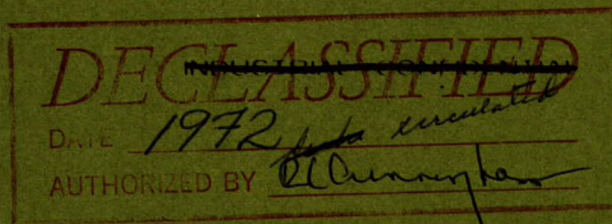


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DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 71-9

**AN EVALUATION OF GYPSUM RESIDUE  
FROM VALLEYFIELD, QUEBEC,  
FOR GYPSUM PRODUCTS MANUFACTURE**

by

**R. K. COLLINGS, D. KARPOFF AND G. A. BROWN**

**MINERAL PROCESSING DIVISION**

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R.K. Collings\*, D. Karpoff\*\* and G.A. Brown\*\*\*

SUMMARY OF RESULTS

Based on the samples received, the results of this investigation indicate that gypsum residue from the phosphate fertilizer plant of St. Lawrence Fertilizers Ltd., at Valleyfield, Quebec, could be used as a substitute for natural gypsum in gypsum products manufacture, in particular wallboard and lath.

Processing of this material, though more complex than that of natural gypsum because of residual acid and other impurities, is nonetheless relatively straightforward. Initial steps include 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 was ground and, being very acidic, neutralized or rendered basic by the addition of various bases including sodium, potassium, and calcium hydroxides before forming into plaster or wallboard.

The resulting product generally compared favourably with natural gypsum when tested as per CSA specifications and produced a satisfactory bond with gypsum wallboard paper.

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Direction des Mines  
Rapport de Recherche IR 71-9

Evaluation des Résidus Gypsifères  
de Valleyfield, Québec, en vue de la fabrication  
des produits en plâtre

par

R.K. Collings\*, D. Karpoff\*\*, et G.A. Brown\*\*\*

Résumé

Les résultats de cette recherche, basée sur les échantillons tels que reçus, indiquent que les résidus gypsifères de l'usine d'engrais phosphatés de la St. Lawrence Fertilizers Ltd, à Valleyfield, Québec, pourraient être utilisés comme un substitut au gypse naturel dans la fabrication des produits en plâtre en particulier des planches mûrales et des lattes.

Le traitement de ce matériau, quoique plus compliqué que celui du gypse naturel à cause de la présence d'acide résiduel et d'autres impuretés, est possible et est assez direct. La première étape comprend un tamisage sous l'eau afin d'enlever la fraction plus 65-mesh la plus impure, suivie d'un lavage à eau pour enlever le maximum d'acide résiduel.

La calcination du gypse moins 65 mesh a présenté quelques problèmes. Le plâtre de Paris obtenu a été broyé et, étant encore acide, neutralisé ou rendu basique par l'addition des bases variées comprenant notamment des hydroxides de sodium, de potassium et de calcium avant la formation du plâtre ou des planches mûrales.

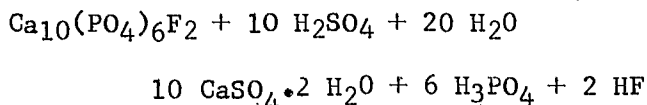
En général, le produit final se compare favorablement avec le plâtre naturel quand il est essayé suivant les spécifications de C.S.A. et donne une adhérence satisfaisante avec le papier pour planches mûrales en plâtre.

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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. The reaction may be represented as follows:



The gypsum is separated from the phosphoric acid by filters, re-slurried with water, and pumped to waste disposal areas. This material is acidic, finely divided, and, on a dry basis, usually contains more than 90 per cent gypsum. Impurities commonly present include unreacted phosphate rock, calcium fluoride, and quartz sand.

Approximately 1½ tons of gypsum are produced for every ton of phosphate rock consumed in the wet process for phosphoric acid manufacture. Production of by-product gypsum in Canada by phosphoric acid 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 product plants. Several such gypsum product plants obtain current requirements of crude gypsum from relatively distant sources, e.g., two Montreal plants obtain gypsum from Nova Scotia, while plants in Vancouver and Edmonton use gypsum from southeastern British Columbia.

This present investigation is part of a larger Mines Branch program of the evaluation of gypsum residue from several areas in Canada for gypsum products manufacture. The work outlined in this report was undertaken on two samples of gypsum residue from St. Lawrence Fertilizers Limited's phosphate fertilizer plant at Valleyfield, Quebec. This plant, located about 30 miles southwest of Montreal, annually discards approximately 200,000 tons of gypsum residue as waste, while the two gypsum products plants in Montreal use 250,000 tons or more of natural gypsum annually. This gypsum, as noted above, is obtained from Nova Scotia at considerable cost.

Previous Mines Branch investigations of the utilization of gypsum residue for gypsum products, undertaken in 1962, 1966, and 1970, are described in Mines Branch Investigation Reports: IR 62-67, "An Investigation of

By-Product Gypsum From a Wet-Process Phosphoric Acid Plant at Port Maitland, Ontario", by R.K. Collings; IR 67-89, "Autoclave Calcination of By-Product, Synthetic Gypsum from a Wet-Process Phosphoric Acid Plant" by R.K. Collings and D. Karpoff; and IR 70-45, "An Evaluation of Gypsum Residue From Phosphate Fertilizer Plants in the Edmonton, Alberta, Area for Wallboard Manufacture" by R.K. Collings and D. Karpoff.

SOURCE AND DESCRIPTION OF SAMPLES

The two gypsum residue samples used in this investigation, samples 1 and 2, were composites of daily filter cake samples collected over a one- to two-week period. Sample 1, weighing 85 lb, was obtained during the early part of June, 1970, and sample 2, weighing 150 lb, was received at the Mines Branch in December, 1970.

These samples were similar in appearance, each being grey in colour and containing up to 25 per cent free moisture. Each was composed of finely divided, prismatic to needle-like crystals of gypsum. Impurities, mainly concentrated in the plus 65-mesh fraction, largely consisted of unreacted phosphate rock and quartz. Another impurity, finely divided carbon, appeared to be uniformly distributed throughout the samples. Both samples contained some residual acid (phosphoric, sulphuric, and hydrofluoric) and gave pH values of 3.0 to 3.5. Sieve analyses follow in Table 1. The wet sieve analysis was made by hand whereas the dry sieve analysis

TABLE 1

Sieve Analyses Wt Per Cent

Mesh Size	Sample No. 1		Sample No. 2	
	Wet	Dry	Wet	Dry
+28	0.4	0.0	Trace	0.0
-28+35	0.6	0.8	0.1	0.1
-35+48	0.7	1.7	0.1	0.3
-48+65	1.1	2.1	0.2	0.6
-65+100	2.3	3.7	2.8	1.2
-100+150	35.0	3.7	15.2	1.2
-150+200	35.4	11.8	37.5	6.8
-200	24.5	76.2	44.1	89.8
Total	100.0	100.0	100.0	100.0

was made with a Ro-Tap shaker. It is interesting to compare these analyses. The mechanical action of the Ro-Tap apparently resulted in more efficient screening, possibly by causing a larger percentage of the needle-like gypsum crystals to pass end-wise through the sieves.

The crystal habit of the gypsum along with that of the calcined product is illustrated in Figure 1 (enlargement 50X).

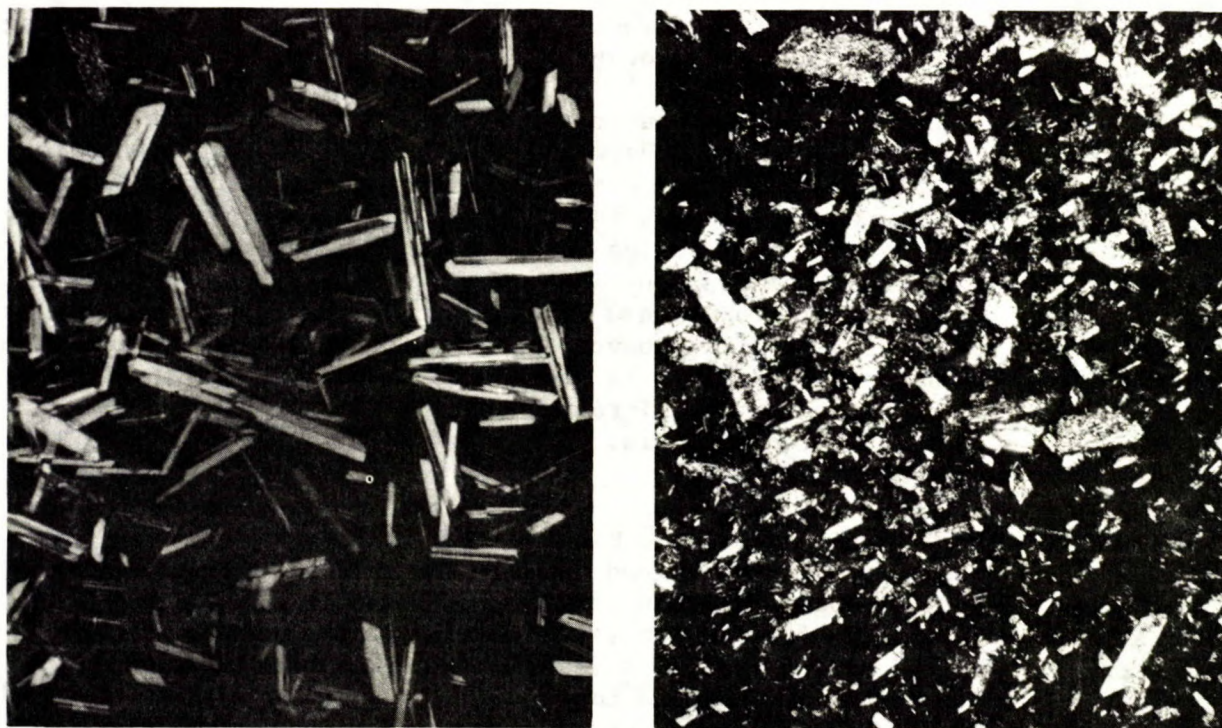


Figure 1. Valleyfield gypsum (left), ground calcined product (right).

Chemical analyses of gypsum residue sample No. 2 and of the washed and calcined products are shown in Table 2.

TABLE 2

Chemical Analyses - Wt Per Cent

Sample	CaO	SO <sub>3</sub>	H <sub>2</sub> O	C	F	P <sub>2</sub> O <sub>5</sub>		
						Water Sol.	Water Insol.	Total
St. Lawrence Fertilizer Head	31.76	44.70	18.64	0.26	0.84	0.02	0.82	0.84
-65 mesh, washed	-	-	18.80	0.29	0.83	0.02	0.81	0.83
-65 mesh, calcined product	-	-	5.71	0.24	0.58	0.02	0.52	0.54

## DESCRIPTION OF EQUIPMENT

The major items of equipment used in this work were two calcining vessels, one a Benco reactor, the other a Mines Branch kettle.

The 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 most calcining tests. The calcining chamber is  $6\frac{1}{2}$  in. in diameter by  $8\frac{1}{2}$  in. deep and holds 5 to 6 lb 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 100 rpm. 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. discharge spout in the bottom of the unit.

A large calcining unit, a Mines Branch kettle, was used in one test. This kettle is fully described on pages 74 to 76 of Mines Branch Report No. 714, The Gypsum Industry of Canada, by L. Heber Cole, 1930. This kettle, patterned after commercial gypsum calcining kettles, is electrically heated and has a cylindrical calcining chamber 18 in. in diameter by 24 in. in height with a concave bottom. The charge, introduced at the top, is stirred by two sets of paddles mounted on a central shaft at right angles to one another. Speed of rotation is 15 rpm. Temperature is recorded via two horizontal thermocouple wells that extend to the center of the kettle and controlled by 4 front-mounted, 4-position, electrical switches. The calcined product is discharged through a 2-in. -diameter spout in the bottom into an appropriate container.

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

## CALCINING AND PHYSICAL TESTS

### Preliminary Treatment

Visual examination of the gypsum residue samples showed that the plus 65-mesh was generally of lower purity than the minus 65-mesh fraction. The coarse, which comprised only a small portion of the total weight, was removed by wet screening and discarded. The minus 65-mesh gypsum was 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. A final pH of from 5.3 to 6.7 was achieved. The sample was filtered and dried at 100°F overnight in an electric oven.

### Calcining Tests

Most of the calcining tests were made with the minus 65-mesh, washed gypsum, the products being ground following calcining to Blaine surface areas between 2600 and 5850 cm<sup>2</sup>/g. However, in one test the gypsum was ground before calcining.

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 1½- to 2-hr period, a maximum temperature of 160°C being achieved (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 2 to 5 per cent of the weight of product, was discarded.

One calcining test was made with the Mines Branch kettle. Little difficulty was experienced apart from the fact that the gypsum, being unground, appeared to be "heavier" in the kettle than normal gypsum. Grinding before calcining would improve this condition. Kettle charge for this test was about 35 lb. A typical temperature/time curve for this kettle is included in Figure 2. Adequate ventilation is desirable during calcining to remove the somewhat unpleasant and possibly harmful fumes that are emitted.

### 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 GSA, 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 was 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, was 1200 psi, well above the 750 psi minimum specified in GSA Standard A82.22.

### Characteristics of Stucco

The calcined product (stucco), in all tests, was more acidic than the kettle 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 setting time was extended 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 allowed to age over several months.



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

#### Bond Development

Bond or adherence to paper is perhaps the most critical aspect of the wallboard manufacturing process, especially when employing gypsum residue as 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 are inclined to believe that crystal habit (in part determined by impurities in the gypsum), neutralizing agent (type and quantity used), and the amount of starch added are perhaps the more important from the standpoint of bond development.

Starch addition is necessary to ensure a satisfactory and permanent bond. Previous work by the authors (noted above) indicated that the quantity required is related to both the surface area and its reactivity with the neutralizing agent employed. With Valleyfield gypsum residue, it would appear that bond is relatively independent of surface area, possibly because of the crystal structure, but its reactivity with the neutralizing agent, in particular sodium hydroxide, must be taken into account. Sodium hydroxide, when used in excess, will hydrolyze the starch and thus render it less effective as a bonding agent. Neither calcium hydroxide nor potassium hydroxide appears to thus degrade the starch. From the standpoint of bond to paper, the best results with sodium hydroxide were achieved when the amount used was kept to a minimum, 0.05 to 0.1 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 either the calcium or potassium hydroxide. Good bonds were obtained with 0.1 per cent of the former, however, slightly more of the latter (0.2 per cent) appeared necessary for good bond development. In all cases, good bonds were achieved with as little as 0.5 per cent starch.

#### CONCLUSIONS

Based on the samples received, gypsum residue from the plant of St. Lawrence Fertilizers Ltd. at Valleyfield, Quebec, 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 Valleyfield, Quebec can be used in gypsum products manufacture. This material may have some commercial application in gypsum products manufacture in certain areas, particularly Montreal, where natural gypsum is not available but must be obtained from distant sources. We recommend that its use for this purpose be investigated by industry on a pilot plant level. Figure 3 is a suggested Flow Sheet for processing this gypsum residue.

#### ACKNOWLEDGEMENTS

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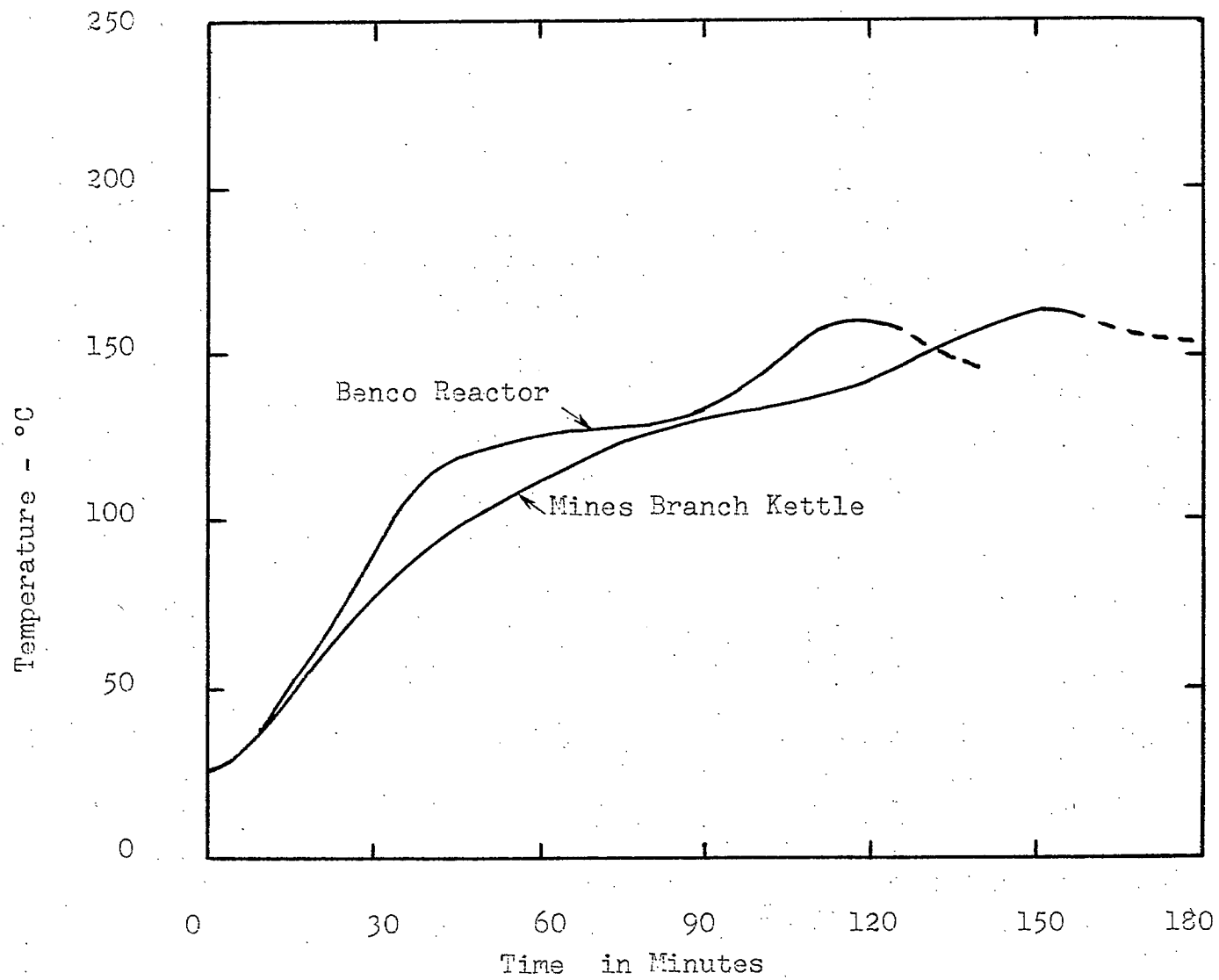


Figure 2 - Typical Calcining Cycles

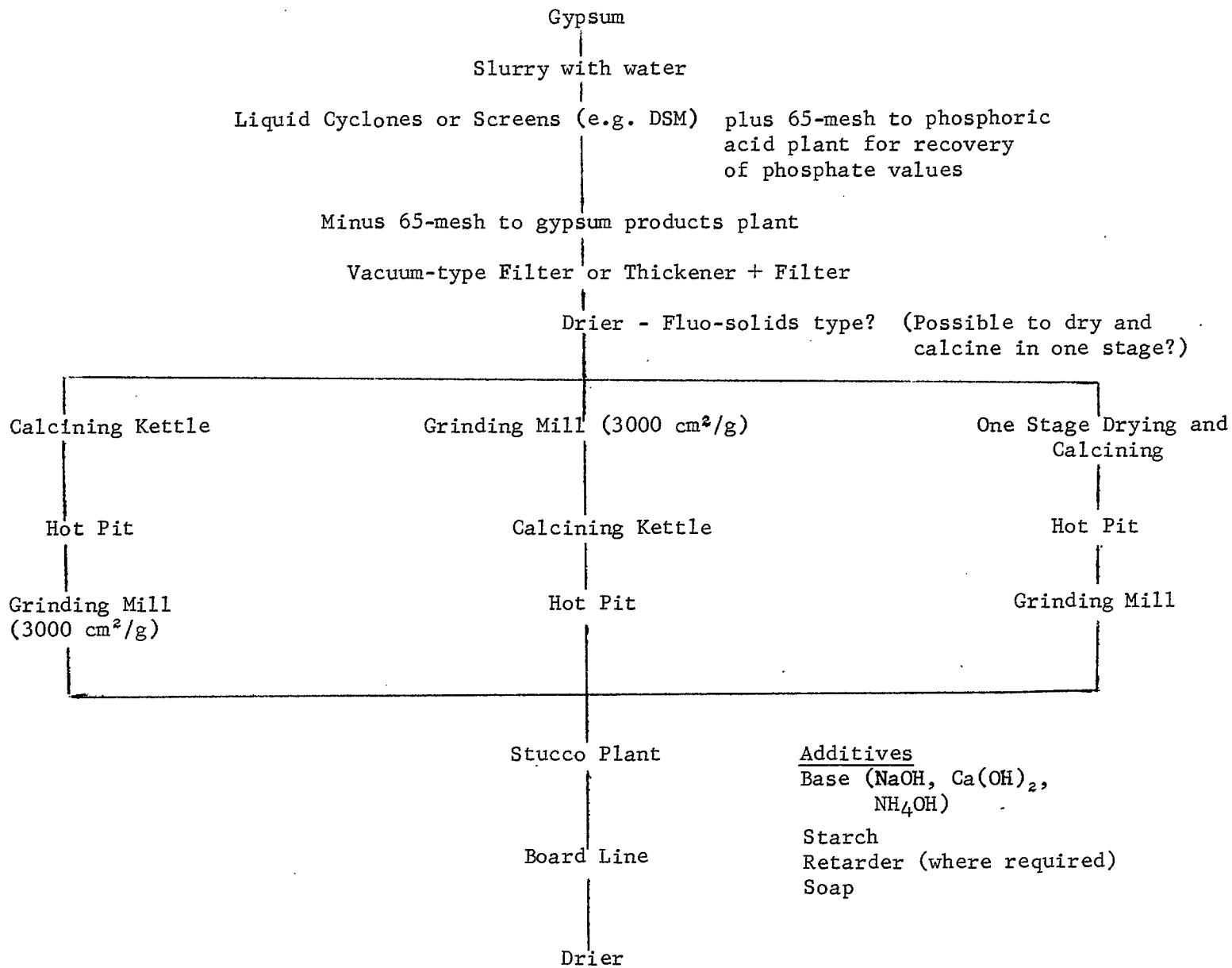


Figure 3 - Suggested Flow Sheet for Treatment of Gypsum Residue

TABLE 2

## Test Data - Gypsum and Stucco Samples

## Gypsum Samples Nos. 1 (11) and 2 (16)

Calcin. Test No.	Stucco Test No.	Grind			Calcinine			Additives				pH				(4) Mixing Consist.	Time of Set min	(5) Adherence		Remarks		
		Unground	Ground	(1) Surface Area cm <sup>2</sup> /g	Unit	Time min	(2) Water %	Base	%	"			Before Calcin.	After Calcin.	(3)			Ivory	Grey			
										Starch	Retarder	Soap			After Add.						24 hr after Add.	
11-70-1	1	-65	After Calcining	900	B.R.	92	6.5															
	2		"	5850				NaOH	0.5	0.6	0.06	0.03	6.2	4.0							Excess NaOH, due to reaction with starch, tends to inhibit bond; retarder appears to have little effect on set; acid stucco sets very quickly to give good bond.	
	3		"	"				"	0.2	"	"	-	-			12.0	-	70	10	no		no
	4		"	"	"				"	0.1	"	-	-			11.6	-	"	9	some		some
			"	"				"	-	0.06	0.03				9.3	-	"	5	good	good		
11-70-2	1		Before Calcining	2952	B.R.	86	7.1	NaOH	0.05	0.5	-	-	6.0	4.0	6.3	-	70	8	good	good	Good bond achieved by reducing quantity of NaOH.	
	2		"	"				"	0.075	0.5	-	-			7.3	-	"	8	"	"		
11-70-3	1		After Calcining	2609	B.R.	88	6.9	NaOH	0.075	0.5	-	-	6.7	4.5	7.2	6.6	70	10	good	good	Good bond regardless of whether ground before or after calcining.	
	2		"	"				"	"	"	-	-			6.7	6.9	68	12½	"	"		
11-70-4	2		After Calcining	3255	B.R.	88	7	NaOH	0.2	0.5	-	-	5.3	3.9	10.1	7.6	73	5	good	good	Good bond, even with 0.2% NaOH; retarder, at lower concentration of NaOH, appears to extend set. Stucco tests 6 and 7, made with stucco that was aged 4 to 5 months, indicate that ageing prolongs set and possible promotes bond - compare with 11-70-1-4 and 11-70-5-8.	
	3		"	"				"	0.15	1.0	-	-			10.2	7.6	76	7½	"	"		
	5		"	"				"	0.1	0.5	0.04	0.02			10.2	7.2	72	13	"	"		
	6		"	"				"	-	"	"	"			5.0	5.7	70	11½	"	"		
	7		"	"	"			"	0.05	"	"	"			6.2	6.8	70	22	"	"		
11-70-5	1		After Calcining	3042	M.B.	158	5.9	NaOH	0.1	0.5	0.04	0.02	5.7	4.4	7.2	6.9	70	7	good	some	Good bond obtained with NaOH, 0.1%, and Ca(OH) <sub>2</sub> , 0.1%; little bond with KOH, 0.1%, the amount added being too little to neutralize acid stucco.	
	2		"	"				"	"	"	"	"			9.9	6.8	"	9	"	"		
	3		"	"				Ca(OH) <sub>2</sub>	"	"	"	"			10.6	6.9	"	10	"	good		
	4		"	"				"	0.05	"	"	"			7.0	6.2	"	9	"	some		
	5		"	"				KOH	0.1	"	"	"			6.5	6.3	"	8	some	no		
	6		"	"				"	0.05	"	"	"			5.7	5.6	"	7½	no	no		
	7		"	"				NaOH	0.1	"	"	"			9.9	6.6	"	10	good	good		
	8		"	"	"			"	0.05	"	"	"			6.6	5.9	"	7½	little	little		
16-70-2	1	-65	After Calcining	1100	B.R.	99	6.4	NaOH	0.1	0.5	0.04	0.03	5.8	5.6	7.8	6.9	70	14	good	good	Very good bonds with NaOH, Ca(OH) <sub>2</sub> and KOH. Note that KOH content increased to 0.2%. Set relatively slow, could be accelerated by omitting or reducing retarder.	
	2		"	3216				"	"	1.0	"	"			9.2	7.0	"	15	"	"		
	3		"	"				Ca(OH) <sub>2</sub>	"	0.5	"	"			9.7	6.6	"	18	"	"		
	4		"	"				"	1.0	"	"	"			9.0	6.5	"	18½	"	"		
	5		"	"				KOH	0.2	0.5	"	"			6.2	6.8	"	15	"	"		
	6		"	"	"			"	"	1.0	"	"			6.0	6.7	"	15	"	"		

(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

B.R. - Benco Reactor

M.B. - Mines Branch Kettle