**RESEARCH ARTICLE**

**INVESTIGATIONS OF THE INFLUENCE OF CALCINED RED MUD ON CEMENT HYDRATION**

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**ABSTRACT**

Utilization of industrial waste materials in the industry has been the focus of research for economical, environmental and technical reasons. Red mud (RM) is a waste material generated to produce alumina from bauxite throughout the world. This waste product calcined at 600°C had the best supplementary cementitious properties. The cementitious activity of calcined red mud was evaluated through the measurements of setting time and compressive strength of blended cement mortars. X-ray diffraction and Scanning electron microscopy techniques were used to follow the extent of hydration reactions and microstructural development of the pastes respectively.

**INTRODUCTION**

Red mud is a waste material of the Bayer process, which is used for the production of alumina from bauxite. For every tone of alumina processed, one tone of RM waste is released [Pera et al., 1997]. The huge deposits of RM and its alkaline nature require large land areas for disposal and need special attention to avoid contamination of soils, surface and ground water. Therefore in order to save the environment, bauxite waste material can be utilized effectively rather than disposing. Now a day’s increasing demand for raw materials and the limited availability of natural resources gave rise to the investigations of the industrial byproduct/waste material for possible reuse. These include applications of RM in the agriculture or waste water treatment, as additive to plastic or ceramic/cement materials [Senff et al., 2011]. The cement based materials are obvious attractive solutions, since production rates are also massive. RM has been used in the production of special Portland clinkers [Singh et al., 1996; Singh et al., 1997].

Different authors [Jobbagy et al., 2009; Srikanth et al., 2005] have been reported on the characterization of RM through heat treatment. According to Na zhang et al. [Na zhang et al., 2011] and Xiaoming Liu et al. [Xiaoming Liu et al., 2011], RM calcined at 600°C had the best cementitious properties. As RM usually contains some quantities of amorphous alumino silicate materials and gibbsite, which they can be transformed into more reactive silica and alumina during the calcinations process, resulting some pozzolanic properties. In the present study, the effect of addition of calcined RM with Ordinary Portland cement (OPC) was analyzed by means of testing setting time, compressive strength and the hydration reactions were evaluated through XRD and SEM techniques.

**MATERIALS AND METHODS**

Ordinary Portland cement (OPC) was a commercially available product. Red mud was obtained from Madras aluminium company (MALCO) Chennai, India. As received RM was calcined in furnace at 600°C for 6 hours followed by air quenching. After cooling, the calcined RM was stored in air-tight polythene bags for further use.

**Setting Time**

The initial and final setting time of OPC, calcined RM blended cement pastes were determined using a Vicat’s apparatus [Shetty, 2004].

**Compressive Strength**

To determine the compressive strength of OPC, OPC blended with calcined RM (OPC + 5% RM and OPC + 20% RM), mortar specimens of cubical size 7×7×7cm were prepared [Shetty, 2004]. After 1 day, the compressive strength of the cured mortars (1, 7 and 28 days) were measured and the average value of three specimens were reported.

**XRD and Sem**

XRD technique was used to analyze the hydration mechanism of OPC, OPC + 5% RM and OPC + 20% RM paste cured at 1, 7 and 28 days. The prepared samples were immersed in acetone to stop hydration. The hydrated samples were heated at 120°C for 2 hours in order to remove the adsorbed water. The dried samples were powdered using agate mortar and stored in a air tight polythene bag. X-ray diffraction patterns of powdered samples were recorded using XRDML Gonio machine equipped with a rotating anode, using Cu-Kα radiation operated at 40 kV and 30 mA. JEOL make SEM was need to observe the hydration products of the OPC, OPC + 5% RM and OPC + 20% RM paste (28 days).
RESULTS AND DISCUSSION

Setting time and strength

The results of initial and final setting time of OPC, OPC + 5% RM and OPC + 20% RM are shown in Fig. 1. The results show that addition of calcined RM accelerates the setting. The 5 and 20% calcined RM blended cements attained a earlier final setting value at 463 and 440 minutes respectively as compared to the 480 minutes of OPC. It indicates that on increase in percentage of calcined RM in cement accelerates the setting. The variation of compressive strength of OPC, OPC + 5% RM and OPC + 20% RM mortar samples with hydration periods are shown in Fig. 2. It is observed that compressive strength increases with increasing curing periods. This strength development is generally attributed to the formation of C-S-H and to the precipitation of primary ettringite. But the compressive strength of OPC + 5% RM and OPC + 20% RM admixtured cement is higher than OPC. Maximum strength of 52.15 MPa has been observed for 20% RM on 28 days which is about 8.44 MPa higher as compared to OPC (43.71 MPa). This increase in strength due to the pozzolanic reactions between calcined RM and OPC.

XRD and sem

X-ray diffractogram of OPC pastes hydrated at different hydration periods are shown in Fig. 3. The most prominent peaks in the OPC paste hydrated at 1 day are portlandite

P-Ca(OH)$_2$; E-AF$\beta$; A-C$_3$A; T-$C_3$S; D-$C_2$S; B-$C_2$S/$C_3$S; O-MgO; F-$C_6$AF; C-CaCO$_3$; S-C-S-H; M- AFm; Fe-$Fe_2O_3$;

CAH- calcium aluminate hydrate

(Ca(OH)$_2$)$_x$ at 18.10$^\circ$; 33.57$^\circ$; ettringite (AFt) at 23.10$^\circ$; 41.25$^\circ$; tricalcium aluminate (C$_3$A) at 26.51$^\circ$; tricalcium silicate (C$_3$S) at 32.20$^\circ$; 51.50$^\circ$; 62.40$^\circ$; dicalcium silicate (C$_2$S) at 32.50$^\circ$; 56.15$^\circ$; tetracalcium alumino ferrite (C$_4$AF) at 44.10$^\circ$; monosuphate (AFm) at 56.64$^\circ$ and calcium silicate hydrate gel (C-S-H) at 29.50$^\circ$. The intensity of clinker peaks reduce as hydration time increases in OPC paste due to formation of hydration products.

The XRD pattern of OPC + 5% RM and OPC + 20% RM pastes at different hydration periods are shown in Figs. 4 & 5. The principle hydration products in calcined RM admixed cement paste are essentially similar as those found in OPC paste. As the percentage of calcined RM increases more amount of Ca(OH)$_2$ is consumed due to pozzolanic reactions and hence the higher amount of C-S-H and CAH is formed. This indicates that the pozzolanic reaction between Ca(OH)$_2$ and amorphous silica and alumina present in the calcined RM. This represents the following equation.

SiO$_2$.Al$_2$O + Ca(OH)$_2$ + H$_2$O $\rightarrow$ C$_3$AH$_x$ + C-S-H ...(1)

Na Zhang et al., [Na Zhang et al., 2011] have also reported that the calcined RM contains some quantities of amorphous aluminosilicate and gibbsite material and these can be transformed into reactive alumina and silica during the calcinations (600$^\circ$C). This amorphous phase may also contributes to the good cementitious activity during the hydration. The OPC + 20% RM have higher compressive strength and it is mainly due to the growth of calcium aluminate hydrate compounds (20=12.10$^\circ$) and C-S-H gel. It is also observed that the intensity of the hematite peak decreases as increase with hydration time.

The SEM micrographs of OPC, OPC + 5% RM and OPC + 20% RM pastes at 28 days are shown in Fig. 6. After 28 days hydration of cement, typical hydration products like ettringite, Ca(OH)$_2$ and significant quantities of C-S-H are seen. Comparing the
Fig. 5 The XRD spectra of OPC + 20% RM paste at (a) 1 day (b) 7 days and (c) 28 days

microstructure of OPC + 5% RM with that of OPC + 20% RM, it can be observed that the paste containing 20% RM is relatively more fibrous and dense structure than the paste containing 5% RM.

Fig. 6 The SEM micrographs of (a) OPC (b) OPC + 5% RM and (c) OPC + 20% RM paste at 28 days

CONCLUSION

The results have shown that RM calcined at 600°C is a good pozzolanic material. The compressive strength of cement containing 20% RM was higher than that of OPC at all hydration periods. The increase in the use of calcined RM in cement, reduce the environmental problem and minimize the requirement of land fill area to dispose of the RM.

References


