Dr. J. Convey

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AN INVESTIGATION OF BY-PRODUCT GYPSUM FROM A WET-PROCESS PHOSPHORIC ACID PLANT AT PORT MAITLAND, ONTARIO

by

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MINERAL PROCESSING DIVISION

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SUMMARY OF RESULTS

The results of this investigation indicate that by-product gypsum from Electric Reduction Company's Port Maitland wet-process phosphoric acid plant is of potential use as raw material for the manufacture of plaster and plaster products. Several of the plasters made with this material satisfied ASTM strength specifications. Of the three gypsum types submitted - Lagoon, Filter, and Filter Cake - the latter two appeared to possess superior strength when made into plaster. However, because of carbon impurity and resulting plaster discoloration, both samples required thorough washing which, because of the fine nature of this material, was difficult and time-consuming. Drying, because of the danger of calcining, had to be conducted below 150°F and resulted in the formation of gypsum cake, which was undesirable because it then had to be reduced to its original fine size. The use of log washers, spiral classifiers, and wet cyclones, with fluo-solid roasting would, of course, greatly facilitate washing and drying.

Removal of the +48 mesh fraction prior to calcining resulted in improved strength characteristics. Pebble mill grinding greatly improved the mixing and stirring qualities of the plaster, but resulted in decreased compressive strength. Additional work on the grinding of this material both before and after calcination is recommended to further investigate the effect of grinding on plaster strength.

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INTRODUCTION

During the latter half of 1961, Electric Reduction Company of Canada, Limited, began the production of wet-process phosphoric acid at its Port Maitland, Ontario, plant. A major by-product of the operation is synthetic gypsum, which currently is produced at a rate of 300,000 tons per year. Dr. J. D. McGilvery, manager of Electric Reduction Company's Central Laboratories in Toronto, contacted the Mines Branch early in 1962 requesting assistance in evaluating this material as a possible source of gypsum for use by the gypsum products industry of southern Ontario.

Currently there are two producing gypsum product plants in Ontario, one at Caledonia and the other at Hagersville. Each obtains its crude gypsum requirements from mines located at or near the plant site. Total consumption of crude by these plants is in the order of 400,000 tons per year. A third plant is being constructed near Clarkson, Ontario, by Western Gypsum Products Limited of Winnipeg. When completed, this plant probably will consume up to 150,000 tons of crude gypsum annually. Western Gypsum Products Limited now is investigating an underground gypsum deposit in the vicinity of Drumbo, west of Paris, Ontario, to determine whether this gypsum is satisfactory for use in plaster manufacture. However, this company also has shown considerable interest in the by-product gypsum currently produced at Port Maitland.

This investigation was undertaken to determine whether a satisfactory plaster, from the point of view of calcination and strength characteristics, could be produced with the by-product or synthetic gypsum from Port Maitland.

EXAMINATION OF SAMPLES

Three synthetic gypsum samples from Electric Reduction Company's Port Maitland plant, each weighing about 100 lb and each contained in two sealed metal drums, were received at the Mines Branch early in February. These were identified as Lagoon, Filter, and Filter Cake. A second sample of Lagoon gypsum was received late in April. To distinguish between the Lagoon samples, the first is referred to as Lagoon No. 1, and the second, Lagoon No. 2, in this report.

All samples contained considerable moisture, especially Lagoon No. 1, and all were composed of extremely fine particles which were mostly 100 mesh in size. The individual grains of gypsum were tabular. The coarser sizes, notably those above 48 mesh, generally were composed of compound grains and appeared to contain relatively large amounts of impurity. The only impurity specifically identified, apart from coloured gypsum, was quartz; however, all samples contained finely divided particles of a black mineral which probably was carbon.

The Filter and Filter Cake samples were distinctly grey in colour, whereas the Lagoon gypsum was white.

TEST PROCEDURE

The free moisture content was determined for each sample by drying overnight at 150°F. Portions of the dried Lagoon No. 1, Filter and Filter Cake samples were calcined in a 5 lb Soil Test laboratory warmer to determine whether calcination would result in any colour improvement and to obtain information about the setting characteristics of the calcined material.

Some colour improvement was noted, but the Filter and Filter Cake samples were badly contaminated with carbon, which floated on the surface of the plaster slurry and produced streaks of grey discoloration in the set plaster. All plasters, in particular that made from the Lagoon No. 1 sample, were spotted throughout with grey to black specks of mineral impurity.

In an attempt to improve the colour and to remove these dark mineral particles, small samples were screened on a 48 mesh sieve and the -48 mesh fractions treated in a Carpco magnetic separator. Magnetic separation removed a considerable portion of the dark particles. The -48 mesh, non-magnetic fractions were then water-washed, dried, and calcined. Only a few dark specks were observed in the set plaster and the Filter and Filter Cake plaster samples were whiter than those made with the unwashed material.

On the basis of this preliminary work the Filter and Filter Cake gypsum samples were thoroughly washed prior to calcining in the 50 lb gypsum kettle. Washing was performed in a 30 in. diameter by 11 in. deep concrete-batch-mixer. The washing cycle consisted of adding about 20 gal of water to 100 lb of gypsum, agitating it for about 5 min, allowing it to settle for 10 min, and siphoning the water. The siphoned water was settled in large tubs for 20 min and the small amount of recovered gypsum returned to the mixer. Each 100 lb sample required continuous washing over an 8 hr period. Upon completion of the washing cycle the samples were dried at 150°F in electric ovens.

Initially, four calcining tests were conducted in the 50 lb kettle. The first was with 50 lb of the Lagoon No. 1 gypsum in its moist, as-received, condition to determine whether drying as well as calcining could be oonducted in the kettle. Following this, samples of the oven-dried Lagoon No. 1 gypsum, and the washed, oven-dried samples of Filter and Filter Cake were screened on a 48 mesh sieve and the -48 mesh fractions were calcined. The samples were then cooled and tested for consistency, time-of-set, and compressive and tensile strength as per standard ASTM methods.

Upon completion of the above test a sample of the Lagoon No. 2 gypsum was dried and screened on a 20 mesh sieve. The -20 mesh material was divided into two equal samples. The +48 mesh material was removed from one and discarded and the remaining -20 and -48 mesh samples were reduced to 100 mesh by a micro pulverizer and separately calcined. The object of these tests was to determine whether removal of the coarse, +48 mesh material, which appeared to contain a large percentage of mineral impurity, would result in stronger plaster.

To determine whether grinding following calcining would have a beneficial strength effect, two plaster samples, one consisting of the -20 and -48 mesh portions of Lagoon No. 2 in the ratio 1:3, the other of a 1:1 mixture of Filter and Filter Cake plaster, were selected and one-half of each sample was ground in a pebble mill for 15 min using 6 lb of pebbles to 1 lb of plaster. The ground and unground samples were then tested for consistency, time-of-set, and strength.

Data pertaining to the above tests follow in summary form in Tables 1 to 5. Also included are calcining curves for each of the six samples calcined in the 50 lb kettle.

RESULTS

The free moisture contents of the gypsum samples follow in Table 1. Sieve analyses of the dry gypsum samples are also included.

TABLE 1

Free Moisture and Sieve Analyses

Gypsum Sample	Free Moisture %	Mesh Fractions, Wt %					
		+35	-35+48	-48+65	-65+100	-100	Total
Lagoon No. 1	24	0.3	0.6	4.3	19.5	75.3	100.0
Filter	15	-	0.2	1.3	9.5	89.0	100.0
Filter Cake	22	-	0.3	1.1	6.6	92.0	100.0
Lagoon No. 2	9	1.3	0.4	1.7	15.7	80.9	100.0

The approximate gypsum content of various mesh sizes of Lagoon No. 2, based on water loss at 450°F, was determined. Results follow in Table 2.

TABLE 2

Gypsum Content, Lagoon No. 2 Sample

Mesh Size	Wt %	Gypsum Content Wt %
+20	0.7	-
-20+28	0.3	72.4
-28+35	0.3	71.5
-35+48	0.4	77.7
-48+65	1.7	88.5
-65+100	15.7	90.8
-100+150	22.1	94.1
-150	58.0	97.4
Total	100.0	

The percentage +48 mesh and the percentage of magnetics in the -48 mesh fraction, removed from typical gypsum samples in an attempt to improve colour or whiteness, follow in Table 3.

TABLE 3

Percentage +48 and Percentage Magnetics in -48 Mesh Fraction

Gypsum Sample	% +48 mesh	% Magnetics in -48 mesh
Lagoon No. 1	1.0	3.7
Filter	0.2	0.6
Filter Cake	3.3	1.2

The Optical whiteness and approximate time-of-set of typical samples calcined in the small Soil Test warmer during preliminary work are shown in Table 4.

TABLE 4

Optical Whiteness and Time-of-Set

Gypsum Sample	Optical Whiteness % (1)			Time-of-Set (min)
	Gypsum	Plaster of Paris	Set Plaster	
Lagoon No. 1				
Head,	75			
Head, calcined		84	82	15
Non mag portion of -48 mesh, calcined		83	80	15
Filter				
Head	69			
Head, calcined		78	77	4½
-48 mesh, washed, calcined		82	86	5
Non mag portion of -48 mesh, washed, calcined		83	86	4½
Filter Cake				
Head	67			
Head, calcined		67	71	6
-48 mesh, washed, calcined		79	78	8
Non mag portion of -48 mesh, washed, calcined		82	81	11

(1) Measured with a Densichron optical density meter adjusted to read 100% with magnesium carbonate standard.

Table 5 summarizes the results of tests conducted on plaster made with Lagoon No. 1 gypsum by calcining samples both as received (wet) and after drying and removal of the +48 mesh fraction, as well as on plaster made with dry samples of -48 mesh Filter and Filter Cake gypsum in a 50 lb laboratory kettle. Results of calcining tests conducted on two samples of Lagoon No. 2 gypsum that had been reduced to -20 mesh and sized to -20 and -48 mesh prior to reduction to 100 mesh also are included and, in addition, the results of comparative tests made on unground and pebble mill ground samples of Lagoon No. 2, and a mixture of Filter and Filter Cake plaster.

TABLE 5

Consistency, Time-of-Set, and Strength Data

Sample	Treatment Prior to Calcining or Testing	Testing Consistency[1]		Time of Set (min)		Compressive Strength (lb per sq in.)		Tensile Strength (lb per sq in.)	
		Gauging[2]	Neat[3]	Gauging[2]	Neat[4]	Gauging[2]	Neat[3]	Gauging[2]	Neat[3]
Gypsum									
Lagoon No. 1 - wet	as received	58	85	23	23	2079	1208	216	83
Lagoon No. 1 - dry	+48 mesh removed	70	90	45	30	975	720	188	126
Filter	+48 " "	75	88	11	12	1788	1641	239	80
Filter Cake	+48 " "	75	95	12	10	1463	1184	185	93
Lagoon No. 2	+20 removed, -20 reduced to 100 m	66	76	11	9	950	825	175	80
Lagoon No. 2	+48 " , -48 " " "	66	76	11	9	1215	1340	201	172
Plaster of paris									
Lagoon No. 2	100 mesh, no grinding	65		9		975		154	
Lagoon No. 2	ground in pebble mill	65		9		755		179	
Filter + Filter Cake	100 mesh, no grinding	75		10		1103		177	
Filter + Filter Cake	ground in pebble mill	75		8		970		199	
ASTM Minimum Strength Specifications						1200	750		

(1) Water, in ml, required for each 100 g of plaster of paris in mixture
(2) Plaster of paris, no sand
(3) Plaster of paris and Ottawa sand in ratio 1:2
(4) Plaster of paris and Ottawa sand in ratio 1:3

FIGURE I

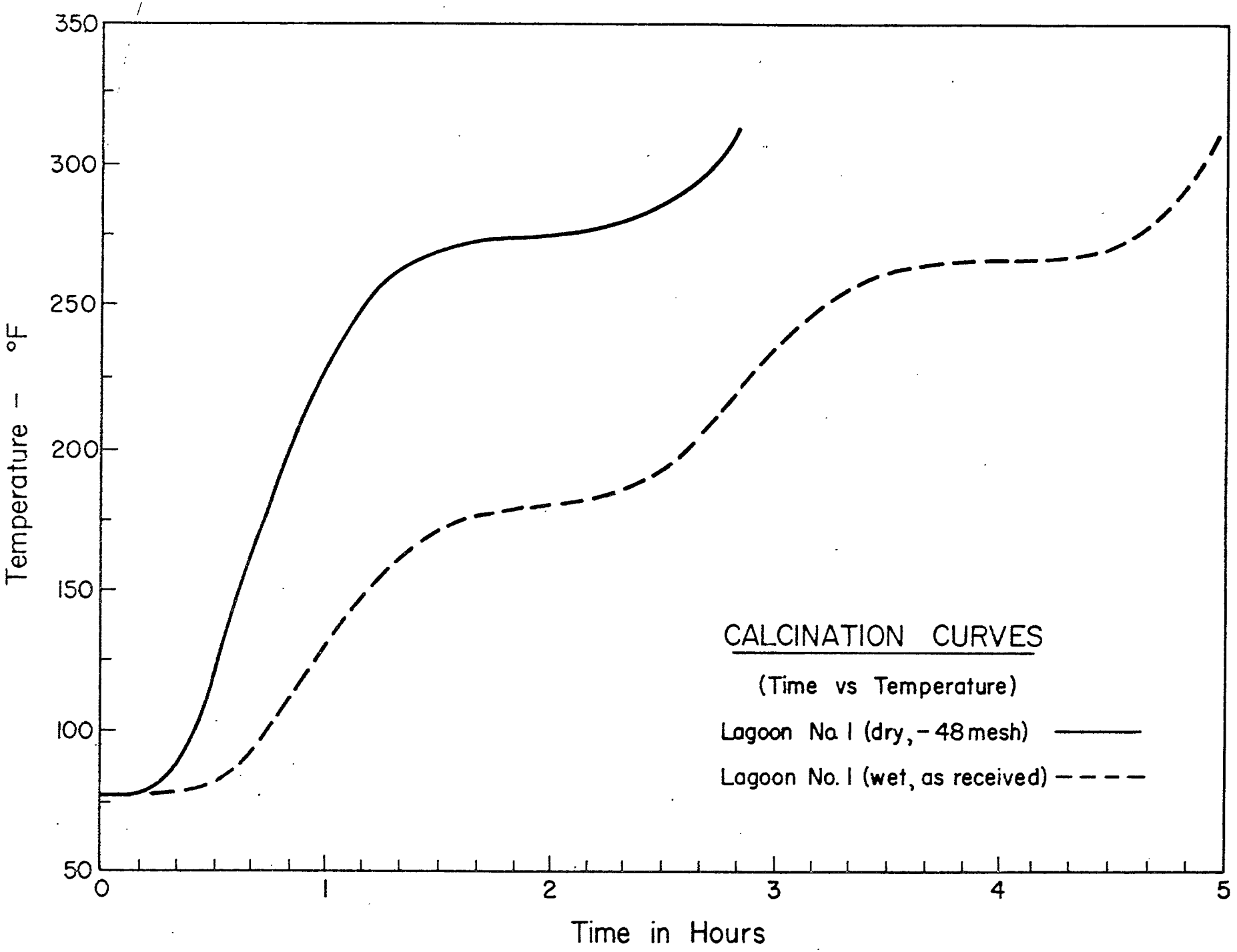

350
300
250
200
150
100
50
Temperature - °F
0
1
2
3
4
5
Time in Hours
CALCINATION CURVES
(Time vs Temperature)
Lagoon No. 1 (dry, - 48 mesh)
Lagoon No. 1 (wet, as received)

FIGURE II

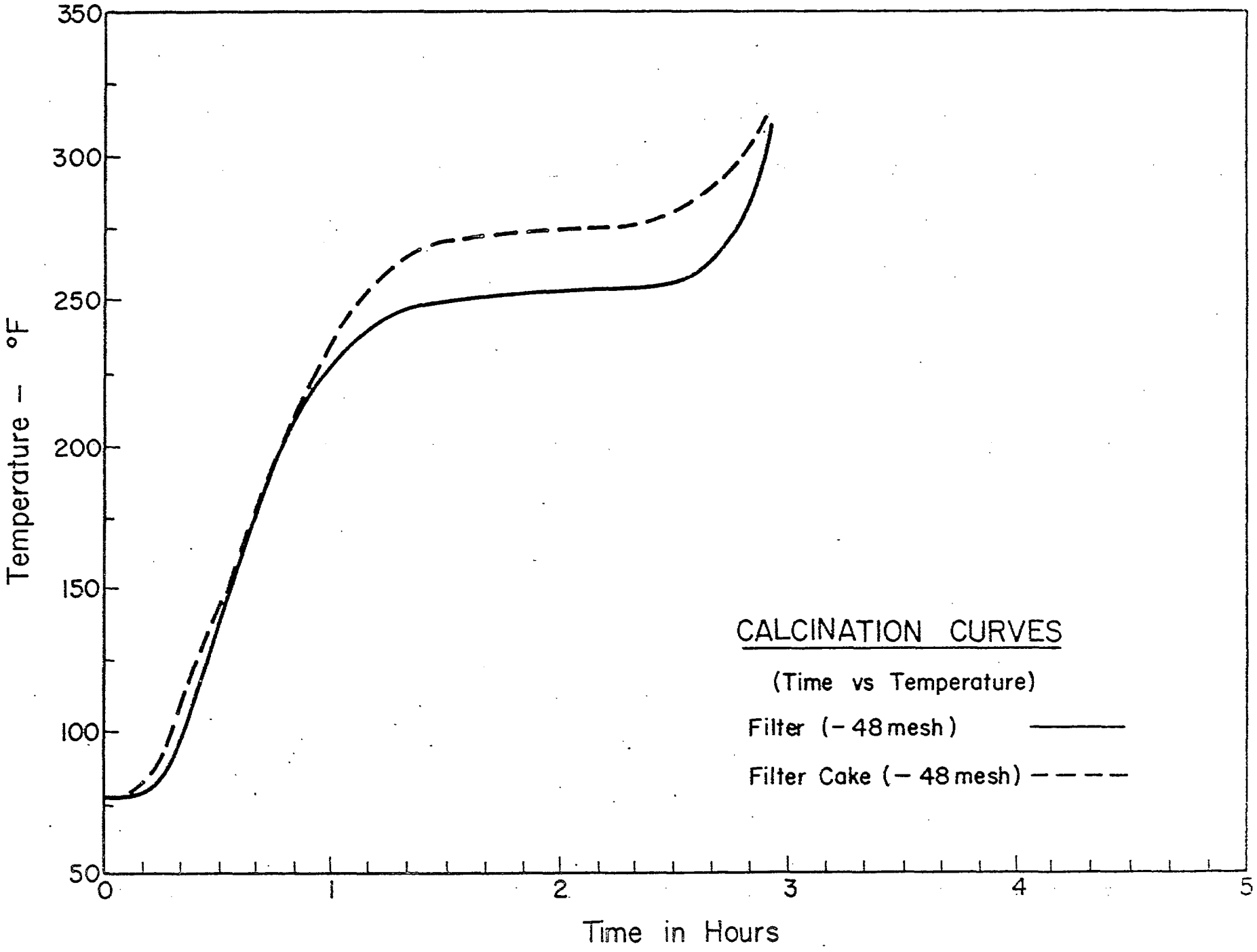
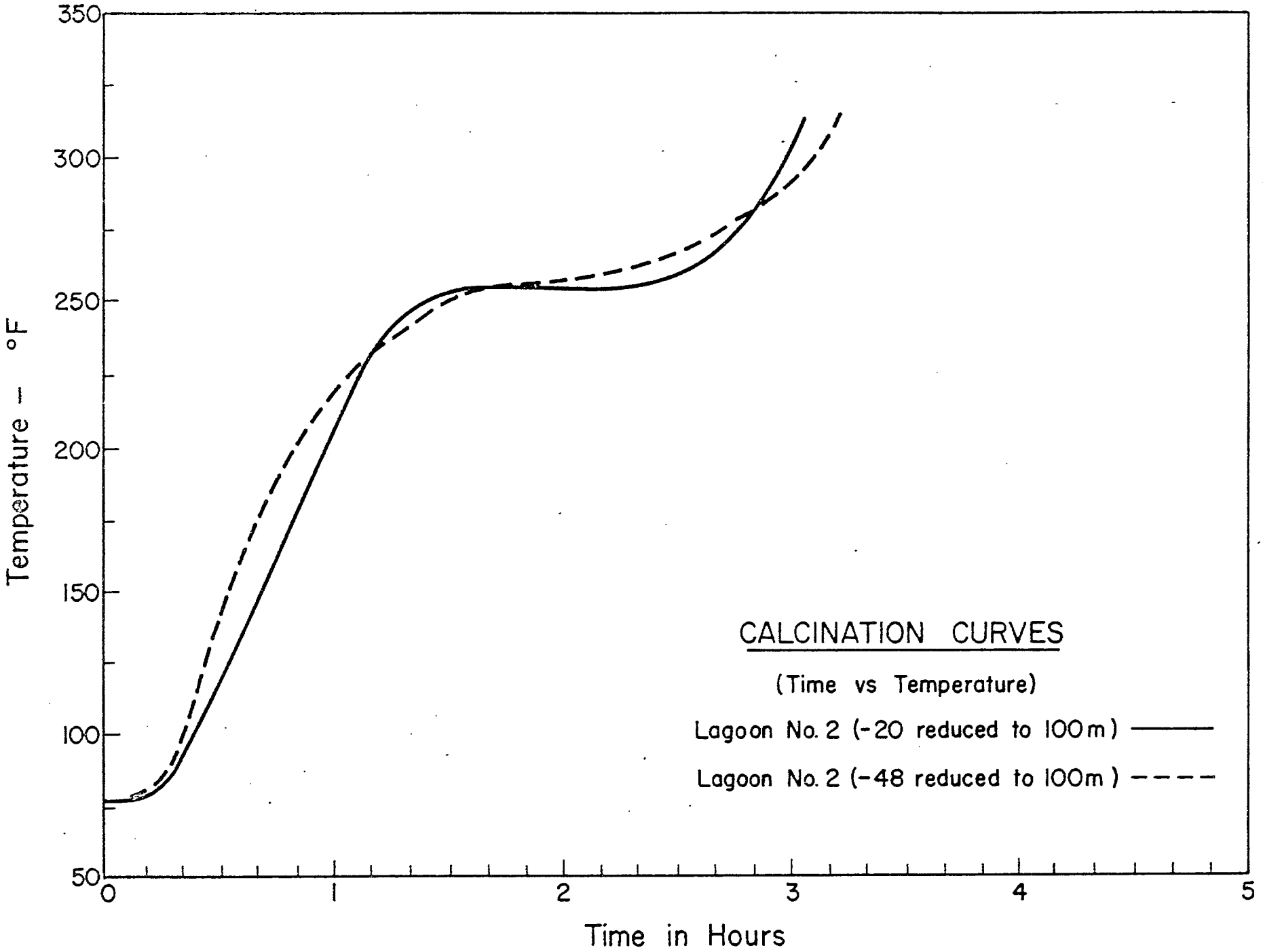

350
300
250
200
150
100
50
Temperature - °F
0
1
2
3
4
5
Time in Hours
CALCINATION CURVES
(Time vs Temperature)
Filter (- 48 mesh)
Filter Cake (- 48 mesh)

FIGURE III


350
300
250
200
150
100
50
Temperature - °F
0
1
2
3
4
5
Time in Hours
CALCINATION CURVES
(Time vs Temperature)
Lagoon No. 2 (-20 reduced to 100m)
Lagoon No. 2 (-48 reduced to 100m)

OBSERVATIONS

Preliminary tests indicated that some colour improvement resulted with calcination alone, but that washing prior to calcining resulted in marked colour improvement. Samples of the Filter and Filter Cake gypsum that were calcined without washing were distinctly grey in colour and, when water was added, a black scum was observed floating on the surface of the plaster slurry. This scum produced streaks of grey discoloration in the set plaster. The optical whiteness values listed in Table 4 give some indication of the colour improvement obtained by water washing and calcination. Removal of the +48 mesh fraction followed by magnetic separation of the -48 mesh material reduced the number of black grains of mineral impurity, especially in the Lagoon No. 1 sample. However, removal of these grains from the Lagoon gypsum was not obligatory as they did not produce grey discoloration and hence were not considered detrimental in the plaster product.

The initial test conducted on a moist, as-received, sample of the Lagoon No. 1 gypsum in the 50 lb kettle was interesting. The moist gypsum did not act favourably in the kettle but was very stiff, would not mix properly and tended to adhere to the kettle side. In addition, because of the free moisture, this sample required 5 hours for calcination as compared with samples that were dried prior to calcining, which required only $2\frac{1}{2}$ to 3 hours. This is illustrated by Figure 1, which shows two, time-temperature calcination graphs, one for the wet Lagoon sample, the other for the dry Lagoon sample. The calcined product formed with the wet sample contained a small quantity of lump material which was up to 1 in. in size. These lumps were removed in a 3 mesh sieve and the +3 and -3 mesh fractions checked for water content. The -3 mesh material contained only 6.8 percent moisture, whereas the +3 mesh lumps contained over 10 percent, indicating that these lumps probably had picked up part of the moisture driven off during calcination. This moisture, upon cooling of the calcined gypsum, would form set plaster which would accelerate the set and probably reduce the strength of plaster made with this material. Because of this the remaining samples were oven-dried before calcining. To avoid calcination, drying had to be carried out below 150°F and, because of the finely divided nature of the gypsum, drying required considerable time, usually 2 to 3 days in the electric oven. In addition, the gypsum tended to cake during drying and had to be broken up prior to calcining. This was done by hand and by forcing it through a 14 mesh sieve followed by a 48 mesh sieve.

The Filter and Filter Cake gypsums required washing prior to drying. Each 100 lb sample required a full 8 hr for washing as per the procedure described earlier.

Careful analysis of the data in Table 5 indicates that many of the plaster samples meet ASTM compressive strength specifications. No specifications are listed for tensile strength but a tensile strength of 150 psi for gauging and 100 psi for neat is generally considered satisfactory.

The low consistency and relatively high compressive strength of Lagoon No. 1 (wet) gauging plaster probably was the result of its being calcined in a steam-saturated atmosphere, which typically results in low-consistency, high-strength plaster. The Lagoon No. 1 (dry) sample weighed only 27 lb and therefore did not properly fill the 50 lb kettle. Some over-calcination undoubtedly occurred and this would account for the relatively long set and low compressive strength.

It is interesting to note that Lagoon No. 2, -48 reduced to 100 mesh, plaster has greater strength than Lagoon No. 2, -20 reduced to 100 mesh, plaster. The superior strength of the former can perhaps be attributed to the fact that the -20+48 mesh fraction, even although it represented only 1 percent of the total weight, contained only 75% gypsum, whereas the -48 mesh portion contained over 95% (Table 2).

Pebble mill grinding greatly improved the mixing characteristics of the calcined gypsum which, prior to grinding, tended to be somewhat stiffer and more difficult to mix than regular plaster of paris. However, the ground product was weaker in compression although stronger in tension than the unground samples (Table 5). Pebble mill grinding prior to calcination might result in better mixing characteristics and greater strength. Most gypsum companies reduce the gypsum to 100 mesh in roller mills prior to calcining. The calcined product, if to be used as wall plaster, is lightly ground in ball mills. This produces a flake-like grain that has superior mixing and spreading characteristics.

The material utilized for plaster manufacture on a production basis probably would be similar to the Filter and Filter Cake samples. Some beneficiation would be required since this material is too dirty as produced for use in the gypsum products industry. The following steps are suggested:

1. Thorough water washing;
2. Removal of the +48 mesh material and slimes;
3. Drying.

Thorough water washing is required to free the finely divided black material (carbon) that causes grey discoloration in the plaster. Washing could be performed in log washers, spiral classifiers, or in large tanks with suitable devices for agitation. Slimes removal could be accomplished by wet cyclone separators and the +48 mesh material could be removed by wet screening before or after washing.

The moisture content of this material should be reduced to less than 2 percent prior to calcining. Initially a substantial reduction of the moisture content could be achieved by atmospheric drying in large storage piles, although some caking undoubtedly would occur. The balance of the moisture could then be removed by carefully controlled fluidized bed roasting at temperatures below 150°F.

This material would, of course, require reduction to 100 mesh for use in gypsum products, but this operation could best be performed at the gypsum plant.

CONCLUSIONS

The results of this investigation, on the basis of the samples received, indicate that by-product gypsum from the Port Maitland phosphoric-acid plant, with beneficiation, can be utilized to produce plaster that meets ASTM specifications for strength, prior to grinding. Grinding to 100 mesh resulted in a reduction of the strength, hence further detailed investigation of the effect of grinding, before and after calcination, is required.

This material is of potential interest for plaster manufacture. However, its acceptance by the gypsum products industry would depend not only on its initial cost but also on its performance during the manufacture of plaster and plaster products and during subsequent application of these products in the building construction industry. Further investigation of this material is therefore recommended. This investigation preferably should be conducted by interested gypsum companies and should include production-scale calcination tests as well as exhaustive tests on products made from the calcined material.