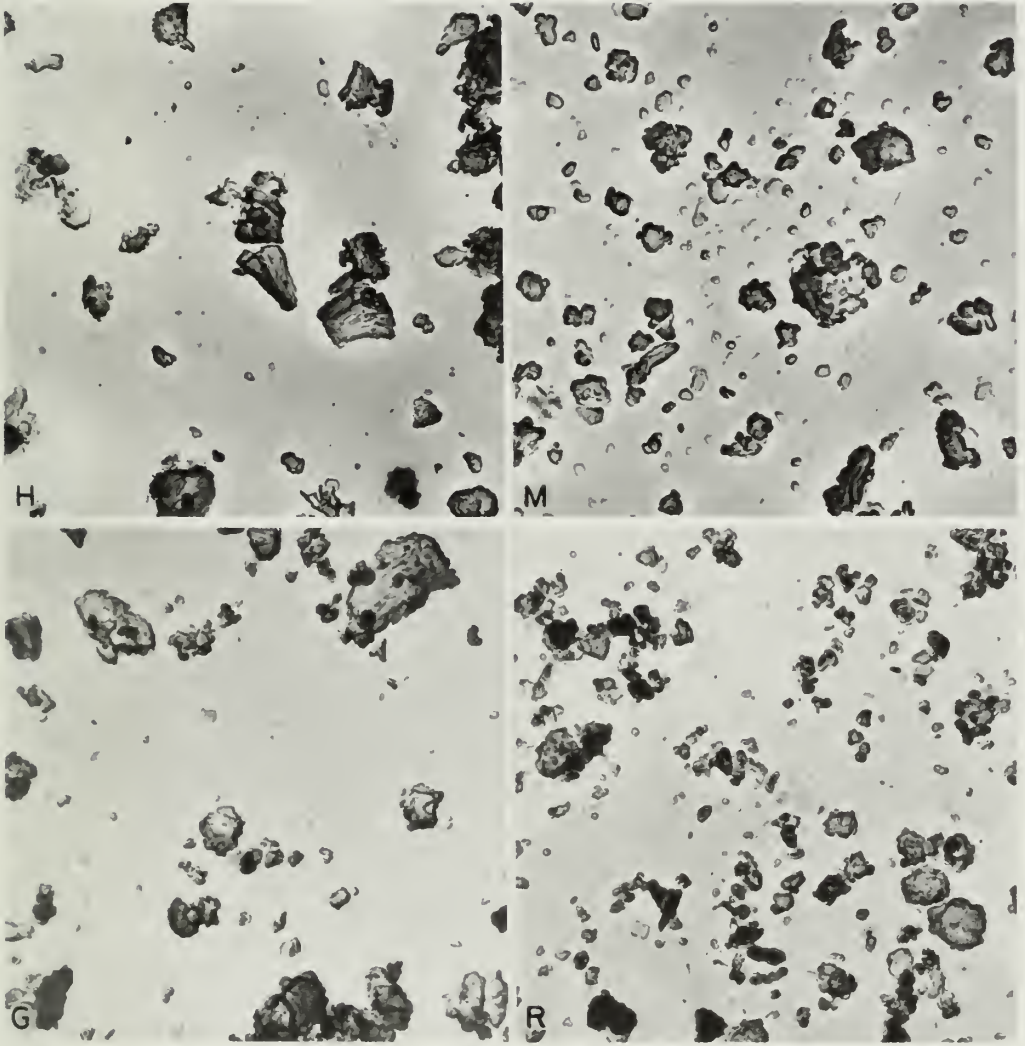
Table 6. - Composition of the Hydrates from X-Ray Patterns  
(as received)

Hydrate	$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{MgO}$	$\text{CaO}$	$\text{CaCO}_3$	Dolomite
H	P	N.P.	N.P.	N.P.	N.P.	N.P.
M	P	P	N.P.	N.P.	N.P.	P
R	P	P	P	N.P.	P	N.P.
G	P	P	P	N.P.	P	N.P.

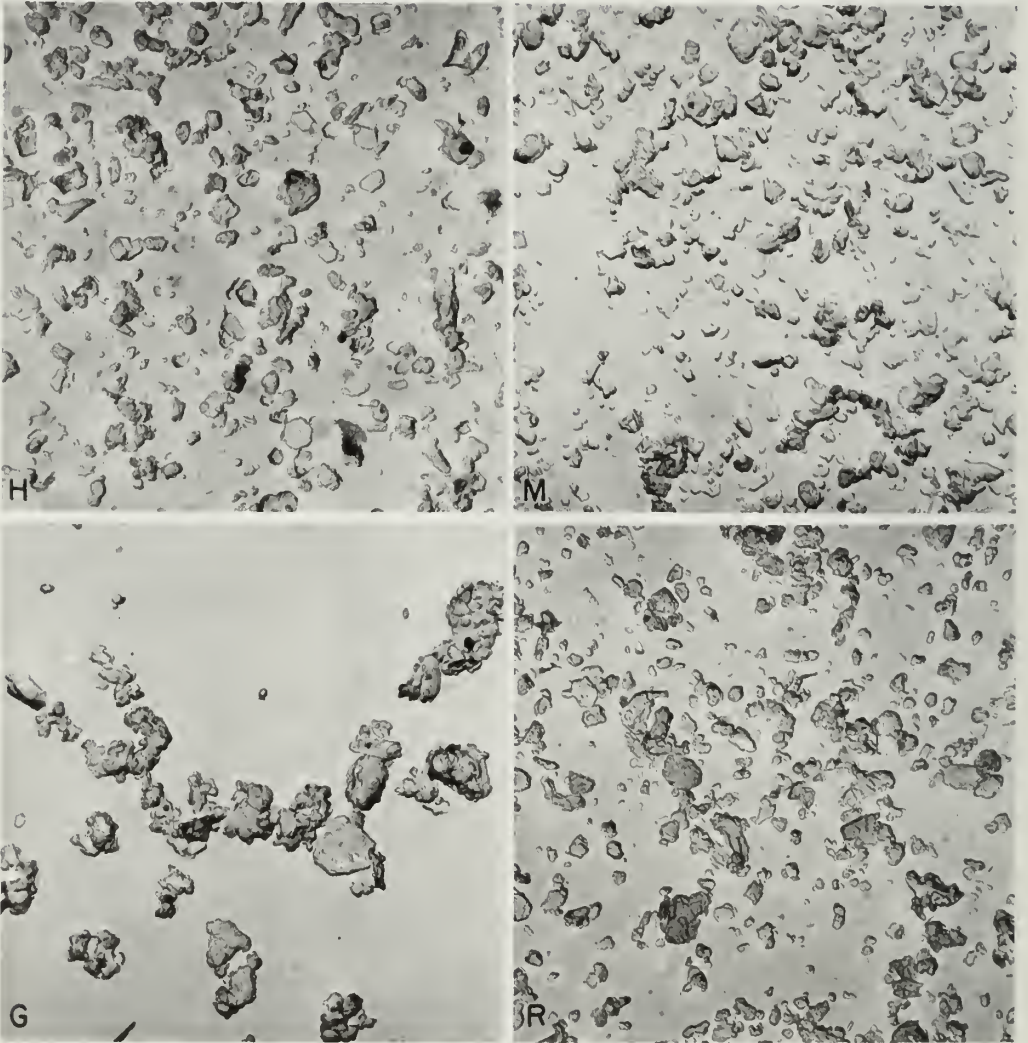
P = component is present.

N.P. = component is not present.





ELECTRON MICROGRAPHS OF HYDRATES H, M, G, AND R. FRACTIONS LESS THAN 2.2 MICRONS. UNSOAKED (X7000).



ELECTRON MICROGRAPHS OF HYDRATES H, M, G, AND R. FRACTIONS LESS THAN 0.86 MICRONS. UNSOAKED (X7000).

The validity of the results given in table 5, from ignition-loss data, for hydrate H is considered fairly reliable because no  $\text{CaCO}_3$  was detected in the X-ray diffraction pattern. However, for hydrates M, R, and G a small amount of carbonate was detected in the X-ray pattern. The compositions calculated from the ignition-loss data are therefore in error, but it is believed that the amount of error is not more than a few percent.

From the X-ray and ignition-loss data it is seen that hydrate H is a very high-calcium lime, whereas the other three hydrates are dolomitic. Hydrate M is a very highly hydrated dolomitic lime containing a small amount of residual dolomite, but hydrates R and G are only partially hydrated inasmuch as both show a considerable amount of  $\text{MgO}$ . They do not show any residual dolomite.

In an effort to learn something about the composition of the various size fractions collected during the course of measuring the particle-size distribution, X-ray patterns of some of the size fractions for hydrates M, R, and G were made. The results are given in table 7.

The results given in table 7, in spite of considerable variation, indicate that the proportion of  $\text{Mg(OH)}_2$  tends to increase in the finer fractions (less than 1 micron) and that the  $\text{MgO}$ ,  $\text{Ca(OH)}_2$ , and dolomite (in hydrate M) show smaller concentrations in the fine fractions. One may infer that, of the components present in these dolomitic hydrates,  $\text{Mg(OH)}_2$  tends to be the finest, and that the residual dolomite,  $\text{Ca(OH)}_2$  and  $\text{MgO}$ , tend to be somewhat coarser. These results are more striking when the diffraction patterns are compared directly, but the above data adequately show the general trends.

#### DISCUSSION OF RESULTS

The results suggest a reason for the particle-size distribution curves of hydrates M, R, and G. Hydrate M contains a larger proportion of  $\text{Mg(OH)}_2$  than either R or G, and, inasmuch as  $\text{Mg(OH)}_2$  tends to be quite fine, this may be the reason that hydrate M contains a considerably greater proportion of very fine particles as compared to hydrates R and G.

Hydrate H is essentially a pure  $\text{Ca(OH)}_2$ , and as seen from table 2 both its soaked and unsoaked plasticities are low. Hydrate M is highly hydrated, and its unsoaked and soaked plasticities are high. Hydrates R and G both have only a fraction of their  $\text{MgO}$  converted to  $\text{Mg(OH)}_2$  during their manufacturing process, and they show a low unsoaked plasticity. However, on soaking, both show large increases in plasticity.

Hydrate M contains a much higher proportion of  $\text{Mg(OH)}_2$  than R and G, and the  $\text{Mg(OH)}_2$  tends to be finer than the other components in these hydrates; therefore, the higher unsoaked plasticity of hydrate M, as compared to R and G, may be due to a greater proportion of fine particles in hydrate M. The surface area of unsoaked hydrate M is somewhat larger than that of hydrates R and G, again indicating that M may have a higher proportion of particles of finer sizes. Plate 1 also shows that M may have a slightly greater proportion of very fine material than have R and G and that the shape of the particles in hydrate M differ from those of H, R, and G. The flat, sheet-like particles of M, as compared to the massive, coke-like pieces in H and G, may help give M a greater unsoaked plasticity.

An explanation of the increase in plasticity on soaking hydrates R and G is not so clearly indicated. If we accept the compositions given in table 5 on the basis that during soaking very little additional carbonation takes place (which is known to be true from data to be reported at a later date), then, even though the

Table 7. - X-ray Identification and Estimates of Concentration of Components in Various Size Fractions for Hydrates M, R, and G Unsoaked

Hydrate	Size fraction	Intensity of X-ray lines* (cm. above background)					Ratio	
		(1) Ca(OH) <sub>2</sub>	(2) Dol.	(3) Mg(OH) <sub>2</sub>	(4) Mg(OH) <sub>2</sub>	(5) MgO	Int. Mg(OH) <sub>2</sub> (18.5°)	Int. Ca(OH) <sub>2</sub> (18.0°)
M	as received	7.5	5.4	5.9	5.8	0		.79
	-20μ	6.7	2.3	5.0	5.4	0		.75
	-2.2μ	7.8	0.8	6.9	7.3	0		.88
	-1.2μ	7.4	0.0	7.4	7.9	0		1.0
	-0.46μ	5.6	0.0	6.8	7.0	0		1.22
R	as received	7.3	0	3.1	3.1	7.8		0.42
	-60μ	6.0	0	-	2.5	5.8		-
	-20μ	6.9	0	3.1	2.5	7.7		0.45
	-4μ	7.8	0	4.2	3.9	7.7		0.54
	-2.2μ	5.8	0	3.2	3.9	5.4		0.56
	-0.86μ	6.4	0	5.4	5.7	5.0		0.85
G	as received	7.0	0	2.8	2.5	7.5		0.40
	-60μ	6.3	0	3.1	2.6	7.0		0.49
	-20μ	6.4	0	3.0	2.2	7.0		0.47
	-4μ	7.6	0	3.9	2.9	8.0		0.52
	-2.2μ	7.6	0	4.8	4.8	7.8		0.63
	-0.86μ	6.5	0	5.5	5.7	5.0		0.85

- \* 1. Ca(OH)<sub>2</sub> line at 18.0° in 2θ.  
 2. Dolomite line at 30.9° in 2θ.  
 3. Mg(OH)<sub>2</sub> line at 18.5° in 2θ.  
 4. Mg(OH)<sub>2</sub> line at 37.8° in 2θ.  
 5. MgO line at 42.8° in 2θ.

absolute values may be in error, the soaked and unsoaked compositions may be compared. Both hydrates R and G show an increase in the amount of  $\text{Mg}(\text{OH})_2$ , which was also substantiated by comparing the X-ray patterns of the soaked and unsoaked hydrates. Since  $\text{Mg}(\text{OH})_2$  tends to be fine, the increase in the plasticity of R and G after soaking may be due to an increased proportion of fine particles. Both R and G show somewhat larger surface areas after soaking, which indicates that the particles may be somewhat finer.

The small increase in the plasticity of hydrate M after soaking may be due to the fact that there is but little free  $\text{MgO}$  available for conversion to  $\text{Mg}(\text{OH})_2$  on soaking, therefore its maximum plasticity is nearly developed in a matter of minutes after tempering with water.

### CONCLUSIONS

It may be concluded that the three dolomitic limes have similar plasticities when soaked. The highly hydrated Illinois dolomitic lime developed nearly its maximum plasticity in a few minutes after tempering with water; the others required an extended soaking period before maximum plasticity developed. This is probably due to differences in the methods of manufacture.

The data relating to high-calcium hydrate containing no  $\text{Mg}(\text{OH})_2$  indicate that pure  $\text{Ca}(\text{OH})_2$  has intrinsically low plasticity. However, when some  $\text{Mg}(\text{OH})_2$  is present in the hydrate, the plasticity rises sharply. This may indicate that  $\text{Mg}(\text{OH})_2$  is a high-plasticity material. The higher Emley plasticity imparted by the presence of  $\text{Mg}(\text{OH})_2$  may be due, at least in part, to the tendency of this material to form a large proportion of fine particles.

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