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Comparison of geopolymer and cement as solidification matrixes for radwaste oil treated with bentonite

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ABSTRACT

Lubricating oils in nuclear power plants may contaminate with radionuclides and become a challenging radwaste for treatment because they decompose in storage and disposal. In addition, conventional methods of immobilization in cement should be checked. This work intends to compare cement and geopolymer used to solidify lubricating oil previously decontaminate using bentonite as sorbent material. Cement is a well-known matrix for radwaste immobilization and geopolymer (alkali-activated material) has been proposed as a new immobilization technology, due to its advantages comparing to cement and bitumen. The geopolymers are cementitious binders formed by aluminosilicates activated in alkaline medium. Synthesis occurs by means of polymerization or polycondensation reactions from the dissolution of SiO_4^{4-} and AlO_4^{5-} ions of the aluminosilicates in a highly alkaline solution. After the treatment of the oil radwaste, the contaminated bentonite was immobilized in geopolymer and cement matrix and the final immobilized waste properties were evaluated: compressive strength and homogeneity. The compressive strength result in cement matrix specimens (13.38 MPa) has been higher than in geopolymer matrix (5.96 MPa). Nevertheless, when the homogeneity was compared, the resultant waste in geopolymer presented an aspect more homogeneous than in the cement matrix. The results showed that the contaminated bentonite was not distributed homogeneously in cement matrix, for this reason the cement was not adequate to solidify the simulated waste. The compressive strength result for the waste in geopolymer matrix did not meet the Brazilian waste acceptance criteria. Therefore, new compositions of geopolymer matrix using less water will be carried out to improve the compressive strength and reach the recommended by Brazilian legislations.

Keywords: **radwaste oil, cement, geopolymer.**

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1. INTRODUCTION

Radioactive wastes are generated from different sources due to human nuclear activities. They should be managed to ensure human health and environmental protection.

Nuclear power plants (NPP) and nuclear accidents constitute the major sources of radioactive waste. The operational activities of the NPP origin many types of radioactive waste, among them, contaminated lubricating oil. Lubricating oils are used in many areas of a NPP and they can be easily contaminated with radionuclides if the oil mixes with water and other contaminants from the nuclear reactor system [1].

This kind of waste must be treated and immobilized for final disposal. Some researchers conducted studies on physicochemical treatment to remove radionuclides from oil. Also, the use of sorption on bentonite to decontaminate lubricant oils is a common practice for the non-radioactive ones. Previous studies have shown that bentonite can be used as sorbent material of radionuclides in simulated radwaste oil [2].

Conventional systems for immobilization of radioactive waste consist of Portland cement, waste and water. Additionally, the nuclear industry may add selective sorbents for radionuclides to the cement formulation, in order to increase the binding power for selected nuclides, e.g. Cs. Examples of substances added for this purpose include zeolites, bentonite and vermiculite [3].

A novel technology has been studied for radwaste immobilization, using alkali-activated material (geopolymer). The geopolymer type materials are made from alkali silicate (sodium, potassium) and metakolin. This type of cement is both new and old: old in the sense that it has a history of patenting and small-scale application extending over more than a century but new in as much as it has only recently been considered for use in structural and large-scale applications. Basically, the reactants are kaolin, a naturally occurring clay mineral, calcined at 700-800ºC so as to expel structural water but at low enough temperature partially to preserve the basic layer structure of the precursor mineral. The resulting powder is mixed with a concentrated aqueous solution of alkali silicate; the sodium silicate is known as “water glass”. Waste is added at the fluid stage [3].

The geopolymer technology results in a product that can be easily handled, stored and monitored, because its production is done with simple technology. The production of one ton of geopolymeric cement from kaolin emits 0.180 ton of CO_2 [4]. To produce one ton of Portland cement, one ton of CO_2 is emitted, because the clinker is calcined at about 1500°C. Thus, the production of geopolymer emits approximately six times less CO_2 than cement [5].

The geopolymer technology has many benefits comparing to other immobilization technologies: less greenhouse gases emission, good mechanical properties, fire and acid resistance. It may also be produced from waste material, like fly ash, blast furnace slags, bauxite residues, clays and tailings, reducing its footprint. Geopolymer concrete products would reduce or eliminate the need for a large energy requirement, as they may be cured at ambient or moderate temperatures, further reducing greenhouse gas emissions [6,7]. However, most alkali-activated cement suffer from severe efflorescence, a reaction originated by the fact that the alkaline and/or soluble silicates that are added during processing cannot be totally consumed [8].

In this study, a company of sand extraction for civil construction, located in Inhaúma, Minas Gerais, Brazil, provided samples of kaolinite, a by-product of their operation. Due to the difficulty of commercialization, the kaolinite is considered a waste, being stored in piles. The goals of this work are to characterize the samples of kaolinite and develop geopolymers from them. This geopolymers and cement will be used to immobilize the bentonite used to remove radionuclides from radioactive waste oil and both matrixes will be compared.

2. MATERIALS AND METHODS

2.1. Kaolinite charcaterization

A company of sand extraction for civil construction, located in Inhaúma, Minas Gerais, Brazil, provided samples of kaolinite, a by-product of their operation. The samples had different greyish colors according to the depth at which they were collected. The gray coloration becomes darker at greater depths. The samples were dried at 120^oC for 24 hours before comminution performed in jaw and planetary mills to reduce the particle size. After sieving in 16 # sieves, the retained portion was disaggregated with the use of rollers. The metakaolin was obtained by calcination of the kaolinite in a muffle kiln at 800°C for 8 hours and heating rate of $10^oC.min^{-1}$.

The samples were characterized by X-ray diffraction, X-ray fluorescence, particle size distribution, specific surface area, density, Fourier transform infrared spectroscopy (FTIR), and thermal analysis. The X-ray diffraction (XRD) was performed to evaluate the mineralogical phases of the material. The analysis was performed in D\Max Última Plus diffractometer with copper Kα radiation, power 40 kV and current of 30 mA. X-ray fluorescence (XFR) was carried out on Shimadzu equipment EDX-720 model and it was used to identify and quantify the elements present in samples of kaolinite. The particle size distribution, specific surface area and density were carried out on Quantachrome Nova 2000 series equipment. Infrared spectroscopy of kaolinite samples before and after the calcination at 800°C (formation of metakaolin) was carried out on ABB Bomem MB equipment. Thermal analysis for the determination of mass loss and endothermic and exothermic events in metakaolin were performed by differential scanning calorimetry (DSC) at 120^{o}C for 24 hours in air, heating rate at $10^{o}C.min^{-1}$, N_2 atmosphere in a STA 449 F3 Júpiter from Netzsch instrument.

2.2. Simulated Waste

Two kinds of lubricating oils, Mobil Turbina 46 and Mobil SHC 624, the most used in the Brazilian Nuclear Power Plants (NPP), were mixed in equal proportions. This mixture was heated until 200°C with air injection. This procedure was conducted to simulate the oil oxidation and ageing, similarly to the real contaminated oil [2].

30 g of bentonite were added to 100 g of the oxidized oil and stirred for 30 min, to simulate the solid oily waste generated after oil decontamination with bentonite. The system was filtered through a membrane filter of 0.45 µm, to separate the loaded sorbent and the oil. The loaded sorbent was considered the “bentonite oily waste” coded as BNO, that will be immobilized in the two different matrixes: cement and geopolymer.

2.3. Geopolymer matrix

The geopolymer samples were synthesized by mixing metakaolin with commercial alkaline sodium silicate solution (Na_2SiO_3, with SiO_2/Na_2O molar ratio = 2.22) and 10 M sodium hydroxide solution. A paste was obtained, placed in polyethylene cylindrical molds (5 cm diameter and 5 cm height) and subjected to stirring on an orbital shaker at 350 rpm for 10 minutes to remove air bubbles. After 24 hours at room temperature, the hardened samples were removed from the moulds. Based on the stoichiometric composition (sc) of 45 wt% of metakaolin (MK), 33 wt% of sodium silicate (SS) and 22 wt% of NaOH solution, seven compositions were made according to Table 1. The best compositions of geopolymer were characterized for compressive strength as described in 2.5.

Table 1: Seven initial compositions of geopolymer based on the stoichiometric composition (sc).

Compositions	MK (wt%)	SS (wt%)	NaOH (wt%)
sc	45	33	22
2	60	25	15
3	55	30	15
4	55	25	20
5	50	35	15
6	50	30	20
7	50	25	25

For the waste incorporation, BNO waste was mixed with metakaolin and the liquid portion was mixed with each other. Finally, the two parts were mixed using a mechanical stirrer until the achievement of homogeneous blend. After mixing, the slurry was cast into 5x5 cm cylindric moulds and was vibrated to remove steam bubbles. The samples were cured in the air at room temperature. After complete curing, 28 days, the mould was removed from the sample and the monoliths were used for compressive strength measurements as describer in 2.5.

2.4. Cement matrix

Previous bench testing was made to establish the highest quantity of BNO to immobilize in the most common cement matrix used at radioactive waste treatment process from Centro de Desenvolvimento da Tecnologia Nuclear - CDTN. The established composition is presented in Table 2.

Table 2: Composition of cement matrix.

Cement	48.0%
Bentonite	4.8%
Water	34.0%
BNO waste	13.2%

The nuclear industry may add selective sorbers for radionuclides to the cement formulation. In accord to waste solidification, CDTN procedure is added 10% of bentonite as mineral additive to the cement formulation.

The order of addition is often important to ensure a homogenous product. Therefore, BNO waste was homogenized manually with cement and bentonite. Water was added and mixed using a mechanical stirrer until the achievement of homogeneous blend. After mixing, the slurry was cast into 5x5 cm cylindric moulds and was vibrated for removing steam bubbles. The samples were cured in the air at room temperature. After complete curing, 28 days, the mould was removed from the sample and the monoliths were used for compressive strength measurements as described in 2.5.

2.5. Compressive strength

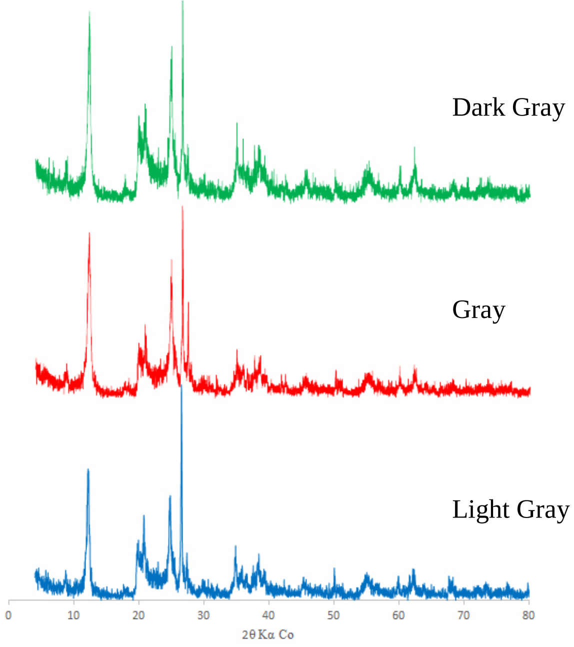
The compressive strength tests were conducted after 28 days of ageing. Five samples were tested for each mechanical test. Compressive strength tests were performed on an EMIC, model PCI 150 testing machine, according to the Brazilian Standard NBR 5739 [9]. Even though the standard refers to cemented products, it was used also to geopolymer because there is no normatization about compressive tests for it [1, 10, 11].

3. RESULTS AND DISCUSSION

3.1. Kaolinite characterization

Despite the difference in coloration, the kaolinite samples showed very similar X-ray curves, with kaolinite as the major phase and quartz as a minor phase (Figure 1). X-ray fluorescence also revealed similarity between the samples, except for the Mn and Cr contents, as well as the loss of mass on calcination, as presented in Table 3. Only the loss of mass on calcination correlates to the color tone, suggesting that the color is related to the presence of organic matter. The results of XRF analysis for light gray sample used to synthetize of the geopolymer presented 51.02% of SiO_2 and 29.20% of Al_2O_3.

Figure 1: *X-ray curves of the samples of kaolinite.*



The molar ratio between SiO_2/Al_2O_3 was 2.93 $g.mol^{-1}$. The results are in accordance with previous studies, that found the bests results in molar ratios between 3.0 and 4.5 [12].

The density of the samples varied between 2.54 $g.cm^{-3}$ and 2.62 $g.cm^{-3}$, probably due to quartz and organic matter contents. The mean particle size varied between 7.75 µm and 11.05 µm.

Thermal analysis of the samples reveals an endothermic peak around 500°C (differential scanning calorimetry, DSC), which is related to the dihydroxylation of kaolinite (Figure 2). Around 250°C there is a small peak that is probably related to the burning of organic matter. There is another small peak around 580°C, which may be related to the transition from alpha-quartz to beta-quartz. At 980°C, there is an exothermic peak, related to mullite formation.

Table 3: Composition of the kaolinite samples (XRF).

Composition	**Sample**		
	Light gray	**Gray**	**Dark gray**
MgO (wt%)	0.16	<0.10	0.20
Al_2O_3 (wt%)	29.23	28.32	25.60
SiO_2 (wt%)	51.02	48.92	48.68
P (ppm)	3421	3385	3593
S (ppm)	111	110	121
K_2O (wt%)	2.14	2.34	2.32
CaO (wt%)	0.38	0.39	0.31
Ti (ppm)	4660	4551	4662
V (ppm)	112	110	113
Cr (ppm)	69	96	42
Mn (ppm)	93	230	150
Fe_2O_3 (wt%)	3.38	3.67	5.10
Ni (ppm)	19	11	16
Cu (ppm)	26	25	26
Zn (ppm)	85	126	80
Zr (ppm)	173	140	180
Ba (ppm)	592	580	591
Loss of mass on calcination (%)	12.73	15.37	16.40

Figure 2: *DSC curves of kaolinite samples.*

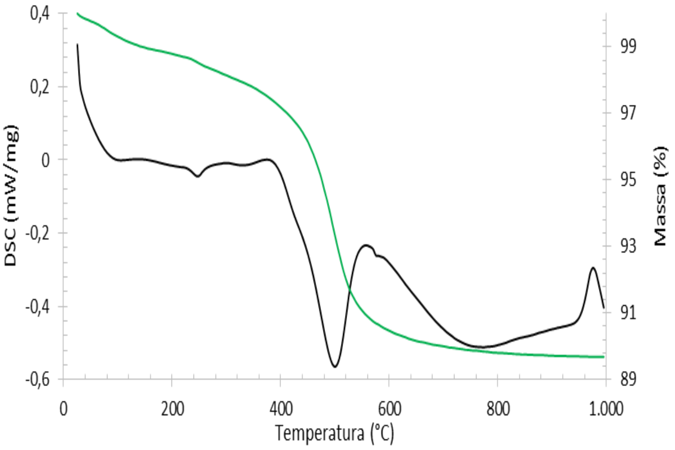
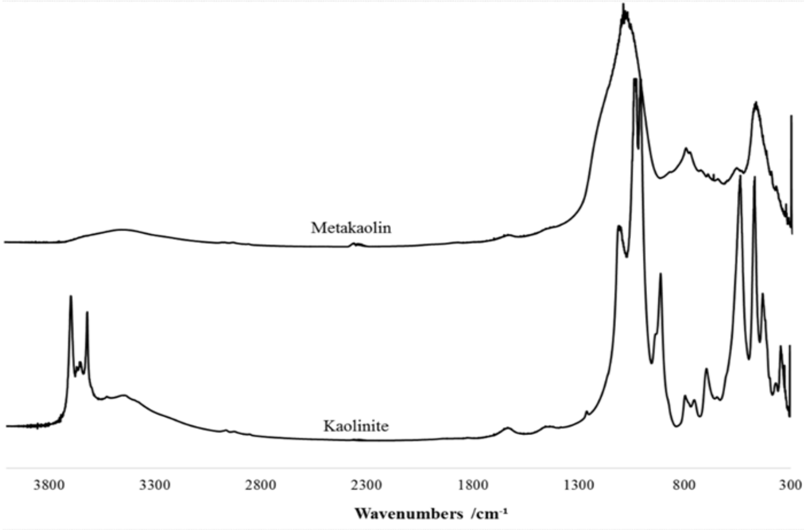


Figure 3 shows examples of infrared spectra of kaolinite samples before and after the calcination at 800°C (formation of metakaolin). Typical bands of kaolinite in the range of 3697-3621 cm^{-1} related to OH stretching disappear after calcination and bands for wavenumbers smaller than 1500 cm^{-1} become indefinite, indicating amorphous material. The loss of crystallinity after calcination could also be observed by X-ray diffraction, except for the presence of quartz that was already present as a minor phase in kaolinite.

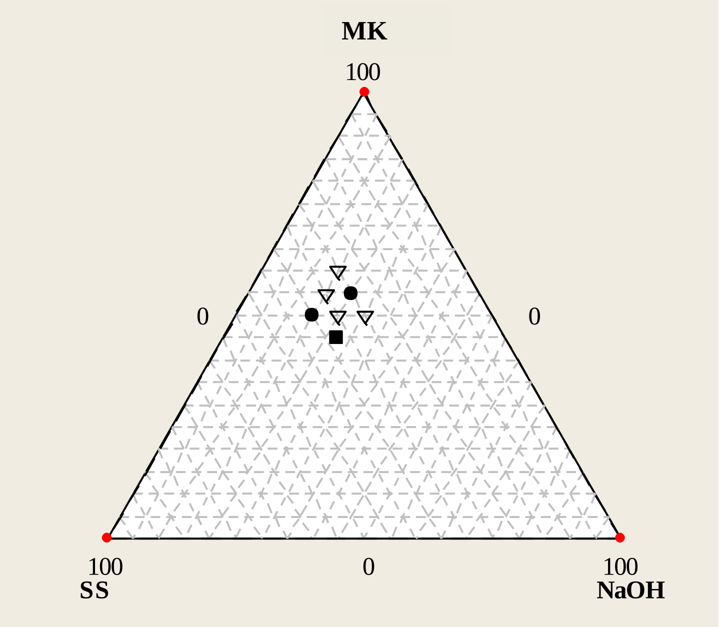
Figure 3: *FTIR spectra of the kaolinite and the metakaolin.*



3.2. Geopolymer matrix

The two compositions that presented the best workability, i.e. the feasibility to obtain a geopolymer paste in consistence that allows the incorporation of the waste and molding, best-solidified product with lower porosity and no efflorescence were chosen and are represented as a circle in the Figure 4. Efflorescence occur due to some unreacted NaOH, which may precipitate after the evaporation of the water or react with atmospheric CO2 during curing. These compositions were referred to as A (55 wt% MK, 25 wt% SS and 20 wt% NaOH) and B (50 wt% MK, 35 wt% SS and 15 wt% NaOH).

Figure 4: *Simplex design where the square is the stoichiometric composition and the circles are the chosen compositions A and B.*



The final composition of the solidified waste form in the geopolymer matrix is presented in Table 4. The highest amount of BNO for immobilization was established through bench testing. Figure 5 shows the paste obtained and the specimens after curing, used for the compressive strength tests, and their visual homogeneity.

Table 4: Composition of geopolymer matrix.

Metakaolin	40.0%
Na_2SiO_3 solution	18.0%
NaOH solution	14.5%
Water	13.0%
BNO waste	14.5%

Figure 5: *Aspects of the slurry geopolymer matrix and the five samples.*

3.2.1 Compressive strength of the geopolymer matrix without waste

The compressive strength result of compositions A and B are presented in Table 5. The geopolymer composition that showed higher compressive strength and metakaolin quantity, composition A, was selected as matrix of solidification for BNO.

Table 5: Compressive strength results to geopolymer's compositions A and B.

Samples	1	2	3	4	5	Mean	CI (95%)
CS A (MPa)	48.26	48.81	63.14	44.77	47.99	50.59	[44.29; 56.90]
CS B (MPa)	38.70	39.97	41.39	41.82	47.06	41.79	[38.99; 44.56]

3.3. Compressive strength of the solidified waste form in geopolimer and cement

The results of compressive strength test for BNO solidified waste form in geopolymer matrix are presented in Table 6.

Table 6: Compressive strength results to BNO in geopolymer matrix.

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**CI (95%)**
CS (MPa)	6.37	5.83	6.77	5.37	5.44	5.96	[5.21; 6.70]

Aspects inside of samples after the compressive strength test are shown in Figure 6. Through visual inspection is possible to identify high homogeneity across the matrix. A thin darker layer is observed on the upper surface of the samples, probably because of some excess of reagent and/or water that did not react. During the preparation of the sludge, it was noted that the water quantity could be lower. The compressive strength result does not meet the Brazilian waste acceptance criteria, set as 10 MPa [13].

Figure 6: *Aspects inside of monoliths (BNO in geopolymer matrix) after the compressive strength test.*

The results of compressive strength (CS) test to BNO in cement matrix are presented in Table 7. Aspects inside of monoliths after the compressive strength test are presented in Figure 7. Through visual inspection is possible to identify many lumps of bentonite that are not dispersed in the matrix. The compressive strength result meets the waste acceptance criteria of 10 MPa. However, the visual aspect do not comply with the homogeneity criteria, because it is established that waste should be solidified into matrix, homogeneously distributed and with minimum segregation [13].

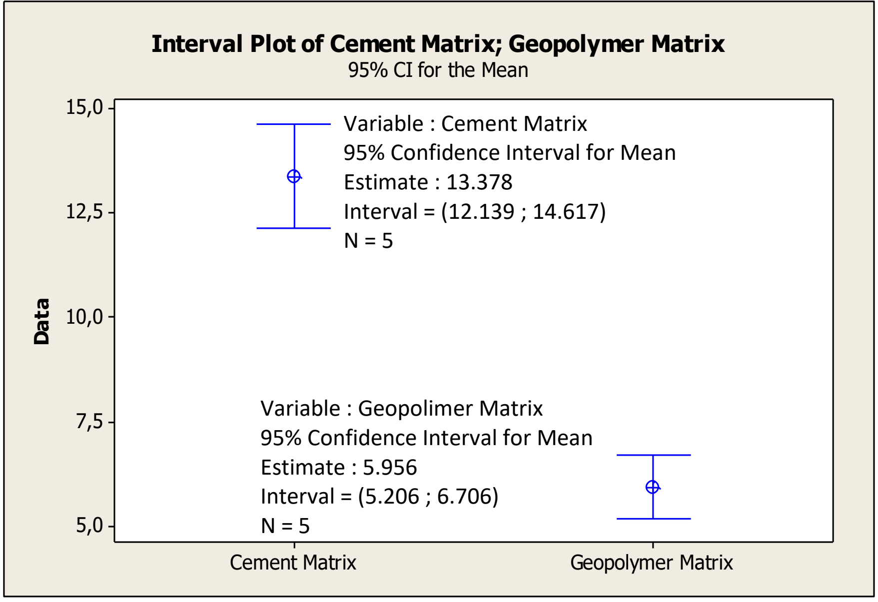
Table 7: Compressive strength results to BNO in cement matrix.

Samples	1	2	3	4	5	Mean	CI (95%)
CS (MPa)	14.01	14.51	13.57	11.98	12.82	13.38	[12.14; 14.61]

Figure 7: *Aspects inside of monoliths (BNO in cement matrix) after the compressive strength test.*

The Paired T-test statistical hypothesis test was done to compare the compressive strength result from the matrixes, with 95% confidence level. The probability or p-value was obtained through Minitab software 16. The p-value was 0,000 and the null hypothesis was rejected, confirming that the compressive strength for cement matrix was higher than for geopolymer matrix. The confidence interval plot for compressive strength mean results to cement and geopolymer matrixes is shown in Figure 8.

Figure 8: *Confidence interval plot to cement and geopolymer matrixes.*



4. CONCLUSION

The kaolinite, by-product from sand extraction, showed satisfactory results in the synthesis of geopolymer. The alkaline activation solution consisting of sodium hydroxide and sodium silicate reacted quickly with the powdered materials and the geopolymer characteristics were consistent with parameters found in literature. The XRD results have shown kaolinite as the major phase and quartz as a minor phase. XRF showed SiO_2/Al_2O_3 ratio = 2.93. The density of the samples varied between 2.54 - 2.62 g/cm^3, probably due to quartz and organic matter contents. The mean particle size varied between 7.75 - 11.05 µm. Thermal analysis of the samples showed endothermic peak which is related to the dihydroxylation of kaolinite and presence of organic matter in the sample. The FTIR analysis showed vibrations that are typical of kaolinite before and after the calcination to metakaolin.

After the treatment of the oil radwaste, the bentonite contaminated was solidified in a geopolymer and cement matrix and the solidified waste form properties were evaluated: compressive strength and homogeneity. The compressive strength result to BNO in cement matrix (13.98 MPa) specimens was higher than BNO in geopolymer matrix (5.96 MPa). Nevertheless, when the homogeneity was compared, the BNO in geopolymer matrix presented an aspect more homogeneous than the BNO in cement matrix. The results showed that the cement matrix had not successfully solidified the BNO simulated waste, because the waste was not distributed homogeneously in the matrix.

The compressive strength result to BNO in geopolymer matrix has not met the Brazilian waste acceptance criteria. Therefore, new compositions of geopolymer matrix using less water will be carried out to reach the recommended by the Brazilian legislation.

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