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Assessment of strength development in Bayer-process residues

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The strength which develops naturally in dried-out lumps of Bayer-process residue (red mud) is investigated for possible use in building material. The ease with which this strength can be reproduced, and its resistance to wet and dry conditions, are assessed in practical-sized building blocks. The evidence suggests that with careful preparation the binding can be exploited to make blocks suitable for the construction of single-floor buildings. The origin of this strength is also investigated by using electron micrography, X-ray diffraction and thermogravimetric analysis (TGA) of selected red mud aggregates. The strength is attributed to the presence of significant quantities of aluminous goethite in the mud. This poorly crystalline material (amorphous to X-rays) is believed to act as a binder by coating the very fine particles present in mud, imparting strength when it dries by providing a rigid bridge between particles.

1. Introduction

The processing of bauxite into alumina by the Bayer process is one of the major industrial operations on the island of Jamaica. When all four of the existing plants are in operation, a total of almost three million tonnes of alumina is extracted for export annually, leaving behind about fifteen million tonnes of slurry-like residue. This waste, which is known locally as red mud because of its characteristic reddish-brown colour and slimy consistency, is usually discharged into natural or artificially created valleys. This method of disposal, practised by the industry for the past three decades, has left behind several large red mud lakes which are, at best, unsightly features of the landscape in certain parts of the island. More significantly however, these lakes are potentially major sources of pollution for the surrounding environment. The situation is described graphically by Bell [1].

These factors have been influential in directing research efforts towards finding some application which would result in large scale use of the mud, and so at least slow down the creation of new lakes. The investigation of its potential use as a building material is one such effort. This has been given impetus by the fact that red mud blocks have the look of conventional clay bricks, while in addition the material is readily available in a form which would be convenient for use in local self-help projects. More important however is the fact that when red mud dries out on the surface of the disposal lakes, brick-sized lumps are sometimes formed. These we have found to be quite hard, (compressive strengths ~ 6.3 MPa or 900 p.s.i. in practical-sized building blocks), and stable in the presence of water.

The purpose of this study is to investigate the reproducibility of this binding and to try to understand its nature and origin in order to facilitate an assessment of the use of red mud for construction.

2. Compressive strength experiments

2.1. Methods

The initial experiments were carried out using mud collected from the surface of a pond (operation B) which is still in use. This meant that the starting material contained about 80% water. In our first attempts at block making, this mud was dried to about 40% moisture content before it was worked by hand and packed into moulds. The average dimensions of the moulds were $0.212 \times 0.106 \times 0.053$ m^3, so that the blocks were about the size of conventional clay bricks used in house building. These were dried to hardness in the sun and their compressive strengths were measured after 28 days using a Controls C901/Z Universal testing machine, employing a loading rate of 0.3 MPa s^{-1} (42.9 p.s.i. s^{-1}).

The compressive strengths of these blocks varied widely; some of this variation was quite obviously due to the extensive cracking which occurred when the blocks dried out. This was due in turn to the shrinkage which occurred during the drying process, as cracks were seen to occur more usually in areas where the shrinkage was not uniform, either because of the presence of foreign material, or because of lumps in the starting material. To reduce this, the mud was dried beforehand and crushed to uniform particle size. Measured quantities of water were added and the blocks formed were again tested for compressive strength.

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2.2. Results and discussion

An acceptable balance between workability and shrinkage was obtained with about 30% water being added to dried mud. The mud was crushed beforehand to $< 425\ \mu m$ particle size. The compressive strengths obtained in blocks were now much more consistent, but strengths comparable to that observed in naturally occurring lumps of mud (i.e. 6.3 MPa) were obtained only when the starting material was ground to a paste in a mortar before being packed into the moulds. Using this method, muds from several different locations were tested as starting material for making practical-sized blocks, and these gave the compressive strengths listed in Table I. These blocks all comply with the minimum 5 MPa specified for non-structural bricks of fired clay in, for example, British Standard BS 3921 [2].

Some measure of the weather resistance of the blocks was obtained by subjecting them to a wet–dry cycling test [3]. Over ten wetting and drying cycles, water absorption remained in the range 22–25%. There was no significant loss of mass due to flaking or slaking, and no noticeable decrease in compressive strength, although the water absorption was somewhat high. The blocks can therefore be considered to be quite acceptable for the construction of at least single-storey residences [3]. Nevertheless, there is obviously significant variation in strength between various mud aggregates. In order to understand why this is so, and ultimately to facilitate the best choice of starting material, we sought to investigate the origin of the binding in these aggregates by looking at the microstructure of the material.

3. Chemistry of strength development

3.1. Chemical content of mud

The equivalent mineral oxide content of red mud used in this project (Operation B) is typically that given in Table II. Iron, the most abundant element, is present mostly as haematite (α-Fe_2O_3), and goethite (α-FeOOH), while alumina is present mostly as gibbsite ($Al_2O_3 \cdot 3H_2O$) and boehmite (γ-AlOOH). Silica is found mostly as quartz, while the titanium minerals anatase (TiO_2) and ilmenite ($FeTiO_3$) are also present.

An X-ray diffractogram (XRD) of the dried mud (Fig. 1) confirms the presence of some of these minerals, which are well known to be present in the parent bauxite [4], but also suggests that some minerals such as bayer sodalite are formed during processing.

TABLE I Compressive strengths of practical-sized red mud blocks

Red mud origin	Compressive strength (MPa)*
Operation A (dry stacked)	6.2
(pond)	6.4
Operation B (pond, site 1)	6.5
(pond, site 2)	7.2
(pond, site 3)	7.6
(pond, site 1)†	8.3

*mean of at least three samples at each site ($\pm$ 0.7 MPa).
†mud dried in open for about two years prior to use.

TABLE II Equivalent mineral oxide composition of Operation B red mud

Oxide	Composition (%)
SiO_2	3.0
TiO_2	7.0
Al_2O_3	16.5
Fe_2O_3	49.5
CaO	5.5
Na_2O	2.3
LOI	11.6

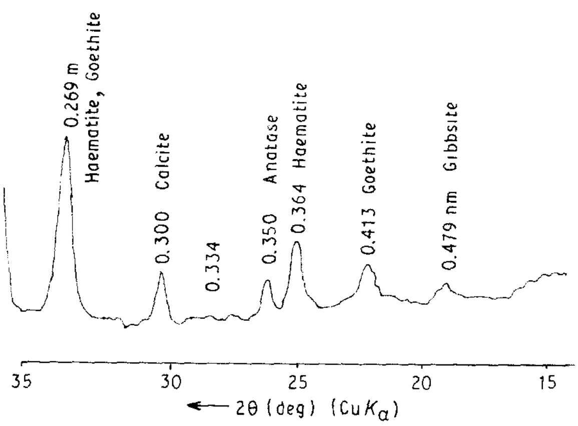

Figure 1 XRD of dried mud (Operation B).

Figure 2 SEM of red mud (Operation B).

3.2. Nature of bonding agents

The electron micrograph shown in Fig. 2 suggests that red-mud particles are held together by an amorphous coating over single or agglomerated particles. Because of the fineness of the particles in the residue, it is safe to assume that the bonding agent must be one of, or a combination of, the components present in relatively high abundance, since the surface area to be covered is large. (More than 70% of particles are less than 1 μm in size). It is therefore likely that the amorphous coating is made up of either alumina gel or amorphous iron oxide hydrate. If not, it is likely to involve some combination of both substances in an amorphous form.

A retrospective look at Fig. 1, where relatively low intensities can be seen for the 0.479 nm peak of gibbsite, and the 0.314 nm peak of boehmite, suggests that a significant amount of the 15% alumina is in an amorphous form. More direct evidence for a strength-giving amorphous alumina phase can be seen when hydrated lime ($Ca(OH)_2$) is added to the mixture. One would expect this to react with the alumina hydrate and so result in a decrease in strength of the resulting dried solid, if alumina hydrate is indeed responsible for the strength of the material. This is in fact observed to occur. Addition of hydrated lime to the red mud paste before it is put into the moulds causes a drastic reduction in strength of the resulting 50 mm cubes, as shown in Table III (50 mm cubes are used simply because they require less material to produce).

The XRD of the resulting material shows two distinct phases as the material hardens (Fig. 3a, b). The former shows crystalline structures with *d*-spacings of 0.332 and 0.742 nm; this changes with time to a second phase, where the 0.742 nm peak disappears and the 0.332 nm peak appears broadened (Fig. 3b). Also of interest is the fact that the 0.413 nm goethite peak appears to be significantly increased over that in the pure mud (Fig. 1). There is an apparent increase in the amount of crystalline goethite present, as a result of the reaction with hydrated lime. This increase can be quantified more precisely by using the method of King [5] to estimate haematite–goethite ratios (H/G) in the samples. The H/G ratio in pure mud turns out to be about 2–3, while in the mud treated with hydrated lime the ratio is nearly one. The implication of this is that iron is also involved in the binding agent, and it is 'released' as goethite, as the binder reacts with hydrated lime.

This would seem to suggest that the binder involves both aluminium and iron and is possibly some form of aluminous goethite, formed by the substitution of

TABLE III. Compressive strength of 50 mm cubes produced from red mud and hydrated lime

Hydrated lime (%)	Compressive strength (MPa)
0	4.2
5	1.3
10	1.4
15	2.2
20	2.0
30	1.9
50	2.1

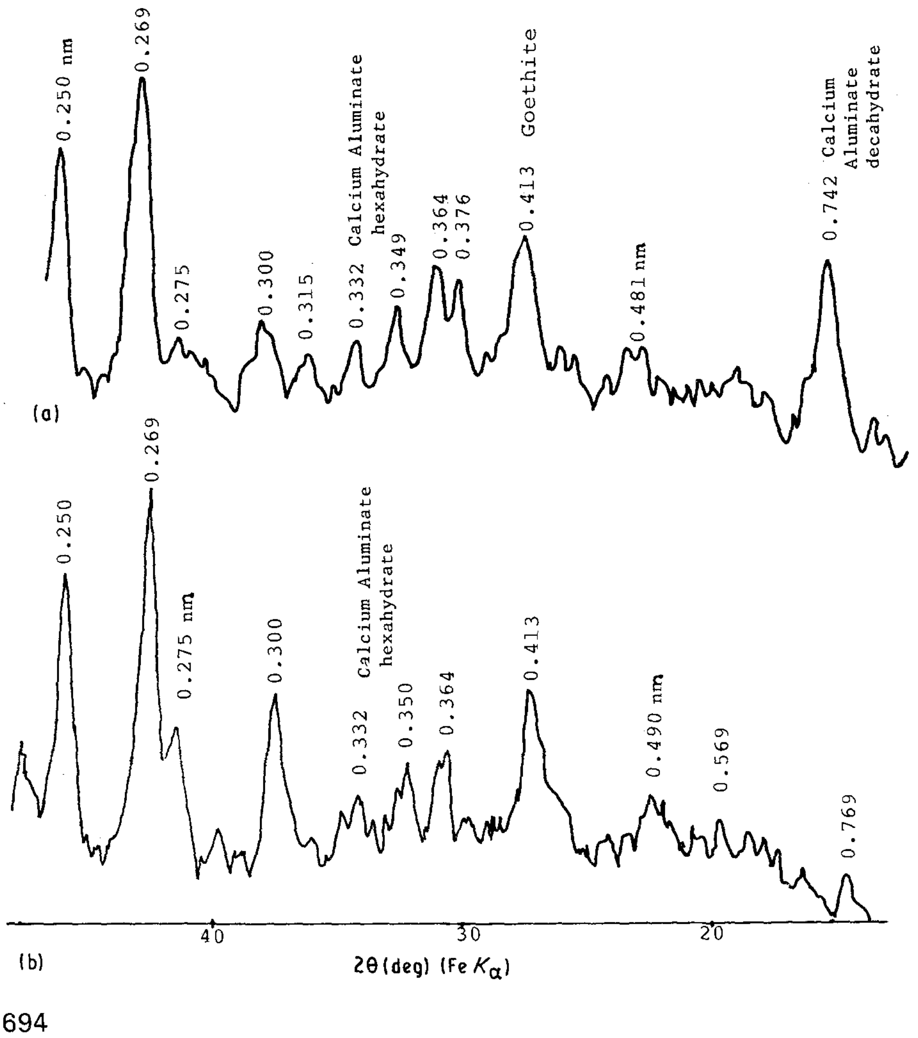

Figure 3 XRD of (a) red mud with 30% hydrated lime after curing for 28 days; (b) after being subjected to sun-drying and four wetting and drying cycles.

aluminium for iron in the goethite structure. This can be represented as $Al_xFe_{1-x}OOH$, where x is the mole fraction of aluminium to goethite, or as $AlFeO_3 \cdot H_2O$ in cases where the degree of substitution is of no concern. This would explain the increase in crystalline goethite content of the mud when the reaction with hydrated lime occurs. The following equations outline the possible reactions

$$2AlFeO_3 \cdot H_2O + 2Ca(OH)_2 + 5H_2O \rightarrow Ca_2Al_2O_5 \cdot 8H_2O + 2FeOOH \quad (1)$$

$$2AlFeO_3 \cdot H_2O + Ca(OH)_2 + 8H_2O \rightarrow CaAl_2O_4 \cdot 10H_2O + 2FeOOH \quad (2)$$

$$2AlFeO_3 \cdot H_2O \cdot 3Ca(OH)_2 + 2H_2O \rightarrow Ca_3Al_2O_6 \cdot 6H_2O + 2FeOOH \quad (3)$$

This would also explain the existence of the two phases seen in the diffractograms of Fig. 3a and b, for the calcium aluminate deca- and octa-hydrates which would be formed initially are unstable at temperatures above 30 °C, and would convert to the hexahydrate according to the following equations [6–8]

$$3CaAl_2O_4 \cdot 10H_2O \rightarrow Ca_3Al_2O_6 \cdot 6H_2O + 2Al_2O_3 \cdot 3H_2O + 18H_2O \quad (4)$$

$$3Ca_2Al_2O_5 \cdot 8H_2O \rightarrow 2Ca_3Al_2O_6 \cdot 6H_2O + 2Al_2O_3 \cdot 3H_2O + 6H_2O \quad (5)$$

The presence of aluminous goethite in process residue has been discussed by Davis [9] in connection with iron mineral transformation in Jamaican bauxites during processing. Schulze and Schwertmann [10] suggest conditions for the preparation of highly substituted aluminous goethite, which are very similar to the conditions which exist in the disposal lakes. They suggest slow oxidation of a 3:1 mixture of $FeCl_3$ and $AlCl_3$ with air, at room temperature and a pH of about 11.7. Both the ratio of iron to aluminium in mud (Table II), and the pH of the mud ($\sim$ 12) are right for the formation of substituted goethites.

The thermogravimetric and differential thermogravimetric (TGA/DTG) scans for the red mud aggregates used in our experiments also support the proposal that Al-substituted goethites are present. The very strong endotherm at 286 °C in Fig. 4a is quite consistent with the DTA patterns observed by Schulze and Schwertmann for their synthetic aluminous goethites [10]. The peaks at 320 and 346 °C are usually attributed in red mud to water loss from gibbsite and goethite, respectively [11]. This being the case, the changes which occur in the red mud aggregate on addition of hydrated lime should be discernible from TGA/DTG scans. Fig. 4a and b shows that the peak at 286 °C disappears and the main endotherm shifts to 355 °C, consistent with the proposal that aluminous goethite is converted to unsubstituted goethite.

The TGA/DTG data support the proposed chemistry in another way, allowing estimates to be made of the percentage increase in goethite by two independent methods. One relies directly on the 346 °C inflexion in the scan, while the other uses the change in aluminous goethite (deduced similarly from the 286 °C peak) in conjunction with the stoichiometries of Equations 1–3, x being taken as 0.33 in accordance with the formation conditons [10]. The agreement is remarkable: both suggest a 6% increase in goethite content following the addition of hydrated lime.

Finally, in an effort to demonstrate the binding properties of aluminous goethite, attempts were made to synthesize the substance, following the scheme given by Schulze and Schwertmann [10]. These preparations were allowed to dry out under conditions similar to those used by us in the manufacture of red mud blocks. None of the products obtained so far are either rigid enough or water-resistant enough to be considered comparable to the natural mud blocks. However our samples appear to be deliquescent and so far have all been dried at elevated temperatures. Attempts are being continued using conditions which are more closely similar to those recommended.

Measurements of compressive strengths have been made on 50 mm cubes fashioned from a variety of muds, and these are compared in Table IV to the content of aluminous goethite, determined on the

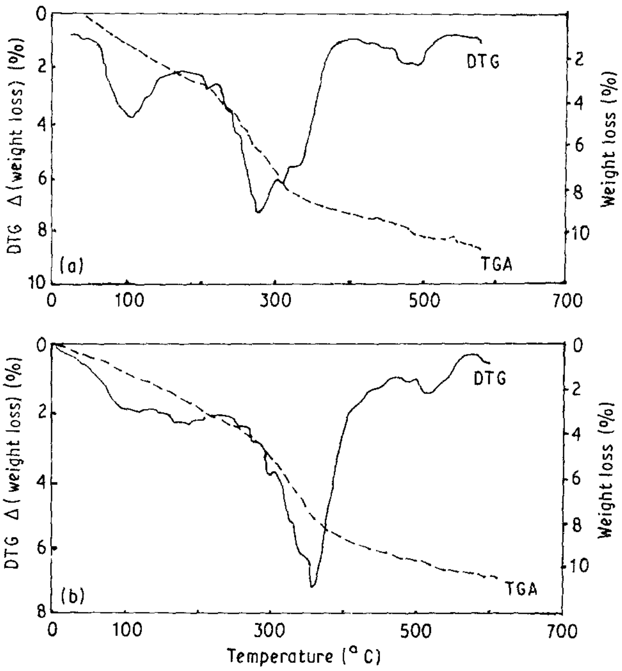

Figure 4 DTG/TGA scans of (a) red mud with 30% hydrated lime after curing for 28 days; (b) after being subjected to sun-drying and four wetting and drying cycles.

TABLE IV Compressive strengths of 50 mm cubes and estimated aluminous goethite content

Sample code	Aluminous goethite (%)	Compressive strength (MPa)
2	4.0	1.9
C2	4.5	2.2
17	6.5	3.2
5	9.9	4.0
36	11.7	3.7
C6	12.2	3.9
B4	15.2	7.4
B6	21.2	7.8

basis of the TGA/DTG endotherm at 286 °C. Although the percentages obtained in this way are only approximate, it seems quite clear that there is a relationship between the strength and content of aluminous goethite as shown in Table IV.

4. Conclusions

The strength of 'red mud only' blocks is adequate for the construction of single-storey buildings. Adequate strength can be obtained reproducibly by a careful procedure which requires crushing, sieving to a uniform, fine particle size (< 0.5 mm), and grinding to a paste with water, before the mixture is packed into moulds.

The strength achieved is probably due to the presence of amorphous aluminous goethites in the mud, coating the particles and bonding them together by itself becoming rigid when it dries out. The resulting material is stable in water and shows good weathering properties over several wetting and drying cycles. The strength of the residue is approximately proportional to the aluminous goethite content of the material (at least up to 21 wt %) as determined by the TGA/DTG endotherm at 286 °C.

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