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AN EVALUATION OF GYPSUM RESIDUE FROM PORT MAITLAND, ONTARIO, FOR GYPSUM PRODUCTS MANUFACTURE

by

R. K. COLLINGS AND G. A. BROWN

MINERAL PROCESSING DIVISION

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R.K. Collings* and G.A. Brown**

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SUMMARY OF RESULTS

Based on the sample received, the results of this investigation indicate that gypsum residue from Electric Reduction Company's phosphate fertilizer plant at Port Maitland, Ontario, could be used as a substitute for natural gypsum in gypsum products manufacture, in particular wallboard and lath.

This material was more difficult to process than natural gypsum because of residual acid and other impurities; however, processing was nonetheless relatively simple. Initial treatment included wet screening to remove the more impure plus 65-mesh fraction and water washing to remove much of the residual acid. Calcination of the minus 65-mesh gypsum presented few problems. The product, ground either before or after calcining, was acidic and required neutralization during the formation of test plaster and wallboard samples. Various bases, including sodium, ammonium, and calcium hydroxides, were used for neutralization.

The test products formed generally compared favourably with those made with natural gypsum when tested as per CSA specifications, especially with respect to plaster strength and bond to paper (e.g., in wallboard test specimens).

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INTRODUCTION

By-product gypsum residue is produced during wet-process phosphoric acid manufacture by the action of sulphuric acid on ground phosphate rock. This material is acidic, finely divided and, on a dry basis, usually contains more than 90 per cent gypsum. Common impurities are unreacted phosphate rock, calcium fluoride and quartz. Production by phosphate fertilizer facilities in British Columbia, Alberta, Manitoba, Ontario, Quebec and New Brunswick currently exceeds 2 million tons annually.

Although phosphoric acid gypsum is or has been utilized for gypsum products in certain countries, e.g., Japan, Britain and Germany, it is not so used on this continent where readily accessible and well-located natural gypsum deposits have been, and undoubtedly will continue to be, the prime source material for many years to come. Nevertheless, several factors - the cost of maintaining disposal areas, the growing concern over land and water pollution, an increasing awareness of the need to conserve native mineral resources, and the possibility of recovering valuable contained phosphate - focus attention on the possible utilization of a portion of this material for gypsum products manufacture, especially where such material is available near gypsum products plants.

This present investigation is part of a larger Mines Branch program of the evaluation of gypsum residues from several areas in Canada for gypsum products manufacture. Although Port Maitland gypsum has been investigated by the authors on two previous occasions, in 1962 and in 1966 (Mines Branch Investigation Reports IR 62-67 and IR 67-69), it was decided to re-examine this material in light of process improvements developed during recent investigations of gypsum residues from other areas in Canada.

SOURCE AND DESCRIPTION OF SAMPLE

The gypsum residue sample used in this investigation, supplied by Electric Reduction Company of Canada, Ltd., was from its Port Maitland, Ontario, phosphoric acid plant. It weighed 190 lbs and was a composite of filter cake samples collected over a three-week period in August, 1970.

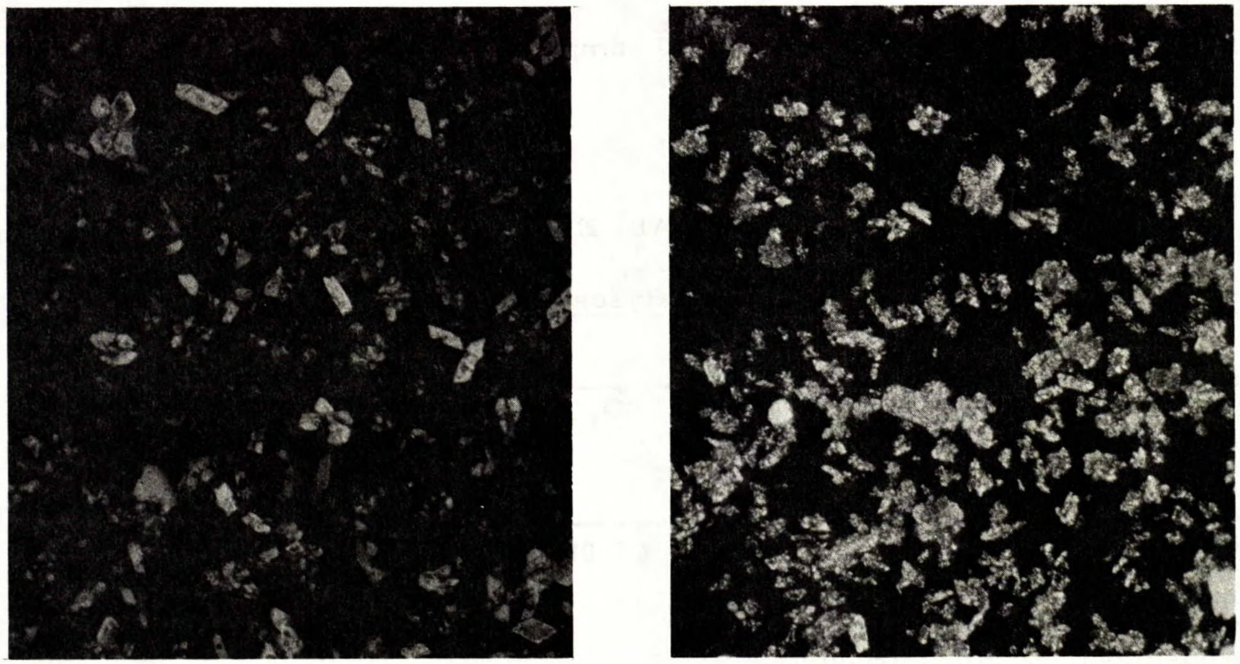
The sample was light brown in color, finely divided, and contained up to 25 per cent free moisture. The gypsum was in the form of crystal agglomerates. Impurities, largely concentrated in the plus 65-mesh fraction, were unreacted phosphate rock and quartz. The sample was acidic (pH = 3.5) due to residual phosphoric, sulphuric, and possibly hydrofluoric acids. The particle size distribution , determined by wet and dry screening, was as follows:-

TABLE 1

Sieve Analyses, Wt Per Cent

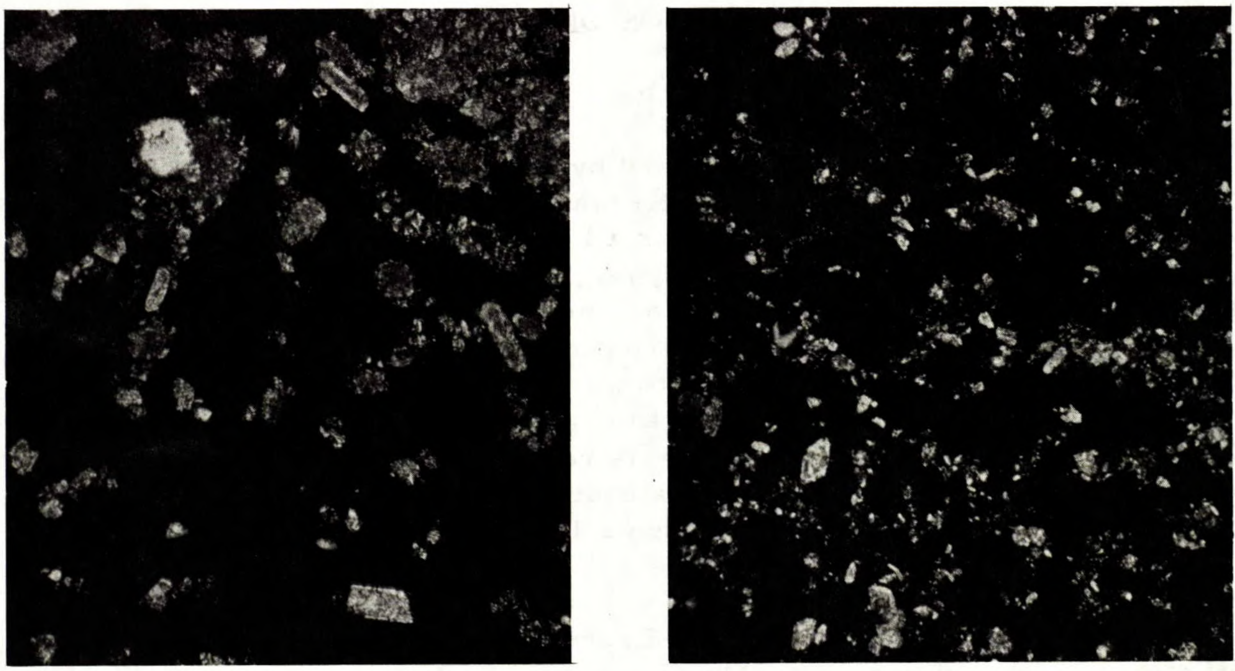
Mesh Size	Dry Basis	Wet Basis
+ 35	2.2	0.8
-35 + 48	3.4	0.7
-48 + 65	5.8	0.7
-65 + 100	13.0	7.0
-100 + 150	15.4	15.7
-150 + 200	24.4	24.6
-200	35.8	50.5
Total	100.0	100.0

The crystal habit of the gypsum and of the calcined products is illustrated in Figure 1.



Head sample, washed.

Minus 65-mesh, washed and calcined.



Minus 65-mesh, washed, calcined, and ground to 5000 cm^2/g.

Minus 65-mesh, washed, ground to 5000 cm^2/g, and calcined.

Figure 1. Port Maitland gypsum and stucco products (enlargement 40X)

Chemical analyses of the head sample and the various products are shown in Table 2.

TABLE 2

Chemical Analyses - Wt Per Cent

Sample	CaO	SO_3	H_2O	F	P_2O_5		
					Water Sol	Water Insol	Total
Head	31.33	43.08	19.55	1.71	0.01	0.94	0.95
+ 65-mesh, wet screen				2.76	0.01	1.02	1.03
- 65-mesh, washed				1.50	0.01	0.81	0.82
- 65-mesh, calcined product			6.96	1.77	0.01	0.95	0.96

DESCRIPTION OF EQUIPMENT

A Benco reactor, manufactured by Bench Scale equipment Company of Dayton, Ohio and assembled by Hayward Gordon Limited, Malton, Ontario, was used at atmospheric pressure for all calcining tests. The calcining chamber is 6.5 in. in diameter by 8.5 in. deep and holds 5 to 6 lbs of gypsum. The chamber is heated by an enclosing insulated heating mantle. Temperature is controllable over a wide range by an external variac. The charge is stirred by a central shaft to which are attached two impeller blades, one at the bottom and the other 3 to 4 in. above. Speed of rotation is variable. The calcining temperature is recorded via thermocouple wells set in the cover of the reactor and extending down into the calcining zone. The calcined product is discharged through a 1-in. spout in the bottom of the unit.

Accessory equipment included screens, washing tanks, filter press, pH meter, and drying ovens. These standard items of laboratory equipment are not described in detail.

CALCINING AND PHYSICAL TESTS

Preliminary Treatment

Visual examination of the gypsum residue samples showed that the coarser, plus 65-mesh was generally of lower purity than the finer, minus 65-mesh fraction. The coarse fraction, which comprised only a small portion of the total weight, was removed by wet screening and discarded. The minus 65-mesh gypsum samples were then water-washed three or four times in an enamel pail, the gypsum being allowed to settle between washings and the water removed by siphon. Final pH values of from 5.4 to 6.2 were achieved. The samples were filtered and dried at 100°F overnight in an electric oven.

Calcining Tests

All calcining tests were made with the minus 65-mesh, washed gypsum, the product being ground before or following calcining to Blaine surface areas between 3087 and 5643 cm^2/g.

Calcining in the Benco reactor presented few difficulties. Approximately 2000 g of gypsum were used in each test. With the impeller speed set at 100 rpm and the variac at 80, a uniform rate of heating (1°C per min) and calcining was achieved. Calcining was continued over a 1.5-to 2.0-hr period to a maximum temperature of 160°C (Figure 2). Owing to the reactor's design, a ring-like build-up of partially hydrated plaster of paris formed in the upper, cooler portion of the reactor. This material, which represented less than 5 per cent of the weight of product,was discarded.

Physical Tests and Results

Water and various additives were mixed with the calcined product (stucco) to form a paste, and various physical tests including consistency, time of set, and compressive strength were made as per CSA, A82 series, Specifications for Gypsum Materials and Products. In addition, the fineness of the stucco, the pH of the paste, and the bond of the paste to wallboard paper were determined. The results of these tests are noted in Table 3.

The compressive strength of the calcined product, as tested with two parts by weight of standard Ottawa sand and neutralized with calcium hydroxide, was 1018 psi and, neutralized with sodium hydroxide, 806 psi compared to the 750 psi minimum specified by CSA Standard A82.22.

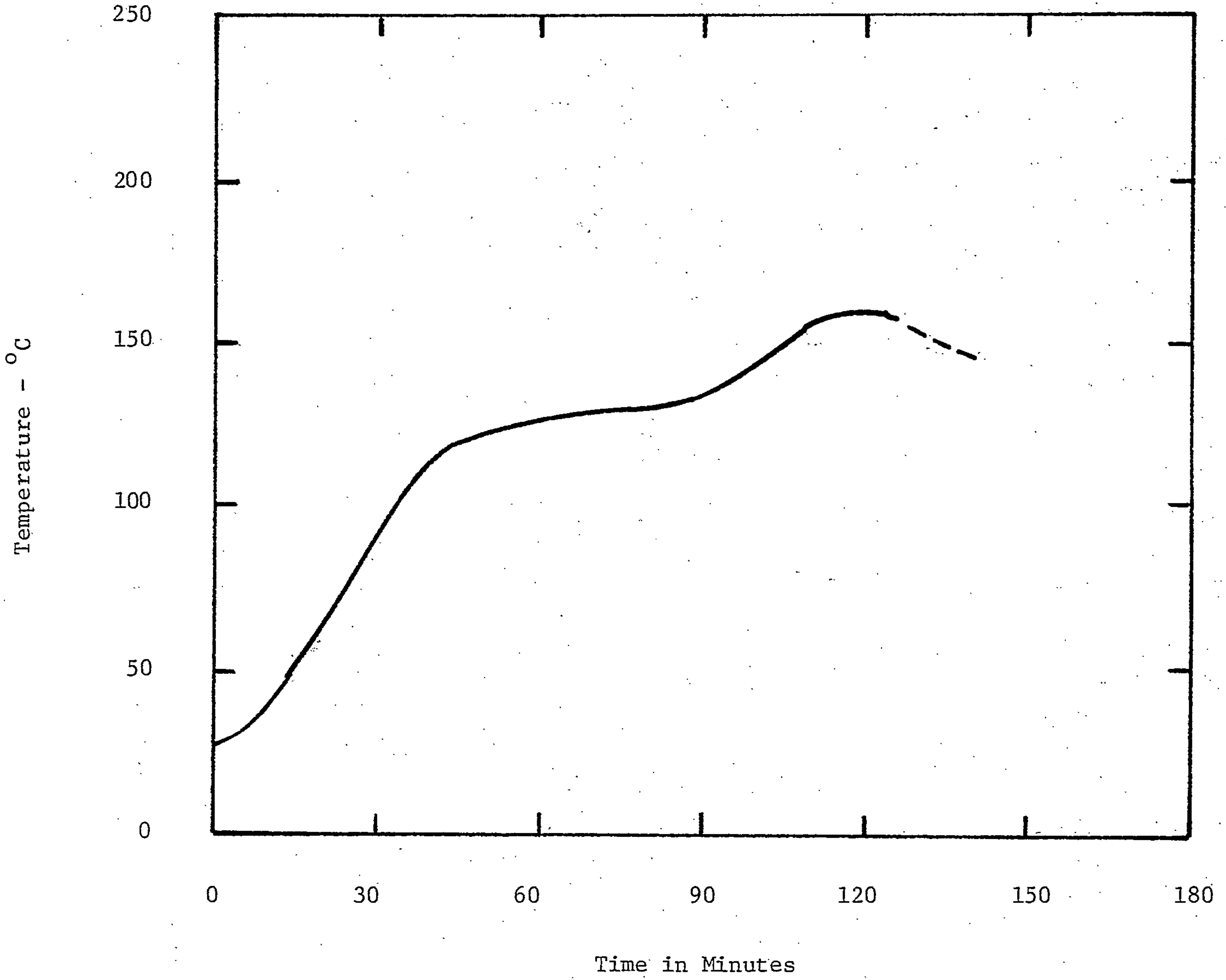


Figure 2 - Typical Calcining Cycle, Benco Reactor.

Characteristics of Stucco

The calcined product (stucco), in all tests, was more acidic than the reactor charge, presumably as a result of the release of acid occluded by the gypsum molecule. When mixed with water to produce a slurry of normal consistency, the stucco set very quickly to form plaster. The set was delayed by the addition of a small amount of commercial retarder - sufficient to allow time for proper mixing and pouring. It was observed that newly formed stucco set more rapidly than stucco that was aged for several months.

Neutralization of the stucco is desirable to prevent a possible reaction between the acid in the plaster and the surface finish (paint) or the enclosing paper (in wallboard). Neutralization was easily achieved by the addition of various bases including calcium and sodium hydroxides.

Bond Development

Bond or adherence to paper is perhaps the most critical aspect of the wallboard manufacturing process, especially when employing gypsum residue as a raw material. Bond to paper is dependent on a number of factors, e.g., crystal habit, surface area, impurities in the gypsum, additives, method of mixing and forming board, pH of stucco, etc. We believe that crystal habit (in part determined by impurities in the gypsum), neutralizing agent (type and quality used), and the amount of starch added are the most important from the standpoint of bond development.

Starch addition is necessary to ensure a satisfactory and permanent bond. Previous work by the authors indicated that the quantity required is related to both the surface area of the stucco and the reactivity of the starch with some of the neutralization agents employed. For example, an excess of sodium hydroxide will hydrolize starch and thus reduce its effectiveness as a bonding agent. Calcium hydroxide does not appear to thus degrade the starch. The best bond to paper was achieved with sodium hydroxide, the amount used being kept to a minimum (0.4 to 0.8 per cent) and added to the mixing water (containing starch and soap) just prior to forming a slurry with the dry stucco. This precaution was not necessary with calcium hydroxide. In most tests from 1 to 2 per cent starch was required for good bond development. (Table 3).

CONCLUSIONS

Based on the samples received, gypsum residue from Electric Reduction Company's phosphate fertilizer plant at Port Maitland, Ontario, could, by means of the process outlined in this report, be utilized as a substitute for natural gypsum in gypsum products manufacture, particularly gypsum lath and wallboard. Products fabricated in our laboratories during this investigation compare favourably with those made with natural gypsum, specifically with regard to setting characteristics, strength, and bond to paper.

RECOMMENDATIONS

It has been shown, in principle, that gypsum residue from Port Maitland, Ontario, can be used in gypsum products manufacture. This material may have some commercial application in gypsum products manufacture in southeastern Ontario, in areas where natural gypsum is not readily available or perhaps costly to obtain. We recommend that its use for this purpose be investigated by interested industrial groups on a pilot plant level. Figure 3 is a suggested flow sheet for processing this gypsum residue.

ACKNOWLEDGEMENTS

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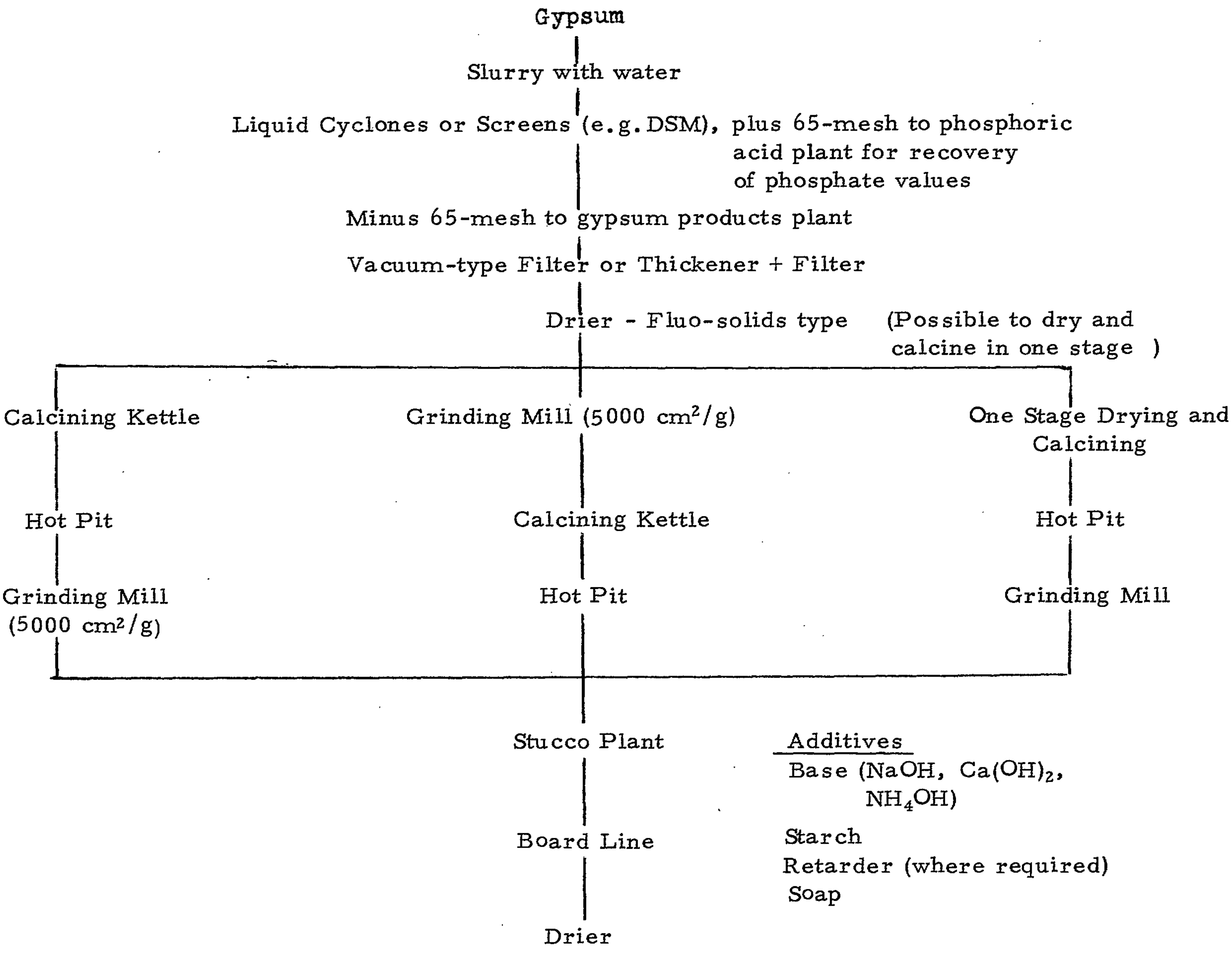

Figure 3 - Suggested Flow Sheet for Treatment of Gypsum Residue

TABLE 3

Test Data - Gypsum and Stucco Samples

		Grind			Calcining			Additives					pH						(5) Adherence		
Calcin Test No.	Stucco Test	Unground	Ground	(1) Surface Area cm^2/g	Unit	Time min.	(2) Water %	Base	%	%			Before Calcin.	After Calcin.	(3) After Add.	24 hr After Add.	(4) Mixing Consistency	Time of Set min.	Ivory	Grey	Remarks
										Starch	Retarder	Soap									
13-70-1	A		After Calcining	3700	B.R.	96	7.6	$Ca(OH)_2$	0.1	0.05	0.03	0.03	5.8	3.3	5.3		70	9.0	No	No	Lack of bond, tests A to I, presumably due to low surface area (3700 cm^2/g). Plaster slurry thickened and set more quickly with NaOH than with $Ca(OH)_2$.
	B							"	0.2	"	"	"			7.2		"	10.0	"	"	
	C							"	"	0.1	"	"			6.6		"	9.0	"	"	
	D							"	0.3	0.5	"	"			7.8		"	12.0	"	"	
	E							"	"	1.0	"	"			7.4	6.4	"	11.5	"	"	
	F							"	"	"	"	"			7.2		"	12.5	"	"	
	G							NaOH	0.5	"	"	"			7.5		"	7.5	Slight	"	
	H							"	0.8	2.0	"	"			12.0		72	8.0	No	"	
	I							"	0.3	"	0.10	"			7.1		70	7.5	"	"	
13-70-2	A		After Calcining	3575	B.R.	93	7.0	$Ca(OH)_2$	0.3	1.0	0.03	0.03	5.5	4.0	7.1		70	10.0	No	No	$Ca(OH)_2$, (0.3%), added to reactor before calcining. Lack of bond, A to D, presumably due to low surface area. Greater surface area, plus addition of NaOH to pH 7 to 8 (F to H) resulted in good bond. No bond with $Ca(OH)_2$ (E) nor in Test I where base was omitted.
	B							"	0.6	"	"	"			9.5		"	8.5	"	"	
	C							NaOH	0.5	"	"	"			7.3		72	8.0	Fair	Slight	
	D							"	0.7	"	"	"			8.0		"	5.0	Slight	No	
	E			4580				$Ca(OH)_2$	0.6	"	"	"			"		70	5.5	No	"	
	F							NaOH	0.7	"	"	"			7.9		72	4.0	Good	Good	
	G							"	0.8	"	0.10	"			7.8		"	7.0	"	"	
	H							"	"	"	"	"			"		74	5.0	"	"	
	I							-	-	"	"	"			4.8		"	9.0	No	No	
13-70-3	A		Before Calcining	5086	B.R.	90	6.8	NaOH	1.0	1.0	0.03	0.03	5.4	3.0	7.3		74	5.0	Good	Fair	Good bond produced with NaOH (pH 7.0 to 7.5) and 1 to 1½% starch, tests A, E, G, H, I & J. Bond with $Ca(OH)_2$ improved by increasing starch content (compare C, D and K). Some bond in G, even although slurry is acid. Additional starch (2%) appears beneficial. Lack of bond in test F possibly due to excess retarder.
	B							"	"	0.5	"	"			7.4		"	4.0	"	No	
	C							$Ca(OH)_2$	0.8	1.0	"	"			7.6		"	9.0	Fair	Some	
	D							"	"	0.5	"	"			7.4		"	8.0	Some	No	
	E							NaOH	1.0	1.0	0.06	"			7.6		"	4.5	Fair	Good	
	F							"	"	"	0.20	"			"		"	5.7	No	No	
	G							"	0.3	2.0	0.10	"			4.6		70	5.0	Some	Good	
	H							"	0.6	1.0	"	"			6.0		"	"	"	"	
	I							"	0.8	"	"	"			6.9		"	4.5	Good	Good	
	J							"	1.0	1.5	"	"			7.5		"	"	"	"	
	K							$Ca(OH)_2$	0.8	2.0	0.03	"			7.6		"	8.0	"	"	
13-70-4	A		Before Calcining	3087	B.R.	80	7.7	NaOH	1.0	1.0	0.20	0.03	6.2	3.3	7.7		72	6.0	No	No	Lack of bond due to low surface area, although some bond in D, presumably due to additional starch.
	B							$Ca(OH)_2$	"	"	"	"			7.5		"	10.0	"	"	
	C							NaOH	"	"	0.10	"			"		"	5.0	"	"	
	O							"	0.8	2.0	"	"			7.3		70	"	Some	Good	
13-70-5	A		After Calcining	4920	B.R.	102	7.2	$Ca(OH)_2$	1.0	1.0	0.20	0.03	6.2	2.9	10.7		72		No	No	Good bond with NaOH provided pH is maintained at 7 to 8 and starch content between 1 and 2%. No bond with $Ca(OH)_2$. Additional starch may have resulted in bond. No bond in test N possibly due to fact that slurry was acid.
	B							NaOH	"	"	0.10	"			8.2		"	5.0	"	"	
	C							"	"	"	"	"			7.5		"	5.5	Good	Fair	
	D							$Ca(OH)_2$	"	"	"	"			10.5		70	7.0	No	No	
	E							NaOH	0.8	2.0	"	"			7.6		"	5.5	Good	Good	
	F							"	0.6	1.0	"	"			7.3		"	5.0	"	"	
	G							"	"	1.5	"	"			"		"	"	"	"	
	H							"	"	2.0	"	"			"		"	6.0	"	"	
	I							"	0.8	1.0	"	"			7.6		"	4.5	"	"	
	J							"	"	2.0	"	"			7.8		"	6.0	"	"	
	K							"	"	"	"	"			"		"	"	"	"	
	L							"	0.6	0.5	"	"			7.2		"	5.0	No	No	
	H							"	0.8	"	"	"			7.7		"	4.5	"	"	
	N							$Ca(OH)_2$	0.2	2.0	0.03	"			5.5		"	7.0	"	"	

TABLE 3 (Continued)

Calcin. Test No.	Stucco Test	Grind			Calcining			Additives					pH				(4) Mixing Consistency	Time of Set min.	(5) Adherence		Remarks
		Unground	Ground	(1) Surface Area cm²/g	Unit	Time min.	(2) Water %	Base	%	%			Before Calcin.	After Calcin.	(3) After Add.	24 hr After Add.			Ivory	Grey	
										Starch	Retarder	Soap									
13-70-6	A		Before Calcining	4904	B.R.	75	7.5	NaOH	0.8	1.0	0.1	0.03	6.0	4.0	11.0		70	5.0	No	No	Good bond with C, high surface area, pH adjusted to 7 to 8 with NaOH, starch content equal to 1%. Tests D, E and F are test plaques, bond generally good.
	B								0.4	"	"	"			7.7		"	"	"	Some	
	C								"	"	"	"			7.3		"	5.5	Good	Good	
	D								"	"	"	"			7.4		"	4.5	"	"	
	E								"	"	"	"			7.4		"	6.0	"	"	
	F								"	"	"	"			7.2		"	5.0	Fair	Fair	
13-70-7	A		After Calcining	5643	B.R.	99	7.0	NaOH	0.4	1.0	0.10	0.03	6.0	3.6	7.2		70	5.0	Good	Good	As expected, bond in A (NaOH) was good. No bond with NH_4OH. Test C to G are test plaques, bond good.
	B							NH_4OH	"	"	"	"			7.0		"	7.0	No	No	
	C							NaOH	"	"	"	"			6.8		"	6.0	Good	Good	
	D							"	"	"	"	"			6.6		"	6.5	"	"	
	E							"	0.5	"	"	"			7.1		"	5.2	"	"	
	F							"	"	"	"	"			"		"	6.0	"	"	
	G							"	0.4	"	"	"			7.3		"	"	"	"	
13-70-9	A		After Calcining	5000	B.R.	111	7.0	NaOH	0.5	1.0	0.25	0.03	5.5	3.6	6.5	6.2	65	7.5	No	No	Note: New retarder was used with samples 13-70-9 and 13-70-10. This retarder was less effective than that used in previous tests. Good bond in one test only (B, 2% starch). Bond failure possibly due to excess NaOH and relatively large percentage of retarder. Extra retarder was employed in an attempt to extend set.
	B							"	0.6	2.0	"	"			7.0	6.2	"	8.5	Good	Good	
	C							"	"	1.0	"	"			7.1	6.3	"	7.0	"	No	
	D							"	"	"	"	"			7.0	6.2	"	7.0	No	No	
	E							"	"	"	"	"			7.3	6.4	"	8.0	Some	Some	
	F							"	"	"	"	"			7.0	6.2	"	8.2	Fair	Fair	
13-70-10	A		After Calcining	4578	B.R.	114	6.2	NaOH	0.5	1.5	0.10	0.03	6.0	3.6	6.0	6.3	70	4.2	No	No	No bond with $Ca(OH)_2$. Bond with NaOH variable. Poor bond possibly due to excess retarder. Compare B, H, K, L. NaOH at 0.7% appear satisfactory, starch at 1.5% appears satisfactory.
	B							"	0.7	"	0.15	"			7.3	6.6	"	6.0	Good	Good	
	C							"	0.8	"	"	"			7.2	6.7	"	5.5	"	No	
	D							"	"	1.0	"	"			"	6.8	"	6.0	"	"	
	E							"	0.6	1.5	0.20	"			6.8		"	7.0	Fair	"	
	F							"	0.6	1.0	"	"			7.0		"	6.2	"	"	
	G							"	0.7	"	"	"			7.1		"	6.7	Good	"	
	H							"	"	1.5	"	"			7.5		"	8.2	"	Fair	
	I							$Ca(OH)_2$	0.8	"	"	"			8.1		"	18.5	No	No	
	J							"	"	"	0.05	"			7.7		"	10.0	"	"	
	K							NaOH	0.7	1.0	0.25	"			7.3		"	8.5	"	"	
	L							"	"	1.5	0.25	"			"		"	9.2	Good	"	

(1) Blaine Air Permeability Apparatus
(2) Per cent water in calcined product
(3) After Add., i.e. after addition of additives
(4) Mixing Consistency - approximately normal consistency
(5) Adherence, i.e. bond to paper as determined visually.