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Processing of Phosphogypsum for the Manufacture of Gypsum Plaster

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Phosphogypsum, a by-product of wet-process phosphoric acid industry, is available to the tune of 2.0 million tonnes per year. It contains impurities, such as phosphate, fluoride, and organic matter, which inhibit its large scale utilisation. A process has been evolved at CBRI for eliminating these impurities and to render phosphogypsum for making gypsum plaster with superior physical properties.

Phosphogypsum is a by-product of wet-process phosphoric acid plants. About 4 to 5 tonnes of it is obtained for every tonne of phosphoric acid produced.

Sixty million tonnes of phosphogypsum is produced annually throughout the world¹. The need to use phosphogypsum as the starting material for the gypsum industry is not the same in all the countries. Japan, a country which does not have the deposits of natural gypsum, consumes all of its by-product gypsum. In 1974, about 4 million tonnes of phosphogypsum was utilised for the production of cement and plaster board². In Central Europe, phosphogypsum is also currently in use in the gypsum industry to some extent³.

In India, about 2 million tonnes of phosphogypsum is available per annum. It is normally produced by the dihydrate process. At present, it is being disposed of either in the river or on the land close to the fertilizer plants. The main cause of its restricted use in the building industry is due to the presence of impurities, such as phosphates, fluorides and organic matter in it. These impurities are known to adversely affect the setting and strength development of plaster produced out of it⁴.

A method, developed at this Institute for processing phosphogypsum to manufacture gypsum plaster of improved properties, has been described in this paper.

Experimental procedure

Characterization of phosphogypsum—Two samples of phosphogypsum were procured from M/s Fertilizer and Chemicals, Travancore, Alwaye and M/s Gujarat State Fertilizer Co. Ltd, Baroda, which were designated as A and B respectively. These samples were produced by the dihydrate process of phosphoric acid manufacture. The samples were analysed for their various constituents following different test procedures⁵⁻¹⁰. The results are given in Table 1.

Processing of phosphogypsum—Neutralization of calcined phosphogypsum has been reported to inactivate the impurities of phosphate and fluoride¹¹. Following this approach, phosphogypsum samples were converted to hemihydrate plaster by calcining it at 160°C for 4-5 hr and then neutralized with milk of lime. The neutralized phosphogypsum samples were analysed for residual impurities of P₂O₅, F and organic matter. The results are given in Table 2.

Table 1—Chemical Analysis of Phosphogypsum Samples

Constituents	A	B
	(%)	(%)
Total P ₂ O ₅	1.03	0.63
Water-soluble P ₂ O ₅	0.72	0.21
Lattice-bound P ₂ O ₅	0.28	0.38
Insoluble P ₂ O ₅	0.03	0.04
Total F	0.76	1.33
Water-soluble F	0.51	0.90
Insoluble F	0.25	0.43
Organic matter	0.26	0.56
SiO ₂	1.64	3.20
R ₂ O ₃ (Al ₂ O ₃ + Fe ₂ O ₃)	1.82	2.88
CaO	32.02	30.33
MgO	0.40	1.93
Na ₂ O	0.36	0.43
SO ₃	43.60	39.44
H ₂ O	18.01	18.99

Production and testing of phosphogypsum plaster—Phosphogypsum samples before and after processing were calcined at 160°C for 4-5 hr to hemihydrate plaster (CaSO₄·½H₂O), cooled and desiccated. The plaster was then ground to pass 150 micron IS sieve and tested for different physical properties as per SSA Int. 317¹². The results are reported in Tables 3 and 4.

Discussion

Data on chemical analysis (Table 1) show that phosphogypsum has impurities of phosphate, fluoride and organic matter. The impurities are mainly classified as water-soluble, insoluble and lattice-bound. The latter type of impurity in phosphogypsum is due to the solid solution formation of CaHPO₄·2H₂O with the CaSO₄·2H₂O because of their similar lattice parameters and they also belong to the analogous space group. The soluble impurities are mainly the free H₃PO₄, Ca(H₂PO₄)₂·H₂O, NaF and Na₂SiF₆ found usually on the crystal surface and in the interstices of agglomerated gypsum crystals. The insoluble portion of

Table 2—Percentage of Impurities in Phosphogypsum After Calcination and Neutralization

Sample designation	Ca(OH) ₂ (%)	Impurities (%)		
		P ₂ O ₅	F	Organic matter
A	4.0	0.94	0.66	0.19
B	4.0	0.57	1.21	0.36

Table 3—Physical Properties of Unprocessed Phosphogypsum Plaster

Sample designation	Consistency (%)	Setting time (min)		Bulk density (kg/m ³)		Compressive strength (kg/cm ²)	
		A.S.	0.1% K.R.	A.S.	0.1% K.R.	A.S.	0.1% K.R.
A	65.0	3.5	16.5	1270	1110	101.36	83.44
B	64.5	3.0	17.5	1280	1109	80.39	70.08

A.S. = As such, K.R. = keratenious retarder.

Table 4—Physical Properties of Processed Phosphogypsum Plaster

Sample designation	Ca(OH) ₂ (%)	Consistency (%)	Setting time (min)		Bulk density (kg/m ³)		Compressive strength (kg/cm ²)	
			A.S.	0.1% K.R.	A.S.	0.1% K.R.	A.S.	0.1% K.R.
A	4.0	62.0	6.5	20	1230	1200	124.42	98.20
B	4.0	63.0	4.0	23	1240	1180	89.20	84.40

A.S. = As such, K.R. = keratenious retarder.

impurity is the unetched phosphate rock consisting chiefly of fluorapatite mineral.

The impurities present in the interstices of agglomerated crystals are difficult to remove just by simple water washing. On calcining phosphogypsum to hemihydrate plaster, P_2O_5 , F and organic matter held up in the interstices of agglomerated crystals are released. At the same time HPO_4^{2-} and AlF_3^{--} ions present in the gypsum crystal lattice are also partially expelled due to change in the crystal system of gypsum from monoclinic to pseudotrigonal. The addition of milk of lime to calcined phosphogypsum plaster provides high alkaline conditions under which the released P_2O_5 and F compounds react with milk of lime and precipitate out as insoluble $Ca_3(PO_4)_2$ and CaF_2 together with the already available water-soluble P_2O_5 and F.

It can be seen from Table 2 that the optimum percentage of $Ca(OH)_2$ required for neutralizing the impurities, P_2O_5 and F, is 4%. It was determined by adding $Ca(OH)_2$ solution in different concentrations to the calcined phosphogypsum ($CaSO_4 \cdot \frac{1}{2}H_2O$) and measuring its pH value. It was found that on adding 4.0% $Ca(OH)_2$, the pH value was increased from 2.9 and 3.3 for unprocessed phosphogypsum samples A and B to 8.5 and 8.0 for the processed phosphogypsum samples. Further addition of $Ca(OH)_2$ did not show any appreciable change in the pH of phosphogypsum indicating thereby the completion of neutralization process. Data in Table 2 show that the level of P_2O_5 and F remained more or less the same in the phosphogypsum before as well as after processing. It may be attributed to the fact that P_2O_5 and F remain intact in the phosphogypsum even after the treatment with $Ca(OH)_2$ and it is only the form of compounds in which they are present after processing gets changed.

Table 4 shows an increase in bulk density and compressive strength values of phosphogypsum

plaster both with and without keratenious retarder. The consistency of plaster is reduced and the setting-time has been found to be prolonged (c/ Table 3). The improvement in various physical properties of processed phosphogypsum plaster over the unprocessed phosphogypsum plaster can be assigned to the conversion of P_2O_5 and F impurities into the insoluble compounds, i.e. $Ca_3(PO_4)_2$ and CaF_2 .

Conclusion

The impurities of phosphate and fluoride present in phosphogypsum can be converted into insoluble form by first calcining phosphogypsum to hemihydrate plaster and subsequently neutralizing the released impurities with 4% of milk of lime. The processed phosphogypsum can be used for the manufacture of hemihydrate plaster with improved properties to be used in the building industry.

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