

~~INTERNAL - CONFIDENTIAL~~

DECLASSIFIED
DATE 1964
AUTHORIZED BY [Signature]

CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 67-89

AUTOCLAVE CALCINATION OF BY-PRODUCT, SYNTHETIC GYPSUM FROM A WET-PROCESS PHOSPHORIC ACID PLANT

by

R.K. COLLINGS AND D. KARPOFF

MINERAL PROCESSING DIVISION

CENTRAL TECHNICAL FILES
C10-IR-67-89
GEOLOGICAL SURVEY

NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.

COPY NO. 7

This document was produced by scanning the original publication.
Ce document est le produit d'une numérisation par balayage de la publication originale.

NOVEMBER 23, 1967

IR 67-89

01-7968887

Declassified
Déclassifié

Industrial Confidential

Mines Branch Investigation Report IR 67-89

AUTOCLAVE CALCINATION OF BY-PRODUCT, SYNTHETIC
GYPSUM FROM A WET-PROCESS PHOSPHORIC ACID PLANT

by

R.K. Collings* and D. Karpoff**

SUMMARY OF RESULTS

The results of this investigation indicate that the production of gypsum plaster by autoclave calcination of by-product, synthetic gypsum, as produced at wet-process phosphoric acid plants, is technically feasible.

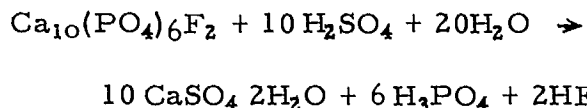
A total of 58 calcining tests were conducted. Initial tests using untreated gypsum resulted in wet plaster (stucco) that thickened slowly and required several days to harden (set) and develop strength. This slow set was, in part, attributed to the presence of phosphoric acid and numerous tests were conducted using various bases, including sodium and ammonium hydroxides, to achieve neutrality. Although some reduction of the setting time was achieved, the products were not satisfactory.

Further study and investigation indicated that unreacted phosphate, which in addition to being concentrated in the plus 100-mesh fraction was also believed to be chemically combined with the gypsum, probably was chiefly responsible for the delayed set. Removal of the plus 100-mesh fraction prior to calcining, coupled with sulphuric acid treatment during calcination and/or following calcination and the removal of excess liquor, effectively nullified the retarding effect of phosphate. Close set control was achieved, in particular, by the addition of controlled quantities of sulphuric acid to the dewatered autoclave stucco. The product set and hardened quickly to form a strong plaster which bonded well with gypsumboard paper and, although acidic, did not appear to exhibit any marked detrimental effects.

*Head, and Scientific Officer**, Non-Metallic Minerals Section, Mineral Processing Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

By-product, synthetic gypsum 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, at most plants, pumped to waste disposal areas. This material is acidic, finely divided and, on a dry basis, usually averages in excess of 90 per cent gypsum. Impurities commonly present include unreacted phosphate rock, calcium fluoride and quartz sand.

Approximately 1 1/2 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 currently exceeds 2 million tons annually and is derived from phosphoric acid facilities in British Columbia, Alberta, Manitoba, Ontario, Quebec and New Brunswick. Large tonnages also are produced in the United States. Production of phosphoric acid and consequently, by-product gypsum in Canada and the United States will increase in direct proportion to the growth of the rapidly expanding phosphate fertilizer industry.

Although phosphoric-acid gypsum is 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, an increasing awareness of water pollution, and the possibility of recovering contained phosphate, valued at up to \$1.00 per ton of waste gypsum - focus attention on the possible utilization of a portion of this material for gypsum-products manufacture. Additionally, several domestic gypsum-product plants, notably those in Montreal and Vancouver, obtain their current requirements of crude gypsum from relatively distant sources (Nova Scotia for the former and southeastern British Columbia, and Mexico for the latter). A gypsum-product plant in southern Ontario continues to obtain part of its requirements for crude gypsum from Newfoundland.

It is appreciated that the consumption of by-product gypsum by the gypsum-products industry, should this material be utilized for this purpose in Canada, would represent only a very small percentage of total production. However, other possible applications, e. g. in land reclamation, in cement manufacture, as an agricultural fertilizer and for the recovery of sulphur, are intriguing and worthy of investigation.

The present investigation was initiated in August, 1966, following discussions with Dr. J. D. McGilvery of Electric Reduction Company Limited, and Mr. S. B. Allen of Ganderstown, Ireland. Its prime purpose was to study the possibility of producing a plaster slurry (stucco) by autoclave calcination of waste gypsum essentially as produced at phosphoric acid plants. The feasibility of utilizing this plaster slurry within a relatively short time of its production for plaster products manufacture, e. g. gypsum wallboard, was also to be studied.

A previous investigation of the utilization of waste phosphoric acid gypsum, undertaken in 1962, was designed to study the feasibility of producing an acceptable dry product for use in gypsum plaster manufacture by the gypsum kettle process in common use by industry. The results, outlined in Mines Branch Investigation Report IR 62-67 by R. K. Collings, were encouraging but indicated a need for further study and investigation.

SOURCE AND DESCRIPTION OF SAMPLES

The gypsum samples, supplied by Electric Reduction Company of Canada, Limited, were from this company's fertilizer complex at Port Maitland, Ontario.

Two samples were received - A, 100 lb, in August and B, 300 lb, in October, 1966. Each was produced at Port Maitland using uncalcined, imported phosphate rock.

The physical appearance of the samples was generally similar. Each was light grey, largely minus 100-mesh, and contained about 20 per cent free water. An examination of various sized fractions of sample A indicated that a large percentage of the impurities were present in the plus 100-mesh size. These impurities, identified by the Ore Mineralogy Section of this Division, were chiefly quartz and apatite (unreacted calcium phosphate). A few crystals of tourmaline and a small amount of carbonate mineral also were observed. Calcium fluoride, although not identified, was also believed to be present.

The gypsum contents of samples A and B, on a dry basis, were respectively 94.2 and 95.9 per cent. (Table 1, page 5).

EQUIPMENT AND TEST PROCEDURE

The autoclave used (Figure 1) was manufactured for the Extraction Metallurgy Division of the Mines Branch by Pfaudler Permutit Incorporated, Rochester, N.Y. It consists of an inner 6-litre, glass-lined steel shell and an outer steel casing, the two being separated by a 1/4-in. air space. Access to the autoclave is by way of a heavy top plate, securely fastened by large bolts. A substantial, glass-coated steel stirrer, driven by an external motor, is seated in the top plate. A pressure gauge and thermocouple well permitted pressure and temperature measurements to be made during test runs. The autoclave was heated by a Fisher gas-fired, blast burner.

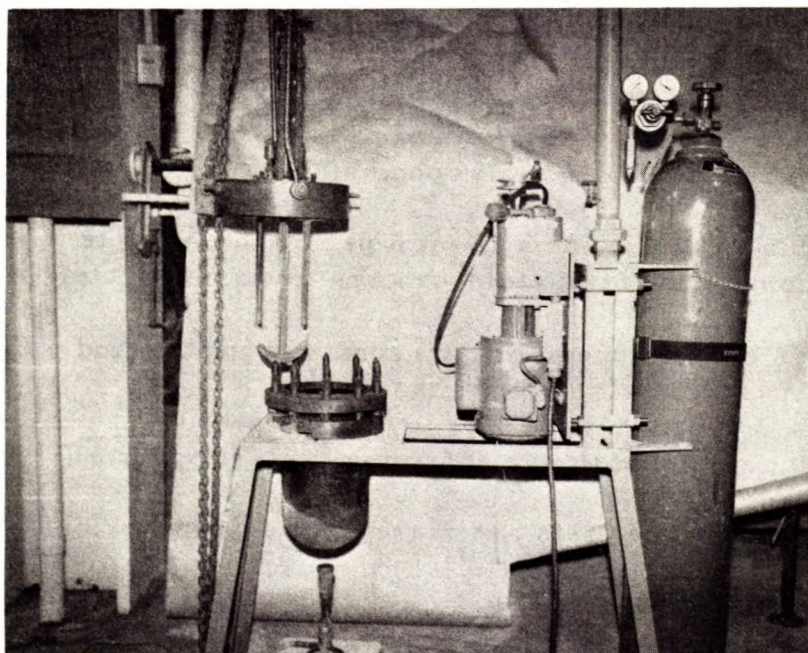


Figure 1 - Autoclave Assembly

A number of preliminary tests were made to study the operating characteristics of the autoclave, e.g. loading and unloading techniques, calcining cycles (time vs. pressure and temperature) attainable, and the effect on the calcining cycle of burner position, impeller speed, auxiliary pressure, and volume of charge. Additionally, these preliminary tests were designed to study the behaviour of the gypsum during calcining, and the effect of preliminary treatment, e.g. washing, sizing, and the

use of additives, both to the autoclave and to the end product, on the characteristics of the calcined product.

On the basis of these preliminary tests, final tests were made using the following general procedure;

1. Wet-screenhead sample on 100-mesh sieve, discard the plus 100-mesh fraction and water-wash the minus 100-mesh material to reduce pH (initially about 2.0-2.5) to about 4.
2. Dry at 60°C overnight.
3. Weigh 1500 to 2000 g of the dry product and slurry with an equal weight of water (50% solids).
4. Place slurry in autoclave, and with impeller speed adjusted to 100 r.p.m., adjust burner position so that the rate of increase of temperature during the initial calcining period is approximately 2°C per min.
5. When pressure reaches 50 psig, adjust the pressure valve to maintain pressure at 50 psig until conclusion of calcining period.
6. Continue calcining for a 10-min period following temperature recovery on completion of the temperature inversion cycle.
7. Remove burner, bleed off and condense vapour and, when pressure returns to 0 psig, open autoclave.
8. Decant remaining liquor and remove plaster paste (stucco).
9. Perform various tests and make such determinations as required on the stucco.

RESULTS

Representative chemical analyses of samples A and B are shown in Table 1.

TABLE 1

Head Sample Analyses* - Wt Per Cent

	Sample A		Sample B	
	Wet Basis	Dry Basis	Wet Basis	Dry Basis
CaO	25.8	31.6	26.5	33.4
SO ₃	35.0	43.0	34.6	42.8
H ₂ O (combined)	16.0	19.6	15.9	19.7
H ₂ O (free)	18.0	-	19.7	-
P ₂ O ₅ (total)	1.7	2.0	0.8	1.0
" (soluble)	0.95	1.1	0.46	0.58
" (insoluble)	0.75	0.9	0.34	0.42
SiO ₂	1.9	2.4	2.0	2.5
F	1.1	1.4	0.5	0.6
Total	100.0	100.0	100.0	100.0
CaSO ₄ ·2H ₂ O	76.8	94.2	77.0	95.9

*Calculated using analytical data provided by Electric Reduction Company.

Wet-sieve analyses were made on representative portions of samples A and B and the fractions from A were forwarded to Electric Reduction Company for analysis. The results are shown in Table 2.

TABLE 2

Sieve and Chemical Analyses*

Mesh	Wt %		Sample A (Dry Basis)							
			P ₂ O ₅		CaO	SO ₃	SiO ₂	F	H ₂ O	Total
	A	B	Total	Water Soluble						
+65	1.9	0.9	25.8	0.3	42.8	5.9	14.4	4.8	6.3	100.0
-65 +100	4.8	2.9	5.9	0.3	35.7	30.0	10.2	4.3	13.9	100.0
-100+150	7.2	6.3	2.0	0.4	31.5	42.1	5.2	2.1	17.1	100.0
-150+200	11.2	26.9	1.0	0.5	32.3	43.3	3.4	1.3	18.7	100.0
-200+325	32.9	33.8	0.9	0.5	32.6	43.5	1.2	1.1	20.7	100.0
-325+400	5.7	7.2	0.9	0.6	32.7	43.5	1.6	1.2	20.1	100.0
-400	36.3	22.0	0.9	0.5	31.7	43.8	2.0	1.4	20.2	100.0
Head	100.0	100.0	1.7	0.5	33.1	41.8	2.7	1.5	19.2	100.0

*Chemical analyses calculated using analytical data provided by Electric Reduction Company.

Unreacted phosphate and phosphate released from the gypsum molecule during calcining were believed to be chiefly responsible for retarding the set of the calcined product. To verify this, samples of products from several tests, including No. 2, in which no sulphuric acid was used and which resulted in a slow-setting plaster, and No. 29, where sulphuric acid was used and a quick-setting product resulted, were forwarded to Electric Reduction Company for analysis.

The phosphate distribution is shown for the two above noted tests in Table 3, along with the per cent reduction in phosphate content.

TABLE 3

Phosphate Distribution - Tests 2 and 29

Test No.	P ₂ O ₅ - Wt %					
	Total	Loss	Water Insol	Loss	Water Sol	Loss
2 (sample A)						
Uncalcined gypsum	2.55	-	1.11	-	1.44	-
Plaster product	1.89	26.0	1.12	-1.0	0.77	46.5
29 (sample B)						
Uncalcined gypsum	1.23	-	0.71	-	0.52	-
Plaster product	0.06	94.5	0.02	97.0	0.04	92.5

Although numerous calcining tests were conducted, significant and typical results may be studied by reference to eight, namely No.'s 1, 8, 12 (sample A) and 18, 30, 31, 34 and 54 (sample B). Test conditions and results for these are shown in Table 4. Figure 2 shows calcining cycles (temperature vs time and pressure vs time) for typical tests conducted with sample A - Figure 3 shows similar information for tests conducted with B. It should be noted that the autoclave was preheated in Tests 18 and 30 in an attempt to nullify the effects of erratic recorder readings at lower temperatures. The cause of this recorder malfunction was not determined, despite numerous checks.

TABLE 4

Typical Test Conditions and Results

Sample and Test No.	Sample Treatment	Autoclave Charge	Impeller Speed and Tank Pressure	Calcining Time, ⁽¹⁾ Temp and Pressure	Stucco, Condensate, Liquor ⁽²⁾ - Vol and pH	Product Treatment	Observations
<u>Sample A</u> 1	head sample, unwashed	2500 g, 60% solids, 50% of vol.	360 rpm 0 psi	2 1/2 hr, 135°C, 29 psi	-	-	Although product thickened within 24 hr, it did not set (harden) for several days - once set, plaster was relatively strong.
8	head sample, washed	3800 g, 85% solids, 65% of vol.	360 rpm 100 psi	1 1/3 hr, 140°C, 85 psi	-	-	Product thickened within 30 min but required several days to set - once set, plaster was relatively strong.
12	-65 mesh, washed once, pH 2.9	2500 g, 80% solids, 35% of vol., 10 g NaOH, pH 5.5	360 rpm 50 psi	1 hr., 113°C, 40 psi	liquor - 180 ml, pH 3.4	-	Product thickened within 30 min but required 16 hr to set.
<u>Sample B</u> 18	-65 mesh, washed seven times, pH 6.1	2530 g, 75% solids, 35% of vol. 7 g NH ₄ OH, pH 7.2	360 rpm 0 psi	35 min, 135°C, 35 psi	stucco - pH 5.8	one portion unwashed - 12g of -65 mesh gypsum added to 600 g of another.	Product thickened within 30 min but required 24 hr or more to set - once set plaster was relatively strong; gypsum noticeably accelerated set.
30	-100 mesh, washed, pH 3.8	2000 g, 50% solids, 35% of vol, 20 ml conc H ₂ SO ₄ , pH 0.8	55 rpm 0 psi	1 hr, 125°C, 30 psi	condensate - 130 ml, pH 2.6 liquor - 525 ml, pH 1.0 stucco - pH 0.8	one portion water-washed, remainder unwashed	Water-washed portion formed weak plaster; unwashed portion set within 10 min to form strong plaster.
31	head sample, unwashed	3600 g, 50% solids, 65% of vol.	55 rpm, 0 psi	1 1/2 hr, 135°C, 45 psi	condensate - 375 ml, pH 1.3 liquor - 775 ml, pH 1.0 stucco - pH 1.2	small amount of conc H ₂ SO ₄ added to pH 0.5	Set very slowly with no acid addition, plaster weak; rapid, 5-min set achieved with H ₂ SO ₄ - plaster strong.
34	-100 mesh, washed to pH 5.7	4800 g, 50% solids, 65% of vol, 44 ml of conc H ₂ SO ₄ , pH 0.6	55 rpm 0 psi	1 1/2 hr, 137°C, 30 psi	condensate - 175 ml, pH 1.8 liquor - 700 ml, pH 0.8	one portion water-washed, one portion acidified to pH 1.3, remainder untreated	Untreated portion set in about 50 min to produce weak plaster; washed portion set quickly but product weak; acidified product set in 10 min to form strong plaster.
54	-100 mesh, washed to pH 4.0	4000 g, 50% solids, 65% of vol, pH 4.0	100 rpm 0 psi	1 hr, 160°C, pressure controlled at 50 psi	condensate - 600 ml, pH 3.0 liquor - 260 ml, pH 1.9	2% gypsum added to one portion, H ₂ SO ₄ added to another to pH 1.2, balance untreated	Untreated portion slow to set and harden; gypsum produced some acceleration of set and product had good strength; acid rapidly accelerated set and resulted in strong plaster.

(1) Calcining Time - total time to discharge of autoclave
 " Temperature - maximum temperature reached prior to temperature inversion
 " Pressure - maximum pressure reached prior to pressure inversion

(2) Decanted liquor

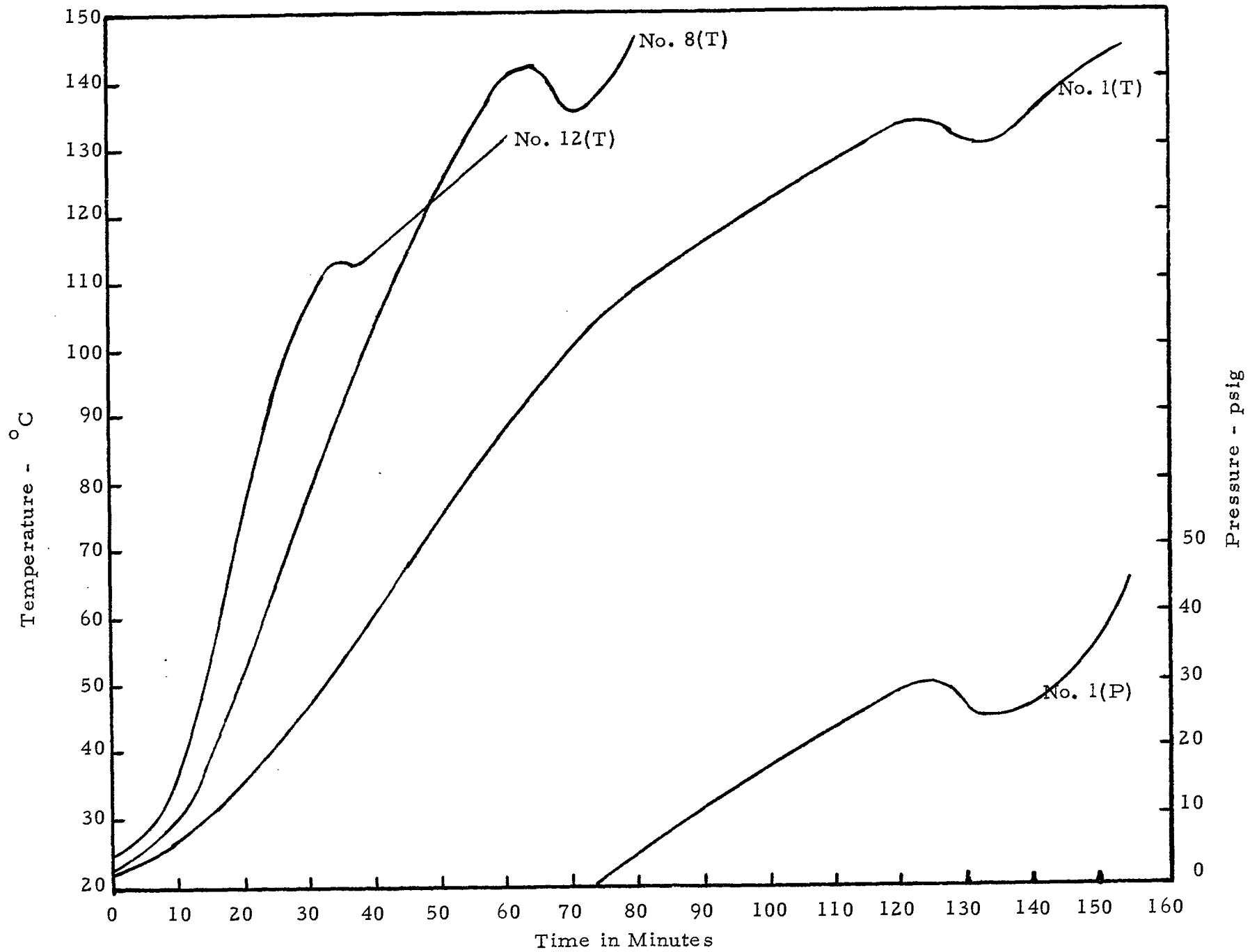


Figure 2. Typical Calcining Cycles - Sample A

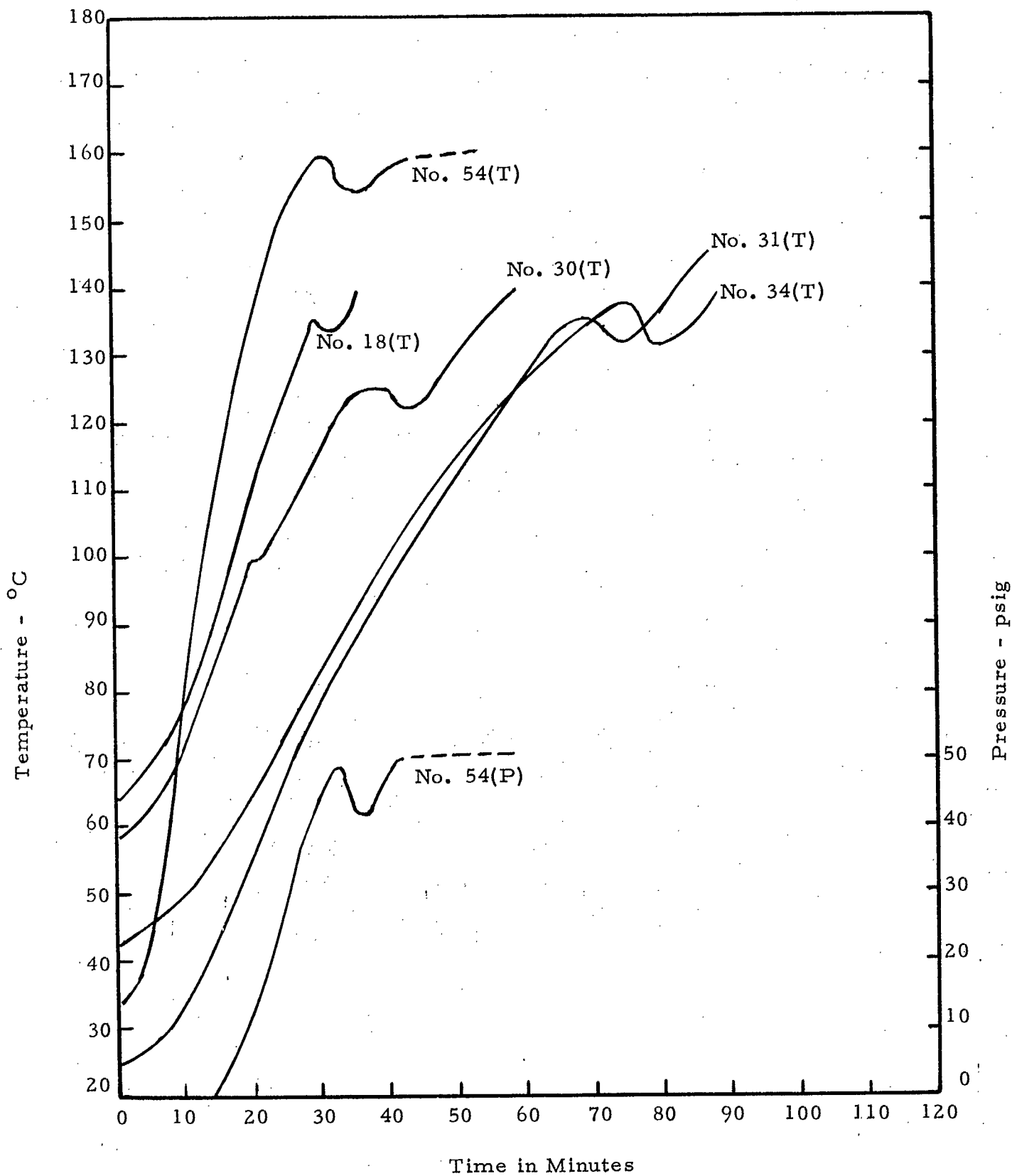


Figure 3. Typical Calcining Cycles - Sample B

DISCUSSION OF RESULTS

The purpose of this investigation was twofold — to investigate the production of a plaster stucco by autoclave calcination of by-product gypsum, and to study the feasibility of using this stucco, as produced and within a relatively short time, for gypsum products manufacture, e. g. plasterboard. To adequately fulfil this role the autoclave product should be the hemi-hydrate form of gypsum (i. e. Plaster of Paris) and should contain only sufficient free water to form a stucco satisfactory for gypsum board or gypsum block manufacture. Furthermore, this stucco should set (become hard) within a 20- to 30-min period and should be responsive to set-control additives.

In all autoclave tests, the conversion of the gypsum dihydrate to hemihydrate was indicated by a marked drop in temperature and pressure (Figures 2 and 3). The temperature inversion was about 5°C and occurred over a 5- to 15-min period. The pressure drop, which coincided with the drop in temperature, was about 5 psig. Discharging the autoclave during the temperature inversion, prior to recovery of the initial temperature, resulted in a product that thickened quickly but developed little strength on ageing. Prolonged heating following temperature recovery did not have any beneficial effect. A 10-min holding period at the conclusion of the temperature inversion cycle appeared sufficient. Samples of the product from several tests, immediately on completion of the calcining cycle, were washed with acetone (to absorb free water), dried and the combined water determined. Results invariably showed approximately 6 per cent combined water, indicating hemi-hydrate calcium sulphate or Plaster of Paris.

The point at which temperature inversion occurs is determined, in part, by the purity of the gypsum, but it is mostly dependent on the temperature and pressure in the autoclave. Temperature and pressure, in turn, are affected by the size of sample, percent solids, rate of heating of the autoclave and, as well, the application of supplementary gas pressure, or the formation of gas by introduced chemicals (e. g. ammonium hydroxide). Presumably an optimum combination of these factors would produce a satisfactory plaster slurry (stucco) with a minimum expenditure of energy. It would appear that the temperature at which inversion occurs is directly proportional to pressure (within limits). In several tests in which auxiliary pressure (compressed air) was used, an increase in the temperature of the inversion point was noted (Test 8, Figure 2). This is undesirable. Later tests were conducted at lower pressures, 30 to 50 psig, created by the natural build-up of steam within the autoclave.

Autoclave calcining tests made with samples of the gypsum as received or water-washed resulted in a product that thickened very slowly and did not harden for several days although the resulting products generally were fairly strong (Test 1, 8 and 31, Table 4). This slow setting action was mostly attributed to unreacted phosphate rock which, as indicated by the chemical analyses, Table 2, was largely concentrated in the plus 65- and plus 100-mesh sizes, as was the silica and fluorine. These fractions, representing only a small portion of the total weight of sample, were usually discarded prior to autoclave treatment.

All head samples were acidic and became increasingly acidic on calcining, even when neutralized with a base prior to or during calcining (Tests 12 and 18, Table 4). This increase in acidity probably was due to the release of CaHPO_4 from the gypsum molecule and to its subsequent dissociation into calcium sulphate and phosphoric acid, which acid was believed to also contribute to the set-retardation effect.

The stucco resulting from samples calcined with sodium hydroxide, added to neutralize or nullify the effect of residual phosphoric acid, thickened fairly quickly but did not develop much strength for many hours. However, most of these products eventually formed high-strength plaster (Test 12, Table 4). Excess sodium hydroxide resulted in the formation of a salt, probably sodium sulphate, on the surface of the plaster. Sodium hydroxide appeared to lower the inversion-point temperature and accelerate the setting action in proportion to the amount added (Test 12, Figure 1- Note: some trouble was experienced with pressure-line blocking in the sodium hydroxide tests. Therefore the pressures recorded may not be entirely accurate). The stucco from samples calcined with ammonium hydroxide, again to nullify the effect of phosphoric acid, thickened and appeared to set very quickly (often in the autoclave itself) but required many hours to harden and develop strength. The products became very strong with ageing. The setting action and strength developed generally appeared to be proportional to the amount of ammonium hydroxide used. The inversion temperatures and pressures were somewhat higher than with sodium hydroxide, perhaps as a direct result of increased pressure due to the liberation of ammonia gas in the autoclave (Test 12 and 18, Table 4 and Figures 2 and 3).

The final series of tests (29 to 54), based on French patents 1,409,248 (Société de Prayon, 1965) and 1,428,193 (Imperial Chemical Industries, Great Britain, 1965) were the most interesting. These indicate that a relatively quick setting, rapid hardening, strong plaster

can be produced by autoclaving phosphoric-acid gypsum with added sulphuric acid (Test 30, Table 4 and Figure 3). The phosphate released during calcining (CaHPO_4) presumably reacts with the sulphuric acid to form calcium sulphate and phosphoric acid. The latter is partly blown off with the vapour following calcination and partly decanted with the autoclave liquor. The results shown in Table 3 indicate a reduction of 94.5% in the P_2O_5 content of acid-treated sample 29 - over three times that of untreated sample 2. The calcium sulphate remains with the stucco and may, in fact, act as a set accelerator. The setting time of the calcined product varies with the amount of acid used, a large quantity producing a more rapid set (within limits). Alternatively the acid may be added to the stucco following completion of the calcining cycle, (Test 31, Table 4). Acid addition following calcination resulted in a marked acceleration of the setting and hardening process. In most tests, an amount of concentrated sulphuric acid equivalent to 2 per cent, or less, of the weight of gypsum (or stucco) appeared adequate.

Good results were obtained with washed, minus 100-mesh gypsum that was acidified with sulphuric acid to pH 0.6 and calcined. The vapour was bled off prior to discharge of the autoclave and the autoclave liquor decanted prior to further acidulation of the resulting stucco. This material set quickly and hardened rapidly (Test 34, Table 4). Samples sandwiched between layers of top and bottom gypsumboard paper appeared to bond well and generally showed no deleterious effects. Unset stucco samples washed or treated with a chemical base following calcination and final acidulation, in an effort to achieve a neutral stucco, generally developed little strength.

Autoclave Test 54, generally similar to 31, showed that a more rapid calcining cycle could be achieved by applying more heat - unfortunately this resulted in a higher calcining temperature (160°C as opposed to 140°C). The resulting product, untreated, was slow-setting and weak. Some acceleration of the set was achieved by the addition of ground gypsum; however, as in previous tests, sulphuric acid addition was required to achieve a rapid set and strong gypsum plaster.

CONCLUSIONS AND RECOMMENDATIONS

The results of this investigation, on the basis of the samples received, indicate that a quick-setting plaster stucco can be produced from wet-process, phosphoric-acid gypsum by the autoclave calcining process outlined. To achieve the desired rapid set, it is imperative that set-retarding phosphates be removed from the system. An initial and substantial reduction of these phosphates was achieved by removal of the plus 65- or plus 100-mesh, high-phosphate gypsum before calcining. Sulphuric acid addition both during calcination, and following calcination and decantation of the residual liquor, effectively nullified the set-retarding effect of the remaining phosphate. Sulphuric acid treatment following calcination is probably the preferred technique as it proved a highly effective method of set control. The resulting stucco, although acidic, bonded well with gypsum wallboard paper and did not appear to exhibit any detrimental effects.

Although the technical feasibility of this process has been demonstrated, detailed investigation by interested groups at a pilot-plant level and a thorough investigation of markets and production costs is required to evaluate the overall economic feasibility.

The recovery of the phosphate values in the plus 65-mesh portion of this gypsum (25.8% P_2O_5 , Table 2) should be considered. Conceivably it may be feasible to remove this fraction by screening and return it to the phosphate acidulation circuit.