

26

Role of catalyst in effecting morphological and mechanical characteristics of high strength α -gypsum plaster

The effect of different salts such as sodium succinate, aluminium sulphate and sodium citrate (0.1 to 0.25 percent) on the morphology and mechanical properties of α -plaster ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) from phosphogypsum under hydrothermal conditions at 1.75 kg/cm^2 steam pressure was investigated. The salts exhibited a quick dehydration of gypsum to α -plaster which is characterised by prismatic, tabular and needle-shaped crystals. α -plaster produced in presence of sodium succinate gave maximum mechanical strength. The formation of hemihydrate was investigated by differential thermal analysis and microscopic studies. The hydraulic properties of α -plaster were studied and it was found to possess considerable high strength (16.20 to 37.80 N/mm^2) depending upon the type of crystals formed.

Calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) or plaster of Paris is an essential component of gypsum plaster which is widely used in building and in the manufacture of sulphuric acid, pottery, ceramics and Portland cement. Calcium sulphate hemihydrate usually arises from the dehydration of dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

There are three crystalline forms of α , β , and γ of gypsum plasters. The most commonly used β -form is made by heating $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at about 130°C - 160°C in an open pan, kettle or a rotary kiln. This plaster has high consistency. Reduction in consistency from 80 - 100 ml to 65 - 70 ml was effected by artificial

ageing treatments comprising of spraying of a fraction of one percent calcium chloride, sodium chloride compounds on to the gypsum prior to calcination or by spraying a predetermined amount of water into the plaster to permit hydration of anhydrite and recrystallisation of hemihydrate¹⁻⁵.

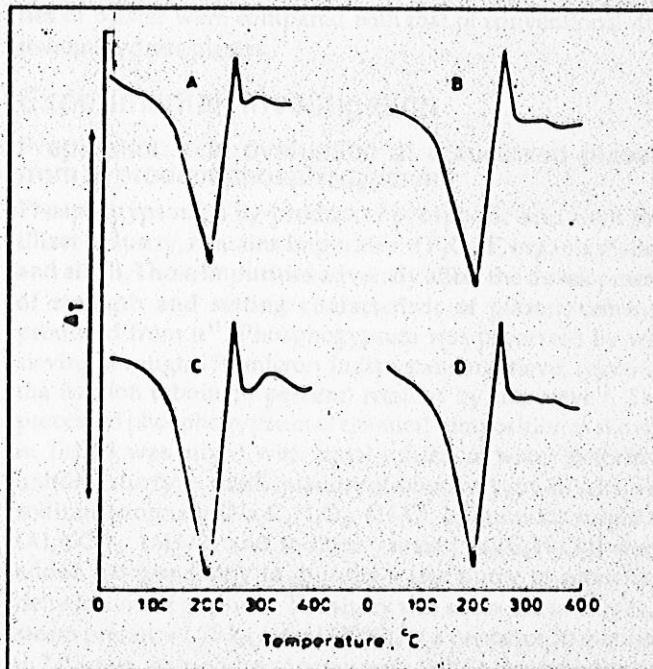


Fig 1 Differential thermograms of gypsum samples autoclaved at 1.75 kg/cm^2 steam pressure for 1 hour in presence of sodium succinate at % : percent, 0.15 percent, 0.20 percent and 0.25 percent respectively

Mary Singh, M. Sc, Ph. D, Scientist, Central Building Research Institute, Roorkee 247 667

Table 1 Chemical composition phosphogypsum

Constituents	Unprocessed phosphogypsum	Processed phosphogypsum
P ₂ O ₅	0.55	0.17
F	1.89	0.74
Organic matter	0.11	0.06
S ₂ O ₃ + insoluble in HCl	0.98	0.90
R ₂ O ₃ (Al ₂ O ₃ + Fe ₂ O ₃)	0.48	0.30
CaO	32.40	32.90
MgO	0.07	0.04
SO ₃	43.00	44.90
N ₂ O	0.38	0.21
Loss on ignition	19.38	19.50

The first practical solution to the problem for making a plaster of much lower consistency popularly known as Hydrocal (α -hemi-hydrate) was offered by Randel and Dailey⁶. Essentially, the method consists of heating gypsum in saturated steam atmosphere (at 1.05 kg/cm²) for 6.0 hours, drying and then grinding. Singh and Rai⁷ corroborated the findings of Randel and Dailey by producing α -plaster at slightly higher steam pressure (1.75 kg/cm²). By this method, the plaster which pours at the consistency of 40-45 ml can be produced. Subsequent to the development of Hydrocal, Gardener⁸ discovered that the consistency of plaster could be reduced to that of Hydrocal by adding a mixture of powdered gum arabic (1 to 2 percent) and certain alkaline reacting materials such as lime, litharge or soda ash. The product is marketed as certrock. The U.S. Gypsum Company⁹ has effected a further lowering of consistency and increase in strength in the product—Hydromite—by the addition of carbamide-formaldehyde resin so that the water requirement of the plaster is practically equal to theoretical requirements.

At the industrial level, the production of high strength

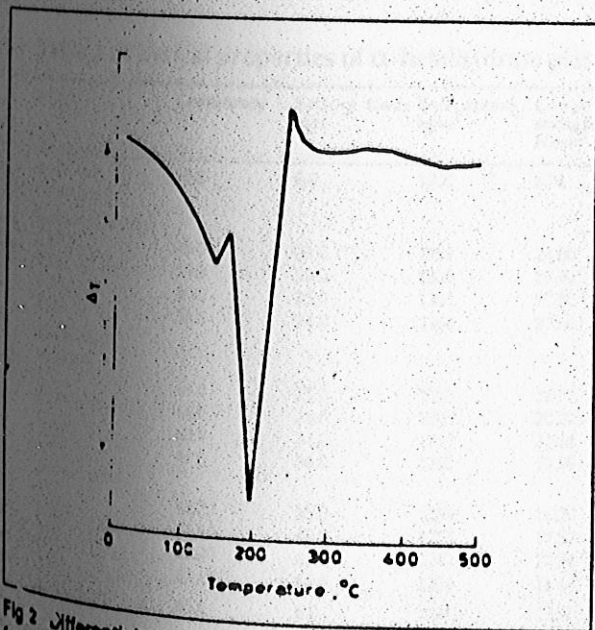


Fig 2 Differential thermogram of autoclaved plaster produced from phosphogypsum without the addition of salts

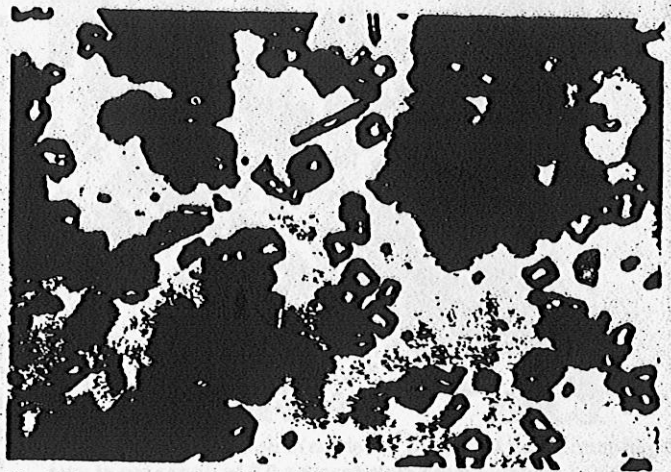


Fig 3 Photomicrograph of α -plaster produced from phosphogypsum in presence of 0.2 percent sodium succinate (X 350)

α -plaster is practised by the process of autoclaving of gypsum. The transformation of gypsum into hemihydrate takes place in long time of 6-7 hours. It has been shown that in the autoclave dehydration of gypsum to form hemihydrate, crystal growth of the hemihydrate from solution may occur in addition to solid state reaction¹⁰. If it is so, it should be possible to accelerate the dehydration process by the addition of salts/nucleating agents. Experiments were therefore carried out to accelerate dehydration of gypsum to form hemihydrate by the addition of different organic and inorganic salts. The formation of α -hemihydrate was evaluated using differential thermal analysis (DTA) and microscopic studies. The properties of plaster were compared with that of conventional dry α -hemihydrate plaster.

Experimental Investigation

Preparation and evaluation of autoclaved plaster from byproduct phosphogypsum

Phosphogypsum, a by-product of phosphoric acid from fertilizer industry, contains impurities of P₂O₅, F, organic matter and alkali. These impurities adversely affect the development of strength and setting characteristic of plaster/cements produced from it¹¹. Phosphogypsum was processed by wet sieving through 150 micron Indian standard sieve, rejecting the fraction (about 15 percent) retained by this sieve¹². The processed phosphogypsum of chemical composition as shown in Table 1 was mixed with equal volume of water to form a uniform slurry. A small quantity of laboratory grade salts, viz sodium succinate (Na₂C₄H₄O₆ · 6H₂O), aluminium sulphate (Al₂(SO₄)₃ · 16H₂O) and sodium citrate [Na₃(C₆H₅O₇)] were added independently to gypsum-water slurry to accelerate dehydration of gypsum. The slurry was subjected to only one steam pressure 1.75 kg/cm² (130°C) for a period of 30 minutes to 2.0 hours. At higher temperature (> 130°C), the dehydration of the small quantity of gypsum was too rapid to permit studies on the acceleration of the reaction by the salts. The autoclaved material was filtered and washed using dried acetone and finally ground to a surface area of 4000 cm²/g (Blaine's) surface area in a ball mill.

Mineralogical examination

Differential thermal analysis (DTA) of the ground plaster samples was performed. For microscopic examination, autoclaved plaster sample was spread in water over the glass plate and examined using a Zeiss petrographic microscope. The physical properties, viz. consistency, setting time, bulk density and compressive strength were determined as per ASTM C 472 - 1979 and IS:2542 (Part 1)-1976.

Results and discussions

Preparation of α -plaster from phosphogypsum

DTA of the steam-treated samples autoclaved in the presence of different salts indicated that with increase in the duration of autoclaving from 30 minutes hour to 2.0 hours associated with increase in salt concentration, the intensity of hemihydrate endotherm (200°C) is increased with the addition of salts upto 0.2 percent. Beyond this concentration, the intensity of hemihydrate endotherm remains more or less the same indicating thereby the dehydration of gypsum is completed at 0.2 percent of salt concentration. At one hour of autoclaving, maximum increase in the hemihydrate endotherm was observed. In case of $Al_2(SO_4)_3 \cdot 16H_2O$ and $Na_3(C_6H_5O_7)_2$ salts, the pattern of increase in hemihydrate endotherm is similar to the pattern found in $Na_2C_4H_4O_6 \cdot 6H_2O$. However, the increase in size of hemihydrate endotherm is comparatively less marked than the endotherm obtained for $Na_2C_4H_4O_6 \cdot 6H_2O$, confirming thereby less formation of hemihydrate phase.

A typical DTA obtained in case of autoclaved α -plaster produced in presence of $Na_2C_4H_4O_6 \cdot 6H_2O$ is shown in Fig 1. DTA shows that the hemihydrate endotherm (200°C) is immediately followed by a sharp exotherm at 240°-250°C which indicates inversion of soluble anhydrate (γ - $CaSO_4$) into insoluble anhydrite (β - $CaSO_4$) phases. It is due to the fact that structure of autoclaved α -plaster is such that after expulsion of the water of crystallisation, very little energy is needed to

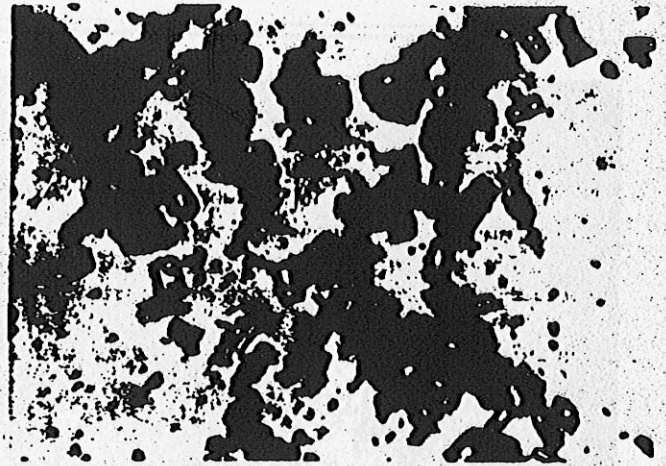


Fig 4 Photomicrograph of α -plaster produced from phosphogypsum in presence of 0.2 percent aluminium sulphate (X 350)

induce inversion to β -anhydrite. Possibly the relatively drastic manufacturing process causes increased strain in the crystal structure and makes the γ - $CaSO_4$ structure even more unstable. Fig 2 shows DTA of α -plaster produced from phosphogypsum without the presence of sodium succinate. Appearance of dehydration endotherm at 150°C indicates the presence of uncalcined gypsum in the plaster.

Microscopic structure of α -plaster

The photomicrographs of α -hemihydrate (1.75 kg/cm² steam pressure for 1 hour) produced in presence of 0.2 percent $Na_2C_4H_4O_6 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 16H_2O$ and $Na_3(C_6H_5O_7)_2$ are shown in Figs 3, 4 and 5, respectively. In Fig 3, a majority of crystals is euhedral prismatic and tabular shaped and well developed needle crystals can also be seen. Fig 4 indicates formation of euhedral prismatic crystals and the meshing characteristic of crystals. Fig 5 shows formation of euhedral columnar prismatic crystals of variable sizes. A majority of the crystals is of short length. The formation of such crystals of hemihydrate can be attributed to its method of preparation wherein a process of recrystallization takes place. Fig 6 shows formation of prismatic, needle and lath-shaped crystals in clusters. Presence of broad lath crystals indicate unconverted gypsum in the plaster.

The basic theory of different salts on the production of α -plaster is not completely clear. The effect of sodium succinate occurs primarily upon the dehydration of gypsum and not upon the recrystallisation of the $CaSO_4 \cdot \frac{1}{2}H_2O$. This finding was corroborated by Hadden¹³ and Ryoza¹⁴. Hadden did the microscopic studies of the α -plaster produced from gypsum of purity more than 90 percent. It was found that α -plaster produced with and without the presence of sodium succinate showed no difference in microscopic appearance or consistency when compared with the $CaSO_4 \cdot \frac{1}{2}H_2O$ produced from the gypsum (greater than 90 percent) in the kettle. Both autoclaved plaster samples found to be prismatic, tabular or needle like. It is presumed that sodium citrate salts and aluminium sulphate also behave in similar fashion. The formation of crystals

Table 2 : Physical properties of α -hemihydrate plaster

Salts	Consistency	Setting time, min	Bulk density, kg/m ³	Compressive strength, N/mm ²
α -Plaster without salt	69.0	6.0	1200	8.76
Sodium succinate				
0.10	45.0	36.0	1299	24.80
0.15	32.3	38.0	1339	27.30
0.20	35.0	35.0	1381	37.80
0.25	36.5	34.0	1366	37.50
Aluminium sulphate				
0.10	46.0	25.0	1283	18.77
0.15	44.0	28.0	1285	20.27
0.20	43.0	34.0	1291	21.64
0.25	44.0	36.0	1280	25.36
Sodium citrate				
0.10	44.20	35.0	1259	16.20
0.15	43.50	40.0	1275	17.52
0.20	42.00	46.0	1282	17.94
0.25	43.40	50.0	1226	16.64
β -Hemihydrate plaster	65.0	8.0	1200	13.50

prismatic and columnar shaped crystals were detected by Vladimir¹⁵ while working on the production of α -plaster from phosphogypsum in aqueous suspension. Koo Jong and Sang Heul¹⁶ have indicated the prismatic form of crystals produced in presence of aluminium sulphate.

Physical properties of α -plaster

The physical properties determined for α -plaster are reported in Table 2. For comparative study, the properties of β -hemihydrate are also reported. Data show increase in bulk density and compressive strength of the plaster with the increase in the concentration of salts up to 0.2 percent. At 0.25 percent concentration, the strength is slightly reduced. The α -plaster produced in presence of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$ gives maximum strength. The increase in the strength can be attributed to the fall in the consistency of the plaster samples. The lower water requirement of the plaster can be understood from the morphology of plaster. Autoclaved α -plaster comprises of large, dense and non-porous crystals with fewer cracks and voids. The particles do not require water to fill pores as found in case of β -hemihydrate plaster. In contrast β -hemihydrate consists of microscopic porous crystals requiring much higher quantity of water to produce a workable slurry satisfying normal consistency.

The setting of α -plaster is more than the setting time of β -hemihydrate plaster. The retardation of setting time in case of α -plaster is ascribed to the formation of large crystals of smaller surface area. On the contrary, β -hemihydrate plaster has a shorter setting time owing to the increase in the number of effective nuclei for the crystallisation of gypsum.

Conclusions

α -hemihydrate plaster of low water requirement, high strength can be produced by autoclaving phosphogypsum for one hour in presence of 0.20 percent sodium succinate, aluminium sulphate or sodium citrate, removing the water and regrinding the product. Every salt added to the gypsum slurry depending upon its concentration has its definite effects

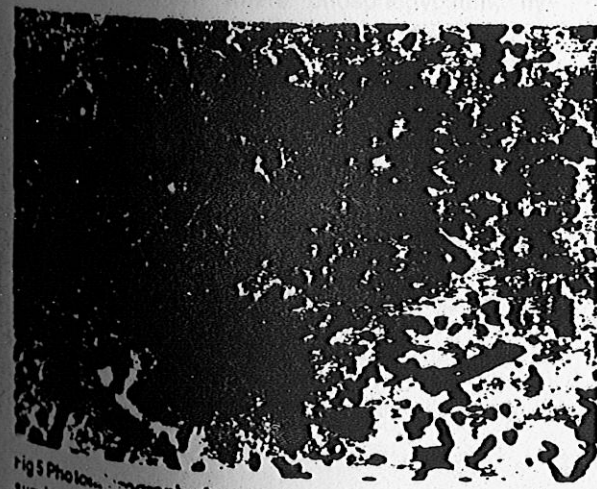


Fig 5 Photomicrograph of α -plaster produced from phosphogypsum in presence of 0.2 percent sodium citrate X 350

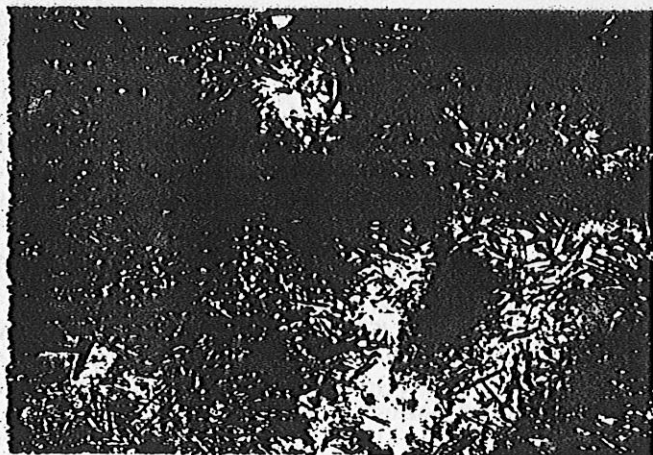


Fig 6 Photomicrograph of α -plaster produced from phosphogypsum without salt addition (X 350)

on the development of shape of the plaster crystals which ultimately lead to the variable strength and setting characteristics. The catalytic effect of salts can be represented as follows : sodium succinate > aluminium sulphate > sodium citrate.

Acknowledgement

This investigation forms part of the research programme of the Central Building Research Institute, Roorkee. The paper is being published with the permission of the Director.

References

1. BROOKLEY, H.E., US patent 1370581, 1921.
2. HOGGATT, G.A., US Patent 1960538, 1934.
3. HOGGATT, G.A., US patent 2002945, 1935
4. HOGGATT, G.A., US patent 2067762, 1937
5. MCANNALLY, S.G., US patent 1713879, 1929.
6. RANDEL, W.S., and DAILEY, M.C., US patent 1901051, 1935.
7. SINGH, MANJIT AND RAI, MOHAN, *Journal of Chemical Technology and Biotechnology*, 1988, Vol. 43, pp. 1-12
8. GARDENER H.L., US patent 1996372, 1935.
9. U.S. Gypsum Company Building, I.C.L. 19.
10. COMBE, E.C., and SMITH, D.C., *Journal of Applied Chemistry*, 1968, Vol. 18, p. 307.
11. SINGH, MANJIT, *Building Research Note No.9*, Central Building Research Institute, Roorkee, 1988.
12. SINGH, MANJIT, REHSI, S.S., and TANEJA, C.A., *National Seminar on Building Materials - Their Science and Technology*, New Delhi, 1982, p. III.
13. HADDEN, C.L., and CAFFERATA, B., British patent 563019, 1944.
14. RYOZO INOUE, YASUHIRO, OKOJIMA, JUNICHI TANAKA and NOBUKO KOBAYASHI, *Chemical Abstract*, 1978, Vol. 89, 16837d.
15. VLADIMIR, SATAVA, OTAKAV, VEPREK, and FRENTISCK, SKVARAG, *Chemical Abstract*, 1979, Vol. 91, 61723f
16. LEE, KOOJONG, CHOI, SANG HEUL, *Chemical Abstract* 1989, Vol. 110, 23755j