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**DOI: 10.1590/0366-69132017633652057**

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## Alkali-activated binder containing wastes: a study with rice husk ash and red ceramic

### *(Aglomerante álcali-ativado contendo resíduos: um estudo com cinza de casca de arroz e resíduo de cerâmica vermelha)*

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#### Abstract

In addition to several positive aspects in technical properties, geopolymeric binders have considerable advantages in the environmental point of view, with lower energy consumption and lower CO<sub>2</sub> emission. In this study, it was conducted an overview about the utilized materials by some Brazilian researchers in geopolymers production, and also an experiment employing two types of wastes (red ceramic waste and rice husk ash). The compressive strength of the resulting material developed very fast, reaching a value of 11 MPa after one day. The microstructure was evaluated by scanning electron microscopy, revealing a compact microstructure and the presence of starting materials from the red ceramic waste that not completely reacted. The results indicated the feasibility of producing geopolymeric material without using commercial sodium silicate and cured at room temperature, showing an option for building materials production with lower environmental impacts.

**Keywords:** geopolymer, alternative materials, sustainability, building materials.

#### Resumo

Além de vários aspectos positivos nas propriedades técnicas, aglomerantes geopoliméricos têm consideráveis vantagens do ponto de vista ambiental, com menor consumo de energia e menor emissão de CO<sub>2</sub>. Neste estudo, conduziu-se uma revisão sobre os materiais empregados na produção de geopolímeros por alguns pesquisadores brasileiros, e também um experimento empregando-se dois tipos de resíduos (resíduos de cerâmica vermelha e cinza de casca de arroz). A resistência à compressão do material resultante desenvolveu-se muito rapidamente, alcançando valor de 11 MPa após 1 dia. A microestrutura foi analisada por microscopia eletrônica de varredura, revelando uma microestrutura compacta e a presença de materiais precursores do resíduo de cerâmica vermelha que não reagiram completamente. Os resultados indicaram a viabilidade de se produzir material geopolimérico sem usar o silicato de sódio comercial e curado em temperatura ambiente, apresentando uma opção para a produção de materiais de construção com menores impactos ambientais.

**Palavras-chave:** geopolímero, materiais alternativos, sustentabilidade, materiais de construção.

## INTRODUCTION

During the 70<sup>th</sup> General Assembly of the United Nations opening speech, the Brazilian president assumed the commitment of reducing the greenhouse gases (GHG) emissions of the country in 43% until the year of 2030, based on emissions of 2005 [1]. The development and the application of technologies able to emit less GHG are interesting for the country and also for the world, mainly by reducing global warming, affecting less the climate change. Ordinary Portland cement (OPC) is the binder most consumed in the world. In Brazil, in the year 2013, the total consumption of cement was 71 million tons, which results in 353 kg/inhabitant/year [2]. Despite its advantages,

due to the excellent mechanical performance, the OPC is highly environmentally impactful. It is estimated that the production of 1 ton of OPC releases 1 ton of CO<sub>2</sub> to the environment [3], thus contributing significantly with a GHG emission. All these numbers show the need of searching an alternative binder, produced by the alkali-activation of an aluminosilicate source, usually (but not always) designed as “geopolymer” in current literature. Other common names are: geocement, alkali-activated binder, inorganic polymer, mineral polymer and alkali-bonded ceramic [4]. This product was defined as a complex material made by the mixture of a reactive aluminosilicate with alkaline solutions [5].

Geopolymer is formed in an open hydrothermal system, having semi-crystalline or amorphous structure. An

interesting characteristic of this material is the use of different raw materials in its formulation [6], such as industrial [7], agricultural [8] and civil construction [9] wastes. When compared to an OPC concrete a geopolymeric concrete has an energy consumption 45.8% lower, and it emits about 72% less carbon dioxide to the environment [10]. Despite these advantages in environmental aspects, the alkali-activated binder has some disadvantages to overcome, such as the unproven durability, the challenging rheology [11], the lack of specific technical standards, and the absence of a uniform nomenclature to the inorganic polymers [12]. The strength-porosity relationship is applicable to a very wide range of materials (for example: cement, mortar, concrete and plaster of Paris). In order to obtain a high strength material, the geopolymer microstructure is changed. The pore size is reduced and also its interconnection [13]. The discontinuity in the pore network improves the material durability. As previously discussed, an alkali source is necessary to produce this kind of material. In this way, a mixture of NaOH and sodium silicate (SS) is the most common activator for geopolymerization [14], which is the name of the reaction that generates the geopolymer. Meanwhile, in the geopolymer production, SS synthesis is what contributes most significantly to the environmental impact (Fig. 1).

Since there is the global requirement to reduce environmental impacts, geopolymer is seen as an alternative, and the interest in expanding this technology is rising. Table I shows some of the works developed with geopolymers in the last ten years in Brazil, with the materials employed for each one. These works were developed with different materials. Metakaolin, fly ash and blast-furnace slag are the most used ones. Accurately metakaolin was employed in more than 70% of the researches. This calcined clay was used mainly in Southeast and Northeast Brazilian regions. Bearing in mind that the coal-based thermal power plants operating in Brazil are located in South region [58], it was realized that more than 75% of the researches with fly ash are coming from

this geographical location, enhancing the recycling interest. Furthermore, it was observed the application of rice husk ash (RHA) as another material on geopolymer production, used by [20, 55, 56]. Although, the rice planting is higher in South Brazilian region [59], this waste is a commercial product available in other regions of the country. None of the Table I researches that employed RHA is from South Brazilian region. Brazil has the rice harvest prediction of about 14 million tons during the 2019/2020 [60]. Following data reported by [61], it is possible to bring forth 504,000 tons of RHA in the period. So, if the entire rice husk was used as an energy source, it could have a large quantity of RHA available for this purpose. Another material in large quantities available in Brazil is red ceramic waste (RC). Data reported by [62] estimated the RC generation in Brazil of 3.9 to 6.5 million tons, and in São Paulo State of 0.780 to 1.3 million tons. RC was applied by [19, 45] researches. Due to the availability of metakaolin, RHA and RC in Brazil, it was decided to apply these materials in this research to give them an usage, avoiding the disposal in landfills, and to improve environmental and sustainable issues.

Considering the alkali activator, the use of SS in Table I studies is much often than NaOH. SS was present in more than 60% of the cited experiments in Brazil, despite its environmental disadvantages. The researchers are still using SS due to the important role which this alkaline activator plays in mechanical properties of the alkali-activated binders by improving the mechanical performance [63]. Viscosity acts in the properties of the geopolymer, which is controlled by the chemical proportion of the species in solution. The  $H_2O/Na_2O$  ratio should be constrained between 10 and 20 and the  $SiO_2/Na_2O$  ratio between 1 and 2 [64]. SS is a high viscosity solution that reduces the flow of the geopolymer, so the increase in SS causes low workability [65]. The ways to change the geopolymer rheology are different from those used in OPC products [64], since many of the admixtures are not effective in enhancing the alkali-activated binder

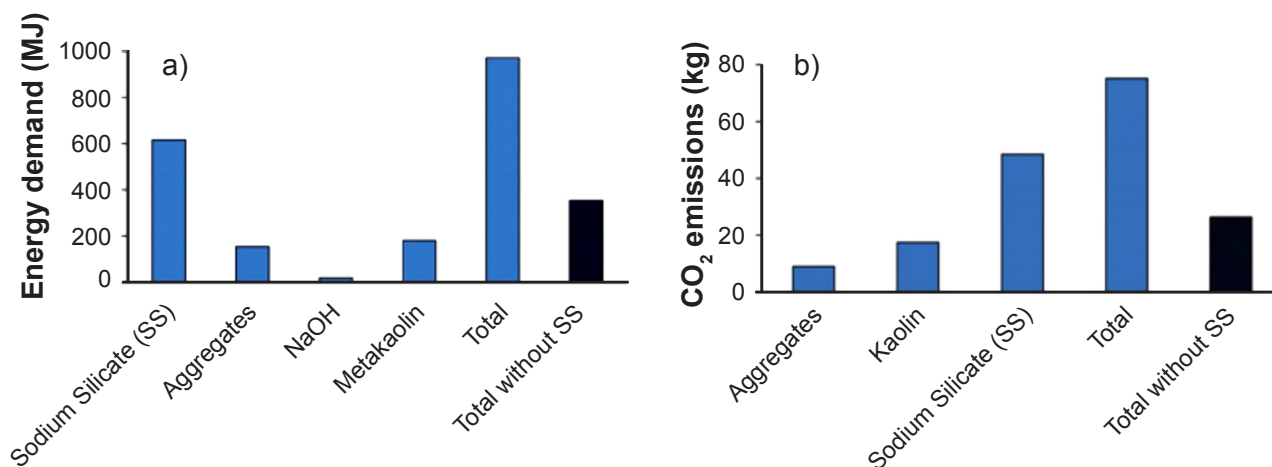


Figure 1: Energy demand (a) and carbon dioxide emission (b) in the production of 1 m³ of geopolymeric concrete (approximate data). Adapted from [10].

[Figura 1: Demanda energética (a) e emissão de dióxido de carbono (b) na produção de 1 m³ de concreto geopolimérico (dados aproximados). Adaptado de [10].]

Table I - Materials applied on geopolymers production made by Brazilian researchers.

[Tabela I - Materiais aplicados na produção de geopolímeros feitos por pesquisadores brasileiros.]

Geopolymer material	Year	Ref.
Metakaolin, granulated blast-furnace slag, SS, KOH	2005	[15]
Fly ash, NaOH, $\text{Ca(OH)}_2$	2006	[16]
Metakaolin, potassium silicate, KOH	2007	[17]
Metakaolin, SS, KOH, Portland cement with blast-furnace slag (CPII-E)	2008	[18]
Metakaolin, kaolin, kaolin waste, red ceramic waste, tropical red weathered soils, SS, NaOH, KOH	2008	[19]
Granulated blast-furnace slag, metakaolin, rice husk ash, calcined egg shell, SS, KOH	2008	[20]
Fly ash, blast-furnace slag, Portland cement with blast-furnace slag (CPIII-RS), metakaolin, SS, microsilica, KOH, NaOH	2008	[21]
Metakaolin, Portland cement with blast-furnace slag (CPII-E), SS, KOH	2009	[22]
Electric arc-furnace slag, NaOH	2009	[23]
Metakaolin, soil, potassium silicate, SS	2009	[24]
Quasicrystalline alloy system Al-Cu-Fe, metakaolin, SS	2009	[25]
Metakaolin, SS, Portland cement with pozzolan (CPII-Z), KOH	2010	[26]
Fly ash, flue dust, NaOH	2010	[27]
Fly ash, flue dust, NaOH	2011	[28]
Fly ash, NaOH, KOH	2011	[29]
Metakaolin, phyllite, Portland cement with blast-furnace slag (CPIII), SS, KOH	2011	[30]
Soil, metakaolin, SS, NaOH, Portland cement with filler (CPII-F), wash water from the biodiesel production	2011	[31]
Bauxite residue, microsilica, metakaolin, $\text{Ca(OH)}_2$ , KOH	2012	[32]
Metakaolin, quasicrystal powders, SS	2012	[33]
Metakaolin, SS	2012	[34]
Metakaolin, quasicrystal powders, SS	2012	[35]
Fly ash, sand casting, metakaolin, NaOH, SS	2012	[36]
Metakaolin, SS, NaOH, KOH, polyethylene glycol	2012	[37]
Kaolin waste, $\text{Ca(OH)}_2$	2012	[38]
Kaolin waste, $\text{Ca(OH)}_2$ , SS	2012	[39]
Metakaolin, soil, NaOH, SS	2012	[40]
NaOH, kaolin waste, granite powder waste	2013	[41]
Metakaolin, $\alpha$ -alumina, NaOH	2013	[42]
Bottom ash from coal burning, calcined paper sludge, NaOH, SS	2013	[43]
Metakaolin, weathered soil, SS	2013	[44]
NaOH, red ceramic waste	2013	[45]
Metakaolin, NaOH, SS	2013	[46]
Metakaolin, NaOH	2013	[47]
Metakaolin, SS	2013	[48]
Fly ash, NaOH, SS	2013	[49]
Fly ash, sugarcane bagasse ash, blast-furnace slag, NaOH, SS, potassium silicate, KOH	2013	[50]
Aluminum industry waste, additive, metakaolin, carbon powder, filler, NaOH	2013	[51]
Metakaolin, weathered soils, SS, potassium silicate	2014	[52]
Fly ash, NaOH, $\text{Ca(OH)}_2$	2014	[53]
Metakaolin, granulated blast-furnace slag, commercial soluble silicate, KOH	2014	[54]
Bauxite waste, rice husk ash, metakaolin, NaOH	2014	[55]
Metakaolin, NaOH, SS	2014	[10]
Rice husk ash, metakaolin, silica fume, $\text{Ca(OH)}_2$ , NaOH, KOH, SS, sodium carbonate, sugarcane bagasse ash	2014	[56]
Metakaolin, amorphous silica, potassium metasilicate solution	2015	[57]

flow [11]. Additional water can be incorporated aiming to improve the workability [65]; but, on the other hand, the increase in the water/solid mass molar ratio decreases the compressive strength of geopolymer [66]. Vargas [16] did not use SS in his work. Different curing temperatures were employed for a period of 24 h (50, 65 and 80 °C) to evaluate the influence of the curing temperature on the binder properties. The material cured at the highest temperature achieved the best compressive strength, being higher than 23 MPa after 28 days. In the same way, Vassalo [47] produced a geopolymer from metakaolin alkali-activation without employing SS. The specimens cured at room temperature provided compressive strength of about 11 MPa after 28 days.

Geopolymers have been generated from red clay brick waste cured at low temperatures [9], as well as from RHA [67]; however, the two materials have not been employed simultaneously. Na<sup>+</sup> preferably forms Si-O-Al bonds [68] that make the solid network. Overall, the alkali activation of waste materials is a suitable alternative to the clay burning process involved in fired brick production. In this study, data were collected with the purpose of evaluating some initial aspects of a geopolymer containing wastes. A building material was produced without commercial SS, not using elevated curing temperatures, optimizing the environmental benefits, and providing a starting point for further investigations. The focus was the use of this product for building materials, using wastes that are easily available in Brazil. Metakaolin (MK) geopolymers are considered a model system for such investigation [13]. For this feasibility step, MK is maintained in the formulation and then partially replaced with RHA and RC.

## EXPERIMENTAL

Geopolymers were prepared using rice husk ash (RHA) as a silicon source, and metakaolin (MK) and red ceramic waste (RC) as supplementary sources of silicon and aluminium. Their role in the mixture is detailed in Table II. The RHA is a waste from agriculture and manufactured by Silica Verde do Arroz Ltd. The final product is a powder with 97.9% passing on a 44 µm sieve. The RC is a waste from red ceramic tiles production, manufactured by Pó Piacentini. RC was ground and the powder had 98% passing on a 44 µm sieve. The MK used was the MetaStar 501 from Imerys Minerals Ltd. The chemical compositions and main elements of these materials were determined by X-ray fluorescence spectroscopy (Table III) using a wavelength dispersive X-ray spectrometer (Shimadzu XRF 1800).

Commercial NaOH in flakes was dissolved in water (7.9 M) and used as an alkali activator. Natural sand with a fineness modulus of 2.9 was added to the mixture for the mortar preparation. The starting powder materials were continuously stirred with the NaOH solution in a Fisatom 715 mixer for 5 min. The sand was gradually added to the paste and it was mixed until the achievement of homogeneous blend (more 5 min). After mixing, the slurry was cast into

Table II - Materials used and their role in the mixture.

[Tabela II - Materiais usados e suas funções na mistura.]

Material	Role
NaOH	Alkaline activator
RHA, MK, RC	Sources of silicon and/or aluminum
Water	Dissolution/workability
Sand	Aggregate

Table III - Chemical composition with the main oxides of MK, RHA and RC (wt%).

[Tabela III - Composição química com os principais óxidos do MK, RHA e RC (% em massa).]

Oxide	MK (%)	RHA (%)	RC (%)
SiO <sub>2</sub>	50.4	93.3	64.5
Al <sub>2</sub> O <sub>3</sub>	43.9	0.1	12.3
TiO <sub>2</sub>	1.0	-	1.5
Fe <sub>2</sub> O <sub>3</sub>	0.5	0.05	11.2
Na <sub>2</sub> O	0.2	-	-
K <sub>2</sub> O	0.2	1.05	6.3
MgO	0.1	0.3	1.6
CaO	-	0.6	1.2
Moisture	2.6	1.1	-

cubic moulds (50 mm × 50 mm × 50 mm). The specimens were cured in air at room temperature (average of 25 °C and relative humidity of 60%) until the testing age. The resulting component ratios were SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.38, SiO<sub>2</sub>/Na<sub>2</sub>O = 1.2, H<sub>2</sub>O/Na<sub>2</sub>O = 12.1, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1.0, and binder:sand = 1:6.2.

The specimens were submitted to compressive strength testing at 1 and 90 days to evaluate the strength development over time. Compressive strength tests were performed on a Versa Tester testing machine (maximum load of 150 kN). X-ray diffraction (XRD) patterns were collected in a Philips Analytical X-ray (X'Pert-MPD) with CuKα radiation (1.54060 Å), 40 kV, 40 mA, and in the 2θ range from 5 to 60°. Scanning electron microscopy (SEM) studies were conducted using a SEM-EDX LEO microscope, Oxford 440i, with 20 kV and 100 pA.

## RESULTS AND DISCUSSION

The mixture presented a fast setting time due to the relative high silicon content used in the mixture as previously described by [9]. The compressive strength was 11 MPa after 1 day, which is already higher than that required by Brazilian technical standards for non-structural hollow soil-cement blocks [69], hollow ceramic blocks for non load-bearing masonry [70], and hollow concrete blocks for concrete masonry [71], considering the age of 28 days. The geopolymerization kinetics and curing are faster for sodium hydroxide activation of metakaolin [72]. These results show an interesting possibility for precast companies and suggest



that additional sand can be used, the amount of geopolymer can be reduced, and the material properties are more suitable for brick applications. The strength after one day cured at room temperature was comparable to that of the strength of

geopolymer made with red clay brick waste cured for 3 days at 65 °C [9].

The high silica content in RHA opens the possibility of applying it in geopolymer production. An alternative SS, produced with silica RHA dissolution was proposed by [8]. This originated a material with compressive strength results very similar to materials produced with conventional SS. In this work, RHA did not have any kind of previous step to dissolve the silica. Probably, a previous dissolution could allow even higher results. After 90 days, the geopolymer strength was 22 MPa. A higher or a lower strength would be possible depending on the alkali-activating solution. The strength after three months was comparable to that of alkali-activated ground fly ash made with a NaOH solution [5] and optimal strength geopolymers made with red mud and RHA [67]. From XRD analyses (Fig. 2), in addition to the crystalline structures of quartz in the sand and RC, the amorphous nature of the geopolymer was visible with maxima at  $2\theta$  of 27°. Between the  $2\theta$  values of 22° and 27°, two peaks from RC were observed and confirmed by separate XRD analyses of this raw material.

SEM images of the geopolymer microstructure at 1 day (Figs. 3a to 3c) and 90 days (Figs. 3d to 3f) show unreacted materials and interconnected pores, as reported for geopolymers having a Si/Al ratio comparable to these experiments [13] and for geopolymers with ceramic wastes [9]. In Fig. 3f, crystal formation after 90 days is evident and also visible in the geopolymer made with RHA [67]. When exposed to controlled temperature (23 °C) the geopolymer presented low signals of efflorescence with time, as also observed with EDX. This observation was found in previous work when curing was conducted at room temperature [73].

As recently highlighted, geopolymers might have a great influence in other impact categories than global

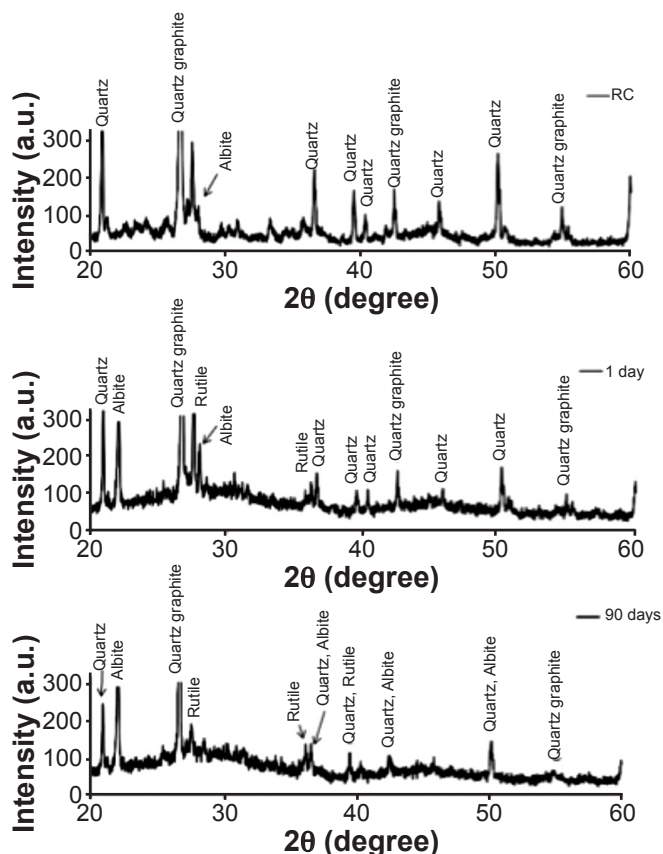


Figure 2: X-ray diffraction patterns of the specimens.  
[Figura 2: Difractogramas de raios X das amostras.]

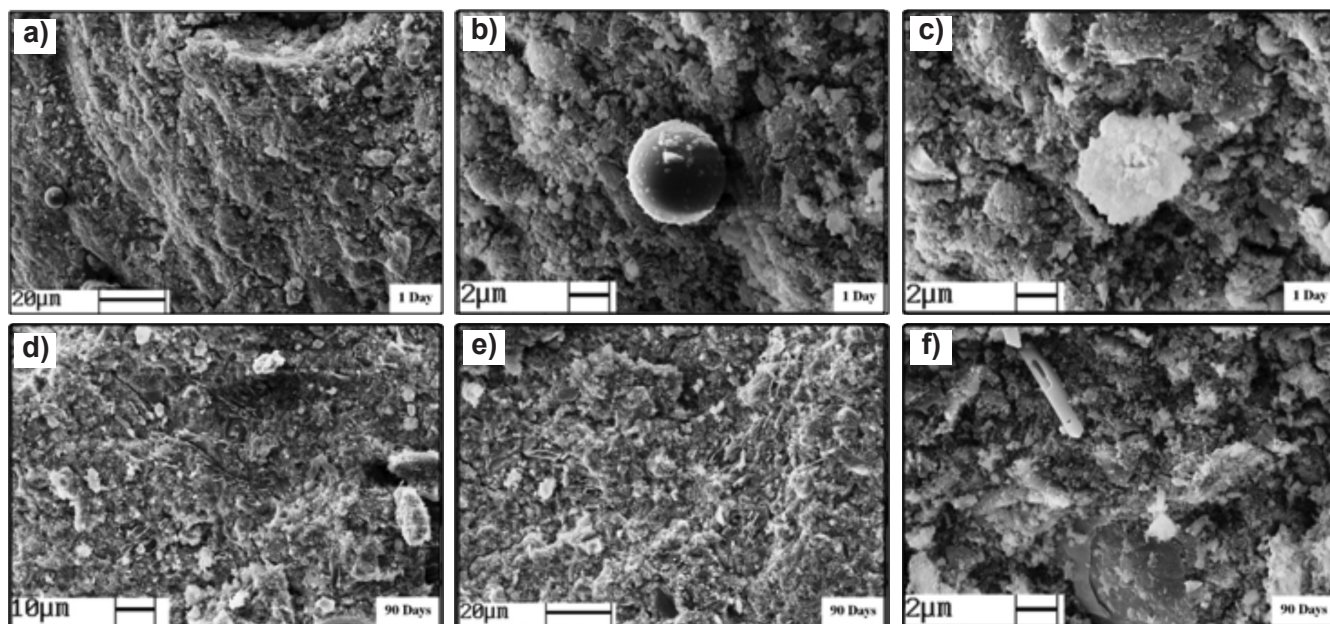


Figure 3: SEM micrographs of geopolymers after 1 day (a, b, c) and 90 days (d, e, f).

[Figura 3: Micrografias obtidas por microscopia eletrônica de varredura dos geopolímeros após 1 dia (a, b, c) e 90 dias (d, e, f).]

warming, due to the use of SS solution [74], and remain as an alternative to reduce greenhouse gas emissions [75]. The strength of alkali-activated material correlates with NaOH content. At lower alkali activation, geopolymers have a compressive strength of 13 MPa [76]. The required strength of a brick for a wall is around 5 MPa. Reducing the alkali activation process and further improving the environmental assessment of the geopolymer are the next research steps.

## CONCLUSIONS

This work studied the civil construction and agriculture wastes to produce an alkali-activated material to be employed as building materials. In Brazil there are few studies using this kind of wastes to make geopolymer binders, and the most of the works uses commercial sodium silicate which causes high environmental impact. Geopolymers containing red ceramic waste and rice husk ash achieved compressive strengths of 11 MPa after 1 day and 22 MPa after 90 days. X-ray diffraction and scanning electron microscopy indicated the amorphous stage of the geopolymer, and also the crystal formation. This showed that the building materials production is feasible, and the strength can be diminished to reach the values recommended by the standards. The sand content must be increased, and the Na solution molality can be reduced. Further studies include the alkali activation process optimization to produce geopolymers that are suitable for eco-friendly bricks with metakaolin and materials locally available in Brazil, the rheology of geopolymerization with recycled materials and the resulting porosity of the products. It is possible to have high-strength building materials by increasing the Si/Al ratio which means to increase the material reactivity. In the near future, it will be possible to optimize this binder by using materials that are locally available with less environmental impact.

## ACKNOWLEDGEMENTS

We acknowledge the National Council for Scientific and Technological Development - CNPq, CAPES and FAEPEX-UNICAMP for their financial support. We thank Prof. Guillaume Habert for his assistance and comments in writing. Prof. Carlos Eduardo Marmorato Gomes is gratefully acknowledged for supplying the RHA and Flaviano Fernandes for the assistance in the XRD analyses. The metakaolin was kindly provided by Bill Bryant from Imerys.

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(Rec. 02/03/2016, Rev. 05/05/2016, Ac. 13/06/2016)