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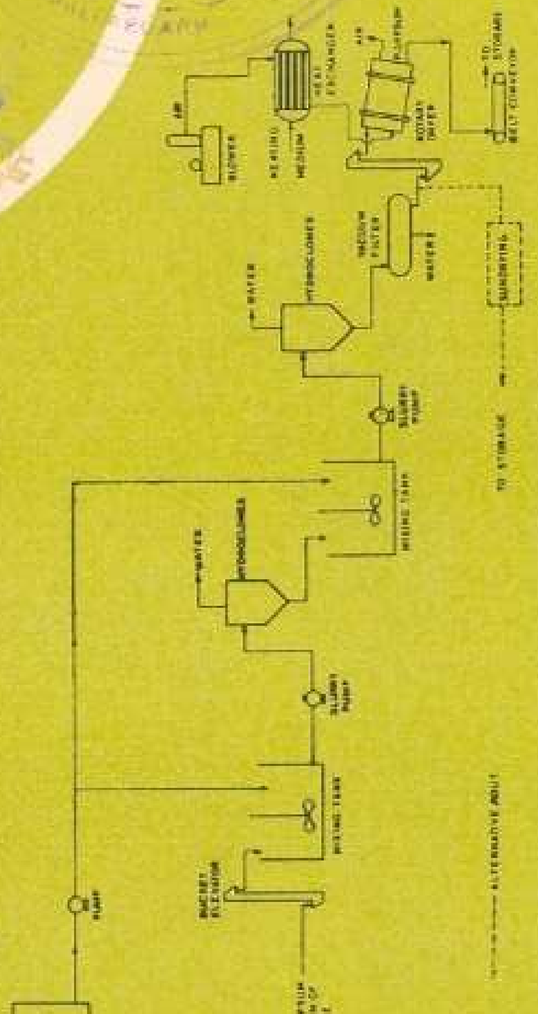
February 1981

CRI TECHNOLOGY DIGEST



CEMENT RESEARCH INSTITUTE OF INDIA

BY PRODUCT PHOSPHO-GYPSUM AS SET CONTROLLER FOR CEMENT

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This Technology Digest briefly focusses attention to the feasibility of using byproduct gypsum from phosphoric acid manufacture as set controller for ordinary Portland cement. The advantages of phosphogypsum over mineral gypsum for cement plants not favourably located with respect to the latter and the manner of processing phosphogypsum for regular use as set controller are discussed.

THE CASE

Although India has good reserves (nearly 1000 million tonnes) of natural gypsum, these are mainly concentrated in three states, namely, Rajasthan (80 percent), Gujarat and Tamil Nadu. The cement plants on the other hand are relatively more widely distributed over the country owing to which they have to transport mineral gypsum of the required quality over long distances, involving large physical and financial resources. On the other hand, a number of chemical industries, such as manufacture of phosphoric acid and hydrofluoric acid yield large quantities of byproduct gypsum in the form of anhydrite, hemihydrate and phosphogypsum (dihydrate) creating considerable disposal and environmental problems. The bulk of byproduct gypsum is available in the form of phosphogypsum, a dihydrate form of calcium sulphate which is a potential source of gypsum for cement industry. The proximity to cement plants of some of the sources of phosphogysum in India indeed makes it an economical alternative to natural gypsum for such plants. From the view-point of its SO_3 content too, phosphogypsum is richer than natural gypsum because of which marginally lesser quantities would do. Despite all these advantages, phosphogypsum was not being used as set controller in Indian cement industry while in some countries including Japan it is being used successfully. This was owing to reservations on the effect of some impurities in phosphogypsum on the performance of cements and possibly absence of data on the economic viability of treating phosphogypsum to free it from the impurities. These have now been cleared by the comprehensive technoeconomic studies including plant trials carried out by Cement Research Institute of India.

PHOSPHOGYPSUM — CHARACTERISATION

Between the dihydrate and the hemihydrate-dihydrate processes of making phosphoric acid, most Indian plants employ the dihydrate process. The process, which involves reaction between calcium phosphate rocks and sulphuric acid, gives phosphoric acid and crystalline calcium sulphate in slurry form containing 15-40 percent moisture. The phosphogypsum, on an average, contains more than 90% $CaSO_4.2H_2O$ and is hence richer in SO_3 content compared to cement grade gypsum which is normally of 80-85% purity. As is the case with all chemical processes using natural raw materials, byproduct phosphogypsum is always contaminated with impurities like P_2O_5 in the form of mono and dicalcium phosphates, undecomposed phosphate rocks, residual acid, fluorides and traces of radioactive material like radium. While P_2O_5 content varies from 0·5 to 0·9% and fluorids range from 0·6 to 1·15%, the residual acid content corresponds to a *p*H of 2·7 to 6·4. These impurities effect the setting time of cements and reduce strength development at early ages while later age strengths are either unaffected or even improved. The influence of impurities on setting is not only different amongst themselves but becomes truly complex in conjunction with clinkers that the general set-retarding trend of the impurities is even reversed with some clinkers. Thus, phosphates and fluorides retard the setting time while free acids generally have the opposite effect. Together with the C_3A and alkalis in clinker, which have their own effects, the overall setting behaviour is altered depending upon their relative contents. All in all, the general behaviour of cements made with phosphogypsum is erratic. In any case, since the role of phosphogypsum as set controller is conditioned to a great extent by the composition of the clinker with which it is to be used, compatibility between a clinker and a phosphogypsum is essential for the latter to be used as set controller.

BENEFICIATION OF PHOSPHOGYPSUM

Since it is the impurities in phosphogypsum which adversely effect its performance as a set retarder, it has to be treated to remove/minimise the impurities. It is equally important to render the phosphogypsum of uniform quality. Thus, any process of beneficiation has essentially to achieve both these objectives. Above all, it has to be simple and economical. Further, it should not introduce any new problem. In this context, washing with water comes out to be the most acceptable as soluble impurities can be removed. Though washing may not be able to remove the lattice-bound impurities, such as P_2O_5, it generally leads to increase in early strengths of cement, which in effect offsets the drawback associated with the use of phosphogypsum.

The process of washing phosphogypsum should include its drying, on the one hand, and its compaction to some extent, on the other. This is so not only because handling of the material in slurry or wet state is inconvenient but also its transport would be costlier owing to its water content. On the other hand, handling and transport of dry powders too has its problems, hence its compaction to nodules/pellets with limited water content. The plant for washing phosphogypsum should be an adjunct to the fertilizer plant for reasons of economy and ready availability of infrastructural facilities. For the rest, there are 4 variants of the process as below which differ in the modes of washing, drying and/or compaction of the product :

Process I—The phosphogypsum is washed in hydrocyclones and the slurry filtered in a horizontal continuous vaccum filter. The filter cake is dried to 2% moisture and sent to storage. Alternatively, the filter cake could be dried in sun to reduce the moisture to 5-6%.

Process II—Here, the washing is done in agitated tanks, the rest remaining the same as Process I.

Process III—Phosphogypsum, discharged from the vaccum filter in the phosphoric acid process as a slurry, is pumped into a helical conveyor centrifuge. The phosphogysum is separated, washed, again separated and is discharged on to a conveyor which feeds the material with controlled moisture content to a roll press that pelletises the product. The pellets are then sent to storage.

Process IV—Phosphogypsum slurry from the phosphoric acid process is pumped into a wash tank, agitated with compressed air and the solids separated in a batch, top suspended centrifuge. The solids with controlled moisture content are fed to the roll press and the pellets sent to storage.

Of these, process I with sun drying and process III are the more economical. Between the two, Process III is more advantageous since the product in pellet form is easier to handle in transport as well as feeding to the ball mill in cement plants.

CEMENT PLANTS AND PHOSPHOGYPSUM SOURCES CLOSE TO THEM

S. No	Cement Plant	Phosphogypsum Source	Distance km
1	Andhra Cement Ltd, Vijayawada	Coromandel Fertilizer Ltd	280
2	Associated Cement Cos Ltd (ACC), Kistna	-do-	295
3	Cement Corporation of India Ltd (CCI), Mandhar (MP)	-do-	530
4	Travancore Cements Ltd Nattakom	Fertilizer and Chemicals Travancore Ltd, Alwaye	45
5	Dalmia Cement (Bharat) Ltd Dalmiapuram	EID Parry Ltd, Enmore	305
6	India Cements Ltd Sankaridurng	-do-	325
7	ACC, Sevalia	a) Gujarat State Fertilizers Ltd, Baroda	35
		b) Fertilizer Corporation of India Ltd (FCI), Trombay	315
8	ACC, Shahabad	a) Albright, Morarji & Pandit Ltd, Ambernath	325
		b) FCI, Trombay	415
9	Bagalkot Udyog Ltd, Bagalkot	a) Albright, Morarji & Pandit Ltd, Ambernath	315
		b) FCI, Trombay	405
10	India Cements Ltd, Sankarnagar	Southern Petrochemical Industries Corpn, Tuticorin	23
11	ACC, Sindri	FCI, Sindri	Negligible
12	Durgapur Cement Works Durgapur	FCI, Haldia	190
13	Dalmia Dadri Cements Ltd Charkhi-Dadri	Hindustan Copper Ltd, Khetri	90
14	Udaipur Cement Works, Udaipur	Hindustan Zinc Ltd, Debari	20

COST ANALYSIS

The fixed and the working capital costs for processing phosphogypsum by all the four processes have been estimated. These vary respectively from Rs 85 lakhs to Rs 20 lakhs and Rs 1·5 lakhs to Rs 3 lakhs. The cost of processed phosphogypsum works out to between Rs 83 and Rs 59/tonne assuming a raw material cost of Rs 25/tonne. The landed cost, after providing for normal returns on capital, octroi, handling and transport over 500 km works out to Rs 193 to Rs 154/tonne.

Plant trials at a cement plant with phosphogypsum obtained from about 500 km away showed a net saving of Rs 5-6/tonne of cement produced. This plant otherwise transported natural gypsum over 1300-1400 km for its regular use.

OUTLOOK FOR PHOSPHOGYPSUM AS SET CONTROLLER

As mentioned at the outset, use of phosphogypsum as set controller would be economically attractive to those cement plants which are more favourably located with respect to phosphogypsum sources than those of mineral gypsum. There are at least 14 such cement plants as given in the Table.

Towards the commercial utilisation of phosphogypsum as set controller, Cement Research Institute of India, as pioneers in the technoeconomic evaluation of the byproduct, is in a position to help interested cement plants.

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