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ORIGINAL ARTICLE

Fracture and flexural assessment of red mud in epoxy polymer mortars

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Abstract Waste reuse has become increasingly important in construction, especially when it deals with the reduction on the consumption of natural materials and use of waste from other industries. The purpose of this work was to evaluate the use of red mud waste, alumina metallurgical residue, as natural aggregate substitute in epoxy polymer mortars. Various weight fractions of sand 5, 10, 20, 30, 40 and 50 % are replaced by the same weight of red mud waste. Fracture and flexural properties of the obtained composites were measured and calculated. A significant improvement of their post-peak flexural behavior in specimens up to 30 % of red mud content is observed. The main results of this study demonstrate an alternative to reuse red mud waste contributing to the environment preservation.

Keywords Red mud · Waste · Fracture · Flexural · Polymer mortar

1 Introduction

Industrial unwanted waste from manufacturing processes should not be viewed as an environmental issue but rather used as raw materials to produce new materials to be used in different fields. One of the challenges of the industrial and scientific community is to identify productive uses for materials that are currently regarded, as wastes.

The aluminum contains mainly bauxite and the industrial production consists of refining bauxite to produce alumina (aluminum oxide). The alumina industry has changed—and this process will continue, as will demands for improved performance from both internal and external forces. Metallurgical grade alumina production has risen from 48 million tonnes in 2000 to 80 million tonnes in 2010—over 65 % growth. New sources of bauxite and new operating parameters also bring new challenges and new opportunities.

Significant new alumina capacity has been added in the South American, Asian and Oceania regions, but dwarfed by the dramatic growth in Chinese capacity and production. From 4 million tonnes in 2000 to 28 million tonnes in 2010, China has jumped to become the world's leading alumina producer accounting for over 35 % of global metallurgical grade alumina production [1].

The Bayer process is the principal industrial means of refining bauxite into alumina. This method consists in digestion, clarification, precipitation and calcination [2–5]. The digestion consists of washing crushed bauxite with a hot solution of NaOH at 200–240 °C under pressure (30 atm). This converts the aluminum oxide in the ore to soluble sodium aluminate. The clarification is one of the most important step in the process where occurs the separation between the solid (insoluble

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residue) and liquid (liquor) phase. This insoluble residue called red mud is composed by insoluble oxides, iron, quartz, sodium aluminosilicates, calcium aluminate carbonate and titanium dioxide [6]. Red mud is normally disposed in landfill lagoons and left. The chemical composition of the red mud depends on the nature of bauxite. Normally, the red mud retains all the iron, titanium and silica present in the bauxite and also the aluminum that was not extracted in the refining process [7]. According to Environmental Protect Agency (EPA) [8], the red mud is a non-toxic waste, but some researchers disagree. Hind et al. [3] consider the red mud risks due to its of high calcium and sodium hydroxide content and Collazo et al. [9] ponder about the red mud high alkalinity.

Many researchers consider the use of red mud in the civil industry as a construction material [10–16]. The results showed a significant improve in the red mud concrete behavior when compared to ordinary cement concrete.

Different results were found by Rathod et al. [17] when red mud was used in the concrete mixture. As red mud content increase the compressive strength and splitting tensile strength decreases.

No sintering, drying or grinding pre-treating process, and no emission of SO_x or CO_2 are some of advantages of such a polymer mortar, compared to ceramic products and burnt clay bricks [14]. Studies on the environmental compatibility on the reuse of Bayer red mud gave encourage results: the red mud generally showed a high metal trapping capacity and the metal release at low pH was typically low [18]. In general, polymer mortars manufactured with red mud may have an excellent potential application in the construction materials market.

In this paper, the impact of red mud as aggregate replacement in the epoxy polymer mortars fracture and flexural properties is investigated. Red mud waste represents an important environmental liability to the aluminum industry, due to the environment contamination risk and the high cost associated to handling and disposal, which worth the research on the matter.

2 Materials and methods

2.1 Materials

Polymer mortars were prepared by mixing foundry sand and red mud with epoxy resin. Resin content was 12 % by weight and no filler was added in both formulations. Previous studies [19] considering an extensive experimental program, allowed an optimization of mortars that is now being used in the present work.

Table 1 Properties of the epoxy resin

Property	Epoxy
Viscosity at 250 °C μ (cP)	12,000–13,000
Density ρ (g/cm^3)	1.16
Heat distortion temperature HDT (°C)	100
Modulus of elasticity E (GPa)	5.0
Flexural strength (MPa)	60
Tensile strength (MPa)	73
Maximum elongation (%)	4

The epoxy resin system was based on a diglycidyl ether of bisphenol A and an aliphatic amine hardener. This system has low viscosity and is processed with a maximum mix ratio to the hardener of 4:1. Epoxy properties provided by the manufacturers are presented in Table 1.

The aggregate was foundry sand with a homogeneous grain size, with uniform grains and a mean diameter of 300 μm, with finesses modulus between 3 and 5. The aggregate content was 88 % by weight. The specific gravity of the foundry sand was 2.63 g/cm^3. Before being added to the polymeric resins to reduce moisture content, the foundry sand was dried, insuring a good bond between polymer and inorganic aggregate.

The red mud waste was obtained from alunorte S/A, which is the largest alumina manufacturer in the world [6]. The chemical composition of the red mud can be found elsewhere [6] and is mainly composed by SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, SO_3 with traces of V, Ga, P, Mn, Mg, Zn, Th, Cr, Nb oxides [20]. XRD patterns are shown in Fig. 1.

As shown in the XRD pattern, activated minerals hematite, Fe_2O_3, was the major crystal found in red mud waste followed by Sodalite and Anatase, TiO_2.

Red mud is composed by fine particles, with a surface area of 13–22 m^2/g and has a high alkalinity (pH 10–13) [3, 21]. Its density (specific gravity) is 1.4 g/cm^3. The granulometry of the fine aggregates and the red mud to be used was determined according to ASTM D422-63 [22] and displayed in Table 2.

Fig. 1 The XRD pattern of the red mud waste

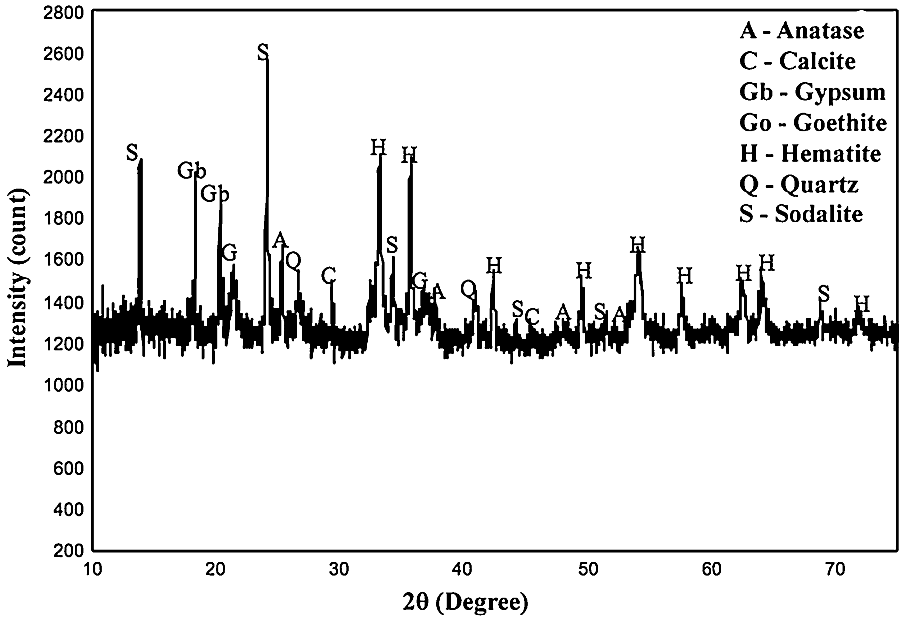


Table 2 Characterization of aggregates

Sieve	Cumulative passing (%)	
	Foundry sand	Red mud
2.38 mm	–	100
1.19 mm	100	99.9
590 μm	84.8	96.0
297 μm	6.7	47.5
150 μm	0.5	4.8
0.075	0	1.4

Thermogravimetry (TGA) experiments were performed according to ASTM E1131 [23] in equipment Shimadzu, model DTG-60H. The temperature range chosen was from ambient (26 °C ± 2) up to 500 °C, with heating rate of 5 °C/min, using 50 ml/min pure nitrogen as carrier gas. For each sample aluminum pans suitable for TGA analyzers were filled with aprox. 20 mg of red mud and introduced in the TGA equipment. The TGA/DTG thermogram of the red mud is shown in Fig. 2.

It can be seen at Fig. 2 that the total mass loss between room temperature and 500 °C is 9.56 % (TGA). Also, it could be seen from the DTG results that the weight loss occurs in five stages: first between 50 and 150 °C corresponds to the loss of water present in the sample. Between 200 and 400 °C is related to the gypsum decomposition due to its complete phase change in alpha alumina [24]. At this temperature range goethite can decompose forming hematite.

Mixtures containing red mud aggregates in different weight fractions are prepared. The ratio used in these mixtures was 5, 10, 20, 30, 40 and 50 % in weight, substituting aggregates in the mixture. The index number represents the red mud percentage, in weight, as foundry sand replacement.

Fracture test specimens with 30 mm × 60 mm × 250 mm and a 20 mm notch and flexural samples with 40 mm × 40 mm × 160 mm were made. The specimens were initially cured at room temperature and then post-cured for 3 h at 80 °C.

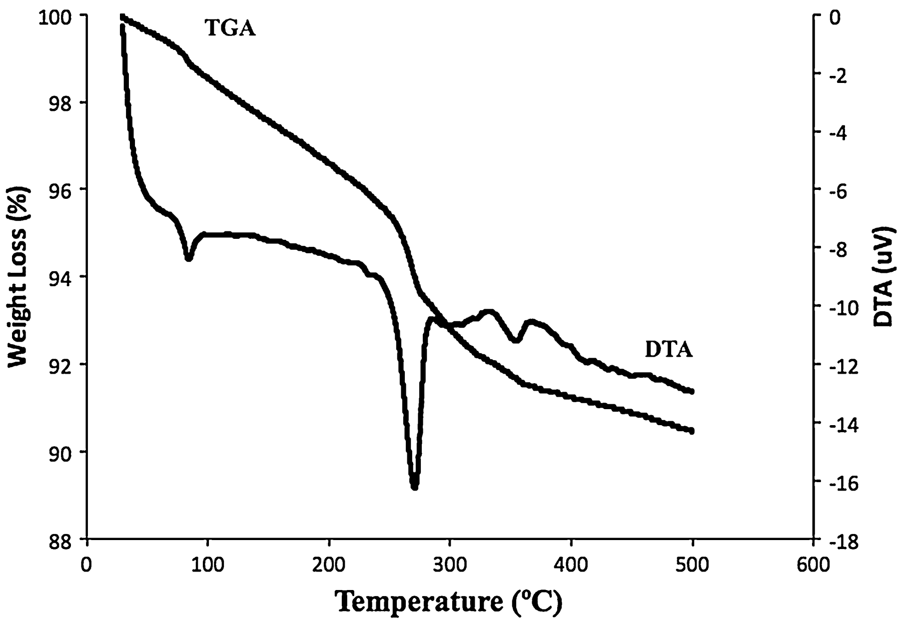
The red mud polymer mortars (RMPM) were manufactured following the specifications of RILEM TC113/PC-2 [25].

2.2 Methods

To determine fracture and flexural properties red mud polymer mortars were tested under different loading conditions.

To determine the fracture properties, three-point bending tests were conducted using a universal testing machine with a cross-head speed of 0.5 mm/min. The crack mouth opening displacement (CMOD) was measured using a COD gauge clipped at the bottom

Fig. 2 TGA-DTA profiles of red mud waste



of the beam and held in position by two 1.5 mm steel knife edges glued to the specimen.

Fracture toughness, K_{Ic}, Fracture energy, G_f, and elasticity modulus, E, are determined according to RILEM [26, 27].

To identify the fracture toughness of RMPC, a direct method, the Two Parameter Method (TPM) [26] was used. This method is used to calculate critical stress intensity factor, K_{Ic}, which is a measurement of a material's resistance to crack extension when the stress state near the crack tip is predominantly plane strain, limiting the plastic deformation, and the opening mode monotonic load is applied and can be expressed as, in (MPa $\sqrt{m}$)

$$K_{Ic} = \frac{3P_{max}S}{2W^2B}\sqrt{\pi \underline{a} F(\alpha)} \quad (1)$$

in which $\underline{a}$ is the effective critical crack length

$$F(\alpha) = \frac{1}{\sqrt{\pi}}\frac{1.99 - \alpha(1-\alpha)(2.15 - 3.95\alpha + 2.7\alpha^2)}{(1+2\alpha)(1-\alpha)^{3/2}}, \quad (2)$$

where α is a/W, P_{max} is the measured maximum load (N), S, W and B are the span, depth and width, respectively.

The elasticity modulus (E) can also be calculated by TPM [26]

$$E = \frac{6Sa_0V_1(\alpha)}{(C_iW^2B)} \quad (3)$$

in which S is the specimen loading span, a_0 is the initial notch depth, C_i is the initial compliance and W and B are the beam depth and width, respectively. $V_1(\alpha)$ can be determined by

$$V_1(\alpha) = 0.76 - 2.28\alpha + 3.78\alpha^2 - 2.04\alpha^3 + \frac{(0.66)}{(1-\alpha)^2} \quad (4)$$

and

$$\alpha = \frac{(a_0 + H_0)}{(W + H_0)}. \quad (5)$$

The fracture energy, G_f, according to the RILEM Technical Committee [27], in single edge notched beams (SENB) when three point bending tests are performed on the specimens can be calculated as

$$G_f = \frac{W_0 - mg\delta_0}{A_{lig}}, \quad (6)$$

where W_0 is the area under the load versus deflection curve (N/m), mg is the self-weight of the specimen between supports (kg), δ_0 is the maximum displacement (m), and A_{lig} is the fracture area [$d(b-a)$] (m^2); b and d are the height and width of the beam, respectively.

Table 3 Fracture and flexural properties epoxy PM with red mud (average/St. dev.)

Polymer mortars	K_{Ic} (MPa)	G_f (Nm)	E (GPa)	σ_f (MPa)
0RMPM	1.56 ± 0.16	396.54 ± 12.94	10.04 ± 0.33	16.44 ± 1.54
5RMPM	1.65 ± 0.09	364.34 ± 24.45	14.66 ± 0.74	18.58 ± 0.84
10RMPM	1.81 ± 0.17	356.19 ± 41.51	17.93 ± 2.47	26.11 ± 1.66
20RMPM	2.03 ± 0.02	244.64 ± 8.42	19.51 ± 0.95	34.17 ± 3.03
30RMPM	2.13 ± 0.06	212.24 ± 1.54	22.52 ± 2.12	36.77 ± 3.15
40RMPM	1.27 ± 0.11	156.06 ± 5.44	4.40 ± 0.54	3.41 ± 0.39
50RMPM	0.17 ± 0.09	27.32 ± 2.44	1.32 ± 0.11	2.06 ± 0.09

Three-point bending up to failure tests, according to the RILEM specification TC113/PCM-8 [27, 28], in prismatic red mud polymer mortar beams was made at a loading rate of 1 mm/min, with a span length of 100 mm. Tests were performed in specimens with similar geometry and span length to ASTM C348 [28, 29]. The shear effect is not considered in neither of the aforementioned standards, to calculate the flexural strength, despite the very short span compared to the thickness. Red mud polymer mortars are considered an isotropic material and the plane cross-section theory was assumed.

For each kind of formulation five specimens each were produced.

3 Results and discussion

Fracture and flexural properties obtained from 3 point bending tests conducted on epoxy PM manufactured with red mud in substitution to fresh aggregates are presented in Table 3, where the index number represents the red mud quantity used as fresh aggregate replacement.

Analyzing Table 3 it can be seen that red mud contributes to improve fracture and flexural properties of epoxy polymer mortars when used as fresh aggregate replacement. Replacing foundry sand by red mud waste by 5 % and increase in the fracture toughness of 5.8 % is calculated, 46 % in the modulus of elasticity and 13 % in the flexural strength. Despite the increase in such properties, the fracture energy, which is the amount of energy that is supplied by the elastic energy in the body and by the loading system in creating the new fracture surface area, decrease. When 5 % of red mud is used as foundry sand replacement it can be seen an 8.1 % lower fracture energy.

As red mud waste was replacing fresh foundry sand in the epoxy polymer mortars mixture, fracture toughness, modulus of elasticity and flexural strength continue to grow reaching the maximum value when 30 % of red mud waste was used. When 30 % of red mud waste replaced fresh foundry sand the fracture toughness increased 36.5 %, modulus of elasticity increased 114.3 and 123.7 % higher flexural strength is observed. Quantities beyond 30 % show a significant decrease. For 40 % of red mud, 18.6 % decrease in the fracture toughness is calculated, 56.2 % lower modulus of elasticity and a diminish of 79.3 % in the flexural strength is observed. Using 50 % of red mud as fresh foundry sand replacement results continue to decrease. Fracture toughness lowered 89.1 %, modulus of elasticity diminishes 86.9 % and flexural strength decreased 88.9 %. This can be explained by the small size of the red mud leading to a difficulty in the workability. The aggregates wettability was prejudiced by the large quantities of the red mud.

The results of fracture energy show an overall decrease meaning that less energy is necessary to create a fracture surface area. Figure 3 presents the typical load versus CMOD curves for different quantities of red mud in epoxy polymer mortars.

According to Antunes and Santos [24] red mud can be characterized for presenting high cohesion, even dry, very low porosity, intense capillarity phenomenon and some plasticity. These properties such as high cohesion can lead to high properties as quantity of red mud content increases but the low porosity will obstruct matrix penetration during the mixture. Therefore, high quantities of red mud (40 and 50 %) produce very low properties.

As shown in Fig. 3, increasing the quantity of red mud as fresh foundry sand replacement in epoxy polymer mortars up to 30 % produces the highest load

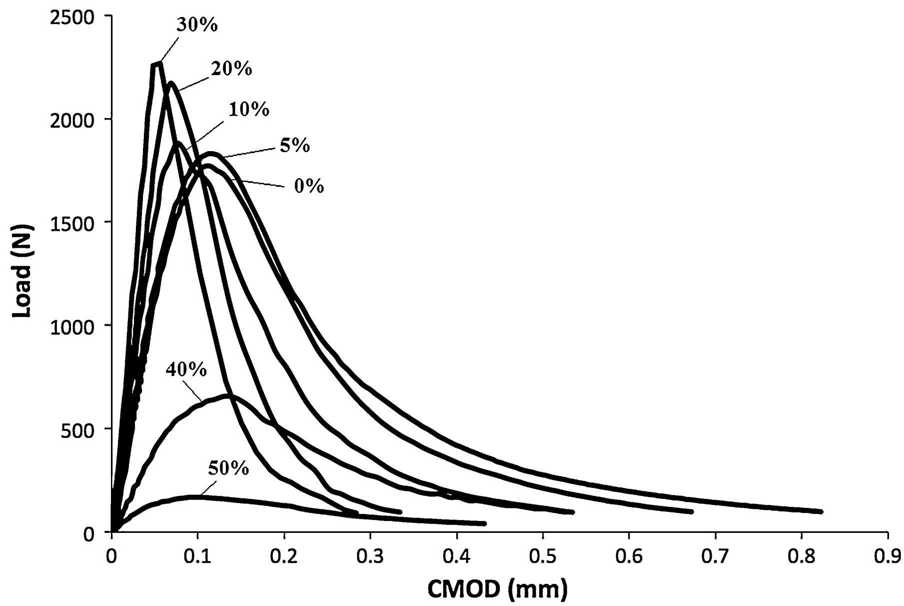


Fig. 3 Typical load versus CMOD for different quantities of red mud in epoxy polymer mortars

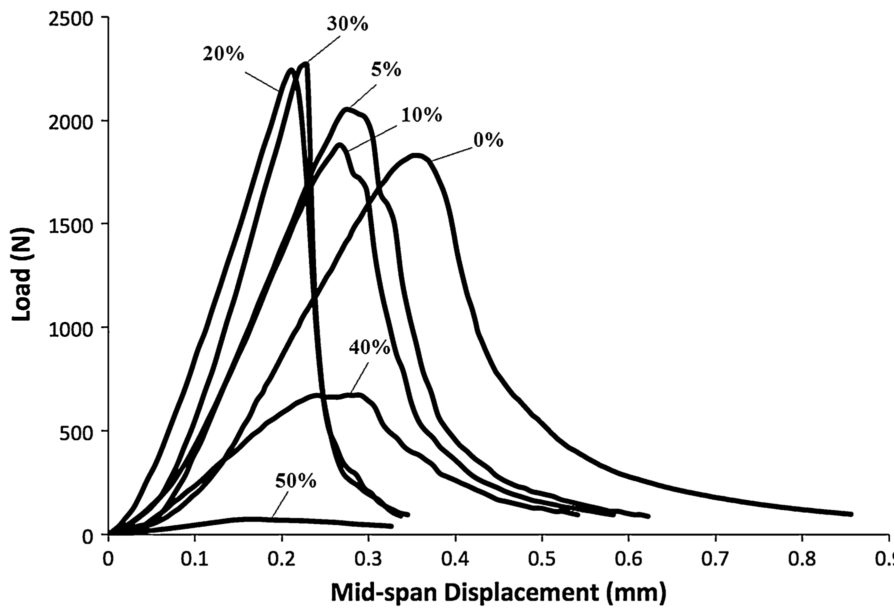


Fig. 4 Typical load versus mid-span displacement for different quantities of red mud in epoxy polymer mortars

leading to the highest toughness. Also, it can be seen that the angle of the linear graph slope raise until 30 % of red mud content, then a significant decrease in observed. This angle increase in the slope led to higher values of fracture toughness and modulus of elasticity. Since red mud has a tendency to agglomerate under low humidity [29, 30], dry red mud particles were observed in the red mud polymer mortars with 40 and 50 % content after samples failure. That led to a poor matrix/particles adhesion contributing to poor properties.

Figure 4 displays the typical load versus mid-span displacement curves for different quantities of red mud in epoxy polymer mortars.

According to Fig. 4 it can be seen that red mud up to 30 % increase maximum load by the fracture energy decrease as red mud waste content increase. The fracture energy is governed by the work of fracture,

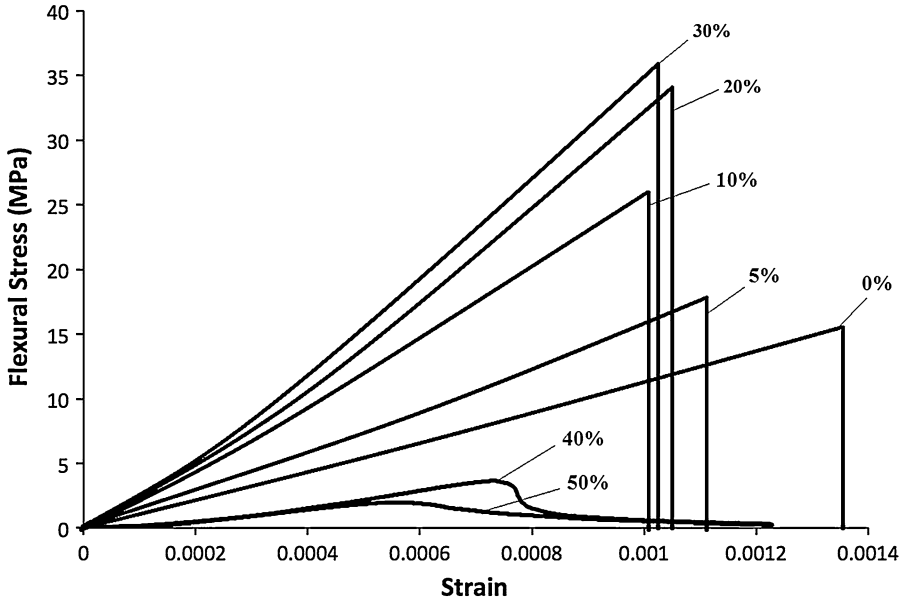


Fig. 5 Typical flexural stress versus strain for different quantities of red mud in epoxy polymer mortars

which is the area under the load versus mid-span displacement, and red mud contributes do lower that area. Also, the red mud waste affects epoxy polymer mortar brittleness. Increasing red mud waste content up to 30 %, catastrophic failure is observed. Polymer mortars with 40 and 50 % of red mud waste content show a less brittle behavior.

Figure 5 presents the flexural behavior of epoxy polymer mortars when red mud waste is used as fresh foundry sand replacement.

Analyzing Fig. 5 it can be seen that 30 % of red mud waste as fresh foundry sand replacement in epoxy polymer mortars produces the best result. It was calculated the highest flexural strength and highest stiffness. Lower strain at failure is observed as red mud waste content increase leading to more brittle behavior. Again, to 40 and 50 % of red mud content the results are very low in comparison to plain epoxy polymer mortars. It was also observed dry red mud particles in the broke specimens. As happen to previously tested specimens, fracture ones, this poor resin impregnation led to very low flexural properties.

4 Conclusions

In this research work, the effect of red mud waste from the aluminum industry as aggregate substitute in epoxy polymer mortars was investigated. Fracture and flexural properties were evaluated and quantified. It is suggested from seven groups of experiments that the optimal proportions of red mud epoxy polymer mortar are when 30 % of red mud is used as fresh sand substitute. Fracture and flexural properties increase when red mud waste is used up to 30 % and then a significant decrease is observed. High red mud content (40 and 50 %) has dry particles dispersed in the composite, low matrix impregnation, contributing to low fracture and flexural properties.

Red mud epoxy polymer mortars may have a good application in the construction materials market because of its lower energy consumption and costs in current processes, and may play an important role to eliminate the storage of the red mud in Brazil.

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