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Use of Red Mud as Addition for Portland Cement Mortars

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Abstract: The aim of the present research work was to investigate the possibility of adding red mud, an alkaline leaching waste that is obtained from bauxite during the Bayer process for alumina production, in the raw meal of Portland cement mortars. The red mud is classified as dangerous, according to NBR 10004/2004, and world while generation reached over 117 million tons/year. This huge production requires high consuming products to be used as incorporation matrix and we studied the influence of red mud addition on the characteristics of cement mortars and concrete. In this paper the properties of Portland cement mortars incorporating high amounts of red mud was evaluated: pH variation, fresh (setting time, workability or normal consistency and water retention), and hardened state (mechanical strength, capillary water absorption, density and apparent porosity). Results seem promising for red mud additions up to 20 wt%.

Key words: Cement mortars, properties, red mud, reuse.

1. Introduction

Nowadays, the search for recycling alternatives of several industrial wastes or by-products is a common practice, conducted under legislation pressure but also attempting to eliminate cost of disposal and to avoid soil and water contamination. Many of these undesirable industrial rejects contain significant amounts of inorganic ingredients, such as silicon, aluminium, calcium and iron oxides [1].

The red mud is the main waste generated in aluminium and alumina production by the Bayer process from bauxite ore. Bauxite mines are located in three main climate regions: the Mediterranean, Tropical and Subtropical [2]. World production of bauxite in 2008 was 205 million tons, and the main producing countries were Australia, China, Brazil, Guinea, India and Jamaica. Occupying the 3rd position in the world ranking in 2008, Brazil produced 26.6 million tons of bauxite. It also has the world's third largest bauxite ore reserves (around 3.5 billion tons), mainly concentrated in the north of the country (Pará state) [3].

Red mud is an alkaline waste generated during ore leaching conducted to remove soluble impurities. It is generally classified as "hazardous" (class I), according to the Brazilian NBR 10004 standard. Roughly 0.3-1.0 tons of red mud waste is generated for each ton of aluminium produced. About 10.6 million tons of caustic red mud must be disposed annually during recent years in Brazil and world while generation reaches over 117 million tons/year [4, 5]. It is generally discharged as highly alkaline slurry (pH 10-13.5) with 15-40% solids, which is pumped away for appropriate disposal. Its chemical and mineralogical composition may temporarily change, depending on the source of bauxite and on the technological processing conditions. It is composed by six major oxides namely Al_2O_3, Fe_2O_3, Na_2O, SiO_2, CaO, and TiO_2, and a large variety of minor elements. Its strong alkaline character (Na_2O + NaOH = 2.0 – 20.0 wt %), restricts the disposal

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conditions in order to minimize environmental problems such as soil contamination and groundwater pollution.

Snars and Gilkes [6] verified that red mud is different although sets produced at different refineries from bauxite collected in the same deposit are quite similar. The origin of the bauxite, conditions used in the Bayer process and any further treatment of the residue influence the mineralogy and chemistry of the red mud.

The search for economically and environmentally viable recycling alternatives include applications of red mud as adsorbent for removal of cadmium, zinc and arsenic, fluoride, lead and chromium from aqueous solutions [7], as component of building materials namely bricks [8], ceramics and tiles [9], glazes [10], as polymer-based composites to substitute wood [11], iron rich cement [1, 12], etc. The use in common construction materials has been suggested as one way that assures high consumption rates [13].

In order to encourage large-scale use of existing red mud stocks in the short term, the building material required, in our view, is one that must be less expensive than conventional materials. It must also be adequately strong and have weather-resistant characteristics at least comparable to that of conventional mortar and concrete.

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. 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 favoured in a high pH environment [13].

The objective of this paper is to study the effectiveness of preparing red mud containing Portland cement mortars. In addition to pH changes on the fresh paste, relevant mortar properties had been evaluated.

2. Experiment

2.1 Materials

The mortar was produced with a Brazilian Portland cement (CPII Z-32, according to the Brazilian NBR 11578 standard), which is equivalent to ASTM C 596 (Pozzolan-modified Portland cement). This cement has pozzolan addition and is one of the most widely used cements in the state of São Paulo, Brazil. The coarse aggregate was dense, crushed granitic stone and the fine aggregate was natural siliceous sand, available in São Carlos, SP, Brazil.

Red mud from Bayer process was sampled from red mud stork-yard of an alumina plant in Poços de Caldas - MG, Brazil. It is a mixture containing about 60% of solids. Chemical and mineral compositions of red mud samples were analyzed.

The materials characterization involved X-ray diffraction (Rigaku Geirgeflex ME 210GF2 Diffractometer) and X-ray fluorescence (Philips PW1480 X-ray Fluorescence Spectrometer) analyses, while physical parameters such as the specific surface area (estimated by BET, using a Micrometrics Gemini 2370 V1.02 equipment) and specific gravity (Helium Pycnometer Accupyc 1330 V2.01 from Micrometrics) were also determined.

2.2 Methods

The mix proportion of the concrete was 1.0 (Portland cement): 3.0 (fine aggregate) and the water/cement ratio was 0.6. The cement consumption was 470 kg/m^3. After mixing, a vibrating table was used to ensure efficient compaction. Mortars containing distinct additions of red mud (10, 20, and 30% in weight) were prepared and analysed.

2.2.1 Mortar Fresh State Properties

The normal consistency (workability), water retention and setting times of cement mortars were determined using a Vicat apparatus according to the European Standard EN 196-3 (Methods of testing cement – determination of setting time and soundness, 1994).

The pH was evaluated by using a pen type pH Meter

NA 2000, Microprocessado.

2.2.2 Mortar Hardened State Characterization

Cylindrical specimens of 100 mm in length and 50 mm in diameter were used to determine the capillary water absorption (sorptivity), mechanical strength, apparent porosity and density. To determine the apparent porosity and density, 40 mm thick slices were cut from the centre of each specimen, in order to minimize heterogeneities and to assure water saturation.

The hardened mortar test pieces were stripped after 24 h and stored at 100% relative humidity and 23 °C (curing storage conditions). At these conditions the pores are continuously water-filled and the cement hydration can take place unhindered. A minimum of five samples per composition was used. Values over 5% deviations from the average were excluded and new samples were tested instead.

The apparent porosity and density was verified using the technique based on the Archimedes principle. The samples were weighed in the dried condition (M_s). They were then left immersed in water for 24 hours until they became fully saturated, after which the immersed mass (M_i) and the wet mass (M_u) were determined. Thus, the apparent porosity (P_A) and the apparent density (D_A) were calculated according to Eqs. (1) and (2), respectively.

$$P_A(\%) = 100.\rho_L.\frac{(M_u - M_s)}{(M_u - M_i)} \quad (1)$$

$$D_A(g/cm^3) = \rho_L.\frac{M_s}{(M_u - M_i)} \quad (2)$$

Where ρ_L is the liquid density (in this in case, water, ρ_L = 1.0 g/cm^3 at 25 °C).

The determination of capillary water absorption (sorptivity) of the mortar is very important. Excessive absorption can induce proliferation of fungi and bacteria and, in extreme conditions, it might generate mortar detachments or painting stripping. Also, the capillary pressure determines the mechanical behaviour of cementitious materials and thus the change of the microstructure [14]. The sorption behaviour of a porous material is given by the pore structure and by the interaction between matrix and water.

This test was conducted in accordance to standard DIN 52617/87. Cylindrical specimens of 200 mm in length and 100 mm in diameter were used. The lateral side of the specimens was sealed with silicon up to 3 cm in height, so that only one circular face of the specimen was exposed to water. The water level during the test was kept constant and 5 mm above the surface of the specimen in contact with water.

The weight of the specimen was monitored in a period of time throughout the contact with water. Sorptivity, S (kg/m^2.min$^{0.5}$), corresponds to the volume of water penetrating per unit of area and time, and is obtained empirically from the slope of the cumulative volume of water absorbed per unit of area of inflow surface versus square root of time, as represented in Eq. (3).

$$\frac{V_w}{A_c} = S.\sqrt{t} + S_o \quad (3)$$

Where V_w is the mass (or volume) of water absorbed (Kg), A_c is the cross-sectional area of each specimen (m^2) and t is the time of exposure (min).

The axial compressive strength of samples was measured by using an Instron 5500R universal testing machine under a load of 1.5 mm/min, following the Brazilian NBR 7222 standard.

3. Results and Discussion

3.1 Materials Characterisation

The used Portland cement has a specific surface area of 0.93 m^2/g and its specific gravity is 3.11 kg/dm^3. The sand has a specific surface area of 0.68 m^2/g and its specific gravity is 2.70 kg/dm^3. According to Brazilian NBR 7211 standard, it is classified as fine sand.

The red mud was received as a paste, containing about 40% free water. In the present study, the material was dried and crushed, and then used as a powdered additive. Ideally, if proved its potential as concrete constituent, red mud incorporation should be tested in the as-received condition, so accounting to the free water present in the mud as mixing mortar component. The specific surface area of bauxite waste is 20.27 m^2/g and the specific gravity is 2.90 kg/dm^3. In accordance to the particle fineness shown in Fig. 1, maximum particle size is under 40 μm and the mean value is only about 5 μm.

Table 1 gives the chemical composition of the waste, while Fig. 2 shows the corresponding XRD pattern. As expected, alumina and iron oxide are the dominant components, but the relative amounts of SiO_2 and Na_2O are also relevant. Some of those oxides are also detected by XRD, in addition to aluminium hydroxide and a complex $Na_5Al_3CSi_3O_{15}$ phase.

Table 2 presents the results of leaching and solubilisation tests that classify the red mud as "hazardous" (class I). The main problem of this waste is its high pH (12.95), over the limit (12.5) for non-hazardous wastes, defined by the Brazilian NBR 10004/2004 standard. The aluminium, arsenium, selenium, sodium and fluorides contents are higher than the maximum allowed in the solubilisation test according to the Brazilian NBR 10004/2004 standard.

It was not verified the presence of iron in the solubilised extract, probably because NBR 10004/2004 standard requests that material should rest in distilled water for 7 days and the high pH might induce metal precipitation. When filtered iron precipitates might be retained.

3.2 Effects on Mortar Fresh State Properties

3.2.1 pH

As shown previously, the high pH of red mud (12.5) is its main environmental problem. However, the use of materials with this feature is good when added to Portland cement matrices, such as mortar and concrete, since hydration reactions are favoured in strong alkaline environments [13]. Previous studies also show that this highly alkaline environment helps to inhibit corrosion of steel bars in reinforced concrete [15].

It can be seen in Table 3 that the red mud addition allows an increase in pH values of pastes, from about 13.5 (no mud) to 14.6 (30 wt% addition). Although one might expect a high value of pH, the values obtained were surprised by larger than the red mud pH. This happens, probably, due to the formation of large concentration of free OH^- ions in the pore solution of mud containing pastes.

3.2.2 Normal Consistency Index (workability) and Water Retention

To assure the desirable flowability, the mortar paste should have a consistency index not less than 140 mm in the flow table. Fig. 3 shows that red mud addition significantly reduces the workability, due to the fineness of particles and also to the tendency to demand more water for wetting and kneading. It is worth remembering that the amount of water used in all mixtures was fixed. Once the workability is assured, the gain of consistency has a positive effect: lower quantity of free water in the mixture means less porosity and higher mechanical strength of hardened paste and also better resistance to the penetration of aggressive agents (chlorides and carbonation).

A similar tendency might be observed by looking to the variation of water retention index (Fig. 4). Greater water retention by the mortar means smaller loss to the environment (evaporation) and, especially, less exudation, i.e., lower migration of free water upon the curing process.

3.2.3 Setting Time

The addition of red mud tends to accelerate the

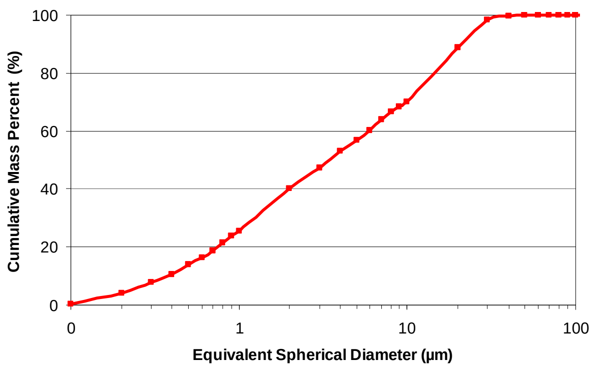

Fig. 1 Particle size distribution of the dried red mud.

Table 1 Chemical composition of red mud estimated by XRF.

Component	Al_2O_3	Fe_2O_3	Na_2O	CaO	SiO_2	K_2O	MnO	TiO_2	Others	LOI*
Content (%)	19.87	19.85	7.35	4.61	14.34	1.87	0.21	2.66	1.01	27.20

*LOI = loss of ignition

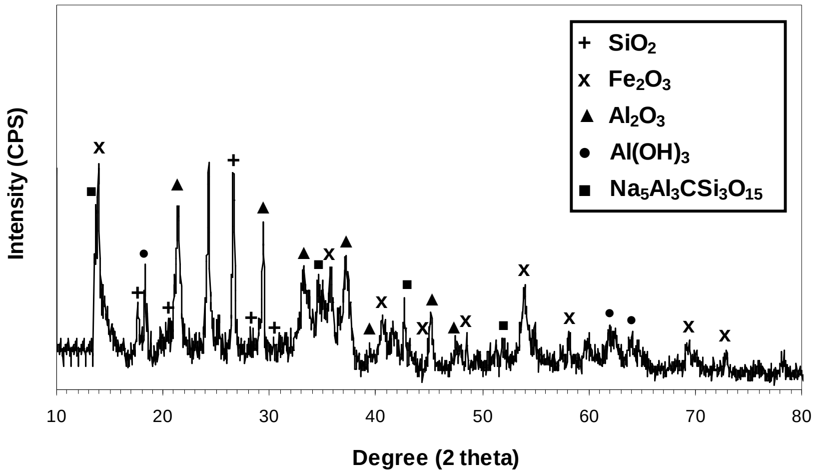

Fig. 2 X-ray diffraction (XRD) pattern of dried red mud.

Table 2 Result of the leaching and solubilization test, according to the NBR 10004/2004 standard, which classifies the red mud as a hazardous waste (class I).

Parameters	Leaching		Solubilization	
	Result (mg/L)	MVA*	Result (mg/L)	MVA*
Aluminum	x	#	41.8	0.2
Arsenium	nd	1.0	0.082	0.010
Barium	nd	70.0	nd	0.700
Cadmium	nd	0.5	nd	0.005
Lead	nd	1.0	nd	0.010
Chromium Total	nd	5.0	nd	0.050
Phenols	x	#	0.007	0.010
Manganese	x	#	nd	0.100
Mercury	nd	0.1	nd	0.001
Silver	nd	5.0	nd	0.050
Selenium	nd	1.0	0.019	0.010
Sodium	1510.0	#	1665.0	200.0
Iron	x	#	nd	0.300
Chlorides	x	#	54.6	250.0
Fluorides	2.3	150.0	78.0	1.5
Vanadium	x	#	x	#
Nitrates	x	#	0.2	10.0
Sulfates	x	#	43.0	250.0
Surfactants	x	#	0.81	5.00

x = not required by the NBR 10004/2004 standard./nd = not detected.
# = absence of a limit established by the NBR 10004/2004 standard.
* MVA = maximum value allowed by the NBR 10004/2004 standard.

setting process (Fig. 5). The end of the setting time changes from 345 to 300 minutes for mortars without red mud and containing 20% waste, respectively. This effect might be explained by the presence of aluminium and sodium hydroxides (known as curing accelerators [5, 16]) in the mud, and also by its high alkaline character. The fineness of waste particles might also partially retain the water, competing with cement. Since the water content is constant in all formulations, the remaining free portion, available to be combined with cement particles, will be consumed shortly [5].

3.3 Effects on Mortar Hardened State Properties

3.3.1 Density and Apparent Porosity

Figs. 6 and 7 showed the evolution of density and apparent porosity, respectively, as a function added mud amount to the mortar cured for 28 days. The mentioned particle fineness of bauxite waste promotes an increase of mortar compactness (density). However, above a certain addition level, packing difficulties might occur, since paste workability is diminishing, and density might then decrease (porosity augment). This tendency was verified. There was an initial increase in density and a decrease in porosity due to better packing of particles (filler effect). However, above 20% red mud addition the behaviour is reserved, due to extra difficulties in moulding and shaping of samples.

3.3.2 Sorptivity

Fig. 8 shows the sorptivity values of concretes having distinct amounts of red mud, estimated from capillary water absorption tests. As previously mentioned, finer red mud particles tend to diminish the relative amount of capillary pores up to certain limit. Consequently, the capillary suction decreases, from 0.284 $kg/m^2.min^{0.5}$ (no red mud added) to 0.254 $kg/m^2.min^{0.5}$ (15% and 20% red mud). However, in a similar way that was discussed about density and porosity changes, samples having more than 20 wt% mud show increasing S values. The expected increase of porosity might include capillary pores or might establish better connection channels between the existing pores.

Table 3 pH of Portland cement mortars as a function of red mud content.

Red mud content	0%	10%	20%	30%
pH	13.48	14.39	14.57	14.61

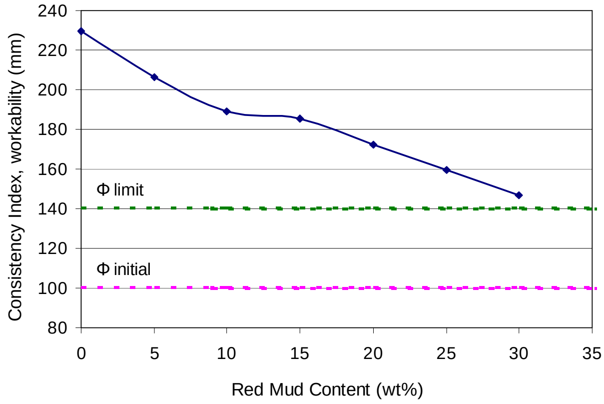

Fig. 3 Normal consistency index (workability) of Portland cement mortars as a function of red mud content.

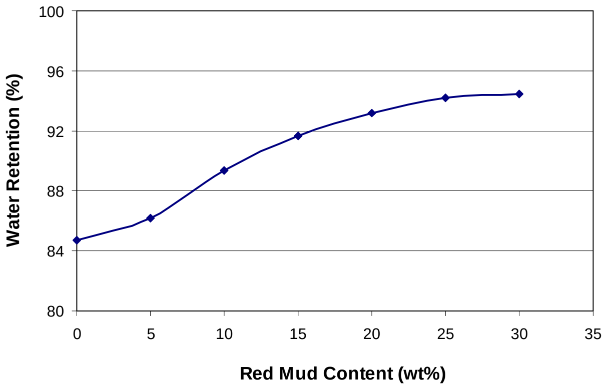

Fig. 4 Water retention of Portland cement mortars as a function of red mud content.

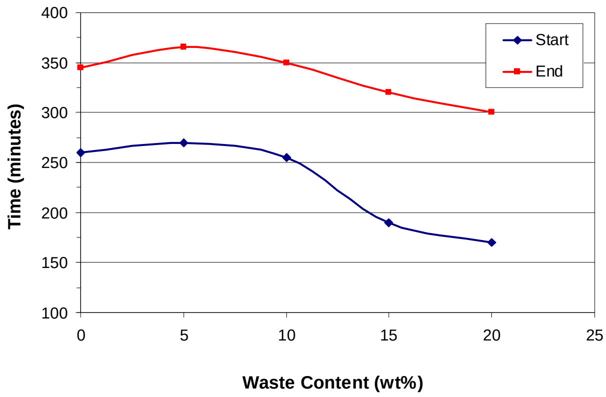

Fig. 5 Setting time of Portland cement pastes as a function of red mud content estimated for mixtures prepared with a fixed amount of water.

3.3.3 Mechanical Strength

The addition of red mud induces a slight increase in strength, as seen in Fig. 9. This gain in strength was around 10.2% (24.43 and 26.92 MPa for 0 and 15 wt% mud containing mortars). However, the mentioned difficulties in casting and the consequent increase of porosity on samples containing more than 20 wt% mud are responsible for the observed resistance degradation. However, we should remark that samples containing 30 wt% mud addition still have better resistance than reference samples, i.e. without compromising the original mortar quality.

Gordon et al. [13] found similar values of strength (20 MPa) for red mud containing Portland cement composites. According to Pinnock & Gordon [17] and Majumdar et al. [18], hydrated lime reacts 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. The reaction of lime with alumina is considered to be a type of pozzolanic reaction as well. Also, according to Delagrave et al. *apud* Pruckner and Gjørv [16], the compressive resistance of cementitious matrices increases with increased concentration of sodium hydroxide because the addition of NaOH originates a finer pore network.

4. Conclusions

Tests performed in the actual work suggest that red mud generated from the alumina and aluminium production by the Bayer process is an interesting candidate to be used in mortars and concretes for non-structural applications, in addition to Portland cement in the mixture. From the research presented herein, the following conclusions can be derived:

The addition of red mud promotes an increase of pH of fresh paste. This is due to a higher concentration of hydroxyl ions (OH^-), from the sodium and aluminium hydroxides detected in the red mud;

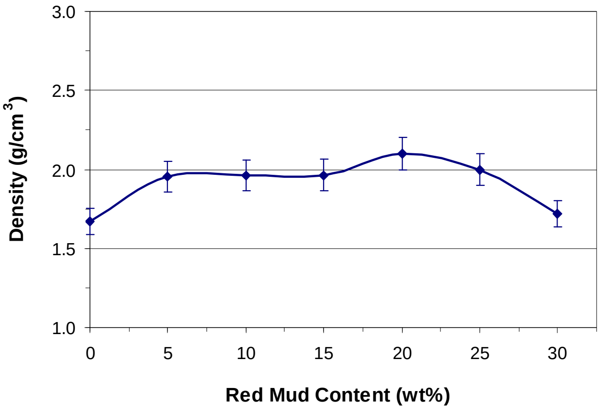

Fig. 6 Density of Portland cement mortars (28 days curing) as a function of red mud content.

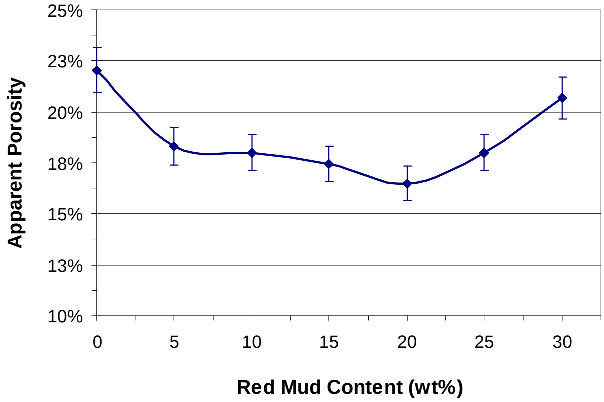

Fig. 7 Apparent porosity of Portland cement mortars (28 days curing) as a function of red mud content.

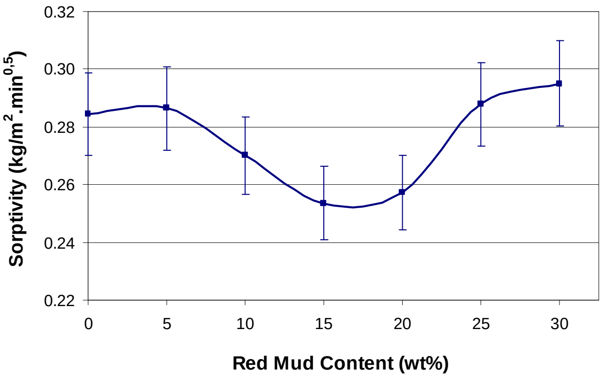

Fig. 8 Capillary water absorption of mortar specimens (28 days curing) as a function of red mud content.

The mortar workability is considerably reduced by adding the red mud. Moreover, water retention is reasonably increased. These two phenomena occur due to the high fineness of red mud particles, which require greater amount of water for wetting and kneading;

Formulations prepared with a fixed amount of mixing water and having increasing amounts of red

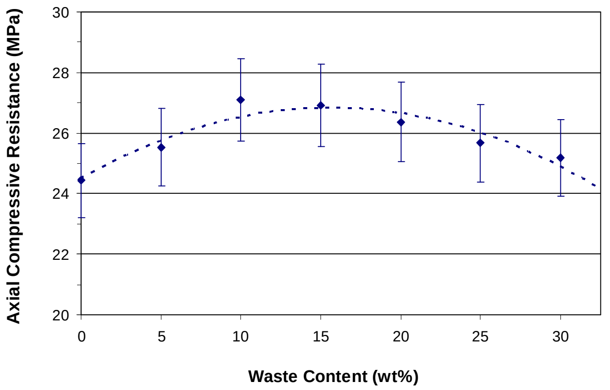

Fig. 9 Axial compressive mechanical strength of mortars (28 days curing) as a function of red mud content as addition of Portland cement.

mud tend to set quickly, due to the fineness of the waste and also due to its composition (rich in aluminium and sodium hydroxide). The fineness of particles might also partially contribute to retain the water, competing with cement;

The red mud addition promotes an initial increase of density and axial compressive mechanical strength of the mortar, while sorptivity tends to diminish. This is due to a better packing (filler effect). Above a certain level (15-20 wt% mud) the behaviour is reserved, due to extra difficulties in moulding and shaping the samples caused by the loose of workability.

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