Pergamon

Waste Management, Vol. 16, No. 8, pp. 665–670, 1996

0956-053X/96 $15.00 + 0.00

PII: S0956-053X(97)00004-4

ORIGINAL CONTRIBUTION

PREPARATION OF SPECIAL CEMENTS FROM RED MUD

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ABSTRACT. Red mud from HINDALCO (Hindustan Aluminium Corporation) Industries Limited, Renukoot, India, contains significant quantities of alumina, iron oxide and silica. Presence of the said constituents makes it a suitable ingredient for the preparation of special cements. Preparation of three varieties of cements was investigated, namely: (a) aluminoferrite (C_4AF)–belite (β-C_2S) using lime + red mud + fly ash; (b) aluminoferrite–ferrite (C_2F)–aluminates (C_3A and $C_{12}A_7$) utilising lime + red mud + bauxite; and (c) sulfoaluminate ($C_4A_3\bar{S}$)–aluminoferrite–ferrite using lime + red mud + bauxite + gypsum. The effects of composition (proportions of lime, red mud, fly ash, bauxite and gypsum), firing temperature and duration on the properties of cements produced were studied in detail. Cements made from lime + red mud + bauxite or lime + red mud + bauxite + gypsum exhibit strengths comparable or superior to ordinary Portland cement (OPC). On the other hand, those prepared using lime + red mud + fly ash did not have sufficient strength. Moreover, it was not possible to replace bauxite by fly ash (as a source of alumina) in any significant quantity.† © 1997 Elsevier Science Ltd

INTRODUCTION

Red mud is the solid waste residue of the caustic soda digestion of bauxite ores (Bayer process). At all the world's 85 alumina plants, 1.0–1.6 tons of this bauxite tailings (red mud) is generated per ton of alumina and it is estimated that over 66 million tons of this waste is impounded annually in the world, with two million tons in India.[1,2] Red mud is a complex material whose chemical and mineralogical composition varies widely depending upon the source of bauxite and the technological process parameters. It contains six major constituents, namely, Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O and CaO and small quantities of numerous minor/trace elements (as oxides) such as V, Ga, Cr, P, Mn, Cu, Cd, Ni, Zn, Pb, Mg, Zr, Hf, Nb, U, Th, K, Ba, Sr, rare earths, etc. Every red mud is composed of as many as 14–21 mineral phases.[3–8]

The disposal of such a large quantity of this alkaline waste sludge (bauxite tailings) is expensive (up to 1–2% of the alumina price), requires a lot of land (approximately 1 square km per five years for a 1 Mtpy alumina plant) and causes a number of environmental problems.[1–5] Hence, it is imperative that apart from developing efficient disposal methods, ways of economic utilization be found, but, despite some 40–50 years of R&D efforts, no significant quantity of red mud is actually being utilized anywhere in the world.

During the last two decades, extensive work has been done by the Extractive Metallurgy Division of Banaras Hindu University to develop various processes for utilisation of red mud. Various applications that have been investigated include (i) production of constructional grade bricks;[4–10] (ii) recovery of titania and ferrotitanium;[4–8] (iii) preparation of low density (foamed or hollow) bricks;[4] (iv) recovery of iron powder;[4] (v) as additive to cement mortars and concretes;[5–8] (vi) preparation of stabilized (cold bonded) constructional blocks;[9] and (vii) preparation of special cements. Since the use of red mud for production of constructional materials

†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, $\bar{S}$: SO_3, T: TiO_2.

RECEIVED 17 MAY 1996; ACCEPTED 22 JANUARY 1997.

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Acknowledgements—Thanks are due to the Head, Department of Metallurgical Engineering, Banaras Hindu University (Varanasi) for provision of the laboratory facilities for these studies. The authors are grateful to Dr E. C. Subbarao (Executive Director) and Dr Pradip of TRDDC (Pune) for their help, constant encouragement and constructive criticism during the course of this work.

has the potential to consume it in bulk quantities, special attention has been paid to developing such products all over the world.

Ferrite phase (C_4AF), an important constituent in any cement, is formed if the raw mix contains Fe_2O_3 and Al_2O_3. Even though this phase does not contribute much to early day strength, it gives a high later day strength.[11–14] In recent times, calcium sulfoaluminate ($C_4A_3\overline{S}$) phase has attracted considerable attention as a component of cements possessing high early day strengths as well as ultimate strength and also dimensional stability similar to that of ordinary Portland cement (OPC). They are usually referred to as low energy, expansive or sulfoaluminate cements. In such cements the high early day strength is due to the rapid formation of ettringite ($C_3A.3C\overline{S}.32H$) phase.[11,12,16–21]

This paper deals with the possibility of preparing different types of special cements using lime, red mud, fly ash, bauxite and gypsum. The effects of different process parameters like composition of raw mixes and firing temperature and time on the phase formation, strength, density and color were investigated.

MATERIALS AND METHODS

As received uncausticised red mud and bauxite (in the form of lumps) from HINDALCO (Hindustan Aluminium Corporation) Industries Limited, Renukoot, fly ash from its captive power plant (Renusagar Power Company) and locally available hydrated lime and gypsum of commercial grade were used in these investigations. Chemical compositions of the raw materials used are given in Table 1. Whereas the first three were dried and powdered to $-150\,\mu m$, the latter two were ground to $-200\,\mu m$ size.

Procedure for Making Cement Samples

To prepare each sample, 100 g of the raw materials in predetermined proportions were taken and ball milled for 45 min for homogenization. The resultant blend was made into a thick paste using an appropriate quantity of water and moulded into cube (5 cm size) shapes, dried overnight in a hot air oven at 100°C and then fired (clinkered) in an electric muffle furnace. A heating rate of approximately 200°C/h was employed and the firing temperature kept at a predetermined level (1150–1350°C) up to 2 h. The clinkered products were cooled in the furnace up to 700°C and then overnight to room temperature. The clinkers so produced were ground in an agate mortar and pestle and sieved through $150\,\mu m$ mesh.

In order to find the right chemical composition which would give cements having the desired strength, five sets of samples were fired (Table 2) at 1250°C for 2 h. The amount of red mud and fly ash/bauxite were varied in steps of 5%. The effects of firing temperature (1150–1350°C) and duration (0.5–2.0 h) were studied on six representative samples of the three sets. Tables 2 and 3 give the details of the firing schedule.

Testing for Compressive Strength

Compressive strengths of the cement samples were determined using small cylindrical pellets of the cement paste made by compacting 5 g of cement sample with 2.0 ml of water in a die of 1.6 cm ID under a 2 kg load (put on top of the plunger for 5 min). Pellets so prepared were kept on the top of a wet piece of cloth for a day and then immersed in water for 28 days. The samples were then ground to a uniform height of 1.5 cm using emery paper. Compressive strengths of these pellets were determined

TABLE 1
Chemical Analyses of the Raw Materials (wt%)

	Lime	Gypsum	Red mud	Bauxite	Fly ash
Fe_2O_3	0.65	0.13	33.1	16.5	3.70
Al_2O_3	0.65	0.07	18.2	48.0	37.80
SiO_2	1.00	0.89	8.8	3.0	45.60
CaO	67.13	37.41	2.7	0.5	5.35
TiO_2	—	—	19.6	8.5	—
Na_2O	—	0.27	5.8	—	—
SO_3	—	53.35	—	—	—

TABLE 2
Compositions (wt%) of Different Raw Mixes Fired at 1250°C for 2 h

	Lime	Gypsum	Red mud	Bauxite	Fly ash
Series A	65.0	—	0–35.0	—	35–0
Series B	50.0	—	5.0–50.0	45.0–0	—
Series C	47.5	7.5	0–45.0	45.0–0	—
Series D	50.0	25.0	0–25.0	—	25.0–0
Series E	35.0	10.0	5.0–30.0	45.0–20.0	5.0

using an Amsler Universal Testing Machine. The strength of ordinary Portland cement (OPC, Indian Standard Grade 33) was also obtained in a similar fashion. Due to the non-standard method of testing the compressive strength, the values obtained indicate only the relative and not the actual strength values.

Identification of Phases

To determine the phases formed on firing of the raw mixes and on hydration of cement pastes, the samples were ground to $-75\,\mu m$ and XRD patterns obtained employing a Rigaku-Geigerflex XRD machine using Ni-filtered Cu Kα radiation at 40 kV and 25 Ma. The complex nature of the samples made the identification and quantitative evaluation of different phases by XRD quite difficult. The large number of phases present in any sample gave overlapping peaks. Moreover, the diffraction peak shifts occur due to doping effects caused by the presence of impurities. Hence, no attempt was made to quantify the phases present, but only a qualitative identification of the phases was attempted.

RESULTS AND DISCUSSION

Effect of Composition of Raw Mixes

The clinkers prepared out of Series A compositions (lime + red mud + fly ash) were observed to be soft,

TABLE 3
Compositions (wt%) of Representative Samples of Raw Mixes Fired at Different Temperatures (for 2 h) and for Varying Durations (at 1250°C)

	Lime	Gypsum	Red mud	Bauxite	Fly ash
A3	65.0	—	10.0	—	25.0
A6	65.0	—	25.0	—	10.0
B3	50.0	—	15.0	35.0	—
B7	50.0	—	35.0	15.0	—
C4	47.5	7.5	15.0	30.0	—
C7	47.5	7.5	30.0	15.0	—

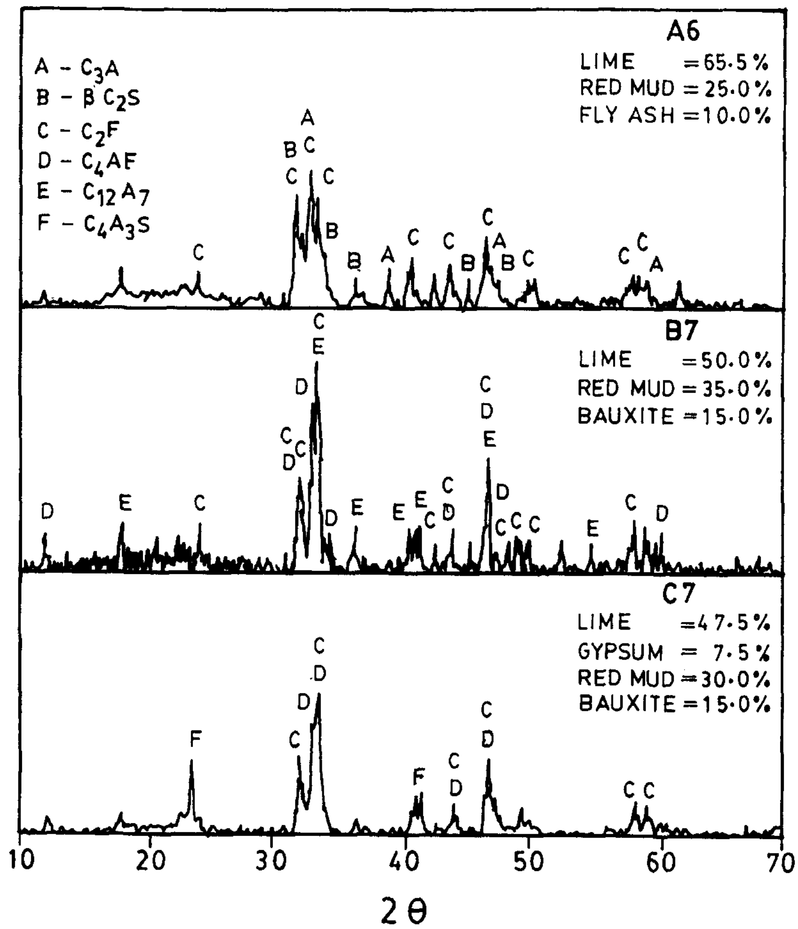

FIGURE 1. X-Ray diffraction patterns of A6, B7 and C7 cement samples made by firing at 1250°C for 2 h.

friable and of cream color. While the samples A1–A3 (red mud = 0–10%, fly ash = 25–15%) did not have any appreciable strength, the samples A4–A6 (red mud = 15–35%, fly ash = 10–0%), hardened. However, their strengths were found to be far below that of ordinary Portland cement because of the development of cracks. Phase identification (XRD) study on A6 cement showed formation of strength giving C_3A and β-C_2S along with poorly hydraulic C_2F, but C_4AF phase was not detected (Fig. 1).

The clinkers obtained using compositions of Series B (lime + red mud + bauxite) were hard and dark brown in color. Their hardness, 'glassy' nature, relative density and intensification of color increased with red mud content. Figure 2 shows that peak strength values were obtained for compositions with red mud content between 25–40% (i.e. F/A = 0.8–1.2%). XRD study of the samples indicated the formation of C_3A, $C_{12}A_7$, C_4AF and C_2F phases (Fig. 1). It was also observed that with the increase in amount of red mud (F/A ratio from 0.5–1.5) the amount of C_3A and $C_{12}A_7$ phases formed decrease with corresponding increase in C_2F phase. The amount of C_4AF phase formed is maximum when F/A ratio is close to unity (sample B5; red mud = 25% and bauxite = 25%). Hence the strength of pellets made from these cements is consistent with the observation regarding the maximum formation of C_4AF. The XRD study of sample B7 hydrated for 28 days indicated the presence of unhydrated C_2F and formation of $C_3(A,F)H_6$.

The clinkers of Series C (lime + gypsum + red mud + bauxite) exhibit a light brown color and were found to be soft and friable. With increase in red mud content the color became darker and density increased. The strength of pellets also increased with red mud content (Fig. 3). XRD work indicated that $C_4A_3\bar{S}$, C_4AF and C_2F were the major phases formed (Fig. 1). Further, with increase in red mud content (hence F/A ratio) there was an increase in the formation of C_4AF and C_2F phases and also a corresponding decrease in the $C_4A_3\bar{S}$ phase. XRD analysis on hydrated cement sample C7 indicated that the strength development was essentially due to the formation of $C_3A.3C\bar{S}.32H$ (ettringite) and $C_3(A,F)H_6$.

Results of the previous set showed the possibility of preparing sulfoaluminate — ferrite based cements using lime + gypsum + red mud + bauxite. Therefore, in the Series D (lime + gypsum + red mud + fly ash), bauxite was replaced with fly ash as a source of alumina. The cements so made did not develop any strength. The XRD study on the D3 (red mud = 10%, fly ash = 15%) cement showed a little formation of $C_4A_3\bar{S}$ and β-C_2S along with unhydraulic C_2F and $2C_2S.C\bar{S}$ as major phases.

In the Series E (lime + gypsum + red mud + bauxite + fly ash) the effect of partial replacement (5%) of bauxite with fly ash was studied. It was found that the incorporation of fly ash in any raw mix definitely exerts a deleterious effect on account of the increased formation of non-hydraulic $2C_2S.C\bar{S}$ and C_2AS phases.

Effect of Firing Temperature

All the samples exhibited an increase in strength with firing temperature up to 1300°C. At 1350°C the clinkers fused and stuck to the walls of the crucibles in which they were fired. While cements of Series A showed only marginal increase in strength, the cements of Series B and C exhibit a regular increase in strength with firing temperature. In fact the strength of samples of Series B and C fired at 1300°C for 2 h were much higher than that of OPC (Fig. 4). XRD tests on cements fired at different temperatures showed that in the case of Series B cements the proportions of $C_{12}A_7$ and C_2F increased with temperature

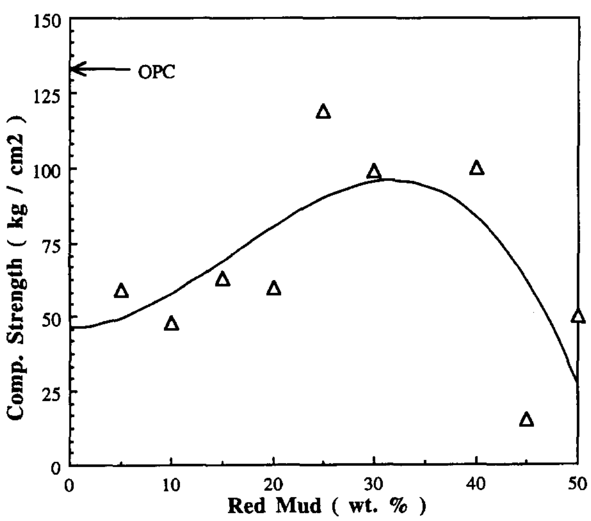

FIGURE 2. Effect of quantity of red mud on the 28-days strength of cements of Series B.

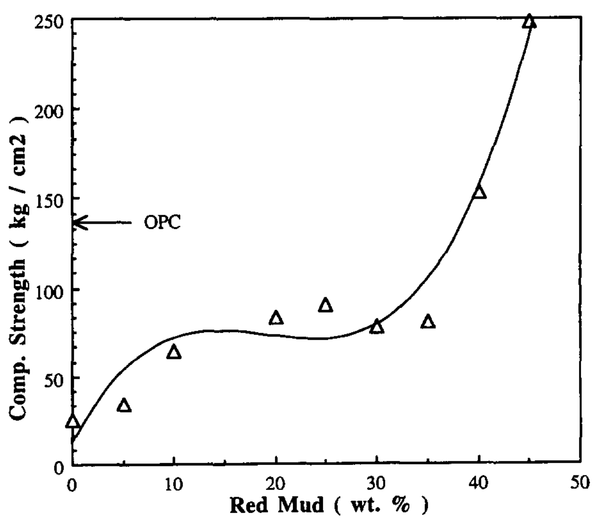

FIGURE 3. Effect of quantity of red mud on the 28-days strength of cements of Series C.

up to 1250°C and then decreased with a corresponding rise in the proportion of C_4AF. In the case of the cements of Series C there was an increased formation of C_4AF at the expense of C_2F and the proportion of $C_4A_3\overline{S}$ remained unaffected. Very high strength values of the samples fired at 1300°C were attributed to the maximum formation of C_4AF phase observed at the said temperature in both the cases.

Effect of Duration of Firing

While the firing time (between 0.5–2.0 h) had no significant influence on compressive strengths of either sample of Series A (the strengths remained far below that of OPC) the cements of Series B and C exhibited increase in strength till 1.5 h and a decrease thereafter (Fig. 5). Phase identification studies (XRD) revealed that for samples of both the cements of Series B and C, the proportion of C_2F decreased and C_4AF increased with the increase in firing duration up to 1.5 h. But in the sample fired for 2 h, the latter phase appeared to dissociate back to C_2F. Additionally, in the case of Series C cements the amount of $C_4A_3\overline{S}$ formed seemed to remain nearly unaffected by the duration of firing.

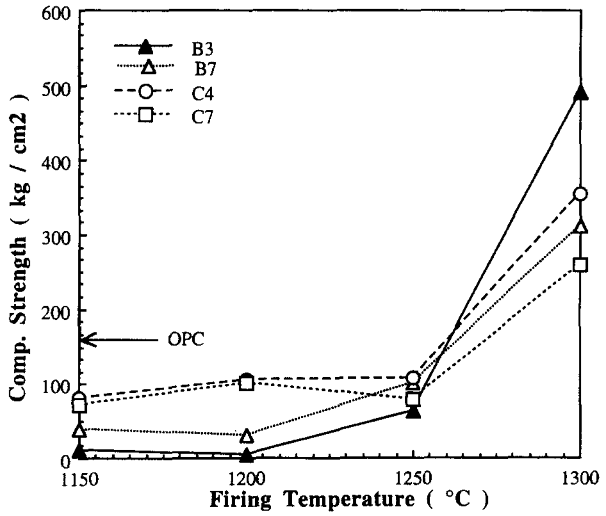

FIGURE 4. Effect of firing temperature on the 28-days strength of cements of Series B and C.

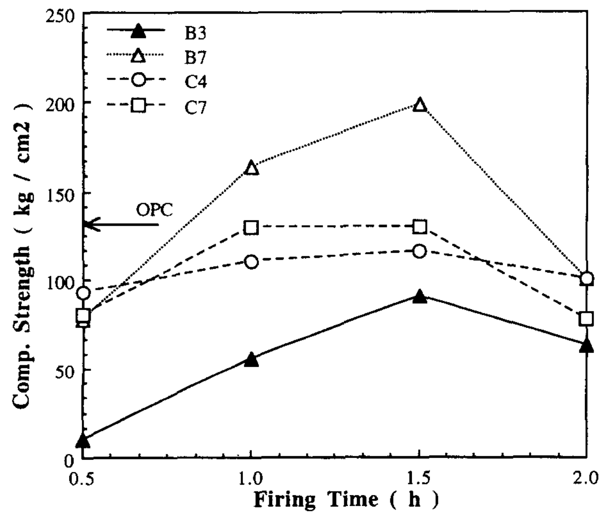

FIGURE 5. Effect of firing time on the 28-days strengths of cements of Series B and C.

Optimum Conditions

The above results indicate that it is feasible to produce good quality special cements possessing strengths comparable to that of ordinary Portland cement (OPC) using raw mixes containing red mud + bauxite + lime or red mud + bauxite + gypsum + lime. The temperature of firing found necessary (1250°C) is much lower than that used for the production of OPC. Though the exact compositions have to be determined by further experimentation, the most promising proportions seem to be 30–35% of the HINDALCO red mud + 15–20% bauxite + 7.5–10% gypsum + 45–50% lime depending on the type of cement desired. Colors of such cements are pleasing reddish-brown. The incorporation of HINDALCO's fly ash in the raw mixes reduces the strengths of the cements produced.

CONCLUSIONS

The following conclusions emerge from the present investigations on the preparation of special cements utilizing HINDALCO's red mud, fly ash and bauxite:

1. It is possible to prepare cements having 28-days strength comparable to that of OPC using raw mixes containing lime + red mud + bauxite or lime + gypsum + red mud + bauxite.
2. It is not feasible to produce cements having strength as good as that of OPC from any raw mix containing fly ash. Even partial replacement of bauxite by fly ash results in a deterioration in the quality of cements.
3. The strengths of the cement samples made from lime + red mud + bauxite or lime + gypsum + red mud + bauxite increase with temperature. Unusually high strengths (compared to OPC) can be obtained by firing at 1300°C.
4. An iron oxide to alumina (F/A) ratio of 0.8–1.2 in the raw mixes and a firing temperature of 1250°C for 1.0–1.5 h give the best results for preparing the special cements.
5. The strength development may be attributed to the formation of C_4AF, C_3A and $C_{12}A_7$ phases in the case of cements made from lime + red mud + bauxite and C_4AF, $C_4A_3\overline{S}$ and C_3A in the lime + gypsum + red mud + bauxite cements.

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Open for discussion until 31 December 1997