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Treating waste phosphogypsum for cement and plaster manufacture

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Abstract

In the investigation reported in this paper, treatment of phosphogypsum with aqueous citric acid solution was attempted to purify phosphogypsum and improve its quality to make it fit for manufacture of cement and gypsum plaster for the first time. The treatment of gypsum converts phosphatic and fluoride impurities into water-removable citrates, aluminates and ferrates. The findings of chemical and physical tests and differential thermal analysis of the phosphogypsum with and without citric acid treatment established improvement of the treatment for purifying phosphogypsum. The purified phosphogypsum was found to have lesser amount of impurities of phosphates, fluorides and organic matter than the impure material. The Portland and Portland slag cements produced with purified phosphogypsum were found to have strength properties similar to those produced from mineral gypsum, whereas gypsum plaster produced conformed to the relevant Indian Standards. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphogypsum; Fluoride; Waste management; Portland cement

1. Introduction

Phosphogypsum is an industrial byproduct of phosphoric acid manufacture using a single (dihydrate) or two-step (hemihydrate–dihydrate) process. Over 6.0 million tons of phosphogypsum is produced per annum in India and poses various environmental and storage problems. Phosphogypsum contains impurities of free phosphoric acid, phosphates, fluorides and organic matter that adhere to the surface of gypsum crystals and also substituted in the crystal lattice of gypsum [1–3]. Phosphogypsum also contains radioactive elements such as U^{238}, U^{234}, Ra^{226}, Pb^{210} and Po^{210}, which are derived from the phosphate rocks [4,5]. The contents of radioactive elements vary in a wide range, depending on the composition of rock phosphate. In India, most of the phosphogypsum is produced out of the Morroco phosphate rock; as a result, the level of radioactivity does not exceed 13.5 pCu/g specified by Euratom [6]. It is essential to remove these impurities to use phosphogypsum for controlling the cement hydration. Some beneficiation processes comprising washing with water, thermal as well as chemical treatments have been applied to gypsum sludge [7]. It has been found that water-soluble impurities can be removed by washing with water, whereas HPO_4^{2-} and FPO_3^{2-} substituted in the crystal lattice of gypsum with SO_4^{2-} ions form solid solutions and are difficult to remove by washing. In heating phosphogypsum towards hemihydrate stage, HPO_4^{2-} ions get freed, which form inactive compounds on neutralization with $Ca(OH)_2$ [8,9]. The impurities of phosphates and fluorides can be reduced by treating phosphogypsum with a mixture of sulphuric acid and silica [10], ammonium hydroxide [11] or aqueous ammonium sulphate solutions [12]. Recently, a process has been developed at the Central Building Research Institute for the beneficiation of phosphogypsum wherein impurities, particularly undecomposed phosphate rock, organic matter, alkalis, quartz, etc., retained over a 300-μm sieve, are discarded as they are rich in impurities while the bulk of gypsum passing through the sieve is further washed, centrifuged and dried for making value-added building materials [13].

In the present study, investigations were carried out to mitigate the level of P_2O_5, fluorides, organic matter and alkalis in the phosphogypsum and make it suitable for use in the manufacture of cement and gypsum plaster by treating with small quantity of aqueous citric acid solution and subsequent washing with plain water. The properties of Portland cement and Portland slag cement and that of gypsum plaster have been reported and discussed in the paper.

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2. Experimental

2.1. Raw materials

Phosphogypsum samples were collected from two fertilizer plants in India (Table 1). Samples DA and HDS were produced by the dihydrate and hemihydrate–dihydrate processes, respectively. These samples were analysed for their chemical constituents as per standard test procedures [14,15].

Table 1
Phosphogypsum samples

Sample code	Source of phosphogypsum
DA	Albright Morarji And Pandit, Ambernath (Maharastra)
HDS	Southern Petrochemical Industries, Tuticorin (Tamilnadu)

2.2. Reagent grade chemicals

- Reagent grade citric acid $(C_6H_8O_7)_2$
- Phosphates: $Ca(H_2PO_4)\cdot H_2O$, $CaHPO_4\cdot 2H_2O$ and $Ca_3(PO_4)_2$
- Fluorides: NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF_2.

2.3. Cement clinker

Cement clinker of composition SiO_2 24.17%, Al_2O_3 6.01%, Fe_2O_3 3.38%, CaO 62.42%, MgO 3.21%, SO_3 0.41%, Na_2O 0.31%, K_2O 0.40%, insoluble matter 0.24% and loss on ignition 0.46% was used to produce cement. The phase composition of cement clinker as calculated from the Bogue analysis method was C_3S 43.40%, C_2S 28.30%, C_3A 11.28% and C_4AF 10.25%.

2.4. Granulated blast furnace slag

Granulated slag of chemical composition SiO_2 30.0%, FeO 0.72%, Al_2O_3 26.80%, CaO 31.50%, MgO 7.32%, MnO 2.29%, sulphide 0.62% and glass content 92.0% was used to produce Portland slag cement.

2.5. Solubility determination

The solubilities of various phosphatic and fluoride compounds were determined in water at 30 °C as suggested by Stephen and Stephen [16] by shaking the known quantities of the reagent grade chemicals in distilled water and subsequently drying the extract at temperature below 100 °C.

2.6. Purification of phosphogypsum

The phosphogypsum samples were thoroughly shaken with 2–5% aqueous citric acid solution in a mechanical shaker for 15–25 min at 30 °C, filtered through a Buchner funnel and washed with 0.5–1.0% aqueous citric acid solution then washed with plain water two to three times. The purified gypsum samples were dried at 42 °C and analysed for residual impurities.

Table 2
Chemical composition of phosphogypsum

	Phosphogypsum samples	
Constituents (%)	DA	HDS
SiO_2	0.60	0.96
$Al_2O_3+Fe_2O_3$	5.86	0.05
CaO	27.76	32.07
MgO	0.25	0.01
SO_3	39.65	45.08
H_2O	17.84	19.68
P_2O_5	0.95	0.66
F	1.5	1.46
Organic matter	0.13	0.59
Alkalies (Na_2O+K_2O)	0.46	0.27

The removal of impurities was monitored by differential thermal analysis (DTA) of the purified gypsum. DTA was performed on a Stanton Redcroft (UK) DTA unit using alpha quartz as a control material at the rate of 10 °C/min.

2.7. Preparation and testing of cement and gypsum plaster

Portland cement was produced by intergrinding cement clinker with the impure phosphogypsum samples at 1.8% SO_3 content (3.87% pure $CaSO_4\cdot 2H_2O$) to a fineness of 320–330 m^2/kg (Blaine). The Portland slag cement was produced by intergrinding the granulated blastfurnace slag and cement clinker with 5.0% gypsum to a fineness of 400–420 m^2/kg (Blaine). The cements produced were tested for setting time, compressive strength and autoclave expansion as per IS 4031–1988 [17].

Gypsum plaster (β-$CaSO_4\cdot 1/2H_2O$) was produced by calcining phosphogypsum at 130–170 °C in the gypsum calcinator [18]. The plaster, after grinding in the ball mill to a fineness of 310 m^2/kg (Blaine), was tested for various physical properties as per Ref. [19].

3. Results and discussion

3.1. Characterization of phosphogypsum

The results of the chemical analysis of the phosphogypsum samples are shown in Table 2. Data show that phosphogypsum sample HDS has comparatively lower levels of P_2O_5, F and alkalis than the phosphogypsum sample DA. However, the organic matter was higher in HDS than DA; probably, the metamorphic rock could have been used in the manufacture of phosphoric acid.

In phosphogypsum, P_2O_5 generally exists as H_3PO_4, $Ca(H_2PO_4)_2\cdot H_2O$, $CaHPO_4\cdot 2H_2O$ and $Ca_3(PO_4)_2$. P_2O_5 found adhered to the surface of gypsum crystals is water-leachable, whereas P_2O_5 present in the crystal lattice is difficult to be removed by simple water washing. The

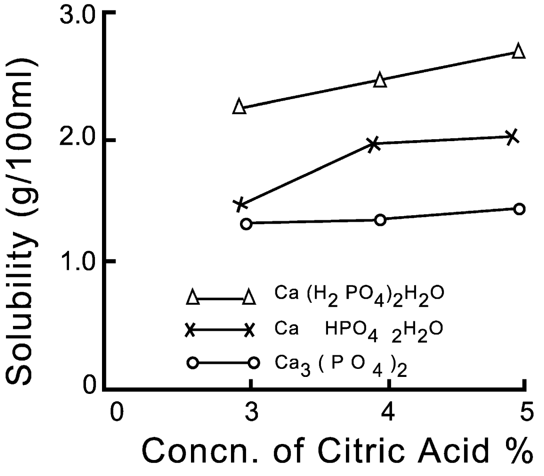

Fig. 1. Solubility of phosphates in aqueous citric acid at 30 °C.

fluorides are normally present as a mixture of NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF_2 compounds, which are derived from the rock phosphate on acidification with sulphuric acid. The organic matter is composed of aliphatic compounds of carbonic acids, amines and ketones.

3.2. Solubilities of impurities in aqueous citric acid

The solubility of reagent grade phosphatic and fluoride compounds in water and aqueous citric acid solutions is shown in Figs. 1 and 2, respectively. It can be seen that with increase in the citric acid concentration, the solubility of the phosphatic and fluoride compounds increased. Maximum solubility was recorded for compounds $Ca(H_2PO_4)_2 \cdot H_2O$ and NaF.

3.3. Purification of phosphogypsum

In fact, impurities of phosphates present in phosphogypsum combine with aqueous citric acid and form water-soluble phosphoric acid (H_3PO_4), whereas fluorides combine with aqueous citric acid and form water-soluble sodium citrate ($Na_3(C_6H_8O_7)$), hydrofluoric acid (HF), hydrofluorosilicic acid (H_3SiF_6), hydrofluoroaluminate (H_3AlF_6) and hydrofluoroferrate (H_3FeF_6) compounds as per the following chemicals equations.

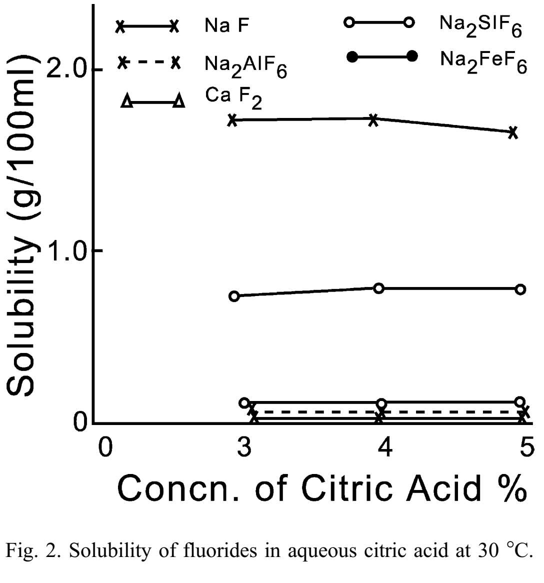

Fig. 2. Solubility of fluorides in aqueous citric acid at 30 °C.

Reaction with phosphatic compounds:

$$\underset{\text{Citric acid}}{C_6H_8O_7} + \underset{\text{Monocalcium phosphate}}{3Ca(H_2PO_4)_2 \cdot H_2O}$$
$$\rightarrow \underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

$$C_6H_8O_7 + 3CaHPO_4 \cdot 2H_2O$$
$$\rightarrow Ca_3(C_6H_5O_7)_2 + 2H_3PO_4 + 2H_2O$$

$$C_6H_8O_7 + Ca_3(PO_4)_2 \rightarrow Ca_3(C_6H_5O_7)_2 + 2H_3PO_4$$

Reaction with fluoride compounds:

$$2C_6H_8O_7 + 3NaF \rightarrow \underset{\text{Sodium citrate}}{Na_3(C_6H_5O_7)_2} + \underset{\text{Hydrofluoric acid}}{3HF}$$

$$C_6H_8O_7 + 3Na_2SiF_6 \rightarrow Na_3(C_6H_5O_7)_2 + \underset{\text{Hydrofluorosilicate}}{H_3SiF_6}$$

$$C_6H_8O_7 + 2Na_3AlF_6 \rightarrow Na_3(C_6H_5O_7)_2 + \underset{\text{Hydrofluoroaluminate}}{H_3AlF_6}$$

$$C_6H_8O_7 + 2NaFeF_6 \rightarrow Na_3(C_6H_5O_7)_2 + \underset{\text{Hydrofluoroferrate}}{H_3FeF_6}$$

$$2C_6H_8O_7 + CaF_2 \rightarrow \underset{\text{Calcium citrate}}{Ca_3(C_6H_5O_7)_2} + 3HF$$

These water-soluble compounds can be easily removed with a stream of water.

The residual impurities of P_2O_5, F organic matter and alkalis in the citric acid treated phosphogypsum are given in Table 3.

Table 3
Impurity content in phosphogypsum after treatment with aqueous citric acid

Phosphogypsum design	Concentration of aqueous citric acid solution	Constituents (%)			
		P_2O_5	F	Organic matter	Na_2O+K_2O
DA	2.0	0.56	0.78	0.08	0.30
	3.0	0.50	0.73	0.07	0.26
	4.0	0.46	0.65	0.03	0.20
	5.0	0.46	0.65	0.03	0.21
HDS	2.0	0.42	0.99	0.39	0.22
	3.0	0.41	0.90	0.38	0.18
	4.0	0.41	0.90	0.38	0.20

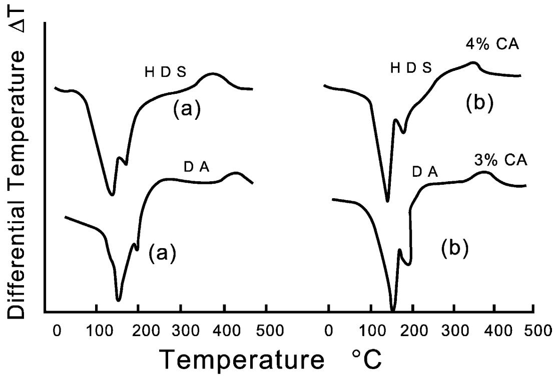

Fig. 3. Differential thermograms of (a) impure phosphogypsum and (b) aqueous citric acid-treated phosphogypsum (CA, citric acid).

The results show that the impurities are reduced in every sample of phosphogypsum. The optimum quantity of citric acid was found to be 4.0% and 3.0% for the samples DA and HDS, respectively. The lower requirement of citric acid for the sample HDS may be ascribed to the presence of initially lower content of impurities. The removal of impurities in the purified phosphogypsum samples was confirmed by DTA (Fig. 3), which shows a fall in the inversion temperatures of exotherms [$CaSO_4(III) \rightarrow CaSO_4(II)$] from 390–450 °C (impure phosphogypsum) to 370–390 °C (purified phosphogypsum), implying removal of impurities from the phosphogypsum.

3.4. *Effect of phosphogypsum on the properties of Portland cement and Portland slag cement*

The effect of impure and purified phosphogypsum sample DA on the properties of Portland cement and Portland slag cement is shown in Tables 4 and 5, respectively. It can be seen that the setting times of the cements are considerably retarded and the compressive strength reduced to a greater extent compared to natural selenite gypsum. The effect of phosphogypsum can be attributed to the formation of the protective coatings of $Ca_3(PO_4)_2$ and CaF_2 compounds as the inactive substances produced by the impurities(PO_4^{3-} and F^-) on the surface of cement grains during the mixing.

$$H_4P_2O_7^{2-} + 4OH^- \rightarrow 3H_2O + 2PO_4^{3-}$$

$$2PO_4^{3-} + Ca^{2+} \rightarrow Ca_3(PO_4)_2 \text{ (Calcium phosphate)}$$

$$SiF_6^{2-} + 6OH^- \rightarrow 6F^- + SiO_3^{2-} + 3H_2O$$

$$2F^- + Ca^{2+} \rightarrow CaF_2 \text{ (Calcium fluoride)}$$

Table 4
Properties of Portland cement produced by intergrinding cement clinker and phosphogypsum samples DA and HDS

Sl. number	Gypsum used	Treatment	Fineness (m^2/kg) (Blaine)	Setting time (min) Initial	Setting time (min) Final	Compressive strength (MPa) 1 day	3 days	7 days	28 days
1	Mineral selenite gypsum	As such	330	79	254	8.0	19.6	28.0	36.8
2	DA phosphogypsum	Impure	330	250	500	5.0	11.2	17.5	30.0
3	DA phosphogypsum	Treated with 4.0% aqueous citric acid	334	130	270	7.5	24.5	28.2	35.5
4	HDS phosphogypsum	Impure	321	200	320	7.0	18.5	26.0	34.6
5	HDS phosphogypsum	Treated with 3.0% aqueous citric acid	319	100	260	9.0	26.5	29.0	39.0
IS 269-1996			Min	Min	Max	–	Min	Min	Min
Limits			225	30	600		16	22	33

Table 5
Properties of Portland slag cement (PSC) produced by intergrinding granulated slag, cement clinker and phosphogypsum sample DA

Sl. number	Gypsum used	PSC composition S:	C:	G	Fineness (m^2/kg) (Blaine)	Setting time (min) Initial	Setting time (min) Final	Compressive strength (MPa) 1 day	3 days	7 days	28 days
1	Impure phosphogypsum	40	60	5	400	255	380	11.5	19.0	34.8	46.0
		50	50	5	420	275	390	10.6	18.0	31.6	44.0
2	Purified phosphogypsum	40	60	5	400	185	260	15.0	22.0	41.0	47.0
		50	50	5	420	245	330	14.8	21.9	36.5	43.6
3	Mineral selenite gypsum	40	60	5	403	180	220	15.5	23.2	42.6	47.5
		50	50	5	408	230	286	14.0	22.8	37.5	37.0
IS 455-1989		–			Min	Min	Max	–	Min	Min	Min
Limits					225	30	600	–	16	22	33

S, slag; C, cement clinker; G, gypsum.

Table 6
Physical properties of gypsum plaster

		Setting time (min)		Bulk density (kg/m^3)		Compressive strength (MPa)	
Gypsum plaster design	Consistency (%)	UR	R	UR	R	UR	R
Impure phosphogypsum							
DA	80.0	2.0	7.0	940	930	5.9	5.0
HDS	63.0	5.0	20.0	1280	1260	13.9	13.0
Purified phosphogypsum							
DA	66.0	10.0	20.0	1200	1200	10.68	8.90
HDS	59.0	16.0	28.0	1290	1280	14.20	13.12
Mineral selenite gypsum	60.0	25.0		1290	1270	14.70	13.00
IS 8272-1981		Min—20		–		Min—7.6	
Limits		Max—35					

UR, unretarded; R, retarded.

As a result, the hydration of the cement is temporarily suppressed. Further, the action of species such as PO_4^{2-} and F^- may take place through two retarding mechanisms:

(i) The ability of these complex species to serve as bridges or cross-linking agents between hydrating grains, involving chemical bonding to more rigid and systematic protective zones compared with simple deposition.
(ii) The action of lattice-bound PO_4^{2-} and F^- can be due to slow, controlled release of these impurities during dissolution of gypsum, resulting in more efficient dispersion of the protective materials throughout the system.

These findings corroborate the retarding mechanisms reported by Tabkikh and Miller [20].

On addition of purified phosphogypsum, the setting time is shortened and the compressive strength augmented because of the removal of impurities of P_2O_5, F, organic matter and alkalis on treatment with aqueous citric acid. The autoclave expansion of Portland cement as well as the Portland slag cement complied with the standard requirements. The heat of hydration of Portland slag cement was found to be within the maximum specified limit of 65 and 75 cal/g at 7 and 28 days.

3.5. Properties of phosphogypsum plaster

The physical properties of gypsum plaster ($\beta CaSO_4 \cdot 1/2H_2O$) produced from the impure and purified phosphogypsum are given in Table 6. In case of purified phosphogypsum plaster, the normal consistency was reduced, while the setting time, bulk density and the compressive strength increased compared to the impure gypsum plaster. The decrease in normal consistency and an increase in the strength of purified gypsum plaster can be attributed to the removal of impurities to a large extent. The gypsum plaster can be used for making building products like boards, blocks, tiles, bricks and a variety of cementitious binders.

4. Conclusions

1. The byproduct phosphogypsum can be purified by treating with 3–4% aqueous citric acid solution and subsequent washing with water.
2. The impurities of phosphates and fluorides are removed as water-soluble phosphoric acid, sodium citrate, hydrofluoric acid, hydrofluorosilicate, hydrofluoroaluminate and ferrate.
3. The purified phosphogypsum can be used as an additive in place of mineral gypsum in the manufacture of ordinary Portland cement and Portland slag cement conforming to Indian Standards.
4. The purified phosphogypsum can be used for the production of gypsum plaster for use as a building material.

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