SYNTHESIS OF GEOPOLYMERS FROM RICE HUSK ASH AND ALUMINIUM ANODIZING RESIDUE

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This study aimed to synthesize geopolymers from the mix of rice husk ash with aluminium anodizing residue, the first as source of silica and the last as source of alumina, both required for the production of polisialates. The wastes were characterized (FRX and laser diffraction) and ground. NaOH and sodium silicate were used for the alkali activation according to a statistical experimental design where the factors were the molarity of the alkali, the ratio between rice husk ash and Al anodizing residue and the temperature of synthesis. The geopolymer samples were subjected to a diametral compression test (1 MPa/s) in order to determine their compressive strength, deformation under maximum load and elastic modulus. As a result, geopolymers can be obtained from the combination of rice husk ash and aluminium anodization residue. The only treatment required for both residues is particle size reduction. The compressive strength depends on the interaction among the molarity of the alkaline solution, the synthesis temperature and the mixing ratio of the waste. The modulus of elasticity depends on the molarity of the alkaline solution and the synthesis temperature. In turn, the deformation depends on the molarity of the base and the ash/aluminium residue ratio.

1. INTRODUCTION

Geopolymers are aluminosilicates that can be formed similarly to the geological process of transformation of some volcanic rocks into zeolites, a process that occurs at low pressures and temperatures during the formation of sedimentary rocks. The sialate network (silico-oxo-aluminate) consists of SiO_4 and AlO_4 tetrahedrons alternatively bonded by sharing of oxygen atoms. Positive ions such as Na^+, K^+ and Ca^{2+} should be present in the spaces of the network to balance the negative charge caused by the Al^{3+} ion in the tetrahedrons. Poly(sialates) are chain or ring polymers with Si^{4+} and Al^{3+} in tetrahedral coordination with oxygen. Their empirical formula is $M_n(-SiO_2)_z-AlO_2)_n.wH_2O$ where z is 1, 2 or 3, M is a monovalent cation such as K^+ or Na^+, and n is the degree of polycondensation. Thus, the complex structure of geopolymers consists of interconnected units of SiO_4 and AlO_4 tetrahedrons forming linear, lamellar and tridimensional networks [1-5].

Although geopolymers have been used in a number of applications, their broader use is limited due to lack of detailed scientific understanding and long-term durability studies. The current lack of commercialization and application of the geopolymer technology is partly due to confusion and inconsistency in designing their chemical nature. The variation of mechanical and thermal properties is also a source of concern for commercial and industrial maturity of geopolymer materials. Experimental variations can be induced by poor sample preparation or a low quantification of the system parameters. The main barrier that geopolymerization must overcome to become acceptable to the industry is mainly related to the retrograde position of regulators. Another issue to consider is that the industry is very conservative in adopting new technologies and products to replace existing ones. To overcome these barriers, continuous and more intensive efforts by the scientific community are needed.

Therefore, this work aims to use solid waste, rice husk ash and residue from aluminium anodizing, for geopolymer synthesis. For this purpose, the wastes were characterized in order to determine their chemical composition and they were processed by grinding. For the synthesis of the geopolymer system, sodium hydroxide and sodium silicate were used, according to a statistical experimental design, where the molarity of the NaOH, synthesis temperature and the relation between the rice husk ash and anodization residue were the main factors under study.

2. MATERIALS AND METHODS

10 kg of aluminium anodization sludge and wet rice husk ash were collected. For the alkaline synthesis NaOH of analytical grade and sodium silicate (SiO_2:Na_2O=3:1) were used. The residues were dried and calcined in an electric furnace (700 °C) for 4 h. They were then dry milled for 30 min in a planetary mill, using a load of 70 vol. % of small balls and 30 vol. % of large balls. The milled samples were then sieved through a 45 µm mesh and used on a dry basis. The ash and waste were characterized by XRF to determine their chemical composition and by laser diffraction to determine their particle size distribution (PSD) after milling.

Based on the chemical analysis of the ash and Al residue, solutions were prepared with the following stoichiometry: SiO_2:Al_2O_3 = 1 to 3, Na:Al = 0.5 to 1.5 and H_2O:SiO_2 = 2.0. Synthesis was performed by dry mixing the rice husk ash with the Al residue, according to a 2^k factorial design, adding the alkaline solution of NaOH (5 to 10 M) and sodium silicate. The mixture (by weight) was made up of 70% ash+Al residue, 20% NaOH and 10% sodium silicate. The gel was shaken for 5 min on a mechanical mixer.

After mixing, the gel was poured into cylindrical moulds (φ = 30 mm, h = 60 mm) and cured at 20 (room temperature), 50 or 80 °C for 72 h according to the 2^k design. After initial curing, the samples were kept in the moulds at room temperature for 14 days and were sequentially tested. The samples were subjected to diametrical compression tests (universal testing machine, 1 MPa/s, average of 3 specimens) according to ASTM D695 ('Brazilian test').

To analyse the synthesis variables, a 2^k factorial design was used, Table 1. The main factors were the ratio of SiO_2/Al_2O_3 (ash/Al residue), the molarity of the NaOH solution and the synthesis temperature. A central point was used in the experiment. The levels were: ash/Al residue = 1 to 3, NaOH = 5 to 10 M, and temperature = 20 and 80 °C. For the central point the levels were ash/Al residue = 2, NaOH = 7.5 M, and T = 50 °C. Table 1 shows the 2^k factorial design and the results for the compression tests: diametral compression strength, elastic modulus, and elongation at maximum load. The results represent an average of three measurements.

Run	Ash/Al residue	NaOH (M)	T (°C)	$\sigma_{comp.}$ (MPa)	E (MPa)	ε (%)
1	50/50	5	20	5.26	308	2.9
2	50/50	5	80	1.27	88.6	6.0
3	50/50	10	20	1.44	206	2.1
4	50/50	10	80	1.90	365	0.57
5	75/25	5	20	0.855	75.7	1.6
6	75/25	5	80	1.50	127	2.1
7	75/25	10	20	1.62	169	1.4
8	75/25	10	80	3.05	431	2.3
9	67.5/32.5	7.5	50	1.25	73.5	2.5

Table 1. *2^k factorial design for the geopolymer synthesis and results for the compression test*

3. RESULTS AND DISCUSSION

The rice husk ash is mainly made up of silica (~ 97 wt.%) and a small amount of alkali and alkaline earth oxides (1.7 wt.%) and alumina (0, 2 wt.%). Iron and manganese oxides are the main contamination (0.4 wt.%). The anodizing residue contains mainly alumina (~ 82 wt.%) and a large amount of sodium oxide (14 wt.%), and fractions of other oxides. After milling, the ash and the anodizing residue were very fine, suitable for the geopolymer synthesis. The ash had an average diameter of 7.6 μm and the anodizing residue had an average diameter of 14 μm.

For the compressive strength results, the most important factors are the three double interactions among the main factors, namely, SiO_2/Al_2O_3 × NaOH, SiO_2/Al_2O_3 × T and NaOH × T. The reliability of the results is 80% (α = 0.2). The higher compressive strength occurs for synthesis at room temperature, lower NaOH molarity and a lower ratio between ash and Al residue (SiO_2/Al_2O_3 = 1:1), very favourable for the commercial exploitation of this geopolymer system, although the literature points out temperatures of 100 °C for the synthesis of geopolymers. The most important factors for the modulus of elasticity are the NaOH × T interaction and the NaOH molarity alone. The highest values for E occur for the higher synthesis temperature and higher molarity of the NaOH solution, with 80% reliability, regardless of the ratio between ash and anodizing residue. These results limit the commercial exploitation of this geopolymer system. However, great plastic deformation of the samples (~ 2%) was observed, which might have caused the difference between the results of compressive strength and modulus of elasticity.

Finally, the most important factors for the deformation under maximum load are the SiO_2/Al_2O_3 × NaOH interaction and the NaOH molarity alone, again. The reliability of the results is 80% (α = 0.2). The highest deformation under maximum load occurs for the lowest ash/anodizing residue ratio and lower NaOH molarity, regardless of the synthesis temperature, which again favours the commercial exploitation of this geopolymer system.

Therefore, to obtain greater rigidity of the samples – modulus of elasticity – the synthesis must be made under higher temperature and higher molarity of the base. Conversely, if the goal is to increase the strength of the sample – in this case, the maximum load until fracture of the sample, which occurs under plastic deformation – the synthesis must be made under lower molarity of the base, lower synthesis temperature and lower ratio between ash and anodizing residue. Finally, if the goal is to obtain samples with greater deformation, the synthesis must be made under lower molarity of the base and lower ratio between ash and anodizing residue.

4. CONCLUSIONS

Geopolymers can be obtained from the mixture of ash from the burning of rice husk and sludge from the treatment of aluminium anodization residue. The only processing required for both wastes is the reduction in particle size. The interactions between the factors under study, i.e., the molarity of the alkaline solution (NaOH), synthesis temperature and the mixing ratio between rice husk ash and aluminium anodizing residue have affected diversely the properties. The compressive strength depends on the interaction between the molarity of the alkaline solution, synthesis temperature and mixing ratio of the waste. The modulus of elasticity depends on the molarity of the alkaline solution and synthesis temperature. In turn, the deformation under maximum load depends on the molarity of the base and ash/Al residue ratio.

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