

# Preparation of calcium sulphoaluminate cement using fertiliser plant wastes

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## Abstract

Phosphochalks from fertiliser plants contain significant amount of calcium sulphate along with  $P_2O_5$  and fluorine. The presence of these impurities makes them unsuitable for most applications and, hence its availability in millions of tons. We demonstrate that it is possible to prepare calcium sulphoaluminate–aluminoferrite based special cements having strength values comparable to ordinary Portland cement (OPC) using these waste chalks. Such cements are insensitive to the presence of impurities in the raw mixture, clinker at low temperatures ( $1230^\circ\text{C}$ ) and the clinkers produced are soft and friable. An empirical technique has been developed to predict the phase composition of the clinkers given the chemical composition of the starting raw mixture. The proposed low temperature clinkering route appears to be a promising method for converting waste phosphochalks into construction grade cements.

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## 1. Introduction

Fertiliser plants normally produce ammonium sulphate in three steps. In the first step, natural gas is burnt to produce carbon dioxide and in the second step, the carbon dioxide is reacted with ammonia to produce ammonium carbonate. Finally, ammonium carbonate is reacted with gypsum to produce ammonium sulphate and chalk.

In a leading fertiliser plant of India, 300–500 tons of chalk is discharged every day by this process. This chalk is in form of fine powder (70% passing through 250 mesh) suspended in water. The chalk slurry is discharged into ponds and over the years more than a million tons of the chalk has accumulated occupying tens of acres of precious land. The chalk waste besides locking up the land creates air pollution, especially during summers when the fine particles are blown in wind.

Various methods have been suggested for utilization of the chalk waste, but none of them can consume it in quantities large enough to equal the rate of production. With the expo-

stantial increase in the demand of building materials, production of cement from this waste would not only be able to utilise it in large quantities but also add value to a liability waste. Unfortunately, Portland cement is very sensitive to the presence of impurities in the raw material. Hence, Portland cement cannot be produced from this waste.

In the presence of calcium sulphate in the raw mixture, it is possible to produce cement, which does not have the phases present in Portland cement namely dicalcium silicate ( $C_2S$ )<sup>1</sup> and tricalcium silicate ( $C_3S$ ), but instead, it contains calcium sulphoaluminate ( $C_4A_3\hat{S}$ ) [1] phase. This phase on hydration gives monosulphate hydrate ( $C_3A \cdot C\hat{S} \cdot xH$ ,  $x = 12–18$ ) or trisulphate hydrate (ettringite or  $C_3A \cdot 3C\hat{S} \cdot 32H$ ) depending upon the proportion of  $C_4A_3\hat{S}$ ,  $Ca(OH)_2$  and  $CaSO_4$ . The formation of both of these hydrates contributes to the strength but the strength imparted by ettringite is more than that from monosulphate hydrate [2,3].

In recent years the calcium sulphoaluminate based cements have attracted attention because [4–18]:

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<sup>1</sup> The following notation has been used throughout the text: A:  $Al_2O_3$ , C:  $CaO$ , F:  $Fe_2O_3$ , H:  $H_2O$ , S:  $SiO_2$ ,  $\hat{S}$ :  $SO_3$ .

- they are tolerant to the presence of impurities in the raw material;
- they save on energy because of clinkering at 200 °C lower than the Portland cements and the clinkers are soft and friable and
- they are expansive in nature, i.e. the volume increases on hydration, and are ideal components for producing low porosity, low shrinkage concrete.

When the raw mixture composition contains Fe<sub>2</sub>O<sub>3</sub>, there exists a series of solid solutions between C<sub>2</sub>F and a hypothetical C<sub>2</sub>A. Under different burning conditions and different raw material proportions, the solid solution may exist in between C<sub>6</sub>A<sub>2</sub>F and C<sub>6</sub>AF<sub>2</sub>. The ratio Al<sub>2</sub>O<sub>3</sub>:Fe<sub>2</sub>O<sub>3</sub> in the clinker varies with that in the raw mix, but the relationship is not simple. For many clinkers the composition approximates C<sub>4</sub>AF, although, it is not a distinct compound. This solid solution is referred to as aluminoferrite or ferrite phase [4,8,19–21].

When heated at 1200–1250 °C and if CaO/SiO<sub>2</sub> > 2, CaSO<sub>4</sub> does not decompose and volatilization of SO<sub>3</sub> is suppressed. The silica present in the composition reacts with lime and CaSO<sub>4</sub> to form 2C<sub>2</sub>S·C $\hat{S}$ . This light green phase forms in large quantities at 1250 °C and does not hydrate to impart strength. Some published work suggests that above 1200 °C, it is possible to dissociate 2C<sub>2</sub>S·C $\hat{S}$  into strength giving phase C<sub>2</sub>S (belite) and CaSO<sub>4</sub> [7].

When P<sub>2</sub>O<sub>5</sub> is present in the composition, it reacts to form wilkeite, Ca<sub>10</sub>O[(Si,S,P)O<sub>4</sub>]. This phase does not hydrate and hence does not give any strength, but since the percentage of P<sub>2</sub>O<sub>5</sub> is normally very low, it does not affect the overall properties of the cement produced.

This paper deals with the possibility of preparing calcium sulphoaluminate–ferrite based special cements from fertilizer plant phosphor–gypsum with addition of fly ash, bauxite, iron ore slimes and gypsum. The effects of different process parameters like composition of raw mixes, firing temperature and time on the phase formation and strength were investigated. Based on the experimental results, an empirical method for predicting the phase formation is presented.

## 2. Material and methods

### 2.1. Materials

The major raw materials used in the investigation were the chalk wastes from a fertiliser plant. The wastes were obtained from two different sources:

- chalk waste 1 was from an ammonium sulphate plant, and
- chalk waste 2 was from the chalk waste heap.

The other raw materials were thermal power plant fly ash, iron ore slimes, bauxite and industrial grade gypsum.

The chemical analysis of raw materials is given in Table 1. Table 2 gives the list of major phases identified in the raw materials by XRD.

### 2.2. Procedure for making cement samples

For preparing a cement sample, appropriate amounts of raw materials in predetermined proportions were taken and ball milled for 45 min for homogenization. The resultant mix was made into a thick paste using water and moulded into 5 cm cubes. The cubes were dried overnight in a hot air oven at 100 °C and then fired (clinkered) in an electric furnace. An average heating rate of about 200 °C/h was employed and the peak firing temperature maintained at 1230 °C for 2 h. The clinkers so prepared were cooled overnight in the furnace to room temperature and ground in a ball mill using porcelain jar and balls to a fineness of at least 3000 cm<sup>2</sup>/g Blaine surface area tested according to IS: 4031-1968 (method of physical test for hydraulic cement). The ground samples had the fineness between 3000 and 6000 cm<sup>2</sup>/g Blaine surface area.

Following retarders were added to some cement samples to make them more workable:

- 2 wt.% borax inter-ground and mixed with clinker or
- 0.5 wt.% citric acid dissolved in water. The solution was used during the making of cement blocks.

### 2.3. Identification of phases

To determine the phases formed on firing, XRD patterns were obtained employing Ni-filtered Cu K $\alpha$  or Fe K $\alpha$  radiation at 40 kV and 25 mA. Overlapping peaks made the quantitative evaluation of different phases by XRD quite difficult. Moreover, there occurred significant diffraction peak shifts due to doping effects in the presence of impurities. Therefore, only a rough quantitative analysis of the phases was carried out. C<sub>4</sub>A<sub>3</sub> $\hat{S}$ , 2C<sub>2</sub>S·C $\hat{S}$  and C $\hat{S}$  have highest peaks at 3.74, 2.82 and 3.49 *d*-spacing, respectively, and were selected to identify each of these phases. Wilkeite has 80% strength peak at 2.23. Since C<sub>4</sub>AF does not have any major independent peak, so the resultant of the two peaks were taken to identify it. At 2.65, C<sub>4</sub>A<sub>3</sub> $\hat{S}$  has 25% and C<sub>4</sub>AF has 70% strength peak. For rough estimation of the amount of phases, only the height of the peaks was considered. The amount of these phases were calculated using the equation:

$$\text{amount of phase (\%)} = \frac{I_{\text{Phase}}}{\sum_{\text{All phases}} I_{\text{Phase}}} \times 100$$

In the absence of any standard sample having known composition, an internal standard method could not be used; hence, these analyses reported here should only be taken as indicative.

### 2.4. Testing for physical properties

The samples produced were tested for their specific gravity, specific surface area, consistency, setting times, mortar and concrete compression strength according to the Indian Standard (IS)-4031. The chemical analysis, wherever reported, was carried out as per IS 4032.

Table 1  
Chemical analysis of raw materials

	Chalk waste 1 (ammonium sulphate plant) (wt.%)	Chalk waste 2 (heap) (wt.%)	Fly ash (wt.%)	Bauxite (wt.%)	Iron ore slimes (wt.%)	Gypsum (wt.%)
CaO	43.54	43.94	0.57	T.	0.19	37.41
SiO <sub>2</sub>	2.57	3.83	58.86	5.43	13.42	0.89
Al <sub>2</sub> O <sub>3</sub>	0.41	0.57	25.13	45.19	10.59	0.07
Fe <sub>2</sub> O <sub>3</sub>	0.11	0.14	3.14	20.61	68.10	0.13
SO <sub>3</sub>	14.24	10.78	N.T.	N.T.	N.T.	53.35
P <sub>2</sub> O <sub>5</sub>	1.20	3.30	N.T.	N.T.	N.T.	0.008
F	0.29	1.34	N.T.	N.T.	N.T.	0.12
MgO	T.	T.	0.73	T.	0.90	T.
Na <sub>2</sub> O	0.21	0.47	0.17	0.39	0.19	0.27
K <sub>2</sub> O	T.	T.	0.38	0.02	0.06	0.03
TiO <sub>2</sub>	0.45	0.05	1.35	4.35	0.07	T.
LOI	36.97	35.57	9.66	23.98	6.35	7.83

Note: T. = traces, N.T. = not tested, LOI = loss on ignition.

Table 2  
Mineralogical composition of raw materials (wt.%)

Raw material	Mineralogical phases
Chalk wastes	Calcite (CaCO <sub>3</sub> ) and gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)
Fly ash	Hematite (Fe <sub>2</sub> O <sub>3</sub> ), α-quartz (SiO <sub>2</sub> ), mullite (3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ), merwinite (3CaO·MgO·2SiO <sub>2</sub> ) and hercynite (FeO·Al <sub>2</sub> O <sub>3</sub> )
Bauxite	Gibbsite, hematite (Fe <sub>2</sub> O <sub>3</sub> ) and cristobalite (SiO <sub>2</sub> )
Iron ore slime	Hematite (Fe <sub>2</sub> O <sub>3</sub> ), α-quartz (SiO <sub>2</sub> ) and gibbsite
Gypsum	Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O), anhydrite (CaSO <sub>4</sub> ) and bassanite (2CaSO <sub>4</sub> ·H <sub>2</sub> O)

### 2.5. Composition of raw materials

Since the raw materials used for the investigation were complex industrial wastes, it was decided to adopt an efficient search technique to arrive at the optimum or near optimum compositions and firing conditions. Fourteen sets of compositions were fired in order to search the right composition. A Monte-Carlo random search strategy was employed in order to identify the region of optimal composition. The search was carried out in two stages. In the first stage, a coarse search was carried out to define the limits of variables and parameters in which the acceptable compositions are most likely to be found. This was followed by a fine search within these limits to arrive at compositions having either maximum strength or any other appropriate criterion for raw mix design.

The compositions tried are given below:

- chalk waste 1 + fly ash,
- chalk waste 1 + fly ash + bauxite,
- chalk waste 1 + bauxite,
- chalk waste 1 + bauxite + iron ore slimes,
- chalk waste 1 + fly ash + bauxite + iron ore slimes,
- chalk waste 1 + chalk waste 2 + fly ash + bauxite,
- chalk waste 2 + fly ash + bauxite,
- chalk waste 2 + bauxite,
- chalk waste 2 + bauxite + gypsum,
- chalk waste 2 + fly ash + bauxite + gypsum,
- chalk waste 2 + bauxite + iron ore slimes,
- chalk waste 2 + fly ash + bauxite + iron ore slimes,
- chalk waste 2 + bauxite + iron ore slimes + gypsum,
- chalk waste 2 + fly ash + bauxite + iron ore slimes + gypsum.

### 3. Calculation of chemical composition of raw mixture

The chemical compositions of the raw materials listed in Table 1 were used for calculating the composition of the raw mixture in terms of the six major constituents – CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub>. In the calculation, the following assumptions were made:

- The batch undergoes complete and uniform firing irrespective of the firing schedule.
- The volatilisation is accounted for by the loss on ignition (LOI).

The comparison between the calculated and measured values obtained by chemical analysis of selected samples showed good match between the two. Only in the case of P<sub>2</sub>O<sub>5</sub> were the calculated values significantly more than the measured values. This could be due to the volatilisation of P<sub>2</sub>O<sub>5</sub>.

In order to quantitatively estimate the phases formed on clinkering, a simple mass balance was carried out. It was assumed that the formation of phases takes place in the following order: wilkeite > C<sub>4</sub>AF > C<sub>4</sub>A<sub>3</sub>Ŝ > 2C<sub>2</sub>S·CŜ > CŜ. The calculations were carried out as shown in Fig. 1.

Wilkeite was selected first because it would be formed in small quantities and was always observed in the clinkers. C<sub>4</sub>AF was selected next because its formation started at relatively lower temperature and was always observed when Fe<sub>2</sub>O<sub>3</sub> was present in the raw mix. Since C<sub>4</sub>A<sub>3</sub>Ŝ was easier to form as compared to 2C<sub>2</sub>S·CŜ, its formation was not obstructed by the latter. Hence, the presence of SiO<sub>2</sub> had no effect on the production of C<sub>4</sub>A<sub>3</sub>Ŝ and it formed before 2C<sub>2</sub>S·CŜ.

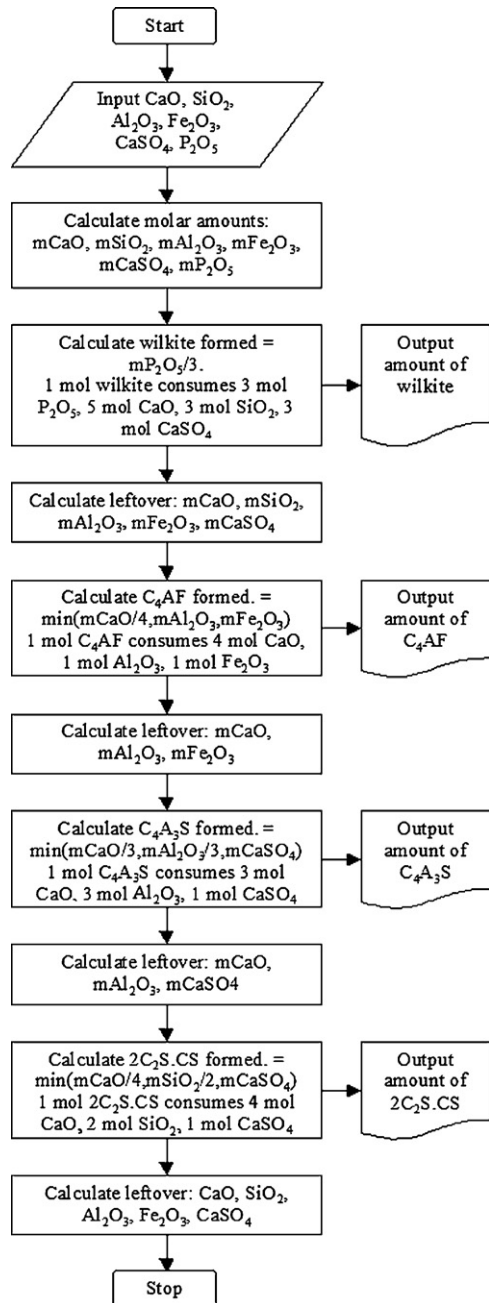


Fig. 1. Flowchart showing the algorithm for predicting the formation of various phases in the clinker.

In order to check the validity of the calculations, the molar amount of phases formed as obtained by calculation was plotted against the ratio of the peak heights obtained from XRD analysis.

## 4. Results and discussion

### 4.1. Effect of composition

The samples from the fourteen compositions were prepared and tested. The representative results of each composition are given in Table 3. As a comparison, the recommended strength for ordinary Portland cement (OPC) as recommended

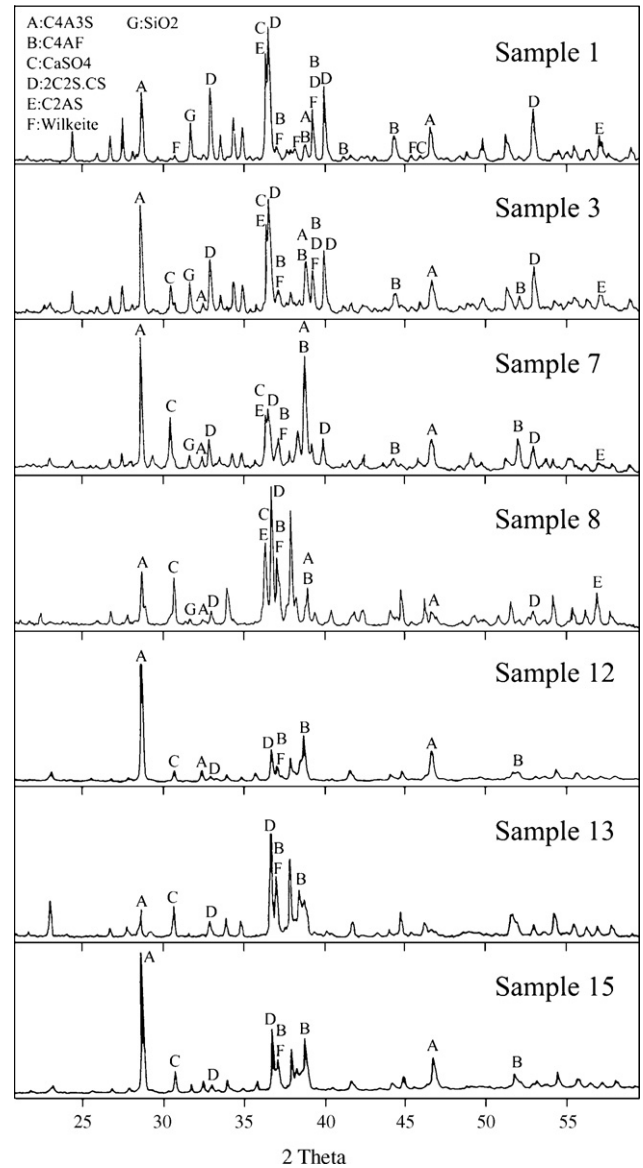


Fig. 2. XRD patterns of some representative cement samples.

by Indian Standard IS: 269-1976 is also included in the table.

The cements produced from composition 1 (chalk waste 1 + fly ash, sample 1) did not develop acceptable strength. This was due to the limited formation of  $C_4A_3\hat{S}$  and  $C_4AF$ , and excessive amount of  $2C_2S\cdot\hat{C}\hat{S}$  and  $C_2AS$  along with  $\alpha$ -quartz and f-CaO (Fig. 2). When fly ash was partially substituted with bauxite in the composition 2 (chalk waste 1 + fly ash + bauxite, samples 2 and 3), cements having acceptable strengths were obtained. This was due to the increased formation of  $C_4A_3\hat{S}$  and  $C_4AF$  at the expense of  $2C_2S\cdot\hat{C}\hat{S}$  and  $C_2AS$ . On the complete replacement of fly ash with bauxite (composition 3, sample 4) high strength cements were obtained, because there was a formation of only  $C_4A_3\hat{S}$  and  $C_4AF$  and very little of  $2C_2S\cdot\hat{C}\hat{S}$  and  $C_2AS$ .

Table 3  
Some representative results for various compositions

Sample	Composition	Chalk waste		Fly ash	Bauxite	Iron ore slimes	Gypsum	Retarder	1:3 Cement sand mortar compressive strength (kg/cm <sup>2</sup> )				
		1	2						1 day	3 days	7 days	28 days	90 days
OPC		Recommendation of IS:269-1976 (Grade 330)								160	220	330	–
1	1	81	0	19	0	0	0	None	80	80	80	Not tested	Not tested
2	2	70	0	7	23	0	0	Citric acid	100	420	430	460	Not tested
3	2	79	0	11	10	0	0	None	Not tested	240	340	400	400
4	3	66	0	0	34	0	0	Citric acid	100	520	540	580	750
5	4	68	0	0	20	12	0	Citric acid	Fail	60	420	490	Not tested
6	4	75	0	0	1	24	0	Citric acid	50	260	210	300	Not tested
7	5	73	0	3	18	6	0	None	230	270	320	480	660
8	6	21	57	12	10	0	0	Borax	60	90	110	120	110
9	7	0	77	12	11	0	0	Borax	70	110	120	200	Not tested
10	8	0	66	0	34	0	0	Citric acid	Fail	Fail	150	280	Not tested
11	8	Sample 10 + 20% gypsum as admixture						None	Not tested	60	400	590	Not tested
12	9	0	53	0	41	0	6	Citric acid	Not tested	296	500	Not tested	Not tested
13	12	0	75	5	16	4	0	Citric acid	92	140	175	345	Not tested
14	12	Sample 13 + 16.7% gypsum as admixture						None	230	440	480	500	Not tested
15	14	0	58	3	30	3	6	None	155	270	500	Not tested	Not tested

When the bauxite was partially substituted with iron ore slimes (composition 4, sample 5), there was increased formation of C<sub>4</sub>AF at the expense of C<sub>4</sub>A<sub>3</sub>S̄. As a result while there was slight fall in strength, the cements still had reasonable strength. In fact almost complete substitution of bauxite with iron ore slimes (sample 6) still gave cements having acceptable strength even though C<sub>4</sub>A<sub>3</sub>S̄ was completely substituted with C<sub>4</sub>AF. Composition 5 (chalk waste 1 + fly ash + bauxite + iron ore slimes, sample 7) showed that while the addition of fly ash to the composition was generally detrimental to the quality of cements, it might be possible to include limited amount of fly ash in the composition.

Direct substitution of chalk waste 1 (composition 2, sample 3) by chalk waste 2 (compositions 6 and 7, samples 8 and 9) did

not give acceptable strength. This was because with increasing substitution, there was a progressive decrease in the amount of C<sub>4</sub>A<sub>3</sub>S̄ with corresponding increase in wilkeite and 2C<sub>2</sub>S·C̄S̄.

In the composition that gave very high strength (composition 3, sample 4), when chalk waste 1 was substituted by chalk waste 2 (composition 8, sample 10), it resulted in poor strength values even though the XRD study showed a large-scale formation of C<sub>4</sub>A<sub>3</sub>S̄. The possible reason for this could be that the complete hydration of C<sub>4</sub>A<sub>3</sub>S̄ required some CaSO<sub>4</sub> for the formation of ettringite and there was a shortage of CaSO<sub>4</sub> in the clinker. In order to test this hypothesis, when gypsum was added as an admixture there was a substantial increase in the strength values (sample 11). Results of composition 8 suggested that the use of chalk waste 2 instead of chalk waste 1 resulted in shortage of CaSO<sub>4</sub>, hence, in composition 9 additional gypsum was included

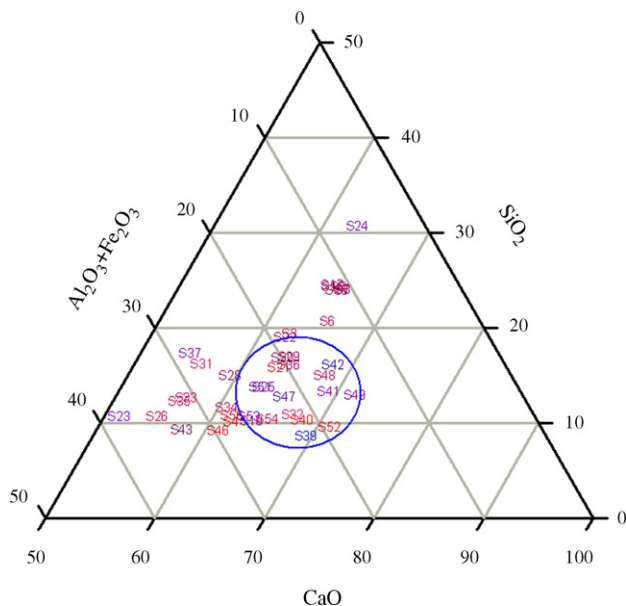


Fig. 3. Composition for optimum strengths of calcium sulpho-aluminate cements.

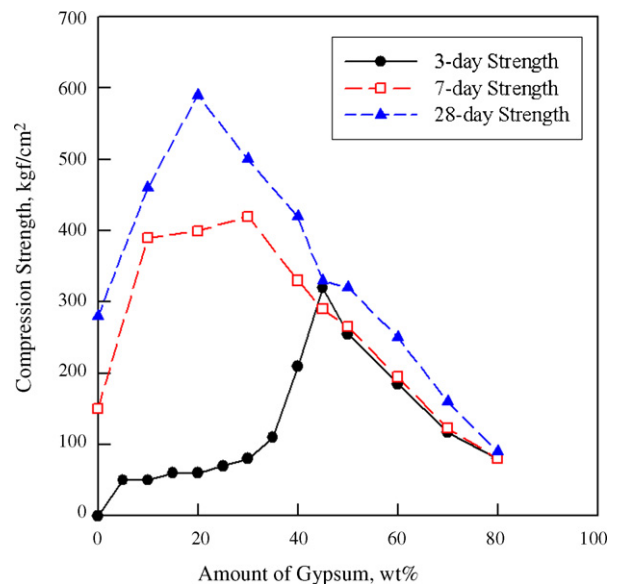


Fig. 4. Effect of gypsum addition on the strength development of sample 10.

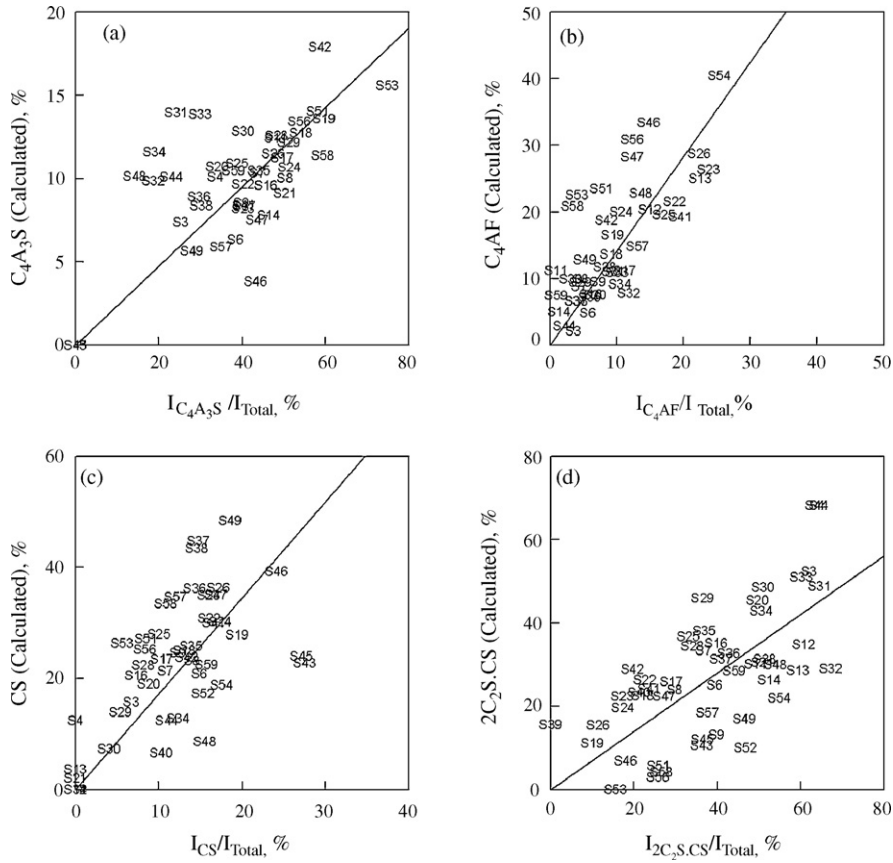


Fig. 5. Relationship between the calculated molar amount of phases and the XRD estimates based on  $I/I_{Total}$  for (a)  $C_4A_3\hat{S}$ , (b)  $C_4AF$ , (c)  $CaSO_4$  and (d)  $2C_2S \cdot C\hat{S}$ .

in the composition. Sample 12 had only chalk waste 2, bauxite and gypsum in the proportion where  $CaO:Al_2O_3:SO_3 = 4:3:1$ , as a result the final product mostly had  $C_4A_3\hat{S}$  and due to low proportion of  $SiO_2$ , there was very less formation of wilkeite and  $2C_2S \cdot C\hat{S}$ . Hence, this composition had very high strength.

When the fly ash was included in the composition 10, expectedly there was a fall in strength due to the formation of  $2C_2S \cdot C\hat{S}$ . The composition 11 also did not perform well due to the excess of  $Fe_2O_3$ , which resulted in the formation of  $C_4AF$  and less of  $C_4A_3\hat{S}$ .

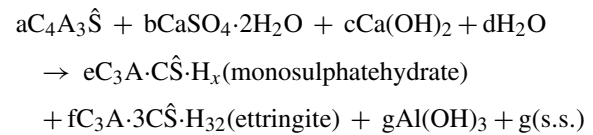
In the composition 12–15, it was possible to manipulate the amount of the chalk waste 2 along with fly ash, bauxite, iron ore slimes and gypsum to prepare cements having high strength due to large amounts of  $C_4A_3\hat{S}$  and  $C_4AF$ .

From the experiments carried out, it is clear that given the right proportion of  $CaO$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$  and  $CaSO_4$ , it is possible to prepare cement having mostly  $C_4A_3\hat{S}$  and  $C_4AF$  in the composition. In the presence of  $CaSO_4$ , these phases hydrate to produce monosulphate hydrate or ettringite that gives high strength. In Fig. 3,  $CaO-SiO_2-(Al_2O_3 + Fe_2O_3)$  is plotted in a ternary diagram.  $CaSO_4$  is not considered in the plot. This is because approximately 16%  $CaSO_4$  is required for the formation of  $C_4A_3\hat{S}$  and this amount is normally available. Gypsum may also be added as admixture to correct small deficiencies. The figure shows that for the preparation of cements having acceptable strength values, the amount of  $SiO_2$  in the composition should be as low as possible. The amount of  $CaO$  should be

between 60 and 72% and the amount of  $Fe_2O_3 + Al_2O_3$  between 15 and 25%. This corresponds quite well for 1:1 molar ratio in  $C_4A_3\hat{S}$  (not accounting for  $CaSO_4$ ) and 2:1 molar ratio in  $C_4AF$ . Hence, for the best result, the composition of the raw material should be as near to stoichiometric proportions of  $C_4A_3\hat{S}$  and  $C_4AF$  as possible.

#### 4.2. Effect of gypsum addition

It is a standard practice to incorporate 4–5 wt.% gypsum in Portland cement as a set retarder. In the case of calcium sulphoaluminate cements, gypsum takes an active part in the hydration reaction.



where s.s. is a solid solution of  $C_3A \cdot C\hat{S} \cdot H_{12} - C_3A \cdot CH \cdot H_{12}$ .

The ratio of monosulphate hydrate and ettringite formed depends upon the relative proportions of  $C_4A_3\hat{S}$ ,  $CaSO_4$  and  $Ca(OH)_2$ . Monosulphate hydrate gives relatively less strength as compared to the ettringite. When there is a deficiency of  $CaSO_4$ , monosulphate hydrate is formed and when there is sufficient amount of it, ettringite is formed. The  $CaSO_4$  can be supplied in the raw mixture or later on as an admixture.

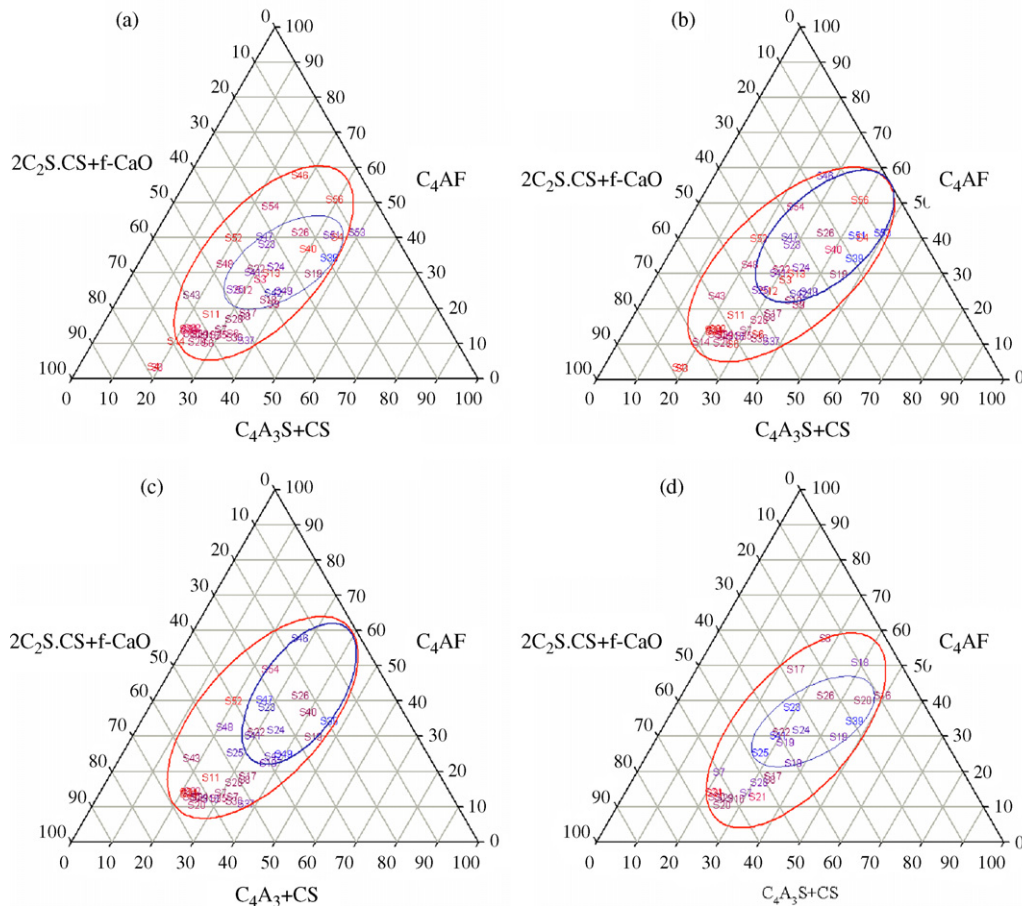


Fig. 6. Composition for optimum strengths for calcium sulpho-aluminate cements (a) 1-day strength, (b) 3-day strength, (c) 7-day strength and (d) 28-day strength.

It was observed that even though sample 10 had significant amount of  $C_4A_3\hat{S}$  but gave poor strength values. Fig. 4 shows the effect of addition of gypsum as admixture on the strength development of cement blocks for sample 10. It is obvious that there is an optimum amount of  $CaSO_4$  that should be present during hydration for proper strength development.

#### 4.3. Clinkering conditions

To understand the effect of firing temperature, one of the compositions, sample 4, was fired at 1150 °C, 1200 °C, 1230 °C, 1250 °C, 1280 °C and 1300 °C for 2 h.

At 1150 °C the main phases were  $C\hat{S}$  and  $C_{12}A_7$  along with small amounts of  $2C_2S \cdot C\hat{S}$ ,  $SiO_2$ ,  $C_4AF$  and  $C_4A_3\hat{S}$ . Wilkeite did not form at this temperature. At 1200 °C the main phases formed were  $C_4A_3\hat{S}$  and  $2C_2S \cdot C\hat{S}$ ; wilkeite also formed along with an increase in the amount of  $C_4AF$ . There was also a significant fall in the amount of anhydrite. At 1230 °C, there was large-scale formation of  $C_4A_3\hat{S}$  and  $2C_2S \cdot C\hat{S}$ . At 1250 °C, the amount of  $2C_2S \cdot C\hat{S}$  was at the highest. On further increase in the temperature to 1280 °C, the clinkers started fusing along with decrease in the amount of  $2C_2S \cdot C\hat{S}$ . At 1300 °C, there was large-scale fusion along with significant dissociation of  $2C_2S \cdot C\hat{S}$  to  $C_2S$ . At temperatures higher than 1280 °C, there was no increase in the formation of  $C_4A_3\hat{S}$

or  $CaSO_4$  even though dissociation of  $2C_2S \cdot C\hat{S}$  did occur, this could be due to the vaporisation and loss of  $CaSO_4$  above 1280 °C. Hence, 1230 °C seems the best temperature for clinkering. Increasing the temperature does not significantly increase the amount of  $C_4A_3\hat{S}$  or decrease the amount of  $2C_2S \cdot C\hat{S}$ .

On hydration both monosulphate and ettringite were formed but the sample fired at 1230 °C had more formation of ettringite compared to the sample fired at 1280 °C. This could again be due to the vaporisation of  $CaSO_4$  at 1280 °C.

To understand the effect of firing time, sample 4 was fired at 1200 °C for 2, 4 and 8 h. The X-ray patterns showed that there was little change in the phase composition of the cement with increase in time and all the reactions seem to be over within 2 h.

#### 5. Calculation of phase composition of raw mixture

Fig. 5 compares the correlation between the calculated amounts of different phases and their respective ratio of  $III_{total}$ . On the whole, there is a general trend between the two. Some of the discrepancies could be due to incomplete reaction, temperature variations inside the furnace and presence of impurities.

Fig. 6 shows the effect of calculated molar amounts of  $(C_4A_3\hat{S} + C\hat{S})$ ,  $(C_4AF)$  and  $(2C_2S \cdot C\hat{S} + CaO)$  on the strength

development. It seems that the best results are obtained when:

- $2C_2S-C\hat{S} + CaO$  is as low as possible and certainly less than 45%,
- $C_4AF = 20-45\%$  and
- $C_4A_3\hat{S} + C\hat{S} = 20-50\%$ .

## 6. Conclusions

The technical feasibility of preparing calcium sulfoaluminate cements using phosphochalk has been demonstrated. The cements have strength properties comparable to the OPC with many advantages: one, they can consume large amounts of industrial wastes; two, are not affected by the presence of impurities; three, are produced at relatively lower temperatures and four, the clinkers produced are soft and friable.

An empirical method for predicting the phases in the clinker is proposed. The calculated amount of phases matches reasonably well with XRD based estimates of different phases.

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