Construction and Building Materials 67 (2014) 29–36

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Microstructure, mineralogy and environmental evaluation of cementitious composites produced with red mud waste

Eliz Paula Manfroi [a], Malik Cheriaf [b], Janaíde Cavalcante Rocha [b,*]

[a] Federal University of Santa Catarina, Post-Graduate Program in Civil Engineering, CEP 88.040-900, Florianópolis, SC, Brazil
[b] University Federal of Santa Catarina, Department of Civil Engineering, CEP 88.040-900, Florianópolis, SC, Brazil

HIGHLIGHTS

- Consumption of calcium hydroxide with red mud.
- Hydration compounds were formed in pastes with up to 15% of red mud.
- Red mud promoted the filling of the empty capillaries.
- Hydration products could be able to assume the fixation of contaminants.

ARTICLE INFO

Article history:
Available online 14 November 2013

Keywords:
Red mud
Waste
Cement
Pastes
Mortars

ABSTRACT

Red mud (RM) is a by-product from aluminum industry, and represents a renewed environmental problem due the significant annual throughput by the plants. The investigation of the microstructure and mineralogical compositions of the cement pastes with up to 15% of dry or calcined RM (600–900 °C) were carried out using scanning electron microscopy, X-ray diffraction and differential thermal analysis techniques, respectively. The environmental evaluation of RM was performed using Toxicology Characteristic Leaching (TCLP) and diffusion tests in mortars. Water absorption by capillarity, wetting angle, compressive strength tests were carried out on mortars with up to 15% RM in replacement of cement. The compounds calcium silicate hydrate, AFm phase, CAH gel and ettringite were identified in the pastes produced with RM. The results showed that the RM waste can be used in replacement to cement to produce cementitious composites with microstructure, mechanical and hygroscopic properties suitable for their use in civil construction.

1. Introduction

Red mud (RM) is a waste generated from the refining of bauxite during the Bayer process for the production of alumina and the posterior production of aluminum. In 2012, the world production of primary aluminum reached the mark of 45.21 million tonnes. Therefore, by estimation, the aluminum industry generated approximately 27 million tonnes of RM for high quality bauxite and 226 million tonnes for low quality bauxite. In spite of the merely illustrative purpose of the estimation, it demonstrates the size of the global environmental problem that RM represents [1,2]. The disposal of RM remains a major problem.

Results reported in the literature are promising regarding the use of RM presents as a pozzolanic material, after calcination, and can be used to produce mortars and concretes [3–5]. In Brazil, studies evaluated the influence of the addition of dry RM on the setting times of Portland cement through the Vicat apparatus and the pozzolanic index of the waste according to Brazilian standard NBR 5752 [6].

It is possible to develop the pozzolanic material for the concrete, but there are gaps in the preparations of the samples regarding the best calcination temperature for the best index of pozzolanic activity. According the literature the chemical and mineral compositions of RM can vary with raw materials used in process and have a significant effect on the pozzolanic properties of calcined RM [4,5].

This article evaluates the pozzolanic property of RM that has been dried and calcined at different temperatures through the procedure of calcium hydroxide consumption. In addition, this article presents the microstructure and the mineralogy of pastes produced with up to 15% of RM in substitution of Portland cement. The evaluation of the compressive strength, water absorption by capillarity and wetting angle of mortars made with RM are also presented in this work.

Lastly, this paper aimed to contribute to the environmental assessment of RM through leaching test described in Brazilian

* Corresponding author. Tel.: +55 48 37215169; fax: +55 48 37219939.
E-mail address: janaide.rocha@ufsc.br (J.C. Rocha).

0950-0618/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.conbuildmat.2013.10.031

standard [7] and to the environmental assessment of mortars produced with RM according to the Dutch standard [8].

2. Experimental

2.1. Materials

The sample of RM was collected in an alumina ponds in the state of Minas Gerais. The analysis of pastes and mortars were carried out on dry and calcined RM. It was dried in an oven at 105 ± 5 °C (for 72 h) and later calcined at 600, 700, 800 and 900 °C for 1 h. The RM samples were ground to particle size less than 0.15 mm.

The chemical characteristics of the RM was carried out using energy dispersive X-ray fluorescence spectrometry (EDX, Model 700 HS, Shimadzu). The chemical composition of dry RM is shown in Table 1.

Fig. 1 shows the X-ray diffractogram of the dry RM at 105 °C obtained by means X-ray diffraction analysis techniques (Model D 500, Siemens). The phases detected in the dry RM were chantalite (1), cancrinite (2), gibbsite (3), hematite (4), quartz (5) and calcite (6).

The particles size distribution of the dry RM obtained by laser grain size measurements (Microtrac Model S 3500) is presented in Fig. 2. According to the measurements 100% of RM particles are smaller than 0.018 mm. The RM dry and calcined at 600, 700, 800 and 900 °C presents the values of the specific area (Blaine), about 6–9 times higher than the Portland cement CPII-F (3200 cm^2/g), i.e., the particles of the RM are lower than the particles of the Portland cement.

The calcium hydroxide (standard analytical) and inert silica flour (particle size < 0.15 mm) were used to evaluate the pozzolanic potential of the RM. The pastes and mortars are produced with Portland cement CPII-F. The mortars were produced with standard sand.

Table 1
Chemical composition of dry RM.

Element (wt.%)	RM
Al_2O_3	30.35
Fe_2O_3	27.50
SiO_2	16.62
Na_2O	10.80
CaO	4.12
TiO_2	3.98
K_2O	2.84
ZrO_2	1.60
P_2O_5	0.40
MnO	0.58
V_2O_5	0.50
NbO	0.30
SO_3	0.06
Cl	0.19
SrO	0.04
Cr_2O_3	0.03
As_2O_3	0.02
ZnO	0.02
CuO	0.02
SnO_2	0.02
CdO	0.01
Rb_2O	0.005
Loss on ignition	13.00

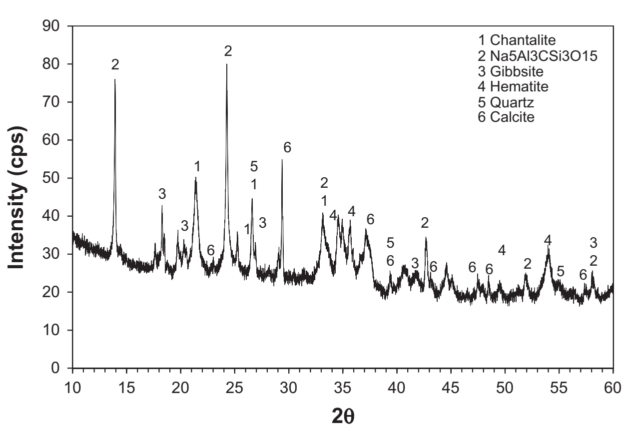

Fig. 1. X-ray diffractogram of the dry RM.

2.2. Methods

2.2.1. Pozzolanic activity of the dry and calcined RM

In order to evaluate the pozzolanic potential of RM the calcium hydroxide consumption method [9,10] was used. For this purpose, pastes were produced with 50% of each type of RM and 50% of calcium hydroxide. The reference sample was prepared with 50% of inert silica flour and 50% of calcium hydroxide. Table 2 shows the compositions of the products used to design the pozzolanic activity.

The pastes with RM and reference paste were cast with a water/solid ratio of 0.60. After the hydration periods, 3, 7 and 28 days, the samples were dried in an oven (T = 50 °C, 24 h), ground (particle size < 0.15 mm) and analysed by differential thermal analysis (DTA). Differential thermal analysis was carried out on samples with a mass of 600 mg with a heating rate of 10 °C/min.

The area of the endothermic peak of residual calcium hydroxide of the thermogram of the paste produced with 50% of RM and 50% calcium hydroxide was compared to peak area of the calcium hydroxide of the reference paste. The relationship between these two areas provided the relative consumption of calcium hydroxide by material considered pozzolanic [9,10].

2.2.2. Hydrated compounds

The investigation of the hydrated compounds was carried out in pastes composed by 5% and 15% of dry and calcined RM, in a mass substitution of the Portland cement CPII-F. The pastes were cast with a water/binder ratio of 0.3 and 0.2 at 0.4% of superplasticizer additive (polycarboxylate ether based). Table 3 shows the compositions of the products used to investigate the hydrated compounds. After the hydration periods (3, 7 and 28 days), samples were dried in an oven (T = 50 °C, 24 h), ground (particle size < 0.15 mm) and analysed by X-ray diffraction (Model X-Pert, Philips) and differential thermal analysis (DTA). The microstructures of the pastes were investigated by scanning electron microscopy analysis (Model JSM-6390LV, JEOL).

2.2.3. Mortars

Mortars were produced according the binder to sand ratio of 1:3 (in mass) and a water/binder ratio kept constant at 0.53. In the mortars with 10% and 15% of RM the superplasticizer additive (polycarboxylate ether based) was used. The cement CPII-F was replaced by 5%, 10% and 15% of dry or calcined RM. The compressive strength was carried out in mortar in accordance with the procedures described in Brazilian standard NBR 13279 [11]. Table 4 shows the mix proportions of the different mortars.

In order to evaluate the water absorption by capillarity of the mortars was used a procedure that consists in the measure of the height variation of a water column contained in a graduated Mariotte tube in function of time [12]. The height variation of the water column is directly related with the amount of water absorbed by the sample. The volume of water absorbed by section of the sample was called absorption index ($I = cm^3/cm^2$). The inclination of the straight (absorption index versus square root of time) corresponds to sorptivity. The wetting angle test in mortars was carried out in accordance with an experimental procedure, and was determined using two different penetrating liquids: water, as the main liquid, and alcohol with perfect wettability, i.e., liquid–solid contact angle equal to 0°. This procedure provides the determination of the apparent wetting angle by means of the evaluation of the capillary rise in test carried out in mortars.

The samples of dry and calcined RM at 600, 700, 800 and 900 °C with a particle size of less than 0.15 mm were tested according to leaching test procedures described in Brazilian standard NBR 10005 [7]. In Brazil there are no standards on environmental assessment of monolithic materials produced with waste. Thus, to evaluate the release of heavy metals from mortars the leaching test was performed in accordance with the procedure established by Dutch standard NEN 7345 [8].

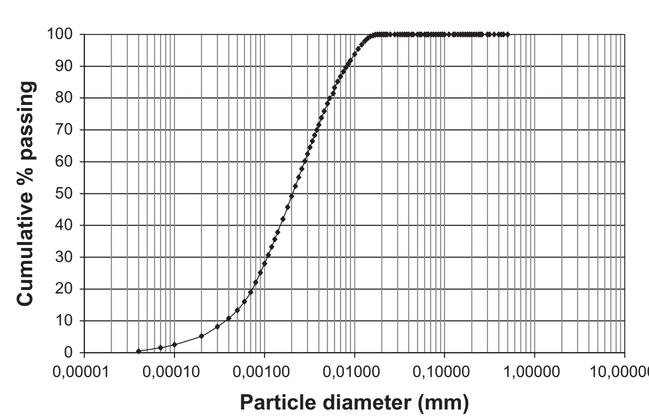

Fig. 2. Particle size distribution of the dry RM.