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A Preliminary Investigation of Strength Development in Jamaican Red Mud Composites

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Abstract

The 28-day strength of 50 mm cubes of composites formed by the addition of various amounts of hydrated lime, condensed silica fume and limestone to Jamaican red mud is investigated. The aim is to produce a red mud composite suitable for use as a construction material, without employing Portland cement as binder. The identities of compounds formed in the composites are deduced from XRD scans, in combination with DTG and electron micrography where appropriate. The strongest composite found in this preliminary study has compressive strength in the range 15–18 MPa at 28 days, with the strength increasing slowly with age to a maximum so far, in the range 18–22 MPa at 122 days. The strength development is observed to be associated with the formation of stratlingite, and possibly also with the formation of complex carbonates such as hydrogrossular. This composite compares favorably, in terms of compressive strength and durability, with the one other composite reported in the literature, which is formed similarly from red mud with additives, not including Portland cement. © 1997 Elsevier Science Limited

INTRODUCTION

The possibility that Bayer-process waste, red mud, could be used to advantage as a component of construction material has been suggested as one way of utilizing the enormous quantities of this waste that are generated each year by the alumina and alumina-related industries in Jamaica.[1] Added impetus has been provided for further investigation of this possibility by the recent apparent shortage of some construction materials such as sand, the relatively high cost of Portland cement, and the chronic island-wide shortage of housing.[2]

In order to encourage large-scale use of existing stocks of red mud in the short term, the building material required, in our view, is one that must be less expensive than concrete. It must also be adequately strong and have weather-resistant characteristics at least comparable to that of conventional concrete. Ideally, also the process of fabrication should be simple enough that the desired strength and durability can be achieved in self-help-type operations.

With these constraints in mind, several possibilities seem to us to be worth considering. These range from the use of red mud simply as a replacement for sand in Portland cement mortars to its use in materials in which there is no Portland cement and binding is derived from compounds formed by the reaction of components of the mud with selected additives. In this preliminary work we have sought to investigate the latter possibility because of the potential it offers for the development of low cost materials and high red mud utilization.

CHEMICAL BASIS FOR ADMIXTURES USED

The most common use of industrial waste in the fabrication of construction materials appears to

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be that of slags and fly-ash in mortars in which they are 'activated' by various means to react with added or free lime to produce cementitious compounds.[3–6] Slags and fly-ashes, which are used this way usually contain siliceous material in a reactive form, so that they react with lime at ambient temperature to produce calcium silicates, which eventually hydrate to produce calcium silicate hydrates which are the compounds responsible for binding in Portland cement concrete. The reaction of the siliceous material with lime, known as the pozzolanic reaction, may be represented as follows:

$$3Ca(OH)_2+2SiO_2 \rightarrow Ca_3Si_2O_7 \cdot 3H_2O$$

The optimum molar ratio between lime and silica is said to be nearer to 2:1 in practice, rather than 3:2 as suggested above, affirming the well-known fact that the real reaction is somewhat more complicated than the equation suggests.[7] Jamaican red mud is not comparable to any of these wastes in terms of its silica content, as the typical mineral oxide composition of mud (in Table 1) indicates. That from operation A (one location where bauxite processing occurs) represents mud derived from the processing of a typically boehmitic bauxite, while that from operation B (another location where processing occurs) represents mud from a more gibbsitic bauxite. Iron is known to be present in red mud mostly as haematite and goethite, while alumina is present mostly as gibbsite and boehmite. The silica present in mud is believed to exist mainly as quartz or bayer sodalite, while the titanium exists as the minerals anatase and ilmenite.[8] Jamaican red mud is fairly caustic, with the pH of pastes being typically in the range 11–13. Except for the residual NaOH left after the final washing in the plant, the components of red mud are usually considered to be relatively inert and unreactive.

Table 1. Equivalent mineral oxide content of two typical Jamaican red muds

Mineral oxide	*% Composition*	
	Operation A	*Operation B*
SiO_2	8.0	3.0
TiO_2	6.0	7.0
Al_2O_3	16.4	16.5
Fe_2O_3	42.3	49.5
CaO	9.1	5.5
Na_2O	4.6	2.3
LOI[†]	10.2	11.6

[†] Loss on ignition.

Despite its apparent inertness and obvious lack of reactive silica, the idea of utilizing the pozzolanic reaction to bind red mud mixtures seemed to be a feasible and potentially low cost alternative for the very simple reason that the mud is highly caustic and the reaction is favored in a high pH environment. The admixtures required would be hydrated lime, with either fly ash, bagasse ash, or silica fume; and all of these are readily available, or can be produced or imported at relatively low cost.

A further possibility for the production of cementitious compounds, is that revealed by our previous work,[9] which suggests that hydrated lime will react with the alumina left in red mud to produce calcium aluminates (CA and possibly C_5A_3). These also hydrate to produce cementitious compounds, in reactions which are fairly well known from the fact that they are responsible for the strengths of high alumina cement mortars.[5] The reaction of lime with alumina is considered to be a type of pozzolanic reaction as well.

In this preliminary investigation the strengths imparted to red mud mortars by admixtures of hydrated lime and condensed silica fume are examined. Limestone is employed as a catalyst in the later experiments. The aim is to produce cementitious compounds through either type of pozzolanic reaction, while incorporating as much mud as possible in the mixtures.

EXPERIMENTAL MATERIALS AND METHODS

The hydrated lime used in these experiments was that available commercially and sold locally as 'white lime'. The condensed silica fume used was that which is sold commercially by a Florida based company. This is itself a waste product from the ferrosilicon industry, and so is a relatively inexpensive imported item. It is used here because it is known to be highly reactive in the finely divided state in which it is available, that is, as a paste with $\approx 53\%$ water. The mud used here was that obtained from operation B. This was dried beforehand, crushed and sieved to particle sizes less than 250 μm. The limestone used initially was similarly crushed and sieved to particle sizes less than 250 μm. Tables 2 and 3

Table 2. Equivalent mineral oxide composition of materials used

Mineral oxide	*% Red mud**	*% Limestone*	*% Silica fume*
SiO_2	3.9	2.4	97
Al_2O_3	16.4	0.2	1.5
Fe_2O_3	48.5	0.4	—
Na_2O	1.7	0.2	—
K_2o	—	0.1	—
CaO	6.2	52.1	0.1
MgO	—	1.0	—
TiO_2	6.7	—	—
LOI	13.1	42.3	1.0

*Composition of mud actually used.

summarize some relevant properties of these components.

The optimum mass ratio of hydrated lime to silica fume, for the formation of calcium silicates, was determined from semi-quantitative examination of the XRD of the products formed from various mixtures of hydrated lime and silica fume, for excess hydrated lime. The ratio was found to be nearly 2:1 by mass, and so this ratio was maintained between the two, throughout our investigations, except in those cases where it was desired deliberately to have hydrated lime in excess. The water:solids ratio was kept near to 0·4 in all cases, because of our finding that this represented a good balance between workability of the mixture and shrinkage of the product during curing.

The materials were used in various combinations, to form 50 mm cubes by blending the ingredients together with a hand-held electrical blender, and then packing the mixture into the moulds, following the procedure recommended in ASTM Standard C109-93.[10] The cubes were demoulded after 24 h and were allowed to cure in a humid environment for 28 days. Compressive strengths were performed on three specimen cubes of each composite at 28±2 days, and the strength is taken as the mean of these three results. Strength testing was done on a Controls C901/Z Universal Testing Machine, using a loading rate of 0·3 MPa s^{-1}. Some measure of the weather resistance of the stronger composites was assessed by determining the weight loss and water absorption which resulted from wet/dry cycling. This was done simply by soaking the cubes in water at ambient temperature, then drying them at 110°C over alternate 24 h periods and determining the mass of the cube after each step. XRD, scanning electron micrography, and thermal gravimetry (TGA/DTG) were employed where they were thought to be appropriate, to give information on the phases present.

RESULTS AND DISCUSSION

Table 4 gives the data obtained for the 28-day compressive strengths of cubes formed in the first set of experiments, which involved the addition of (a) hydrated lime to red mud and (b) condensed silica fume to red mud. The strengths obtained can be seen to be lower than those obtained for cubes made from red-mud-only pastes. With the mud used in this experiment, the strength of red-mud-only cubes was 4·2±0·5 MPa. In the case of the addition of hydrated lime, the decrease in strength is likely to be due to the reaction of lime with alumina gel, as is discussed in our previous paper.[9] This removes the incipient binder and replaces it with calcium aluminate hydrates, which undergo conversion at ambient temperature leading to the reduction in strength observed. With condensed silica fume as the only admixture, there appears to be no significant change in the chemistry of the mixture as the XRD scans remain nearly identical to that obtained from mud-only cube samples.

In our next series of experiments, hydrated lime and condensed silica fume were added together to red mud in the various proportions shown in Table 5, to investigate the possibility that these would combine in the high-pH red mud matrix to form calcium silicate hydrates. The 28-day compressive strengths obtained are again seen to be less than the strength obtained

Table 3. Particle size distribution of some materials used[†]

Material	*Percent retained on sieve*				
	250 μm	*150 μm*	*90 μm*	*75 μm*	*45 μm*
Limestone	0	68.8	77.5	80.4	93.4
Red mud	0	63.5	73.0	77.0	81.4

[†] Silica fume is used in the form supplied, that is, as a paste.

Table 4. Compressive strengths of composites of: (a) red mud and hydrated lime; and (b) red mud and condensed silica fume

% Red mud	*% Hydrated lime*	*% Silica fume*	*Compressive strength*[†] *(MPa)*
100	—	—	4.2
(a)			
95	5	—	1.3
90	10	—	1.4
85	15	—	2.2
80	20	—	2.0
70	30	—	1.9
50	50	—	2.1
(b)			
99	—	1	2.0
95	—	5	3.2
89	—	11	1.7
85	—	15	2.3
80	—	20	2.8

[†]Mean of three (±0·5 MPa).

for red-mud-only cubes in most cases. X-ray diffractograms for (a) red mud with no admixtures, (b) red mud mixed with hydrated lime and (c) red mud mixed with hydrated lime and condensed silica fume, shown in Fig. 1, suggest that the hydrated lime has again reacted with alumina gel to produce calcium aluminate hydrates. Some of these show up as compounds with *d*-spacings of around 0·332 nm in both (b) and (c), but also with a *d*-spacing of around 0·740 nm in (b). The desired reaction between the condensed silica fume and hydrated lime is not occurring, partly, it seems, because the hydrated lime–alumina reaction is occurring more readily and is using up the available hydrated lime.

In an effort to reduce this occurrence our next series of experiments was done with red mud which was treated beforehand with hydrated lime, by making it into a paste with water and 30% hydrated lime. This mixture was kept in a moist state for 14 days before it was allowed to dry out under lab conditions. This pre-treated mud was then blended with lime and silica fume in the proportions used in the earlier series and made into cubes as before. The compressive strengths obtained after 28 days moist curing are shown in Table 6.

Table 5. Compressive strengths of composites made from mixtures of red mud, hydrated lime and condensed silica fume

% Red mud	*% Hydrated lime*	*% Silica fume*	*Compressive strength*[†] *(MPa)*
100	—	—	4.2
85	10	5	2.9
82	12	6	4.9
70	20	10	2.4
55	30	15	3.2

[†]Mean of three (±0·5 MPa).

These show that the pre-treatment does make a difference, with the strength of the composites increasing with increasing proportions of lime/silica in the composite. The diffractogram for the strongest of these composites is shown in Fig. 2. where it is compared to that obtained when hydrated lime and silica are added, with no pre-treatment. This comparison shows up the presence of new reflections at 0·419, 0·438 and 0·469 nm that were not present in the previous case, and there are also new reflections at 0·376 and 0·384 nm. The absence of significant calcium hydroxide reflections at 0·262 and at 0·485 nm suggests that all of the added lime has reacted. Reflections near 0·740 nm indicate that some calcium aluminate decahydrate (CAH_{10}) has been formed and is still unconverted even after 28 days.

Even though it is difficult to interpret the new reflections unambiguously in terms of new compounds formed, it is quite clear that reactions are occurring, which use up the added hydrated lime. The compressive strength tests show that significant improvement in the strength of red mud composites is achieved by the addition of relatively large quantities of hydrated lime, and suggests that some reaction

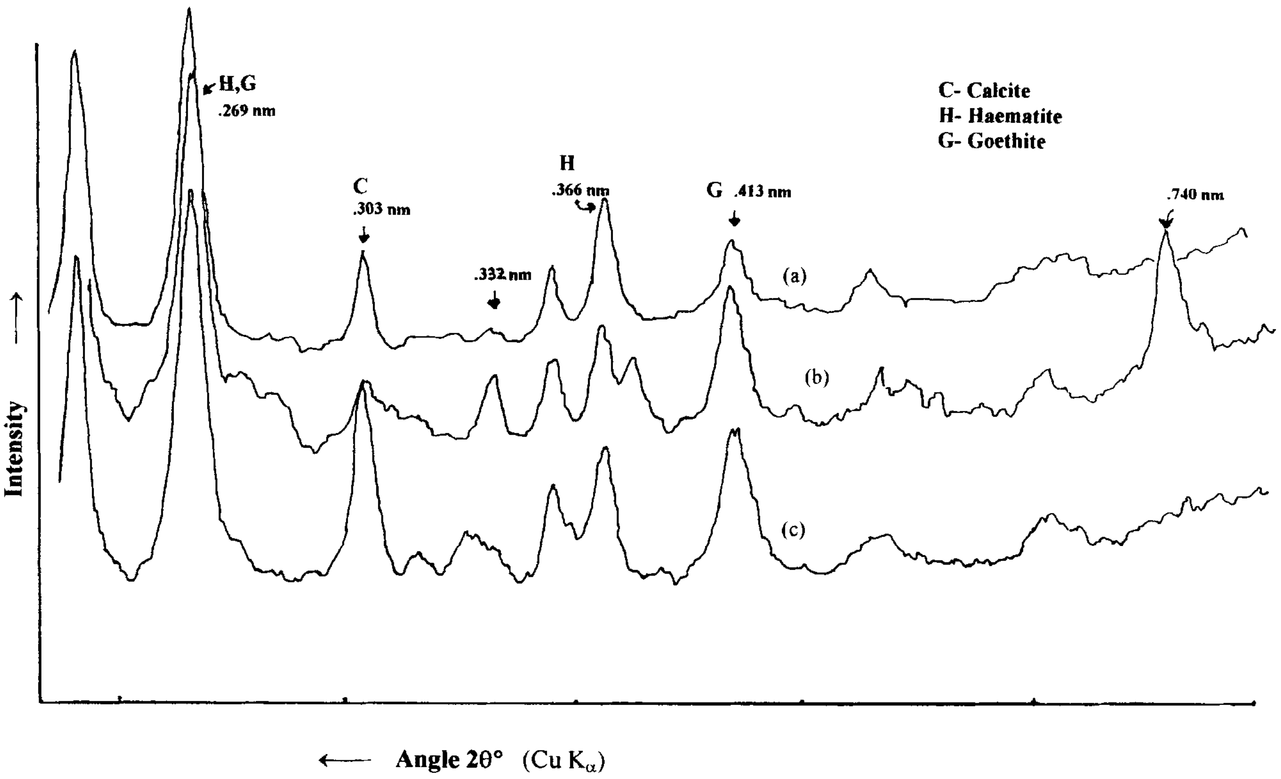

Fig. 1.

between hydrated lime and condensed silica fume is now taking place. Unfortunately this result is not particularly useful for the application we have in mind, because even though hydrated lime is a relatively inexpensive additive under normal circumstances, the cost is not trivial when it constitutes as much as 30% of the composite.

The possibility that limestone could be used to advantage as an admixture to the composite formed by red mud, hydrated lime, and condensed silica fume, was next investigated on the basis of the finding of Alexander[11] that calcium carbonate has a catalytic effect on the lime–silica reaction. This also turns out to be quite an attractive proposition from the economic point of view, because limestone deposits can be found in abundance in close proximity to most Jamaican red mud storage lakes. Table 7 gives the compressive strengths of cubes made from mixtures containing red mud, hydrated lime, condensed silica fume and limestone.

Table 6. Compressive strengths of composites made with red mud pre-treated with hydrated lime, then mixed with condensed silica fume and hydrated lime as indicated

% Red mud	*% Hydrated lime*	*% Silica fume*	*Compressive strengths*† *(MPa)*
85	10	5	4.2
79	14	7	4.9
70	20	10	6.0
55	30	15	7.2

†Mean of three (±0·5 MPa).

Significant increases in strengths can be seen in Table 7, and the strengths are generally better than those obtained even by pre-treating the mud with hydrated lime. The composite showing the highest compressive strength at 28 days turns out to be one containing equal quantities of red mud and limestone, blended with a 2:1 mix of hydrated lime and condensed silica fume. Comparisons of the strengths of composites #6 and #7 with that of composite #4, in Table 7, suggest that the red mud does play some role in the binding achieved in the composite with the highest strength.

XRD analysis of a sample of the composite with the highest strength is shown in Fig. 3, and again reflections are seen in the region between 0·419 and 0·483 nm, as in the case of the pre-treated mud composite. Again, it is true that there are so many possibilities and so many overlapping reflections in this region that precise and unambiguous interpretation is difficult. Majumdar *et al.*[5] have inferred the presence of

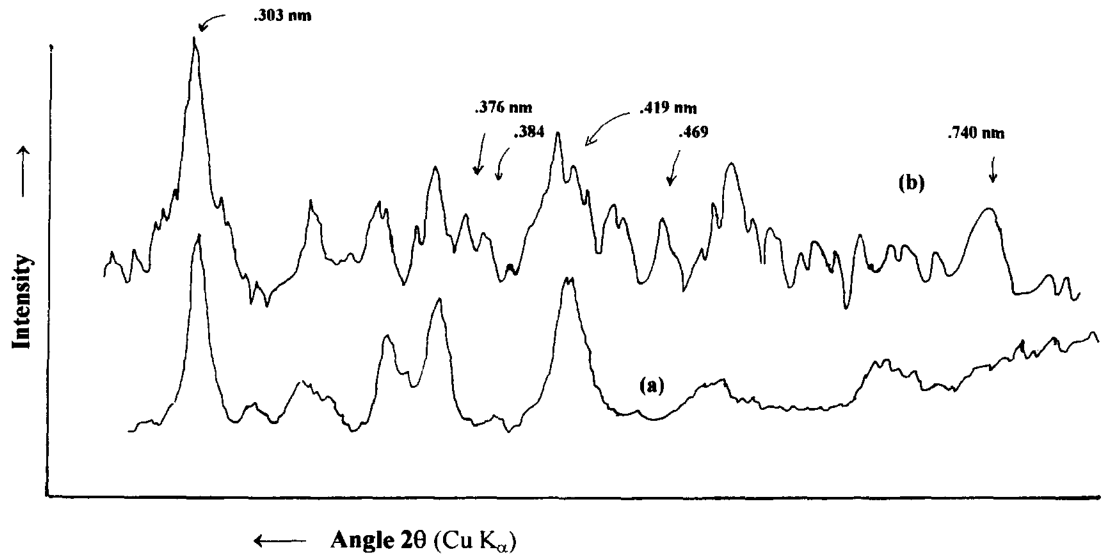

Fig. 2.

Table 7. Compressive strengths of composites made of red mud, hydrated lime, condensed silica fume and limestone

Composite number	*% Red mud*	*% Hydrated lime*	*% Silica fume*	*% Limestone*	*Compressive strength*[†] *(MPa)*
1	20	7	3.5	69.5	12.6
2	45	7	3.5	44.5	13.1
3	20	14	7	59	14.6
4	39.5	14	7	39.5	16.7
5	79	14	7	—	4.9
6	—	14	7	79	13.0
7	—	17	8.5	74.5	14.3
8	32	21.5	6.5	40	13.9
9	21.5	21.5	6.5	50.5	11.2
10	53.5	21.5	6.5	18.5	6.0
11	23.5	47	14	15.5	7.2
12	12	61	18	9	10.2

[†] Mean of three (±0·5 MPa).

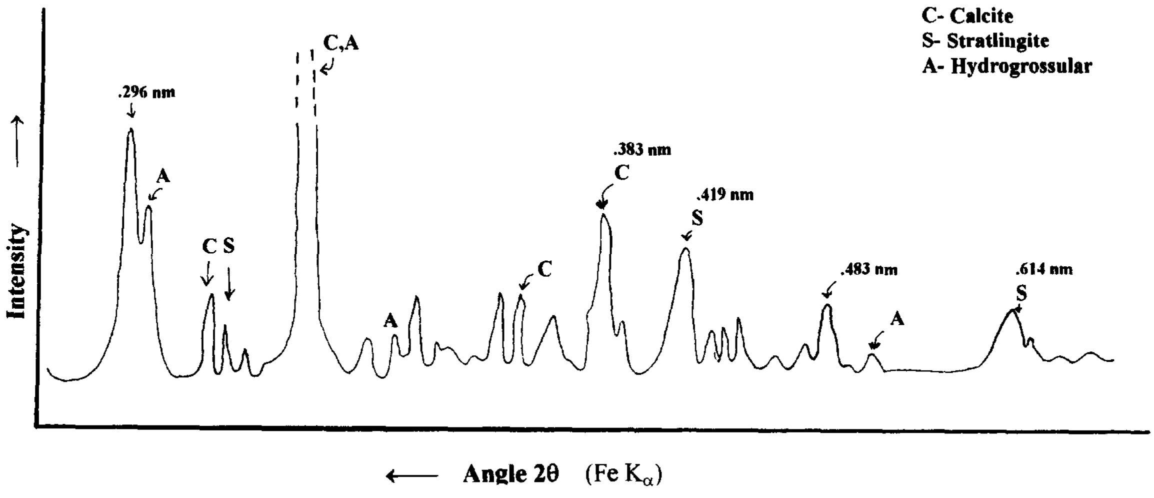

Fig. 3.

stratlingite (C_2ASH_8) as the predominant stable end product associated with strength development in fairly similar mixtures as we have here. It is observed by these workers that stratlingite is formed very slowly, so that its presence is detectable by XRD only after about 28 days. The presence of small amounts of stratlingite in our composite would account for the low intensity reflections observed around 0·627, 0·419 and 0·286 nm in the XRD scan, and suggest that similar strength-giving compounds are being formed in our composite. Though the role of the limestone is intended to be catalytic, it seems likely that the carbonate ion does take some part in the reactions occurring in this composite. XRD reflections at 0·500, 0·325, 0·303 (masked by calcite), and at 0·271 nm suggest the formation of some hydrogrossular (Ca_3Al_2 (SiO_4,CO_3,$OH)_3$), and so suggest that the involvement of the limestone/carbonate ion is more than simply catalytic.

A DTG scan of a sample of composite #4, shown in Fig. 4, shows a weak endotherm between 186 and 200°C, where stratlingite is known to dehydrate/dehydroxylate partially[12] and so is quite consistent with the proposal that stratlingite is present. The microstructure of the material, shown in Fig. 5(b), indicates the presence of thin needle-like crystals, which appear to be interwoven in a mat-like formation in some areas, while some less abundant platy crystals, similar to those identified as stratlingite by Majumdar and Singh,[13] also appear to be present. The microstructure of the composite is clearly very different from that of dried mud, shown for comparison in Fig. 5(a), where the structure can be seen to be almost totally amorphous.

Water absorption tests carried out on the material of composite #4 gave percentage water absorption in the range 22–29% over 10 wetting and drying cycles, with mass loss being about 2% overall after 10 cycles. The density of the composite is $2{\cdot}0 \pm 0{\cdot}1$ kg m^{-3}. The 28-day strength was found to be reproducible within the range 15–18 MPa with limestones from different sources, all crushed to have grain size distributions similar to that given in Tables 2 and 3. Long-term studies of the strength of this composite show a much slower increase in the strength in the period beyond 28 days. This study has lasted so far, only up to 122 days, as shown in Fig. 6, where each data point represents the mean of four or five strength tests. This finding of slow increase in the long-term strength is again quite consistent with the proposal that the strength is associated with the formation of stratlingite, as its formation has been fairly well-documented to continue relatively slowly even up to and beyond five years, in blends of blast furnace slag with high alumina cements.[13]

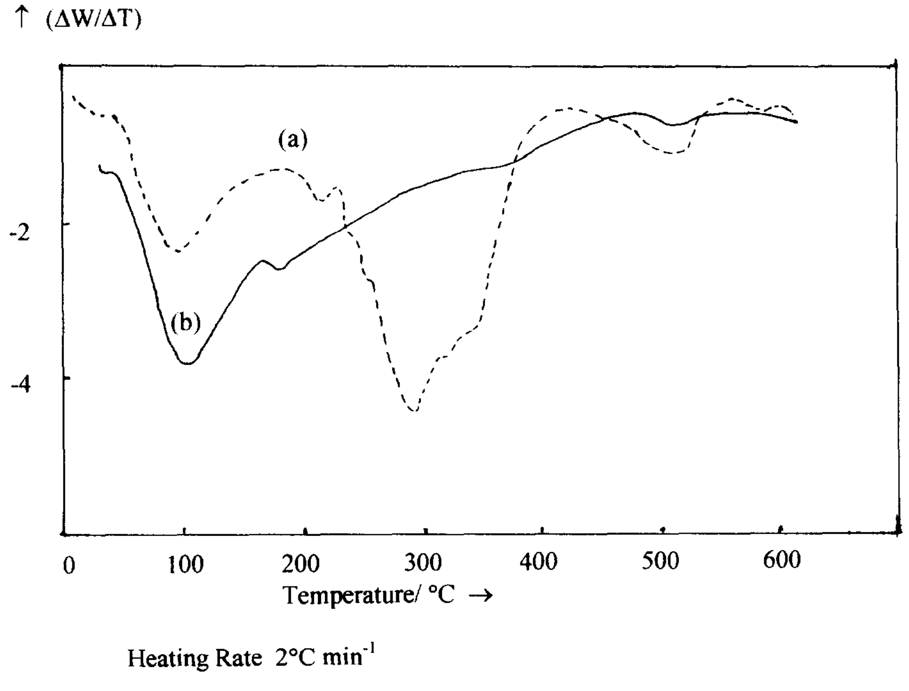

Fig. 4.

This composite compares favorably with the one other red mud composite, containing no Portland cement, which we have found reported in the literature. Ikeda[14] has reported compressive strengths as high as 20 MPa (after 91 days) in composites containing gypsum and Portlandite added to Australian red mud. He found however, that the surfaces of his cubes were not hard, and that the strength decreased as they advanced in age beyond 91 days. The strength of our composite is still increasing even after 122 days, and it seems likely that the strength will continue to increase as the composite increases in age.

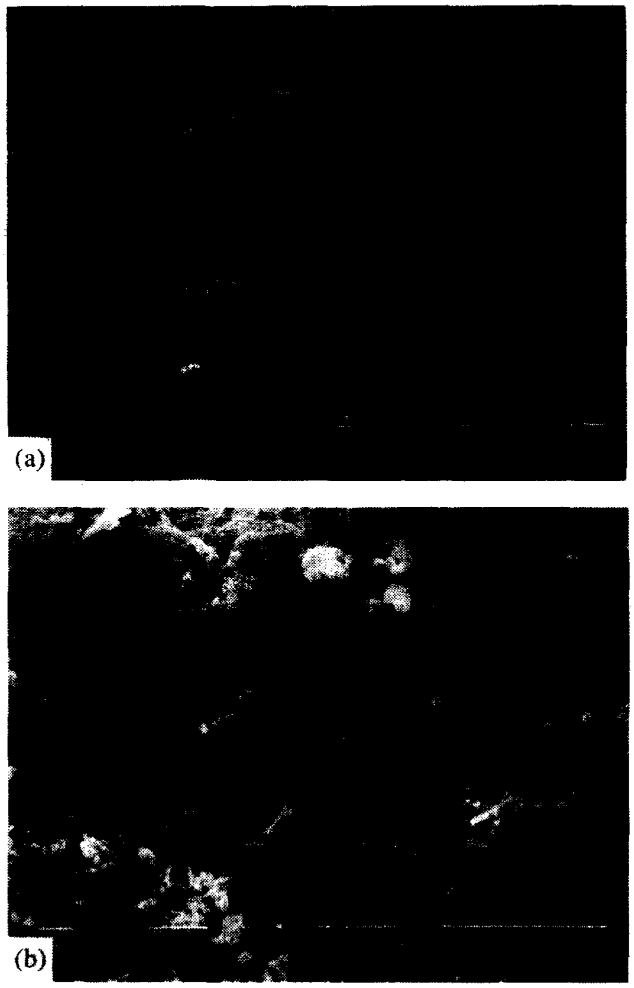

Fig. 5.

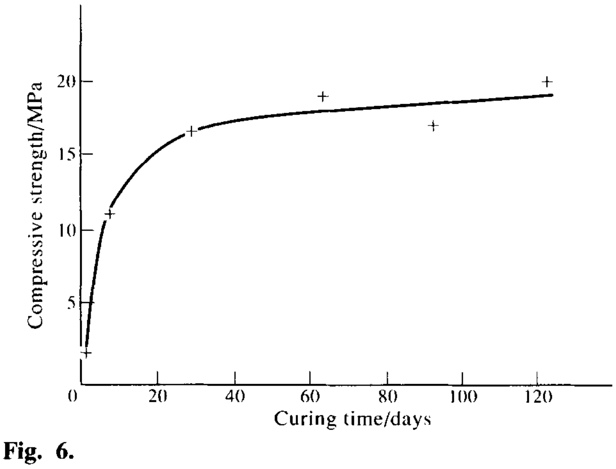

Fig. 6.

CONCLUSION

It appears from these results that it is indeed possible to fabricate, from red mud, materials which have both the strength and durability that are likely to make them useful in the construction industry. Strengths in the range 18–22 MPa are attainable (at 122 days) with relatively inexpensive and readily obtainable additives, which do not include Portland cement. These strengths are not yet comparable to the compressive strengths obtained with Portland cement mortars, which we have found to have strengths in excess of 50 MPa at 28 days, in 50 mm cubes cured under the same conditions. However, it is likely that with better understanding of the strength-giving processes operating in these composites, the mix of components can be optimised to produce higher strengths.

The indication from XRD is that the strength is associated with the formation of stratlingite (C_2ASH_8) in a way that is similar to that observed in high alumina cements blended with blast furnace slags. The XRD data suggest that the formation of complex carbonates might also contribute to the strength of these composites.

The possibility that strengths can be improved by using mixes of components closer to those found in high-alumina cement/slag blends will be investigated in future work. The possibility that a local pozzolanic material, such as bagasse ash, may be used in place of condensed silica fume is also to be investigated.

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