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PREPARATION OF IRON RICH CEMENTS USING RED MUD

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ABSTRACT

Possibility of producing calcium sulfoaluminoferrite (SAF) ($C_4(A,F)_3\bar{S}$)-calcium aluminoferrite (C_4AF) based cements using lime + red mud + bauxite + gypsum has been investigated. The effects of composition, firing time and firing temperature on the properties of cements produced has been studied. The characteristics of the cements produced have been found to be strongly dependent on the raw mix composition and firing temperature but not so much on firing time. Some of these cements possess strengths comparable to and at times even more than ordinary Portland cement (OPC). Since the red mud used contains significant amount of titania, effect of titania on pure sulfoaluminate phase has also been studied. © *1997 Elsevier Science Ltd*

Introduction

In the last few decades, calcium sulfoaluminate ($C_4A_3\bar{S}$) phase has attracted considerable attention as a component of cements exhibiting high early day strengths and having ultimate strength as well as dimensional stability similar to that of ordinary Portland cement (OPC) (1-17).

Calcium sulfoaluminate can include in its structure a number of impurities, for example Al^{3+} can be replaced by Ti^{4+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Si^{4+}, etc. When the raw mix contains a significant proportion of iron oxide, apart from the formation of ferrite and aluminoferrite phases,

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partial substitution of alumina by iron oxide in sulfoaluminate takes place. This is possible because the ionic size of Fe^{3+} is only 20% larger than Al^{3+} (Fe^{3+} = 0.675 °A and Al^{3+} = 0.535 °A). Such a replacement leads to the emergence of a solid solution of $C_4A_3\bar{S}$ (calcium sulfoaluminate, CSA)-$C_4F_3\bar{S}$ (calcium sulfoferrite, CSF) which may be designated as calcium sulfoaluminoferrite ($C_4(A,F)_3\bar{S}$, SAF) phase. The extent to which Fe_2O_3 can substitute Al_2O_3 is not known with certainty and different researchers claim it to be between 9-20% (18-21). According to Krivoborodov et al. (20) in the system CaO-Al_2O_3-Fe_2O_3-$CaSO_4$ apart from the formation of $C_4(A,F)_3\bar{S}$ (where maximum substitution of Al^{3+} by Fe^{3+} can be 9%), some amount of SO_4^{2-} also gets fixed to calcium aluminoferrites. This results in the formation of two other series of cements-high basicity sulfoferrites ($C_2F.C\bar{S}$-$2C_2F.C\bar{S}$) and $C_4A_xF_{1-x}\bar{S}_n$ where x varies between 0.3-1.6 and n between 0.4-1.0.

On hydration sulfoaluminate forms ettringite ($C_3A.3C\bar{S}.32H$) and monosulfate hydrate ($C_3A.C\bar{S}.12H$) depending upon the proportion of $C_4A_3\bar{S}$-$C\bar{S}$-$Ca(OH)_2$-H_2O (11-13). Likewise, on hydration both the high and low basicity calcium sulfoferrite give two hydrated products: $C_3F.C\bar{S}.12H$ (monosulfate) and $C_3F.3C\bar{S}.32H$ (ettringite). According to Krivoborodov et al. (20) in case of $C_4(A,F)_3\bar{S}$ the hydration rate during the first three days falls with the increase in F/A ratio but later it becomes equal to the hydration rate of sulfoaluminate, as a result there would be no visible effect in the latter days. On the other hand, in the case of calcium aluminoferrites the presence of sulfate enhances the hydraulic activities of the solid solutions as compared to the basic aluminoferrite phases (18-21).

The sulfoaluminoferrite based cements have a number of advantages over ordinary Portland cement. These include-energy conservation due to lower clinkering temperature and formation of softer clinkers, ability to use industrial wastes/low grade traditional raw materials, good strength characteristics, good anti-seepage properties, good corrosion resistance, good behavior at low temperature and rapid setting characteristics. Investigations carried out in the recent years have shown that admixing of $C_4(A,F)_3\bar{S}$ with OPC leads to an improvement in strength, reduction in porosity and increase in corrosion resistance characteristics of the cement (18-20).

Red mud is the caustic insoluble waste residue generated at the alumina refineries which use the Bayer process (pressure caustic digestion of bauxite). 1.0-1.6 tons of it is generated per ton of alumina produced, as a result it is estimated that in India and World over 2 and 70 million tons of it is generated respectively. It is a complex material whose chemical and mineralogical compositions vary widely depending on the bauxite and the local plant process parameters. It contains significant quantities of Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O and CaO and trace quantities of numerous other elements such as V, Ga, Cr, Zr, U, Th, Sc, La, Y, Sr, Ba, Hf, K, Pb, Mn, Cd, Ni, Zn, B, Bi, Co and Li (as oxides). Moreover, red muds consist of 14-21 mineral phases (22-23).

Out of different industrial wastes available, red mud was chosen for the present work due to its high alumina and iron oxide as well as low silica contents. Low silica is necessary since in presence of $C\bar{S}$ silica reacts to form undesirable $2C_2S.C\bar{S}$. This paper deals with the preparation of special cements using lime, red mud, bauxite and gypsum. The effects of different process parameters like composition of raw mix, firing temperature and firing time on the phase formation, strength, density and color were investigated. Since the red mud used contains significant proportion of titania, the effect of titania on $C_4A_3\bar{S}$ was also studied.

TABLE 1

Chemical Analysis of Raw Materials (wt.%)

	Lime	Gypsum	Red Mud	Bauxite
Fe_2O_3	0.65	0.13	33.1	16.5
Al_2O_3	0.65	0.07	18.2	48.0
SiO_2	1.00	0.89	8.8	3.0
CaO	67.13	37.41	2.7	0.5
TiO_2	-	-	19.6	8.5
Na_2O	-	0.27	5.8	-
SO_3	-	53.35	-	-

Materials and Methods

Materials. As received uncausticized red mud and bauxite from M/s HINDALCO Industries Ltd., Renukoot were used. Red mud and bauxite lumps were crushed and/or ground, dried and sieved to -150 μm. Commercially available hydrated lime and gypsum, obtained from local market were of -200 μm size. The chemical composition of the four raw materials used is given in Table 1.

Procedure for Making Cements Samples. To prepare each cement sample, 100 g of the 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 an appropriate amount of water and molded into a 5 cm cube. The cube was 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 firing temperature maintained at a predetermined level (1150-1350°C) up to 2 h duration. The clinker so prepared was cooled overnight in the furnace itself to room temperature, ground in agate mortar and pestle and sieved through 150 μm mesh.

To determine the effect of chemical composition, two sets of samples were fired (Table 2) at 1250°C for 2 h. The amounts of red mud and bauxite were varied in steps of 5%. To study the effect of firing schedule on the quality of cement produced, two representative samples of each set (Table 3) were fired at different temperatures (1150, 1200, 1250, 1300 & 1350°C) for fixed time (2 h) and for varying duration (0.5, 1.0, 1.5 & 2.0 h) at a fixed temperature (1250°C).

TABLE 2

Composition (wt.%) of Various Samples Fired at 1250°C for 2h.

	Lime	Gypsum	Red Mud	Bauxite
Series A	47.5	7.5	0-45.0	45.0-0
Series B	32.5	12.5	5.0-50.0	50.0-5.0

TABLE 3

Compositions (wt.%) of Representative Samples Fired at Different Temperatures (for 2h) and for Varying Duration (at 1250°C).

	Lime	Gypsum	Red Mud	Bauxite
A4	47.5	7.5	15.0	30.0
A7	47.5	7.5	30.0	15.0
B3	32.5	12.5	15.0	40.0
B8	32.5	12.5	40.0	15.0

Testing for Compressive Strength. Small sized cylindrical pellets were made by compacting 5 g of each cement sample mixed with 2.0 ml of water in a die of 1.6 cm I.D. using a 2 kg weight (put on top of the plunger for 5 min.). Pellets so prepared were kept on and covered with wet pieces of cloth for a day and then immersed in water for 27 days. Each sample was then ground to a height of 1.5 cm on emery paper. Compressive strengths of such pellets were tested using an Amsler Universal Testing Machine. In order to get some relative idea, pellets made of Ordinary Portland Cement (OPC, Indian Standard Grade 33) were also tested in a similar fashion. Due to the non-standard method of the testing the compressive strength the values obtained gave only a relative idea and not the actual strength values.

Identification of Phases. To determine the phases formed on firing of the raw mixes and on hydration, typical samples were ground to -75 μm and XRD patterns recorded using Rigaku-Geigerflex XRD machine employing Ni-filtered Cu Kα radiation at 40 kV and 25 mA. The

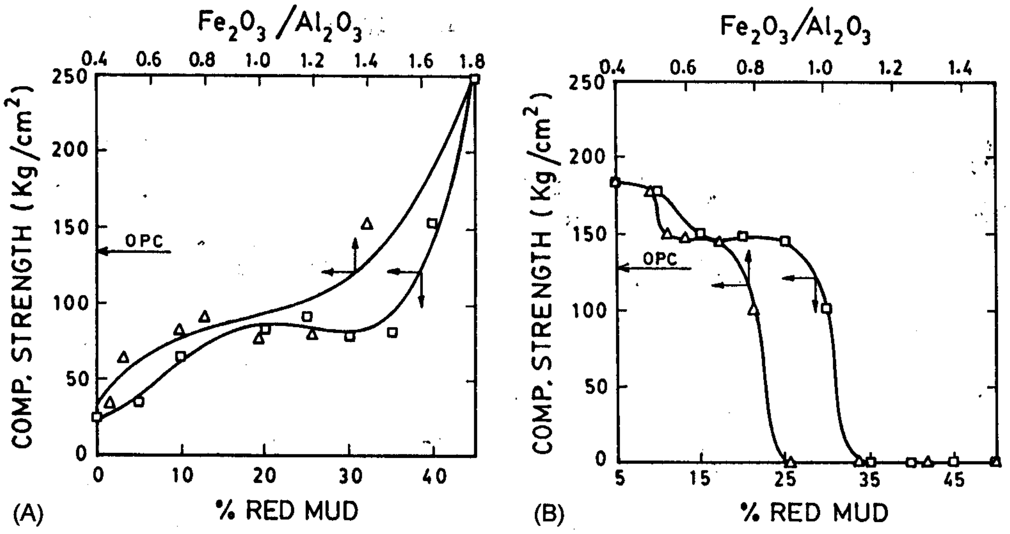

FIG. 1.

Effect of red mud proportion and F/A ratio on the 28-days strength of cement pellets of Series A and Series B compositions.

complex composition of the samples made the quantitative evaluation of different phases by XRD quite difficult. The large number of phases present in any sample resulted in overlapping peaks. Moreover the diffraction peak shifts also occur due to doping effects caused by the presence of impurities. Therefore, only a qualitative identification of the phases was done and no attempt was made to quantify the phases present.

Microstructural Studies. Test pieces of hydrated cement samples were fixed on bronze mounts and coated with a thin layer of gold-palladium alloy using Edwards sputter coater. The coated specimens were then examined employing a JEOL-840 Scanning Electron Microscope (Model JSM-840 A).

Results and Discussion

(a) Effect of Composition. The clinkers produced of Series A composition were light brown in color, soft and friable. With increasing red mud content (hence F/A ratio) their color became darker and density as well as strength increased (Fig. 1). XRD studies showed that there was an increase in the formation C_4AF and C_2F phases with corresponding decrease in the $C_4(A,F)_3\overline{S}$ phase with increase in the F/A ratio.

Though the raw mixes of Series A contained 5.2-11.4% TiO_2, the XRD patterns of these cements did not indicate the presence of any titanate phases. To understand the absence of such phases raw mixes were made using analytical grade CaO, Al_2O_3 and Fe_2O_3 taken in a molar proportion CaO: Al_2O_3: Fe_2O_3 = 4:1:1 to which was added varied amount of analytical grade TiO_2 (0-10%). They were then fired in the fashion described earlier. The phase identification studies (XRD) indicated no formation of titanate phases. Instead there seemed to be complete uptake of TiO_2 in aluminate and ferrite phases. The substitution of Al_2O_3 and Fe_2O_3 by TiO_2 would not change the basic crystal structures of C_4AF or C_2F phases but only distort it resulting in a shift of peak positions depending upon the degree of doping. This was observed in all the cases; e.g. the strongest peak of C_2F was observed at d = 2.681, 2.685 and 2.688 for TiO_2 = 0%, 4% and 8% respectively. Similar work carried out using CaO, Al_2O_3, $CaSO_4$ (CaO: Al_2O_3: $CaSO_4$ = 3:3:1) and 0-10% TiO_2 showed that till 3% addition there was absence of titanate peaks and beyond that CT peaks were present. In the case of $C_4A_3\overline{S}$ phase increasing shifts in peak position with titania dosage was recorded (peak positions of hkl = 422 were at 3.748, 3.762 and 3.764 for TiO_2 = 0%, 4% and 8% respectively). This explains the absence of CT phase in the series A, in which all of the titania got doped in the ferrite and $C_4(A,F)_3\overline{S}$ phases.

The clinkers prepared out of Series B compositions were hard and brownish-black in color. The hardness, "glassy" nature and density of clinkers increased with the red mud content. Unlike the previous set, the strength of the cement samples (B1-B10) decreased with the increase in red mud content (Fig. 1). Furthermore, the samples B7-B10 on curing exhibited significant cracking and deformation due to excessive expansion. $C_4(A,F)_3\overline{S}$ and CT were found to be the major phases formed in these cements. The fall in strength with increase in red mud content was attributed to the increase in CT with corresponding decrease in $C_4(A,F)_3\overline{S}$.

In the case of cements of Series B there was no peak corresponding to ferrite or aluminoferrite phases, which is surprising. A part of Fe_2O_3 got used up in the formation of $C_4(A,F)_3\overline{S}$. In this set of experiments the peak position of hkl = 422 of B3 (F/A = 0.5), B5 (F/A = 0.7) and B8 (F/A=1.1) was observed at 3.764, 3.762 and 3.753 respectively, implying

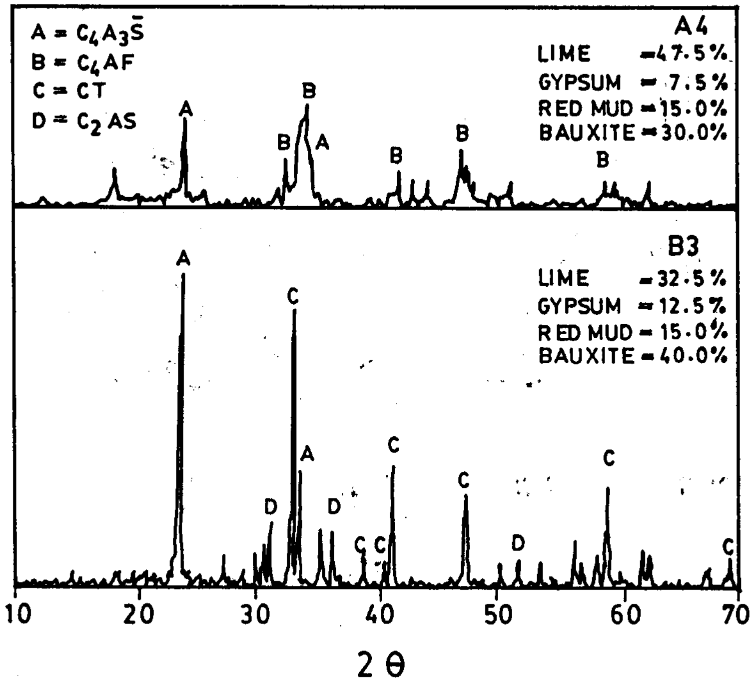

FIG. 2.
XRD patterns of A4 and B3 fired at 1250°C for 2 h.

a progressive increase in doping (18). Such peak shifts were also observed in CT for which the highest intensity was recorded at 2.705, 2.703 and 2.698 respectively. The balance of Fe_2O_3 was found to form "glassy" phase (incorporating Fe_2O_3) which could be observed even visually.

Further experiments carried out using varying quantities of lime, gypsum, red mud and bauxite showed that the cements containing C_2F and C_4AF formed till gypsum content was less than 10% in the raw mix. Beyond that, cement without these phases but those containing CT formed. Cements made using fly ash (as source of alumina) instead of bauxite too showed similar trend, on the other hand when red mud was replaced by iron ore fines (as source of iron oxide and alumina but without titania) this was not observed. This suggests the critical influence of sulfate content in the presence of titania.

XRD analysis of hydrated sample A7 attributed the strength development to the formation of $C_3(A,F).3C\bar{S}.32H$ (ettringite) and $C_3(A,F)H_6$. The hydration of B5 cement resulted in the formation of ettringite and unhydrated CT, whereas on hydration, B8 gave monosulfate hydrate ($C_3(A,F).C\bar{S}.13H$) and unhydrated CT.

The S. E. microscopic study on the hydrated cement samples A7 and B5 showed formation of ettringite crystals of different structures (Fig. 3). Whereas the ettringite formed on hydration of A7 was in the form of long needle-like crystals, that formed on hydration of B5 was in form of compact bundles. The former type of structure is obtained when the ettringite crystals sprout in large cavities, thereby filling the water filled space by long and thinner needles. The latter is obtained when the ettringite is formed in restricted space (3). This may explain the large expansion observed in the case of the samples of B series.

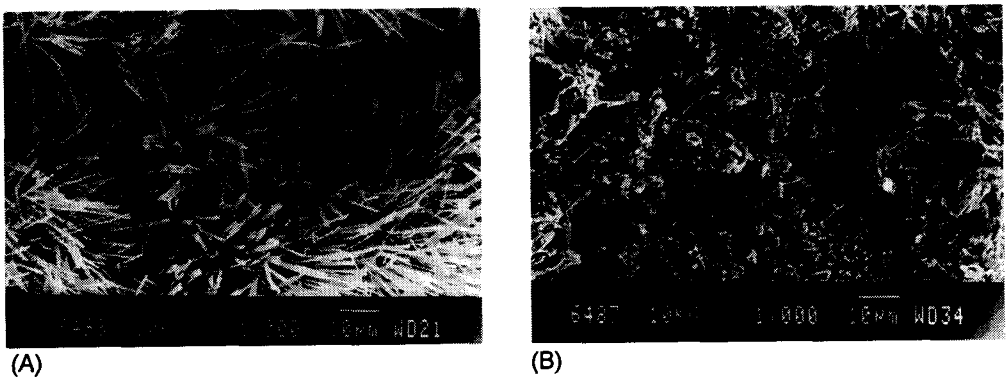
(A) (B)

FIG. 3.
Scanning Electron Micrographs of hardened pastes (A7 and B5) cured for 28 days.

(b) Effect of Firing Temperature. The strengths of cements of Series A (A4 and A7) were observed to increase with the firing temperature till 1300°C (Fig. 4). At 1350°C incipient fusion of clinkers was noticed. The phase identification studies (XRD) indicated that such an effect was due to an increased formation of C_4AF at the expense of C_2F, while the proportion of $C_4(A,F)_3\overline{S}$ remained unaffected.

The strength of cements of Series B (B3 and B8) monotonically decreased till 1250°C and then increased. XRD study of B8 showed the reason for fall in strength to be due to the increased formation of CT while the amount of $C_4(A,F)_3\overline{S}$ phase remained the same.

(c) Effect of Firing Time. All the cements of both series (A4, A7, B3 and B8) had maximum strength when fired for 1-1.5 h (Fig. 4) at 1250°C. While the amount of $C_4(A,F)_3\overline{S}$ remained unaffected in all the cases, in case of Series A the amount of C_4AF and C_3A were maximum between 1-1.5 h where as in Series B the fall in strength for 2 h of firing duration was due to the increased formation of nonhydraulic C_2AS (gehlenite) phase.

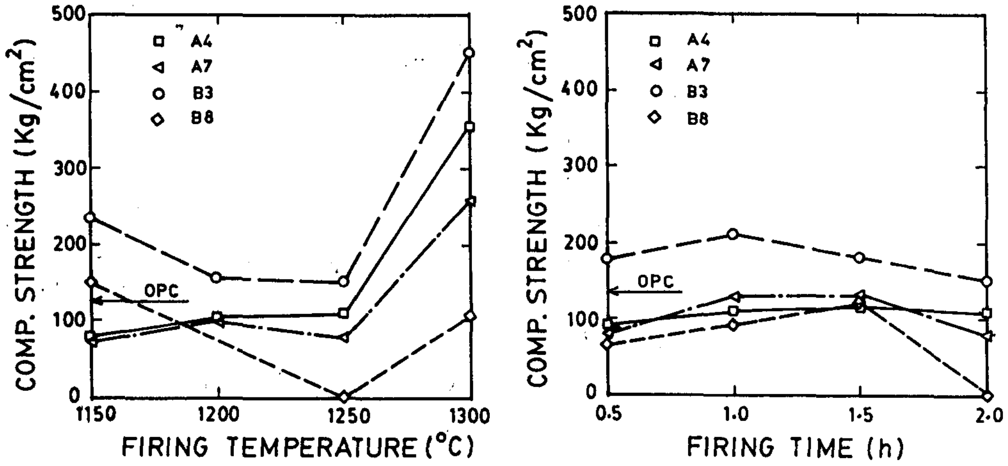

FIG. 4.
Effect of firing temperature and time on 28-days strength of cement pellets.

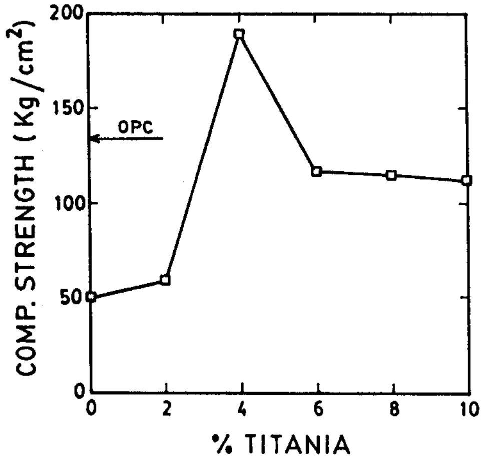

FIG. 5.
Effect of TiO_2 on 28-days strength of $C_4A_3\bar{S}$.

(d) Effect Of Titania On Pure Phases. As the HINDALCO red mud contains significant quantity of titania, the effect of titania doping in $C_4A_3\bar{S}$ (prepared from analytical grade reagents) was studied. The clinkers obtained were soft and friable. While the samples without titania were white in color, and those containing titania exhibited light to deep cream color, the latter being the case with high-titania cements. It was also observed that the strength of cured samples was maximum for the cement containing 4% titania (Fig. 5). The XRD phase identification study indicated absence of peaks of CT till 3% TiO_2 and beyond that increased formation of CT with increase in the titania content. Titania not only formed CT but also substituted the alumina to some extent in $C_4A_3\bar{S}$. On hydration while T1 (0% TiO_2) and T3 (4% TiO_2) hydrated to monosulfate and ettringite; the CT present in T3 remained unhydrated.

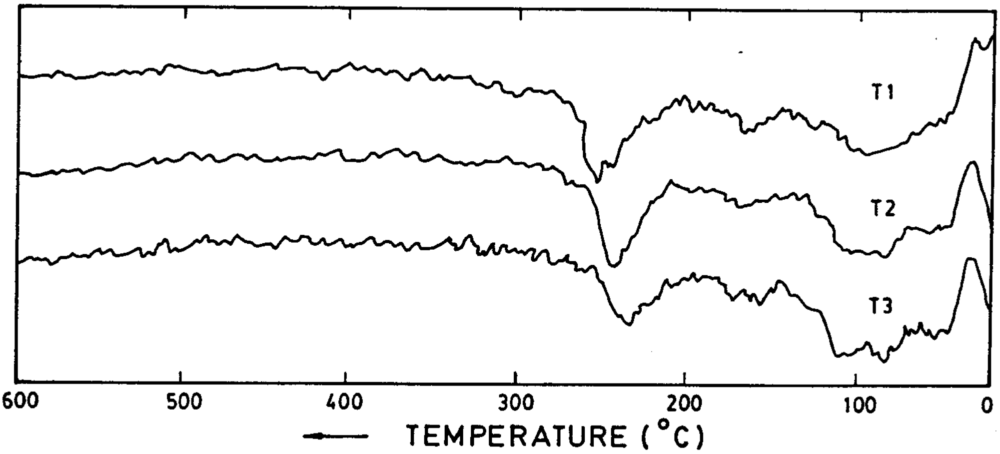

FIG. 6.
DTG of hydrated cements of phase showing fall in the dehydration temperature of monosulfate hydrate on increase in titania content.

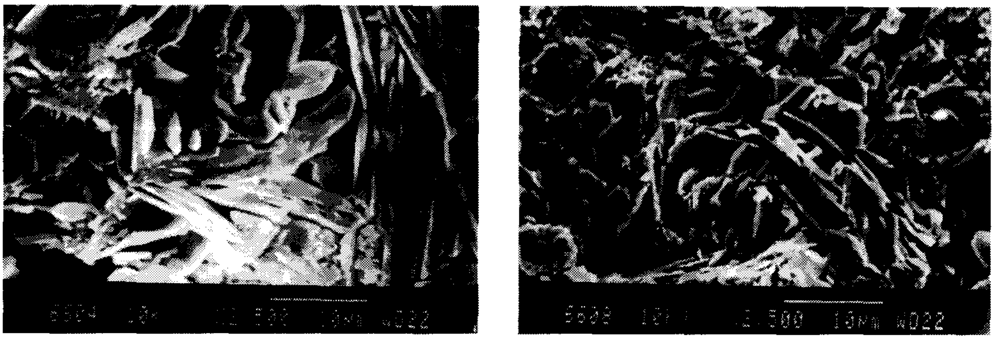

FIG. 7.
SEM of T1 and T3 hydrated samples showing reduction in the size of monosulfate crystals on addition of titania.

Fig. 6 shows the role of titania on the thermal behavior of hydrated samples. (2) The samples showed rapid mass loss at two regions. The first in the range 50-110°C and the second in the range 205-255°C. The first one is characteristic of ettringite and the second is of monosulfate hydrate. While the presence of titania did not seem to significantly alter the temperature at which ettringite dehydrated, the temperature at which monosulfate lost water of hydration decreased slightly with increase in titania content. This may be due to the decrease in the size of monosulfate crystals on addition of titania (Fig. 7).

Conclusions

The following conclusions may be drawn from the present investigations on the preparation of iron-rich cements using red mud as a component of the raw mixes:

1) It is feasible to produce cements possessing acceptable 28 day strength using lime + gypsum + red mud + bauxite, but the properties of cements strongly depended on the proportion of the ingredients.
2) The phases formed on clinkering depend on the percentage of gypsum. When it is 7.5% the major phases that form are $C_4(A,F)_3\bar{S}$, C_4AF and C_2F, and when it is increased to 12.5% the major crystalline phases formed have been found to be $C_4(A,F)_3\bar{S}$ and CT.
3) The strengths of the cement samples increase with the firing temperature and abnormally high strengths (compared to OPC) are obtained at 1300°C. At 1350°C incipient fusion is noticed.
4) A firing duration of 1-1.5 h at 1250°C yields cements having the highest strengths.
5) The presence of titania in $C_4A_3\bar{S}$ increases the strength development of cement paste, lowers the dehydration temperature of monosulfate hydrate and effects the morphological structure of the hydrates.

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References

1. P.K. Mehta and A. Klein, J. Am. Ceram. Soc., 48, 435 (1965).
2. V. Satava and O. Veprek, J. Am. Ceram. Soc., 58, 357 (1975).
3. P.K. Mehta, Cement and Concrete Research, 6, 169 (1976).
4. Y.B. Pliego-Cuervo and F.P. Glasser, Cement and Concrete Research, 8, 455 (1978).
5. C. Tashiro, J. Oba and K. Akama, Cement and Concrete Research, 9, 303 (1979).
6. P.K. Mehta, World Cement Technology, 21, 166 (1980).
7. G. Sudoh, T. Ohta and H. Harada, Proc. 7th International Congress on Chemistry of Cements, 5, 152 (1980).
8. J. Deng, W. Ge, M. Su and X. Li, Proc. 7th International Congress on Chemistry of Cements, 5, 381 (1980).
9. K. Ikeda, Proc. 7th International Congress on Chemistry of Cements, 3, 31, (1980).
10. K. Ogawa and D.M. Roy, Cement and Concrete Research, 11, 741 (1981).
11. K. Ogawa and D.M. Roy, Cement and Concrete Research, 12, 101 (1982).
12. K. Ogawa and D.M. Roy, Cement and Concrete Research, 12, 247 (1982).
13. W. Kurdowski and F. Sorrentino, Structure and Performance of Cements, Applied Science Publishers, London and New York, 471 (1983).
14. W. Yanmou and D. Jun'an, Proc. 8th International Congress on Chemistry of Cements, 2, 300, (1986).
15. I. Kapralik and F. Hanic, Cement and Concrete Research, 19, 89 (1989).
16. F. Hanic, I. Kapralik and A. Gabrisova, Cement and Concrete Research, 19, 671 (1989).
17. F. Hanik, I. Kapralik and M. Drabik, Silikaty, 33, 203 (1989).
18. A. Zdorov and V. Bernshtein, 1st NCB International Seminar, Proceedings, 6, 82 (1987).
19. A.P. Osokin, Y.R. Krivoborodov and N.F. Dukova, 9th International Congress on Chemistry of Cements, Proceedings, 3, 256 (1992).
20. Yu R. Krivoborodov and S.V. Samchenko, 9th International Congress on Chemistry of Cements, Proceedings, 3, 209 (1992).
21. Y. Xi, 9th International Congress on Chemistry of Cements, Proceedings, 4, 377 (1992).
22. P.M. Prasad and J.M. Sharma, Proceedings of Electrometallurgy, Cent. Electrochemical Res. Inst., Karaikudi, 12, (1986).
23. P.M. Prasad, Second International Conference on Aluminium (INCAL-91), Proceedings, Aluminium Association of India, Bangalore, 117 (1991).