







## Preparation and Characterization of Geopolymers Obtained from Alkaline Activated Hollow Brick Waste

Lauren Rayna Lima Colnago<sup>a\*</sup> , Ana Karla Vieira Santos<sup>a</sup> , Bruno dos Santos Potensa<sup>a</sup> ,  
Felipe Pires Chaves<sup>a</sup>, Gleyson Tadeu de Almeida Santos<sup>a</sup> , Agda Eunice de Souza<sup>a</sup> ,  
Silvio Rainho Teixeira<sup>a</sup> 

<sup>a</sup>Universidade Estadual Paulista (UNESP), Faculdade de Ciências e Tecnologia, Laboratório de Caracterização e Gestão de Resíduos Sólidos (LCGRS), Presidente Prudente, SP, Brasil.

Received: April 30, 2024; Revised: July 5, 2024; Accepted: July 12, 2024

Geopolymers are inorganic polymers obtained through the alkaline activation of aluminosilicates. Due to their cementitious properties, they are being studied as a sustainable alternative to Portland cement. Red ceramic waste (RCW), being a source of silica and alumina, can serve as a precursor for producing geopolymers. In this work, we evaluated the feasibility of producing geopolymers from hollow brick (HB) and hydrated lime, using only sodium hydroxide as an alkaline activator. The test specimens were prepared replacement HB by up to 30 wt% of hydrated lime, aiming to evaluate the compressive strength after 7 and 28 curing days of the geopolymer produced. The results showed that samples with 30 wt% of hydrated lime, achieved the highest compressive strength (11.26 MPa) after 28 days of curing, although all values found were above the limit established by Brazilian standards for modular geopolymer bricks. The results therefore show a sustainable and widely viable implementation alternative to reduce the environmental impacts caused by the production of Portland cement.

**Keywords:** *Geopolymer, activating solution, hydrated lime, hollow brick.*

### 1. Introduction

The construction industry is a sector of great importance for global economic development. However, it is also responsible for a significant portion of the environmental impact caused by human actions.

Additionally, in 2021, Brazilian municipalities collected over 48 million tons of construction and demolition waste (CDW), with a notable contribution from red ceramic waste (RCW)<sup>1</sup>.

According to data provided by the National Association of the Ceramic Industry<sup>2</sup>, there are approximately 5,578 ceramics and pottery workshops spread across Brazil, contributing to an annual production of over 5 billion ceramic blocks. During the production process, the ceramic sector generates a considerable volume of waste due to fragmentation, non-conformities, and irregular firing of pieces, often lacking environmentally appropriate management.

Ceramic materials, due to their richness in aluminosilicates, can form geopolymers in an alkaline solution<sup>3</sup>, serving as a promising alternative cementitious agent to conventional cement, given that Portland cement production generates 1.35 billion tons of greenhouse gases annually, accounting for approximately 6% to 9% of global emissions<sup>4</sup>. One innovative approach is to incorporate supplementary cementitious materials that can replace clinker partially in the Portland cement, which can be derived from natural materials or industrial by-products such as fly ash, blast furnace slag,

rice husk ash, silica fume, metakaolin, volcanic ash, calcined clays, pumice, waste glass powder, and palm oil fuel ash<sup>5</sup>. The use of alternative materials, such as ceramic materials rich in aluminosilicates, is, therefore, a viable and sustainable alternative for the production of binder materials and/or materials with cementitious properties like Portland cement.

Geopolymer, as an emerging environmentally friendly construction material, has gained significant attention and application in the field of architecture<sup>6</sup>. In general, the geopolymer is considered a green cementitious material with higher strength and better resistance to acids, sulfate, and heat, compared to Portland cement<sup>7</sup>.

Geopolymers emerged from research conducted by Joseph Davidovits to discover new heat-resistant materials in the form of non-flammable and non-combustible “plastic-like” substances after several catastrophic fires in France during the 1970s. The term “geopolymer” was coined because the raw materials used in its synthesis are primarily minerals of geological origin<sup>8,9</sup>.

The geopolymerization process consists mainly of dissolution, coagulation, condensation, and crystallization reactions, where the first step consists of breaking the Si-O-Si and Al-O-Si covalent bonds when the pH of the solution increases and the groups are transformed into colloidal phase. After this, the bond-breaking products are accumulated and interact with each other to form a coagulated structure which is then led to a third phase with the generation of a

\*e-mail: [lauren.colnago@unesp.br](mailto:lauren.colnago@unesp.br)

condensed structure. With time and temperature, they can develop a crystallization phase<sup>6,10</sup>.

Geopolymers have numerous applications, including materials for thermal insulation, coating, and adhesives resins, biotechnologies (materials for medical applications), foundry industry, cement and concrete, low-energy construction materials, composites for infrastructure repair and reinforcement, high-tech composites for aircraft and automotive interiors, high-tech resin systems, containment of radioactive and toxic waste, arts and decoration, among others<sup>8</sup>.

In this work, a geopolymer was developed using red ceramic waste as a source of aluminosilicate to act as a cementitious precursor, together with sodium hydroxide as an alkaline activator. The results of this study suggest a simple, feasible, and sustainable strategy to mitigate the environmental problems caused by the improper disposal of these wastes, as well as to reduce the impacts caused by Portland cement production.

## 2. Materials and Methods

### 2.1. Preparation and characterization of red ceramic waste

Red ceramic perforated hollow brick (HB) waste was used as a precursor material to geopolymer test specimens. Initially, the waste was subjected to a crushing procedure using a jaw crusher to reduce the initial material size. Subsequently, the waste fragments were added to a pulverizing mill using iron pans and rings (Marconi, MA-360 model) programmed to rotate for 6 minutes. The pulverized waste was sieved through a 100-mesh screen to achieve a particle size of  $\leq 150 \mu\text{m}$ . These particle sizes are important to the geopolymer reaction.

The HB powder was characterized by: (1) X-ray diffraction (XRD) using Shimadzu instruments (XRD-6000), with Cu-K $\alpha$  radiation source,  $\lambda = 1.5444 \text{ \AA}$ , in an angular scan from  $5^\circ$  to  $60^\circ$  ( $2\theta$ ); (2) X-ray fluorescence (FRX) using the Shimadzu (EDX-7000) instrument, with a scanning capability from Sodium (Na) to Uranium (U), and a primary Rhodium (Rh) radiation source, focused on a 5 mm diameter collimator and sample holder containing mayler. The analysis was carried out using a qualitative-quantitative method under a vacuum atmosphere; (3) FTIR analysis using Perkin Elmer Frontier IR equipment equipped with a diamond ATR module, with a measurement range of  $500\text{-}2000 \text{ cm}^{-1}$ .

### 2.2. Preparation and characterization of geopolymer specimens

Initially, an activator solution of NaOH (Synth, 97% purity) 8 mol/L was prepared. Then a solid mixture of pulverized HB with 0, 10, 20, and 30 wt% of hydrated lime was prepared. Next, a geopolymer material was prepared using 16.7 mL of the NaOH activating solution together with 65 g of solid mixture, setting the liquid-solid ratio at 0.26. The geopolymer materials were manually mixed until achieving homogeneity.

The specimens were prepared using a cylindrical mold (3 cm in diameter x 6 cm in height) in a manual hydraulic press (Carlsons) and a compaction pressure of 0.5 ton.

Three specimens were prepared for each hydrated lime concentration, totaling 12 specimens for each curing time (7 and 28 days, at room temperature). Compression tests were carried out on each specimen, using a universal testing machine (Instron/EMIC 23-100), applying a loading rate of 1mm/min with a 10 kN load cell.

Fragments of the specimens after the mechanical test were powdered, and used for FTIR characterization, seeking to evaluate molecular interactions and/or functional groups in the geopolymer after the curing process. FTIR analysis was carried out using Perkin Elmer Frontier IR equipment equipped with a diamond ATR module, with a measurement range of  $500\text{-}2000 \text{ cm}^{-1}$ .

## 3. Results and Discussion

### 3.1. Characterization of the ceramic waste

The mineralogical compositions of the HB waste are shown in Figure 1. According to the X-ray diffraction pattern, some crystallinity peaks were identified in the HB due to the presence of quartz (JCPDF: 89-8936), hematite (JCPDF:79-7), and rutile (JCPDF: 76-319). The identification of quartz is related to the sand present in the “clay” used for brick production. The reddish color of the HB indicates the presence of iron oxides identified by the hematite peaks and rutile by the titanium oxide (TiO<sub>2</sub>) content. These compounds are confirmed by chemical analysis using X-ray fluorescence (Table 1), highlighting the majority presence of silicon aluminum, and iron oxides, commonly found in red ceramics<sup>11,12</sup>.

### 3.2. Characterization of geopolymer specimens

The geopolymer specimens exhibited efflorescence, particularly those cured for 7 days. The occurrence of this phenomenon may have been facilitated because they were not wrapped during the curing period, remaining in contact with the ambient air. Efflorescence, which involves a superficial formation resulting from the deposition of salts leached from alkali carbonation, is a recurring phenomenon in laboratory situations but is not widely researched and reported by the scientific Community<sup>13</sup>. Zhao et al.<sup>7</sup> reported that the formation of geopolymer efflorescence is a rapid process

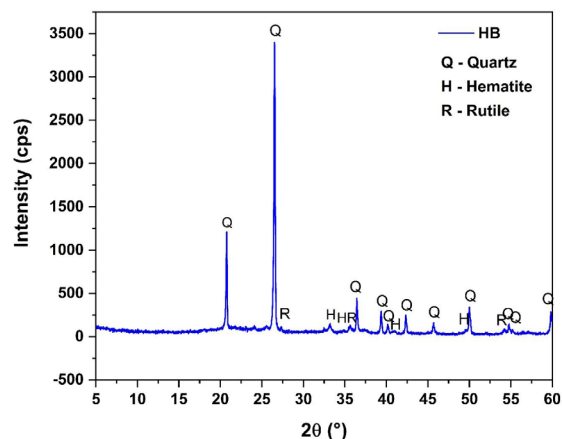
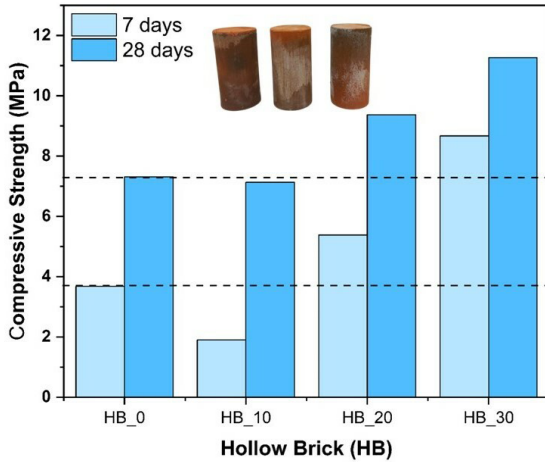


Figure 1. XRD of hollow bricks waste.

**Table 1.** Chemical composition of hollow bricks waste.

Oxide, %	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>	K <sub>2</sub> O	CaO	Other
HB	62.23	17.49	8.61	5.81	2.06	1.77	0.30	1.73

**Figure 2.** Compressive strength of geopolymers.

in the early stage, consistent with the constant leaching concentration of alkali ions after reaching the reaction peak. Therefore, the effects appear after 7 days of healing. According to the authors, less sufficient dissolution of the solid alkaline activator in the geopolymer results in a higher concentration of unreacted alkali in the matrix. This higher concentration of alkali, in turn, could continuously dissolve and leach onto the sample surface along with pore solutions under the action of water capillary pressure, which results in a crystallization characteristic of efflorescence<sup>7</sup>.

Figure 2 shows the efflorescence of some specimens, together with the results of compressive strength tests. It is observed that, for all tests, there was an increase in mechanical strength with the extended curing time of the material. The average mechanical strength of the test samples with the replacement of HB by 30% hydrated lime was higher compared to the others, reaching 11.26 MPa at 28 days of curing. The second highest strength was obtained by replacing HB with 20% of the hydrated lime, resulting in 9.37 MPa. The test without replacing HB with lime shows a higher average strength compared to the 10% replacement. Without the addition of hydrated lime, the mechanical strength of the geopolymer was 7.31 MPa. For the 20% replacement of HB with hydrated lime, the geopolymer achieved a mechanical strength of 7.13 MPa, representing the lowest strength observed. The results indicated that the use of hydrated lime at a concentration of 30% enhanced the hardening and strength of the HB-based geopolymer. All these results are shown in Table 2, including the composition of the geopolymer specimen.

Table 3 shows that the compressive strength results are slightly below other values found in the literature. However, it can be observed that other studies use different parameters, such as the use of two alkaline activators. It is already known that sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) provides both sodium ions (Na<sup>+</sup>) and silicate ions (SiO<sub>4</sub><sup>4-</sup>) directly, which are essential for the formation of the aluminosilicate structure in the

**Table 2.** Specimen data according to test and curing time.

Test	HB (g)	Hydrated lime (g)	NaOH (mL)	Strength (MPa)
7 curing days				
HB_0	65	0	16.7	3.68
HB_10	58.5	6.5	16.7	1.90
HB_20	52	13	16.7	5.38
HB_30	45.5	19.5	16.7	8.67
28 curing days				
HB_0	65	0	16.7	7.31
HB_10	58.5	6.5	16.7	7.13
HB_20	52	13	16.7	9.37
HB_30	45.5	19.5	16.7	11.26

geopolymer. The silicate ions are readily available to react with the aluminum ions present in the solution, facilitating the formation of Si-O-Al bonds, which are the basis of the geopolymer structure. This generates silica-rich structures responsible for forming a denser matrix, resulting in higher mechanical properties. On the other hand, NaOH provides only sodium and hydroxide ions (OH<sup>-</sup>). Although the OH<sup>-</sup> ions help in the dissolution of aluminosilicates present in the raw material, such as HB, the absence of silicate ions requires that all the silicon necessary for the formation of the geopolymer be supplied by the dissolution of the starting material, which can be a slower and less efficient process. Consequently, the final material is less compact and less resistant.

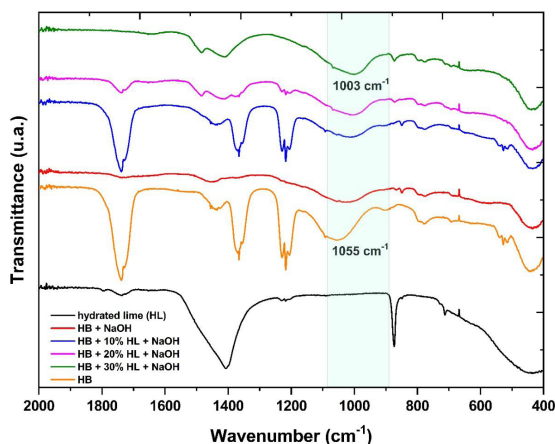
Other factors that may influence the compressive strength results of the works cataloged in Table 3 are the presence of metakaolin and sand in geopolymeric compositions. Similar to Na-Si-based alkaline activators, metakaolin is crucial as it is the main source of reactive silicon and aluminum, promoting the formation of aluminosilicate that constitutes the geopolymer structure. Sand, on the other hand, acts as an aggregate that increases density, distributes stresses, and fills voids, improving the integrity and mechanical strength of the material.

In a study using hydrated lime as a composite activator for the production of modular bricks, it was observed that its utilization contributed to achieving the compressive strength values established by the Brazilian reference standard<sup>18</sup> that corresponds to 2 MPa for geopolymer modular brick. This can be explained by the fact that the addition of hydrated lime facilitated greater dissolution of aluminosilicates, favoring polycondensation and contributing to the enhancement of the geopolymer's mechanical strength<sup>19</sup>.

Figure 3 shows the FTIR spectrum of the materials. It is observed that the unreacted precursor exhibited a band with a wavenumber of 1055 cm<sup>-1</sup>. The material reacted with a 30% substitution of hydrated lime displayed a band with a wavenumber of 1003 cm<sup>-1</sup>. Furthermore, the other reacted materials also exhibited a shift in band position relative to the precursor toward lower wavenumbers.

**Table 3.** Comparative analysis of different geopolymer composition and its strength compressive.

Waste	Sample Composition	Geopolymer composition variations	Alcaline activators	Cure time (days)	Maximum compressive strength	Ref
Red ceramic waste (TW)	60% sand + 20% activators + 20% binder (metakaolin MK+TW)	MK:TW 20:0 13.4:6.6 10:10 6.6:13.4	Na <sub>2</sub> SiO <sub>3</sub> NaOH (13M)	28	~50MPa to binder 10MK:10TW	Sarkar and Dana <sup>14</sup>
Sewage sludge ash (SSA) and Ground granulated blast-furnace slag (GGBS)	50% SSA + 50% GGBS	Addition of 0, 5, 10, 15% of silica fume	Na <sub>2</sub> SiO <sub>3</sub> NaOH	28	57MPa to 10% silica fume	Zhao et al. <sup>7</sup>
Demolition waste powder (DWP) and ground Granulated Blast Furnace Slag (GGBS)	GGBS + DWP	Replacement of 0, 5, 10, 15, 20% of GGBS by DWP	Na <sub>2</sub> SiO <sub>3</sub> NaOH (3, 4 and 6M)	7	~38MPa to 0% DWP and NaOH 6M	Roy and Islam <sup>15</sup>
Iron mine (Hem)	Metakaolin + iron mine	Replacement of 0, 10, 20, 30, 40, 50% of metakaolin by iron mine	Na <sub>2</sub> SiO <sub>3</sub> NaOH	90	~41MPa to 0% iron mine	Santos et al. <sup>16</sup>
Ceramic waste aggregate (CWA): Bricks (BR), floor tiles (FT), roof tiles (RT), sanitary ware (ST)	70% ceramic waste + 30% binder (60% fly ash and 40% alkaline solution)	Replacement of 0, 25, 50% of a sand river by each CWA	Na <sub>2</sub> SiO <sub>3</sub> NaOH (14M)	7, 14, and 28	~47MPa to 50% ST at 28 days	Yanti et al. <sup>17</sup>
Red ceramic: hollow brick (HB)	HB + hydrated lime	Replacement of 0, 10, 20, and 30 wt% of HB by hydrated lime	NaOH (8M)	7 and 28	~11MPa to 50% hydrated lime at 28 days	This work

**Figure 3.** FTIR of hollow brick waste, hydrated lime and geopolymers.

For hydrated lime, the bands at 873 and 711 cm<sup>-1</sup> are related to calcite, CaCO<sub>3</sub>, O-C-O bond. The band around 1408 cm<sup>-1</sup> is related to the CO<sub>3</sub><sup>2-</sup> ion<sup>20</sup>. This band can vary to nearby wavelength ranges, due to the presence of other bonds in the three-dimensional geopolymer network<sup>7</sup>, for example, observed the presence of CO<sub>3</sub><sup>2-</sup> in the 1427-1454 cm<sup>-1</sup> interval. For the authors, the vibration peak of O-C-O is mainly due to the reaction of CO<sub>2</sub> in the atmosphere with OH<sup>-</sup> in the geopolymer, also called subflorescence. When analyzing the unreacted precursor, the bands located at 446 cm<sup>-1</sup>,

528 cm<sup>-1</sup>, and 895 cm<sup>-1</sup> are associated with the flexural vibration of Si-O-Si and Si-O-Al molecules. Additionally, the bands at 693 cm<sup>-1</sup>, 779 cm<sup>-1</sup>, and 1055 cm<sup>-1</sup> correspond to the stretching vibration of Si-O bonds<sup>14</sup>.

The absorption bands at 1080-1050 cm<sup>-1</sup> correspond to the asymmetric stretching vibrations of Si-O-Si, while the bands at 1010-980 cm<sup>-1</sup> represent the stretching vibrations of Si-O-Al<sup>21</sup>. Consequently, the primary evidence of geopolymer formation can be observed by the shift of the broadband from 1055 cm<sup>-1</sup> to a lower wavenumber of 1003 cm<sup>-1</sup>. This band is associated with the fusion of Si-O and Al-O bonds, leading to alterations in the material microstructure and confirming the occurrence of the geopolymerization reaction<sup>22</sup>.

## 4. Conclusions

The results of this study showed that red ceramic waste (hollow blocks) exhibits physicochemical characteristics compatible with cementitious materials in the presence of hydrated lime, using only NaOH as the alkaline activator. The produced geopolymeric specimens showed a compressive strength of up to 11.26 MPa, with a replacement of 30 wt% of hollow blocks with hydrated lime after 28 curing days. All the compressive strength results were above the limits established by Brazilian standards for the production of modular geopolymer blocks. The geopolymeric reactions were confirmed by FTIR, where characteristic bands of Si-O and Al-O bonds were evident. These results, therefore,

demonstrate the versatility of obtaining geopolymers from red ceramic waste, contributing sustainable alternatives to minimize the impacts caused by Portland cement production.

## 5. References

- Abrelpe: Brazilian Association of Public Cleaning and Special Waste Companies. Overview of solid waste in Brazil 2022 [Internet]. 2022 [cited 2024 Apr 11]. Available from: [https://edisciplinas.usp.br/pluginfile.php/7758785/mod\\_resource/content/1/Panorama\\_Abrelpe\\_2022.pdf](https://edisciplinas.usp.br/pluginfile.php/7758785/mod_resource/content/1/Panorama_Abrelpe_2022.pdf)
- Anicer: National Association of the Ceramic Industry. Industry data [Internet]. 2023 [cited 2024 Apr 11]. Available from: <https://www.anicer.com.br/anicer/setor/>
- Maccarini HS. Development of a geopolymer from the use of metakaolin. In: Joinville Center of the Federal University of Santa Catarina (UFSC). Proceedings. Institutional Repository of UFSC; 2015. p. 58
- Alhawat M, Ashraf A, Yildirim G, Aldemir A, Sahmaran M. Properties of geopolymers sourced from construction and demolition waste: a review. *J Build Eng*. 2022;50:104104.
- Madirisha MM, Dada OR, Ikotun BD. Chemical fundamentals of geopolymers in sustainable construction. *Materials Today Sustainability*. 2024;27:100842.
- Zhang Y, Liu X, Wang C, Zhang Z, Jiang S, Ma Z. Development of sustainable geopolymer with excavation soil powder as precursor: cementitious properties and thermal-activated modification. *J Build Eng*. 2024;91:109745.
- Zhao O, Ma C, Lu X, Huang B, Chen Z, Lian C. Effect of silica fume on the efflorescence, strength, and micro-properties of one-part geopolymer incorporating sewage sludge ash. *Constr Build Mater*. 2024;436:136840.
- Davidovits J. Properties of geopolymer cement. Kiev, Ukraine: Geopolymer Institute Alkaline Cements and Concretes; 1994.
- Davidovits J. Geopolymers: ceramic-like inorganic polymers. *Journal of Ceramic Science and Technology*. 2017;8:335-49.
- Zhuang XY. Fly ash-based geopolymer: clean production properties and applications. *J Clean Prod*. 2016;125:253-67.
- Cherene MGP, Xavier GC, Barroso LS, Oliveira JSM, Azevedo ARG, Vieira CM, et al. Technological and microstructural perspective of the use of ceramic waste in cement-based mortars. *Constr Build Mater*. 2023;367:130256.
- Rakcho Y, Mouiya M, Abouliatim Y, Bouazizi A, Sahaqui H, Mansouri S, et al. Effect of firing temperature on porous ceramic properties fabricated by Moroccan red clay and oil shale. *Mater Today Proc*. (In press)
- Longhi MA. Efflorescence in metakaolin-based geopolymers: formation, effects, and mitigation [thesis]. Porto Alegre: UFRGS; 2019.
- Sarkar M, Dana K. Partial replacement of metakaolin with red ceramic waste in geopolymer. *Ceram Int*. 2021;47:3473-83.
- Roy A, Islam GMS. Geopolymer using different size fractions of recycled brick-based mixed demolition waste. *Cleaner Materials*. 2024;11:100224.
- Santos A, Andrejkovičová S, Perná I, Almeida F, Rocha F. Mechanical and thermal properties of geopolymers derived from metakaolin with iron mine waste. *Appl Clay Sci*. 2024;258:107452.
- Yanti ED, Mubarak L, Erlangga BD, Widyaningsih E, Pratiwi I, Rinovian A, et al. Utilization of various ceramic waste as fine aggregate replacement into fly ash-based geopolymer. *Mater Lett*. 2024;357:135651.
- Associação Brasileira de Normas Técnicas. NBR 8491 - Solid Soil-Cement Brick: Specification. Rio de Janeiro: ABNT; 2012.
- Gonçalves LF. C. Study of alkali-activation in the production of ecological modular bricks [dissertation]. Guaratinguetá: São Paulo State University; 2022.
- Cizer Ö, Rodriguez-Navarro C, Ruiz-Agudo E, Elsen J, Van Gemert D, Van Balen K. Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime. *J Mater Sci*. 2012;47(16):6151-65.
- Catauro M, Papale F, Lamanna G, Bollinno F. Geopolymer/PEG Hybrid materials synthesis and investigation of the polymer influence on microstructure and mechanical behavior. *Mater Res*. 2015;18(4):698-705.
- Valcke SLA, Pipilikaki P, Fischer HR, Verkuijlen MHW, Eck ERH. FT-IR and <sup>29</sup>Si-NMR for evaluating aluminium-silicate precursors for geopolymers. *Mater Struct*. 2015;48(3):557-69.