2021 International Nuclear Atlantic Conference – INAC 2021
Virtual meeting, Brazil, November 29 – December 2, 2021

ISBN: 978-65-594-1256-3

Synthesis of geopolymers for immobilization of radioactive waste using sewage treatment plant sludge

A. Casas [1], L. Araujo [1], R. Garcia [1], R. Vicente [1], M. Franco [1], J. Marumo [1]

[1] alexandre.las.casas@usp.br *Alexandre Las Casas*
[1] jtmarumo@ipen.br *Júlio Takehiro Marumo*

1. Introduction

Immobilization of radioactive waste is one step of the waste management required to comply with nuclear regulations and waste acceptance criteria for disposal. The radioactive waste should be solid or immobilized in solid form within a durable and resistant matrix. Portland cement is the most common material used for solidification of liquid waste and sludge, because of its low cost and ease of preparation at room temperature. An alternative material which has been studied recently is the geopolymer, which has a better performance than Portland cement as immobilization matrix [10, 11, 15].

The use of industrial by-products, containing aluminosilicates in the production of geopolymers, has become one of the most advantageous options when compared to Portland cement, due to the potential of these materials in using waste produced in any industrial chemical process [6, 8]

The application and incorporation of residues as a precursor material for use as alkaline activated binders has been found in literature, for instance, coal ash, mining, ceramic, demolition and agro-industry wastes. The objective of this work is to present preliminary results obtained from experiments using ashes obtained from the calcination of sewage sludge to synthetize a geopolymer material for immobilization of radwastes [4, 5, 6, 8]

2. Methodology

The sludge samples were obtained from the three sewage treatment plants of a sanitation company located in state of São Paulo. The samples were calcined at 650 °C for 5 hours. This temperature was used because, above this calcination temperature, there is an irreversible degradation of the sample, increasing the crystalline phase and consequently decreasing the amorphous phase, which is important for geopolymerization and the resulting ashes were grinded in ball mill to obtain size grains between 150 and 200 Tyler [13, 15, 16]

Previously, the sludges were characterized by Inductively Coupled Plasma (ICP OES) technique. For this purpose, the samples were subjected to a chemical attack process with hydrogen peroxide and hydrochloric and nitric acids, until complete elimination of the organic compounds. The analysis was performed with PerkinElmer equipment, model Optma 7000 DV. The ashes were characterized by X-Ray Diffraction and X-Ray Fluorescence (XRF) techniques.

X-ray diffraction analyses were carried out at the Nuclear Fuel Center of IPEN-CNEN/SP, with a Rigaku diffractometer, Multiflex model (Rigaku Co, Tokyo, Japan). All samples were analyzed using Cu-Ka radiation at 800 W, in the range of 2Θ from 3 to 70° with a step size of 0.02° and 8s per step. The results were compared with the reference diffraction in standard database files using Bruker's Diffrac EVA version 3.1 software (Qualitative Analysis), using the PDF2-2003 database.

For the qualitative and quantitative analysis of the crystalline phases present, crystallinity content and analysis of the material's crystal structure, the results were compared with the reference diffraction in standard database files using Bruker's Diffrac Suite Topas version 5.0 software (Analysis quantitative).

Fluorescence was also a technique used to characterize the ash and the respective geopolymers. In this analysis, carried out at the Center for Chemistry and the Environment, a WDXRF Rigaku Co., model RIX 3000 (Rigaku Co, Tokyo, Japan) spectrometer was used. For the analysis, pellets were prepared with samples, previously ground, dried in an oven at 105º C and sieved, to obtain particles with a diameter less than 0.065 mm. The main elements involved in geopolymerization are silicon and aluminum in oxide compounds, with a minimum molar ratio between them necessary for the reaction to occur properly, between 3.5 and 4 [13, 15, 16]

The specimens were prepared in a Pavitest mortar mixer. For this, 50 g of ash were transferred to a steel bowl and moistened with 10 ml of water. This mixture was homogenized for 180 seconds and immediately put in contact with 120 mL of the activating solution and stirred for another 3 minutes. Then, it was transferred to 8 cm3 silicone molds, previously greased with mineral oil, and subjected to vibration for 120 seconds (Quimis sieve vibrator), to eliminate empty spaces. The samples were demoulded after 24 hours and kept at room temperature for 1 day, to be then submitted to the compressive strength test (EMIC model PCE100/20).

3. Results and Discussion

The results of the elemental analysis by ICP-OES are shown in Table 1. The concentrations of the elements differ considerably in the three treatment stations, a fact justified by the type of sewage that each station treats and the treatment process.

These analyzes were important to obtain essential information to produce a geopolymer, that is, to have an approximate value of the aluminum concentration and also to verify the presence of possible interfering agents. It can be seen in Table 1 that aluminum, calcium and iron are the most abundant elements in the ash. Among them, the most important is aluminum, which together with silicon and/or phosphorus can form a geopolymer in the presence of alkalis. Calcium and iron, on the other hand, can negatively interfere in this process [17, 19]

Van Jaarsveld, stated that the calcium content in sewage sludge ash affected the properties of geopolymers, playing a significant role in setting time and in faster development and in higher strength values. However, to obtain a geopolymer with optimal properties, sewage sludge ash should have low calcium content and Fe2O3 content below 10%, among other characteristics [19].

Fernandez-Jimenez, in a study on the characterization and reactivity of sewage sludge ash, observed that Fe2O3 contents above 8% reduced mechanical strength. In this work, contents above 10% were observed, observed in the 3 samples [17].

Table 1. Results of the elemental analysis obtained by ICP-OES

Concentration (mg/L)			
Element	Barueri	Parque Novo Mundo	Bragança Paulista
Al	21.68	37.95	116.5
B	3.231	0.854	0.282
Ba	0.733	0.667	0.819
Bi	0.064	-	-
Ca	14.21	198.8	22.55
Cu	2.113	3.116	1.342
Fe	16.47	77.02	81.63
Ga	0.311	0.326	0.354
K	0.205	9.497	9.943
Li	1.969	1.955	1.961
Mg	-	13.81	4.148
Na	15.12	34.77	83.95
Pb	-	0.061	0.095
Sr	1.096	1.507	1.133
Zn	-	8.392	0.254
Ti	0.948	0.755	0.676
Ni	0.226	0.723	0.791

All these elements are in the form of oxides and their contents are shown in Table 2, obtained by the X-ray fluorescence technique.

Table 2: Results of the X-ray Fluorescence analysis of the ash obtained with the sludge from the treatment plants.

Compound	Content (%)		
	Barueri	Parque Novo Mundo	Bragança Paulista
Al_2O_3	24±1	5.8±0.6	25±1
Na_2O	0.44±0.04	17±1	25±1
SiO_2	35±1	7.6±0.8	21±1
Fe_2O_3	10±1	14±1	13±1
P_2O_5	8.9±0.9	4.0±0.4	10±1
CaO	8.2±0.8	42±1	2.1±0.2
TiO_2	1.8±0.2	0.53±0.05	1.2±0.1
K_2O	2.1±0.4	0.46±0.05	1.2±0.1
MgO	2.0±0.2	1.5±0.2	0.85±0.09
SO_3	5.7±0.6	2.3±0.2	0.46±0.05
ZnO	0.35±0.04	1.3±0.1	0.07±0.01
CuO	0.17±0.02	0.22±0.02	0.03±0.01
Cr_2O_3	0.15±0.02	0.21±0.02	0.03±0.01
NiO	0.08±0.01	0.05±0.01	0.014±0.001
Ag_2O	0.06±0.01	ND	ND
PbO	0.03±0.01	ND	0.013±0.001
Cl	ND	3.8±0.4	0.04±0.01
As_2O_3	ND	ND	<0.010
Br	ND	ND	<0.010
ZrO_2	0.020±0.002	0.011±0.001	ND
MnO	0.13±0.01	0.06±0.01	ND
BaO	0.19±0.02	ND	ND
SrO	0.017±0.002	ND	ND
Rb_2O	<0.010	ND	ND
Y_2O_3	<0.010	ND	ND

It can be seen in Table 2 that the ash from the Parque Novo Mundo treatment plant has the lowest quantities of aluminum and silicon oxides and the highest levels of calcium oxide. These contents could already be an indication of the impossibility of using this material in the production of the geopolymer.

The presence of Mg and Ca can also affect the hardening time of the geopolymer. Thus, according to the MgO and CaO contents observed in the ashes of the three stations, it can be stated that the geopolymers to be produced will present a fast initial setting time of around 30 seconds, which may affect workability [17].

Sulfur, whose role in the geopolymer seems to be not well defined yet, is present in the three sewage sludge ashes, however, only the Barueri ash had a content slightly above 5%, being, therefore, a parameter of little relevance. Sulfur could eventually form ettringite, as occurs in hydrated cement in the presence of sulfates. In the case of cement, according to ASTM C618-03, the sulfate content cannot exceed 5% so that there is no excessive formation of ettringite, which can damage the hydrated cement in the short term. Of the elements analyzed, silicon and aluminum are those that form the geopolymer, together with oxygen, with a minimum ratio between them necessary for the reaction to occur properly [2, 15, 18].

According to Boca Santa, the Si/Al ratio will always be equal to or greater than one. It can be seen in Table 2 that these elements are in the form of oxides and, in this case, according to Davidovits, the molar ratio that should be recommended between SiO_2 /Al_2O_3 is 3.5-4.5. However, just knowing the quantities of these elements or oxides is not enough, as alkaline activation will not occur if energy is not available [15, 18].

The degree of crystallinity in which these elements will define this. The lower the grade, the greater the chance of success in obtaining geopolymers. Hence the need to characterize the material using the X-ray diffraction technique.

Rietveld method was adopted for the analysis of diffractograms which revealed different degrees of crystallinity and types of crystalline phases in the three samples. The crystallinity degrees of Barueri, Parque Novo Mundo and Bragança Paulista were 15, 95.5 and 37%, respectively. Relating these results with those of X-ray fluorescence, it can be concluded that the ash from Parque Novo Mundo is not feasible for the production of a geopolymer since it has almost 100 percent of crystalline phase.

X-ray diffraction by the Rietveld method proved to be relevant and efficient in the study of sewage sludge ash, with satisfactory values of statistical indicators of refinement (GOF and Rwp) being obtained, according to the values presented in GOF: 1.18, 1.91 and 1.32, and in Rwp: 9.92, 19.47 and 11.65 respectively when applied in tests of complex samples, such as sludge ash, which has a large amount of crystalline phases in its composition and with different concentrations. In addition to high linear correlation with the other applied methodologies, particularly with regard to the largest constituents of the samples, essentially quartz-α (SiO_2), alinite, hematite. and clay minerals.

Based on the SiO_2 and Al_2O_3 contents obtained by the fluorescence analysis (calculation base 100g) and the crystallinity percentages, the molar ratios between the two compounds can be calculated. It can be observed that both the ash from the sewage sludge from Barueri and from Bragança Paulista have lower ratios than that suggested by Davidovits, between 3.5 and 4.5. Thus, additions of SiO_2 of at least 12 g to the ash from the sewage sludge from Barueri and 20 g from the sewage sludge from Bragança Paulista will be necessary for the reaction to occur.

The geopolymerization potential of the ash was tested. The preparation of the geopolymer involved mixing of the ash with a sodium silicate activator solution, prepared with sodium hydroxide. Concentrations of 8, 10, 12, 14 and 16 M of NaOH P.A. (Synth) and 2 M of $Na_2SiO_3.5H_2O$ P.A. (Dynamics) were adopted. The best results were obtained with 12 M evidenced by the heat released and workability.

In this case, the samples presented axial compressive strength close to 10 MPa. This value is the minimum acceptable according to CNEN standard NN 6.09 Acceptance criteria for deposition of radioactive waste with low and medium levels of radiation (COMISSÃO NACIONAL DE ENERGIA NUCLEAR, 2002), for waste immobilized in Portland cement. The axial compressive strength close to 10 MPa when comparing with those found in the literature, this value is at least 5 times lower, demonstrating the need for improvement in the preparation method. In addition, it is possible that this result is due only to the solidification of the activator solution, since, even though it does not have the ideal characteristics, the "geopolymer" produced with sewage sludge ash from Parque Novo Mundo also resulted in a product similar to the others. The term has been placed in quotation marks as there is no evidence that it is an actual geopolymer.

Through exploratory tests already carried out it is possible to conclude that geopolymer based sewage sludge is an unconventional mineral precursor with potential for the production of geopolymers by partial substitution of the conventional materials. The use of sewage sludge proved to be an innovative solutions in adding value on sewage sludge, or solutions to emit less pollution, more careful on the environment and mankind, respecting the sustainable development.

4. Conclusions

In view of the objective of this research project to evaluate the influence and feasibility of using sewage sludge ash from sewage sludge as a precursor material in the production of a new geopolymer in general to boost the reuse of this residue level and with the results obtained so far, it can be concluded that: The sewage sludge ash from the three treatment plants has different characteristics; The sewage sludge from the Parque Novo Mundo treatment plant is not suitable for obtaining a geopolymer, given its high calcium content and low aluminum and silicon content; It is necessary to establish a protocol for the preparation of the geopolymer, correcting the Si/Al ratios of the wastewater sludge ash from Barueri and Bragança Paulista and It is necessary to describe in detail the input and output mass flows of the process to compose the feasibility analysis.

References

[1] Adamiec, P.; et al., **Pozzolanic reactivity of silico-aluminous fly ash**. Particuology, Amsterdam, v. 6, n. 2, p. 93–98, abr. 2008.

[2] AMERICAN SOCIETY FOR TESTING AND MATERIALS. **Standard specification for coal fly ash and raw or calcined natural pozzolona for use in concrete.** West Conshohocken, PA: ASTM, 2003. (ASTM C618-03).

[3] Antoni S., Wibiatma Wijaya, and Hardjito D., **Factors Affecting the Setting Time of Fly Ash – Based Geopolymer**, Mater. Sci. Forum, vol. 841, pp. 9097, (2016).

[4] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **Amostragem de resíduos sólidos**. Rio de Janeiro: ABNT, 2004. (NBR 10007).

[5] Barroso, M. D. B**. Desenvolvimento de compósitos com matriz de geopolímeros reforçados com partículas de quasicristais AlCuFe**, Tese Dr., Un. Fed. Paraíba, 2009.

[6] Cantarel V., et al., **Geopolymers and Their Potential Applications in the Nuclear Waste Management Field - A Bibliographical Study – JAEA - Review**, 2017.

[7] Cheng H. K., Lin L., Cui R. C., Hwang, L, Y., Chang, M. T., Cheng W., **The effects of SiO_2/Na_2O molar ratio**

on the characteristics of alkali-activated waste catalyst-metakaolin based geopolymers, Constr. Build. Mater. 95 710–720, 2015.

[8] Cheng, L.; Lin, D. F. **Applications of sewage sludge ash and nano-SiO2 to manufacture tile as construction material. Construction and Building Materials**, Amsterdam, v. 23, n. 11, p. 3312–3320, nov. 2009.

[9] Chindaprasirt P., and Chareerat T., **High-strength geopolymer using fine high-calcium fly ash**, J. Mater. Civ. Eng., vol. 23, no. March, pp. 264270, (2011).

[10] COMISSÃO NACIONAL DE ENERGIA NUCLEAR. **Critérios de aceitação para deposição de rejeitos radioativos de baixo e médio níveis de radiação.** Rio de Janeiro: CNEN, 2002. (Norma CNEN 6.09).

[11] COMISSÃO NACIONAL DE ENERGIA NUCLEAR. **Gerência de rejeitos radioativos de baixo e médio níveis de radiação.** Rio de Janeiro: CNEN, 2014. (Norma CNEN-NN-8.01).

[12] Davidovits J., : **Inorganic polymer Patent FR2464227** (1981).

[13] Davidovits J., Geopolymer **Chemistry and Applications**, 1st edition march 2008, 2nd edition June 2008, 3rd edition July 2011, 4th edition November 2015, 5th edition March 2020.

[14] Davidovits J., Geopolymers - **Inorganic polymeric new materials. Journal of Thermal Analysis** 1991, 37, (8), 1633-1656.

[15] Davidovits J., Sawyer J. L., **Early-strength mineral polymer. US Patent 4509985**, 1985.

[16] Davidovits, J. **"Geopolymer Chemistry and Properties", Proceedings of the Geopolymer'**88, Vol. 1, pp. 25-48., 2015.

[17] Fernandez-Jimenez*A., Palomo A. **Characterisation of fly ashes. Potential reactivity as alkaline cements** 82 2259–2265, 2003.

[18] Santa, R. A. A. B. **Desenvolvimento de Geopolímeros a Partir de Cinzas Pesadas Oriundas da Queima do Carvão Mineral e Metacaulim Sintetizado a Partir de Resíduo da Industria de Papel**. Florianópolis, 2012. 134 f. Dissertação (Mestrado em Engenharia Civil) - Programa de Pós-Graduação em Engenharia Química, Universidade Federal de Santa Catarina, Florianópolis, 2012.

[19] Van Jaarsveld, J. G. S., et al., **The characterisation of source materials in fly ash-based geopolymers**. Materials Letters, 57(7), 1272-1280, 2003.