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DEVELOPMENT OF A POZZOLANIC PIGMENT FROM RED MUD

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ABSTRACT

Red mud is a waste generated by the aluminium industry, and its disposal is a major problem for this industry. Very rich in iron, it can be used as cheap pigment for coloured concrete. The red coloration can be enhanced by calcination in the range of 600 to 800°C. Such operation also transforms the aluminium hydroxides (goethite and boehmite) and clays minerals into pozzolanic admixtures that are able to consume the calcium hydroxide produced by cement hydration. Thus, it is possible to develop a new admixture for concrete: a pozzolanic pigment. The pozzolanic properties of calcined red mud were investigated by monitoring lime consumption of different mixtures of OPC and red mud. The main products of hydration were C-S-H and mono-carboaluminate ($C_4A\bar{C}H_{11}$). A uniform and durable coloured concrete was obtained using white cement interground with 11% of burnt red mud. © *1997 Elsevier Science Ltd*

Introduction

Red mud is a by-product of the Bayer process, which is used for the production of alumina from bauxite. For each part of alumina produced by this process, about one part of red mud is generally discarded as a waste. In Western countries, about 35 million tons of red mud are produced yearly. Disposal of this waste was the first major problem encountered by the alumina industry after the adoption of the Bayer process.

Over the years, many attempts have been made to find a use for red mud, but none have proven to be economically satisfactory. These attempts were based mainly on the use of red mud as a partial substitute for clay in the production of bricks and other ceramic products (1–4). Red mud has a reddish-brown colour and a superfine, fine particle-size distribution as it's physical characteristics, as well as alkalis, iron oxides and hydroxides, aluminium hydroxides, calcium carbonate, titania, and silica in its chemical composition. The superfine particles characteristic of red mud makes this a promising admixture for mortar and concrete (5).

As shown by Péra et al. (6), the aluminium hydroxides (boehmite and gibbsite) develop some pozzolanic behaviours when calcined between 600 and 800°C. Goethite (FeOOH) is transformed into hematite (Fe_2O_3) during the calcination process, and the red colour is reinforced.

TABLE 1
Chemical composition of red mud on a dry basis

Oxides	Composition (%)
SiO_2	4.98
Al_2O_3	15.00
Fe_2O_3	26.62
CaO	22.21
MgO	0.95
K_2O	0.02
SO_3	0.23
TiO_2	15.76
MnO	0.09
Na_2O	1.02
Cr_2O_3	0.33
P_2O_5	0.69
LOI	12.1

Based on these results, this paper describes a process for the production of a pozzolanic pigment from red mud, which is able to limit efflorescences in coloured concrete and is more easily dispersed than the usual pigments.

Experimental

The red mud used for the study was provided by Aluminium Pechiney from its plant at Gardanne, France. Red mud was dried at 50°C for 3 days and desagglomerated to get a product finer than 100 μm. Its chemical composition is given in Table 1. The main crystalline phases present in red mud were determined by x-ray diffraction and are shown in Fig. 1.

The presence of hydrogarnets and perovskite is due to chemical reactions that occur between calcium carbonate and bauxite during the Bayer process. The latter consists essentially of two steps. In the first step, washed and crushed bauxite is treated with a solution of sodium hydroxide at an elevated temperature and pressure (240°C, 3.2 MPa). This process brings all the recoverable alumina from bauxite into solution, and the residue, known as red mud, is discarded as a waste. From the above alumina-rich mixture, alumina is precipitated, filtered, and dried, before being subjected to electrolysis.

The nature of red mud depends mainly on the nature of the bauxite used and on the experimental conditions employed in Bayer's treatment. Essentially, there are two types of constituents in red mud (7). Those originating from bauxite are minerals of undissolved aluminium oxides and hydroxides (boehmite, gibbsite, diaspore), iron oxides and hydroxides (hematite, goethite, limonite), and others (rutile, anatase, calcite, dolomite). The second type includes new phases formed in Bayer's process, such as sodium aluminium hydrosilicates (sodalite, cancrinite), hydrargilite, titanates of Na, Ca, or Mg, calcium, and aluminium silicates, etc.

In the present study, the high LOI (12.1%) is due to the presence of many hydroxides and calcite. The physical properties of dried red mud were determined: the BET surface area is

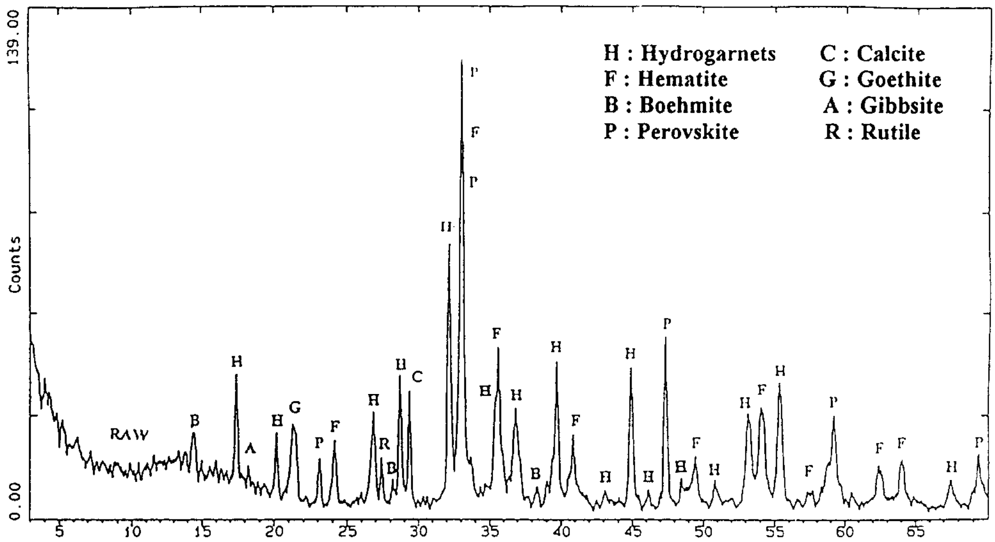

FIG. 1.
X-ray diffraction analysis of red mud.

10.7 m^2/g and the specific gravity 3.05. The specific gravity was determined from the displacement principle by using toluene in a pycnometer, just as for cement.

The cement used in the study was a CEM-I 52.5 (HP) portland cement, according to European standards, which is similar to a Type I ASTM cement. The calcium hydroxide was a from Merck (>96% $Ca(OH)_2$.).

The calcination programme was as follows: calcination for 3 hrs up to a temperature varying from 600 to 800°C, at a step of 50°C; temperature maintained for 5 hrs; and a natural cooling of the furnace.

The pozzolanic activity of calcined red mud was studied by means of pastes cast at a standard consistency and containing 50% red mud and 50% $Ca(OH)_2$. The $Ca(OH)_2$ consumption was studied at different times of hydration by differential thermal analysis (DTA) for periods 3, 7, 28, and 90 days.

Standard mortars, including 10 to 30% of red mud instead of OPC, were cast and investigated for their compressive strength for 90 days. In these mortars, the sand:binder ratio was 3:1. The water:binder ratio was maintained constant at 0.50. Mortars were placed in prismatic moulds (40 × 40 × 160 mm) and compacted by vibration. After casting, the prisms were covered with plastic film to prevent water loss. After 24 hours, the specimens were demoulded and cured in lime-saturated water at 20 ± 2°C for periods of 2, 7, 28, and 90 days.

Results and Discussion

Influence of Calcination on the Mineralogy and Physical Properties of Red Mud

As shown in Fig. 2, the peaks corresponding to boehmite, gibbsite, and goethite disappear as the temperature reaches 600°C. The intensity of the hydrogarnet peak also decreases. Calcite

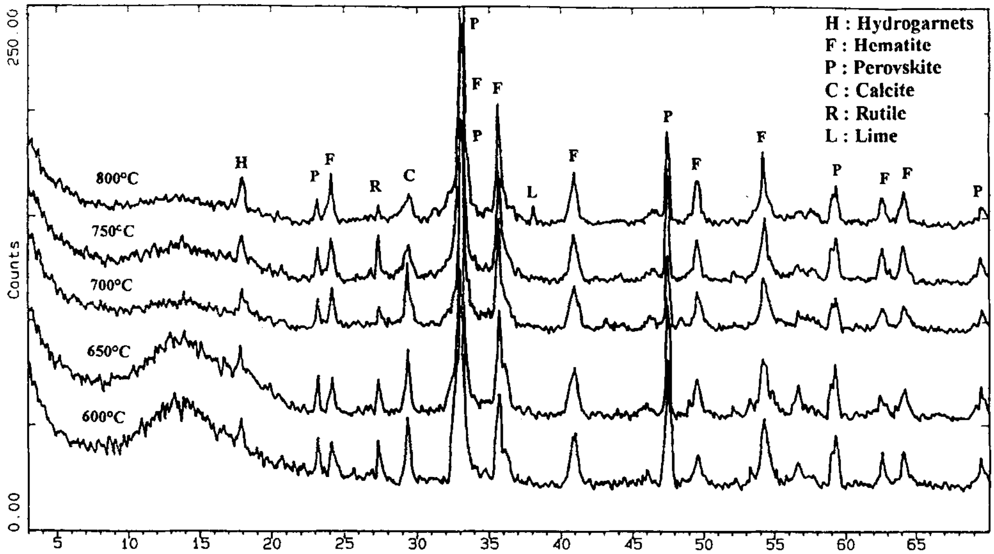

FIG. 2.
XRD of calcined red mud.

is retained until the temperature approaches 750°C. Lime (CaO) appears at 800°C. A "halo" indicative of noncrystalline phases is notable at 600 and 650°C. The halo corresponding to this is present between 2θ = 10° and 2θ = 20°.

The evolution of the halo area is shown in Table 2. The evolution of the BET-specific surface area (also given in Table 2) correlates with the XRD halo area (Fig. 3). The coefficient of the linear regression is 0.89.

Pozzolanic Activity of Calcined Red Mud in the Presence of Calcium Hydroxide

The ratio of water to solid pastes composed of 50% calcined red mud and 50% $Ca(OH)_2$ varied from 0.57 (calcination at 600°C) to 0.60 (calcination at 800°C). There is no direct

TABLE 2
Halo area and BET surface area as functions of temperature

Temperature (°C)	XRD halo area (arbitrary units)	BET surface area (m^2/g)
20	3.0	10.7
600	10.5	12.4
650	11.0	12.0
700	4.0	9.3
750	5.0	9.2
800	4.0	7.5

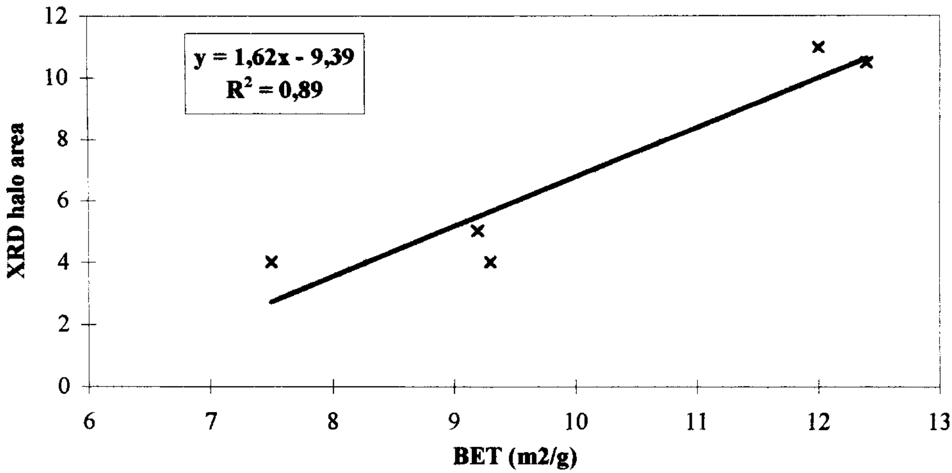

FIG. 3.
Relationship between the BET surface area and the XRD halo area.

relation between this ratio and the BET surface area. The evolution of the $Ca(OH)_2$ consumption versus time is reported in Table 3.

All the calcined red muds are pozzolanic. The reaction starts at 3 days and progresses with time. Samples calcined at 600 and 650°C show less pozzolanic activity, whereas those calcined at 700 or 800°C show greater activity.

Performances of Blended Cements

Pastes. Ten, twenty, and thirty percent of OPC were replaced by calcined red mud in pastes cast at equivalent consistency and standard mortars. The trend in $Ca(OH)_2$ consumption in pastes (Table 4) was the same as that observed in $Ca(OH)_2$, i.e., calcined red mud pastes. The product calcined at 600°C is not very reactive, and the reduction in portlandite content is only due to the dilution effect (replacement of OPC by calcined red mud). When the level of OPC replacement is 10%, calcined red mud only acts as a filler.

The mineralogical investigation carried out by DTA and XRD showed that the main

TABLE 3
$Ca(OH)_2$ consumption in
50% red mud/50% $Ca(OH)_2$ pastes

Temperature (°C)	$CA(OH)_2$ consumption (%)			
	3 days	7 days	28 days	90 days
600	19	20	22	25
650	15	17	17	28
700	24	26	34	35
750	20	25	26	28
800	21	21	38	43

TABLE 4
Portlandite consumption in OPC-calcined red mud pastes

Temperature (°C)	OPC/calcined red mud (%)	Portlandite consumption at 28 days (%)
600	90/10	≈0
	80/20	≈0
	70/30	≈0
650	90/10	≈0
	80/20	6
	70/30	10
700	90/10	≈0
	80/20	10
	70/30	18
750	90/10	1
	80/20	11
	70/30	19
800	90/10	5
	80/20	21
	70/30	38

hydrates formed during the hydration reaction are C-S-H (DTA peak at 130°C), ettringite, portlandite, and mono-carboaluminate ($C_4A\bar{C}H_{11}$). The latter forms from the reaction between portlandite, calcite, and the amorphous alumina resulting from red mud calcination. As shown in Fig. 4, $C_4A\bar{C}H_{11}$ appears in pastes containing more than 20% of calcined red mud.

Mortars. The compressive strengths of standard mortars are shown in Table 5.

Mortars containing calcined red mud exhibit lower strengths than the control mortar. When red mud is calcined at 750 or 800°C, there is a drastic decrease in early-age strength as red mud content reaches 20%. This may be due to the presence of lime (CaO), which appears from calcite decarbonation at these temperatures. Lime first hydrates to give calcium hydroxide, and it consumes water that is no longer available for correct OPC hydration.

To investigate the reasons of such a decrease, the binder activity index was calculated from Feret's equation:

$$R_c(t) = K(t)\left(\frac{V_s}{V_s + V_a + V_w}\right)^2$$

where: $R_c(t)$ = compressive strength at t days,

$K(t)$ = binder activity index at t days,

V_s = volume of the solid fraction in the cementitious paste, calculated on the basis of the mass of added red mud and its density,

V_a = volume of entrained air,

V_w = volume of mixing water.

The results for K(28) and K(90) are shown in Table 6.

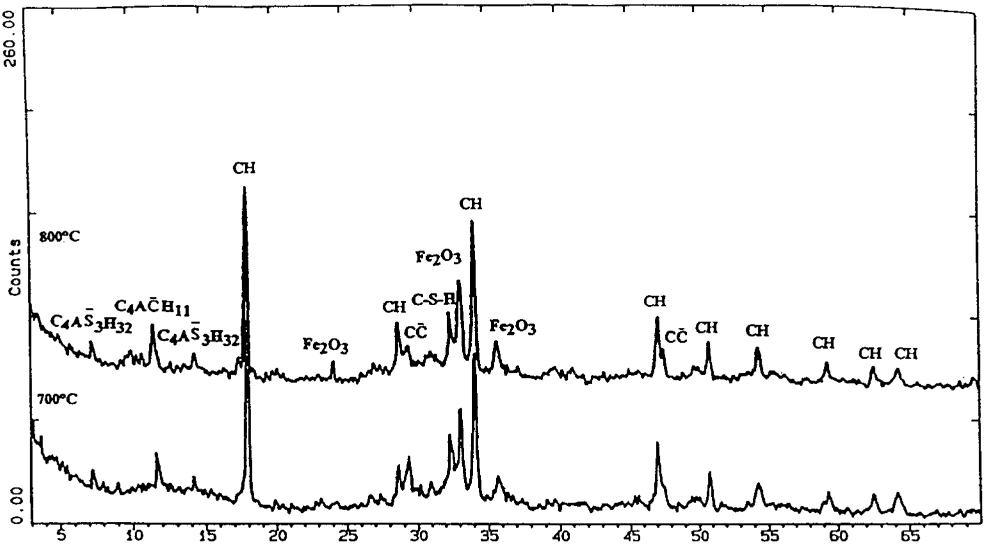

FIG. 4.
XRD of a hydrated paste (90 days) containing 30% of calcined red mud.

TABLE 5
Compressive strengths of mortars (MPa)

Temperature (°C)	OPC/calcined red mud (%)	Compressive strength (MPa)			
		2 days	7 days	28 days	90 days
OPC control	100/0	38.3 ± 0.6	55.6 ± 0.6	65.5 ± 1.2	66.7 ± 1.8
600	90/10	38.0 ± 0.6	55.9 ± 0.4	60.4 ± 1.6	60.9 ± 0.9
	80/20	34.0 ± 0.4	49.1 ± 1.7	58.6 ± 0.6	58.1 ± 1.2
	70/30	28.7 ± 0.7	46.4 ± 0.8	50.2 ± 0.7	49.5 ± 0.5
650	90/10	37.6 ± 0.7	54.0 ± 0.8	59.6 ± 0.7	60.6 ± 0.6
	80/20	33.8 ± 0.3	51.5 ± 0.2	56.6 ± 0.9	55.8 ± 0.6
	70/30	29.0 ± 0.8	47.2 ± 0.6	51.1 ± 1.1	49.6 ± 0.4
700	90/10	36.9 ± 0.5	53.6 ± 0.8	59.9 ± 0.9	63.0 ± 0.9
	80/20	34.2 ± 0.3	51.1 ± 0.4	57.1 ± 1.3	57.5 ± 0.9
	70/30	29.1 ± 0.2	45.1 ± 1.0	48.8 ± 1.0	48.8 ± 0.9
750	90/10	35.7 ± 1.0	54.5 ± 1.7	60.5 ± 1.7	61.6 ± 1.0
	80/20	25.5 ± 0.7	51.6 ± 1.5	52.6 ± 1.9	52.5 ± 0.5
	70/30	3.6 ± 0.2	45.6 ± 0.7	48.5 ± 1.0	40.7 ± 0.7
850	90/10	33.6 ± 1.4	54.5 ± 1.7	58.5 ± 1.1	58.7 ± 1.1
	80/20	1.4 ± 0.7	45.0 ± 1.0	48.7 ± 0.8	48.9 ± 1.1
	70/30	1.5 ± 0.7	39.6 ± 0.8	41.6 ± 2.1	37.7 ± 1.2

TABLE 6
Binder activity indices at 28 and 90 days

Temperature of calcination (°C)	OPC/calcined red mud (%)	K(28)	K(90)
600	90/10	119	120
	80/20	115	114
	70/30	99	97
650	90/10	117	119
	80/20	111	110
	70/30	100	98
700	90/10	118	124
	80/20	112	113
	70/30	96	96
750	90/10	119	121
	80/20	103	103
	70/30	95	80
800	90/10	115	115
	80/20	96	96
	70/30	82	74
Control OPC	100/0	129	131

From Table 6, it can be said that the pozzolanic activity of calcined red mud is low. If this admixture acts as a filler, then the activity index of OPC has to be multiplied by the cement content of each binder to obtain the activity index of the blended cement. If the resulting index is higher than that calculated on the basis of a dilution effect, the admixture can be considered as pozzolanic. In the present study, K(28) and K(90) for plain OPC are essentially the same; therefore, the indices, calculated by taking into account the dilution effect, are as follows:

Blend 90/10 = 117
Blend 80/20 = 104
Blend 70/30 = 91.

Table 6 shows that indices for blended cements are higher than those assuming only a filler effect for a temperature of calcination lower than 750°C and a degree of OPC substitution under 20%.

In order to increase the reactivity of red mud calcined at 750°C and 800°C, it was first hydrated to transform CaO into $Ca(OH)_2$ and then mixed with OPC. When calcined at 800°C, red mud needed 25% of water to completely transform quick lime into slaked lime. The compressive strengths and reactivity indices of blended cements prepared with hydrated red mud calcined at 800°C are given in Table 7. Another batch of OPC was used for this study that gave slightly lower strengths.

Such treatment of calcined red mud increases its reactivity and leads to essentially the same binder indices than those observed when red mud is calcined at 700°C. In comparison with the OPC used in the study, the blended binder indices are higher than those calculated when assuming that the admixture acts as filler. For example, at 28 days, this calcination leads to:

TABLE 7
Compressive strengths and activity indices of mortars prepared with hydrated red mud calcined at 800°C

OPC/red mud (%)	Compressive strength (MPa)				K(28)	K(90)
	2 days	7 days	28 days	90 days		
100/0	38.0 ± 1.0	55.5 ± 0.9	62.3 ± 0.6	65.2 ± 0.9	123	128
90/10	38.0 ± 0.7	55.7 ± 0.4	60.5 ± 1.1	64.3 ± 0.6	119	126
80/20	35.0 ± 1.4	52.0 ± 1.1	57.2 ± 0.6	59.9 ± 1.0	112	118
70/30	30.1 ± 1.0	44.1 ± 0.4	48.6 ± 0.5	50.0 ± 0.5	96	99

Blend 90/10 = 111
Blend 80/20 = 98
Blend 70/30 = 86.
This result demonstrates a good pozzolanic activity of red mud calcined at 800°C and prehydrated with 25% of water.

Tinting Properties of Calcined Red Mud

The tinting property was studied in developing coloured concrete. The mixture proportions of this concrete were as follows:
sand (0/1 mm); 650 kg/m^3
coarse aggregate (5/15 mm); 1250 kg/m^3
white cement; 300 kg/m^3
superplasticizer; 6 kg/m^3
calcined red mud; 33 kg/m^3
The calcined red mud used in the study was that calcined at 800°C and prehydrated with 25% of water. The colour obtained when using 11% calcined red mud was the same as that obtained with 4% of Bayer 130 pigment.

Conclusion

Calcination of red mud at 700°C leads to a pozzolanic material essentially reactive at early ages. When calcined over 750°C, calcite is decarbonated and quick lime is formed, and having negative effects on the reactivity. To recover a good pozzolanic activity, calcined red mud has to be prehydrated with 25% of water. A replacement of 20% OPC by calcined red mud is thus possible. The tinting properties of this new pigment are satisfactory.

References

1. H.J. Pepplinkhouse and W.A. Davern, Acoustic tiles from solid wastes. J. Australian Ceram. Soc. 11, 42 (1975).
2. S.S. Amritphale and M. Patel, Utilization of red mud, fly ash for manufacturing bricks with pyrophyllite. Silic. Ind. 3–4, 31 (1987)

3. A. San Filippo and G. Usai, Recycling of red mud from the Bayer process. Part. 2. Production of vitrified clayware at a firing temperature of over 1000°C. Ziegelind. Int. 4, 133, (1988).
4. C. Allaire, Use of red mud for the production of aluminium reduction cell potlining refractores. Bull. Am. Ceram. Soc. 72, (1993).
5. K. Kohno, K. Amo, Y. Ogawa and Y. Ikezoe, Effect of admixture consisting of finely ground silica and red mud on properties of high strength concrete for products. Proceedings of the 4th EASEC, Seoul, Korea, I, 1437 (1993).
6. J. Péra and A.S. Momtazi, Pozzolanic activity of calcined red mud. Proceedings of the 4th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete. Istanbul, Turkey, V.M. Malhotra, (ed.) SP 132, I, 749 (1992).
7. R.S. Thakur and B.R. Sant, Utilization of red mud, Part I Analysis and utilization of raw material for absorbents, building materials, catalysts, fillers, paints and pigments. J. Scient. Ind. Res. 42, 87 (1983).