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Composition and Stability of a Copper Metallurgy Slag Based Environmentally Friendly Geopolymer Cement

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Abstract: ***The cement industry consumes huge amounts of energy and emits CO_2, the main greenhouse gas. With the promotion of sustainable development, particular attention is drawn to how ecological materials with similar or better properties should be developed than ordinary Portland cement, and geopolymer cement has been recognized as one of the most promising materials. This study investigated the effect of SiO_2/Al_2O_3 ratio and curing time on the mechanical and chemical properties of synthetized geopolymers (SCAA) from activated clay (AA), copper slag (SC) and Na_2SiO_3-NaOH. Five (5) slag geopolymers (SCAA) were synthetized using two different proportions of clay and copper slag: CSAA1 (5 % AA-95% CS), CSAA2 (10 % AA-90% CS), CSAA3 (15 % AA-85% CS), CSAA4 (20 % AA-80% CS), and CSAA5 (25 % AA-75% CS). The best stability properties were observed for the SCAA5 with SiO_2/Al_2O_3 ratio of 2.23 and an acidity index of 1.3.This research has a large environmental impact as it helps to valorise copper slags and immobilize their containing ETMs, therefore it also indirectly aids to reduce the energy use and direct CO2 emissions during the manufacture of ordinary Portland cement.***

Keywords: geopolymer, greenhouse gas, ordinary Portland cement, stability, acidity index

1. Introduction

The cement industry consumes huge amounts of energy and emits carbon dioxide. About one ton of carbon dioxide is emitted to the atmosphere for a production of one ton of cement, leading to global warming conditions (Kong and Sanjayan, 2008). Thus, to reduce the carbon dioxide emission of the cement industry, sustainable development has been recently promoted and has drawn a particular attention on developing ecological materials with similar or better properties than ordinary Portland cement (OPC). Thereby, various materials has been suggested in literature to replace the cement as far as concerning the usage of waste materials like silica fume (Geetha and Madhavan, 2017), fly ash (Geetha and Madhavan, 2017; Lin et al., 2003; Sharma and Khan, 2018; Yu et al., 2018) and granulated blast furnace slag (Escalante et al., 2001; Fernández-Jiménez et al., 1999; J.P.H. Frearson, 1992; Pal et al., 2003; Schneider et al., 2001; Van Rompaey G., 2006).Besides, one of the excellent and most promising alternative is the utilization of geopolymer cements because they do reuse waste materials, and contribute to the improvement of the binder properties such as long-term strength, permeability, and durability (Alp et al., 2008; Gorai et al., 2003; Gülay, 2006).

The current global production of copper slag is estimated to 40 million tonnes (Prem et al., 2018), with more than 13 million tonnes available in the Democratic Republic of Congo. This production of industrial slag derived from the use of pyrometallurgical treatments to extract metals. Copper slags are by-products obtained during matte and conversion smelting, thermal refining of copper, and dry reduction of oxidized ores (Davenport et al., 2002; Gorai et al., 2003; Gülay, 2006; Kabange, 2013).About 2.2 tonnes of slag is generated as a by-product for every tonne of copper metal produced (Gorai et al., 2003). The chemical composition of the copper metallurgical slag consists mainly of FeO, Fe_2O_3 and SiO_2 (Bulut, 2006; Das et al., 2009), with small amounts of Al_2O_3, CaO and MgO, as well as elements (ETM) such as Cu, Co, Ni, Cr, V, Ti, Zn, Pb, As, Co (Çoruh et al., 2006; Ozel et al., 2006), which may be found in metallic, oxide or sulphide forms (Gorai et al., 2003). The natural decay of this copper waste is very complex with harmful by-products that pose a serious management and environmental problems. For example, the copper slag is classified as special waste from mining and mineral processing by US Environment Protection Agency (Achudhan et al.)because of its ETMs content (Davenport et al., 2002; Gorai et al., 2003; Kabange, 2013).Thus, the leaching of heavy metal contained in ETMs limits the disposal of the slag from

storage sites and makes the stabilization costs very exorbitant.

When the copper slag contains an appreciable quantity of copper (> 0.8% by mass) or other metals, it can be reprocessed by various metallurgical processes (melting in an arc furnace, leaching and flotation) in order to recover the metals it contains, and particularly copper (Bulut, 2006; Gülay, 2006; Gyurov et al., 2017; Sarfo et al., 2017; Tong and Yunhan, 2007). Unfortunately, the reprocessing treatment is expensive and environmental unfriendly. Additionally, because of the scarcity of landfill filling area and the lack of natural aggregates in the construction industry which are supported by the stringent environmental regulations in many countries, it is becoming important to develop new costless slag waste management techniques to valorise and manage the slag wastes.

To date, among the possible low cost methods, copper slags have been mostly used as fill material for land reclamation (Lim and Chu, 2006), as glass-ceramic and glass-epoxy composites (Biswas and Satapathy, 2009; Çoruh et al., 2006), or immobilize using red mud and clinoptilolite (Çoruh, 2008). Further, their use as cement supplement or fine aggregate (Al-Jabri et al., 2011; Al-Jabri et al., 2009; Alp et al., 2008; Dhir et al., 2017b; dos Anjos et al., 2017; Kabange, 2013) and artificial aggregates (Achudhan et al., 2018; Dhir et al., 2017a; Geetha and Madhavan, 2017; Prem et al., 2018) has been recently developed. Another simple and less expensive method that can be considered is their use as a raw material in the synthesis of geopolymer (Furlani et al., 2018; Joseph, 2015). Most of the copper metallurgical slags found in R.D. Congo have high level of aluminosilicate glasses and would better adapt themselves to the geo-polymerization reactions (Kabange, 2013). Indeed, the synthesis of the geopolymer materials generally consists of an "alkaline activation" of aluminosilicate materials at room temperature or at slightly high temperature (Joseph, 2015).

This work helps to immobilize the ETMs while indirectly aiding to reduce the energy use and direct CO_2 emissions during the manufacture of OPC (Asavapisit and Macphee, 2007; Deja, 2002; Giergiczny and Król, 2008; Joseph, 2015; Kitobo, 2009). It aims to investigate the strength and durability of environmentally friendly synthetized slag geopolymers. The slag geopolymers were first synthetize through mixture of copper slag from the SiO_2-Al_2O_3-CaO-MgO system with activated clay at 750 ° C. Then, the geopolymers chemical properties were examined and characterised, and their mechanical strengths were analysed according to the SiO_2/Al_2O_3 ratio and the curing time. Finally, the durability was examined trough the chemical stability analysis through study of the SiO_2/Al_2O_3 ratio and curing time impacts on the slags geopolymer weight loss after immersion in three different alkaline and acid solutions.

2. Method

2.1 Materials

The used copper slag (CS) is a by-product of the reprocessing of a slag for matte smelting. It has been fully characterized by Kabange (2013)as vitreous and in the form of coarse gray sands. The utilized clay was provided by a former deposit that has been operated by the Gecamines Quarry and Mines (GCM) for its brickyard. Previous to its used, the clay was heated in an oven at 750 ° C for 3 hours (Garg and Skibsted, 2014), with a temperature rise rate of 4.16 °C/min. The chemical composition of these ground raw materials, was determined using X-ray fluorescence and shown in Table 1. Sodium hydroxide (NaOH) and metasilicate (Na_2SiO_3) used as activators for geo-polymerization reactions were supplied by Glassworld Laboratory.

Table1: Chemical composition of the copper slags and the clay materials

Compound	Slag (%w)[a]	Clay (%w)
Na_2O	0.02	0.08
MgO	7.30	0.03
Al_2O_3	7.10	43.76
SiO_2	37.40	31.66
P_2O_5	0.20	-
SO_3	1.50	-
K_2O	0.80	1.67
CaO	30.90	0.70
$CaCO_3$ (Rietveld)	5.30	-
TiO_2	0.60	0.73
V_2O_5	0.070	-
Cr_2O_3	0.01	0.01
MnO	0.20	0.05
FeO, Fe_2O_3	2.40	10.95
CoO	0.20	-
NiO	0.01	-
CuO	0.20	-
ZnO	0.03	0.01
As_2O_3	0.05	-
SrO	0.03	-
MoO_3	0.01	-
PbO	0.02	-
LOI	5.60	10.33

[a] (Kabange, 2013)

2.2 Slag geopolymers synthesis

Five (5) slag geopolymers (SCAA) were synthetized using two different proportions of clay and copper slag: CSAA1 (5 % AA-95% CS), CSAA2 (10 % AA-90% CS), CSAA3 (15 % AA-85% CS), CSAA4 (20 % AA-80% CS), and CSAA5 (25 % AA-75% CS). Subsequent to activation, the clay was mixed to the copper slag at the need edratio for geo-polymerization. NaOH activator was used at a concentration of 12 M (Hamidi et al., 2016; Yong et al., 2013), and $Na_2SiO_3.5H_2O$ at 5 M. Prior to use, the Na_2SiO_3 solution was prepared and placed in a sealed polyethylene beaker for at least 24 hours to allow depolymerization of the sodium silicate solution. Then, Dassekpo et al. (2017) method was used to formulate the cement pastes. It consisted of adding the clay to the NaOH

solution and mixing the system for 15 minutes. Then, SC and Na_2SiO_3 solutions were consecutively added to the obtained paste and mixing again for 15 minutes. The obtained paste was cast in a three cells prismatic mold of 40 mm*40 mm*160 mm and vibrated for 15 minutes. After vibration, the paste was held at 40 ° C for 24 hours (Bilek et al., 2016; Joseph, 2015; Nath et al., 2014), then take off. Finally, the cured samples were wrapped in plastic films and stored at 25 °C until the test (Kabange, 2013).

2.3 Slag geopolymers analysis

Siemens SRS 3000 X-ray fluorescence device (Université Libre de Bruxelle) was used to determine the chemical composition of the samples. The mechanical strengths at simple compression were measured with a mechanical press. This test was carried out on the hardened samples of 40mm*40mm*160mm. The cure times were 7, 14, 21 and 28 days (Kabange, 2013). The chemical stability of the cured samples was determined using gravimetric difference between the cured fresh and dry weight of the sample after immersion in the test solution (10 % wt. H_2SO_4, 10 % wt. NH_3 et 5 % wt. HCl) for 24 hours (Joseph, 2015; Lee and Lee, 2016; Zhang et al., 2018).

2.4 Data analysis

Statistical analysis was computed to investigate the effect of the various factors on the stability of the copper slag geopolymers. The data was first analysed using Microsoft Office Excel 2007 spreadsheets. Then, the compressive strength and chemical stability variables were subject to one-way ANOVA test and turkey multiple means pairwise comparisons using SPSS (IBM SPSS Statistics, Version 20). The considered factors were theSiO_2/Al_2O_3 ratio and the curing time.

3. Results and Discussion

3.1 Characterization of the geopolymers slags

The chemical and physical properties of the slag and clay mixtures geopolymers was examined using the metal oxides of the chemical identification results (Table 1) and the acidity index. The chemical composition of the copper slag exhibited a high level of oxides such asSiO_2, CaO, MgO, Al_2O_3, $CaCO_3$ and $FeO\text{-}Fe_2O_3$ while the clay revealed high concentrations of Al_2O_3, $SiO_2$and $FeO\text{-}Fe_2O_3$ (Table 1).The observed great concentration of Fe_2O_3 in the clay suggests that the it was of ferruginous type, as showed its red colour which related the presence of iron in the form of hematite. The concentrations of the other identified oxides concerning Ti, V, Cr, Mn, Co, Cu, Zn, Pb, As and Mo were very low, but still can threaten the environment because their concentration are higher than the standards limits requirement (standards and limits).The LOI of the clay was two times higher than that of the copper slag.

The $(CaO + MgO)/SiO_2$ ratio was 1.02, suggesting that the copper slag was neutral and could not be hydraulic. Nevertheless, this result is different from those of intrinsic reactivity studies conducted by Kabange (2013). The calculated SiO_2/Na_2O (Ms) ratio for NaOH and Na_2SiO_3 solutions was equivalent to 2.4 (Allahverdi et al., 2008; Hardjito et al., 2018). On the other hands, theSiO_2/Al_2O_3ratio of the clay mineral was low with value of 0.72; therefore, this ratio must be rose up through the mixture of the clay with copper slag. The computed SiO_2/Al_2O_3 ratio of the SC-AA mixture increased from 2.23 to 4.27 with the increasing ratio of the slag content 75% to 95%, showing a better SiO_2/Al_2O_3 property of the mixtures than the raw clay mineral.

The SiO_2 and Al_2O_3 levels, and SiO_2/Al_2O_3 ratios of the CS and activated clay (AA) mixtures are presented in Table 2. According to (Joseph, 2015), a geopolymer cement should have a SiO_2/Al_2O_3 ratio value between 2 and 3. Thus, the SiO_2/Al_2O_3 ratio is important to determine the structure of a synthesized geopolymer materials.

The acidity index was calculated according to the Eq. (NF-196-1) from the masses of the acidic and alkaline oxides of the CS-AA mixtures, and those of the activator (Na_2SiO_3 et NaOH), and the results are presented in Table 3.

Acidity index = $(S_{tot}+A_{tot}+F)/ (N+C+M+K)$ Eq. (NF-196-1)

The results from Table 3 showed that of the acidity index of the slag geopolymers decreased from 0.97 to 1.3 with the decreasing slag content 75% to 95%, showing a better acidity index for the 25 % AA-75% CS geopolymer mixture.

Table 2: SiO_2, Al_2O_3 and SiO_2/Al_2O_3contents of the slag and clay mixture geopolymers

Slag and clay material	Oxide	Slag and clay mixture				
		CSAA1	CSAA2	CSAA3	CSAA4	CSAA5
CS	SiO_2	35, 25	33, 4	31, 54	29, 69	27, 83
	Al_2O_3	6, 43	6, 09	5, 75	5, 42	5, 08
AA	SiO_2	1, 59	3, 16	4, 75	6, 33	7, 92
	Al_2O_3	2, 18	4, 37	6, 56	8, 752	10, 94
Total	SiO_2	36, 83	36, 57	36, 29	36, 02	35, 75
	Al_2O_3	8, 62	10, 47	12, 31	14, 17	16, 02
SiO_2/Al_2O_3		4, 27	3, 49	2, 95	2, 54	2, 23

Table 3: Acidity indexes of the formulated slag geopolymers.

Chemical compounds (g)	Slags types				
	CSAA1	CSAA2	CSAA3	CSAA4	CSAA5
Fe_2O_3	28, 28	32, 55	36, 83	41, 10	45, 38
Al_2O_3 total	89, 33	107, 7	126, 0	144, 3	162, 7
$SiO_{2\ SC-AA} + SiO_{2\ Na_2SiO_3}$	371, 1	368, 3	365, 4	362, 5	359, 7
K_2O	8, 435	8, 870	9, 305	9, 740	10, 18
CaO	293, 9	278, 8	263, 7	248, 6	233, 5
MgO	69, 37	65, 73	62, 10	58, 46	54, 83
Na_2O	176, 7	176, 7	176, 7	176, 7	176, 7
$(S_{tot}+A_{tot}+F)/ (N+C+M+K)$	0, 97	1, 1	1, 1	1, 2	1, 3

3.2 Mechanical strength of the slag geopolymers

Definition and importance of mechanical strength and slight description of the experimental conditions.

The figure 1 illustrates the trend of the mechanical strengths of hardened specimens as function of their SiO_2/Al_2O_3 ratio and the curing time. It shows that the mechanical strength generally increased with both the increasing SiO_2/Al_2O_3 ratio and curing time. However, a decrease of the mechanical strength was observed at 21 and 28 days immersion when the SiO_2/Al_2O_3 ratios increased from 2.23 to 2.54 and 2.23 to 2.95, respectively. This decrease could be linked to the structural change of the reaction products due to the increasing values of the SiO_2/Al_2O_3 ratios; as an SiO_2/Al_2O_3 ratios between 1 and 2 leads to a three-dimensional structure of the minerals in the slags (Joseph, 2015). However, the three-dimensional structure progressively changed to polymeric structure when the SiO_2/Al_2O_3 ratios reaches a value within a range of 2.2 and 3 (Joseph, 2015). Therefore, within this SiO_2/Al_2O_3 ratios range, the hardened specimens can have two types of structures: geopolymer structure on one hands, and activated cement on the other hands.

The highest compressive strength were obtain after 28 curing days, with value of reaching 61.48 and 64.48 MPa for the 2.23 and 4.27 SiO_2/Al_2O_3 ratios, respectively (compare these values with those of previous researches). The increase in the compressive strength with the increasing SiO_2/Al_2O_3 ratio is mostly due to the raising of the reaction time of the mixture AA-SC and the activator. The result of this reaction is affected by the activating solutions Na_2O/SiO_2 ratio (Joseph, 2015). In the current study, the value of the Na_2O/SiO_2 ratio was 2.4 which conducted to the formation of low solubility amorph and semi-amorph reaction products (geopolymers or zeolites) (Joseph, 2015).At this value of the Na_2O/SiO_2 ratio, there is a high polycondensation and formation of binder phases (geopolymers or zeolites) of three-dimensional and / or polymeric structure that was responsible of the high value of the mechanical strengths (Joseph, 2015). Thus, this structural transformation was responsible of the decrease of the mechanical strength of the slags. When the SiO_2/Al_2O_3 ratio is over 3, the increasing mechanical strength could be linked to the transformation of the structures from geopolymers to activated cement (Roy, 1999). Oppositely to geopolymers, this type of cements are characterized by great values of mechanical strength but with low durability. For these types of cements, the commonly observed reaction phases are mostly the type I CSH, C-A-S-H, N-C-A-S-H, hydrotalcite and even C_4H_{13} when the NaOH and Na2SiO3 have been used as activators (Palomo et al., 1999; Roy, 1999; Wang and Scrivener, 1995).

For values of SiO_2/Al_2O_3 ratio less than three (3), it can be confirmed that the geopolymer binder has a zeolite structure (Wang and Scrivener, 1995). However, the greater content of CaO in the scories does not exclude the presence of C-S-H, (C, M) 4AH3, hydrotalcite or even C-A-S-H [26-28] besides the binder geopolymers. Other studies relates the presence of N-C-A-S-H with intermediate chemical composition between that of C-A-S-H and N-A-S-H (Ismail et al., 2014; Lee and Lee, 2016; Puertas and Fernández-Jiménez, 2003).

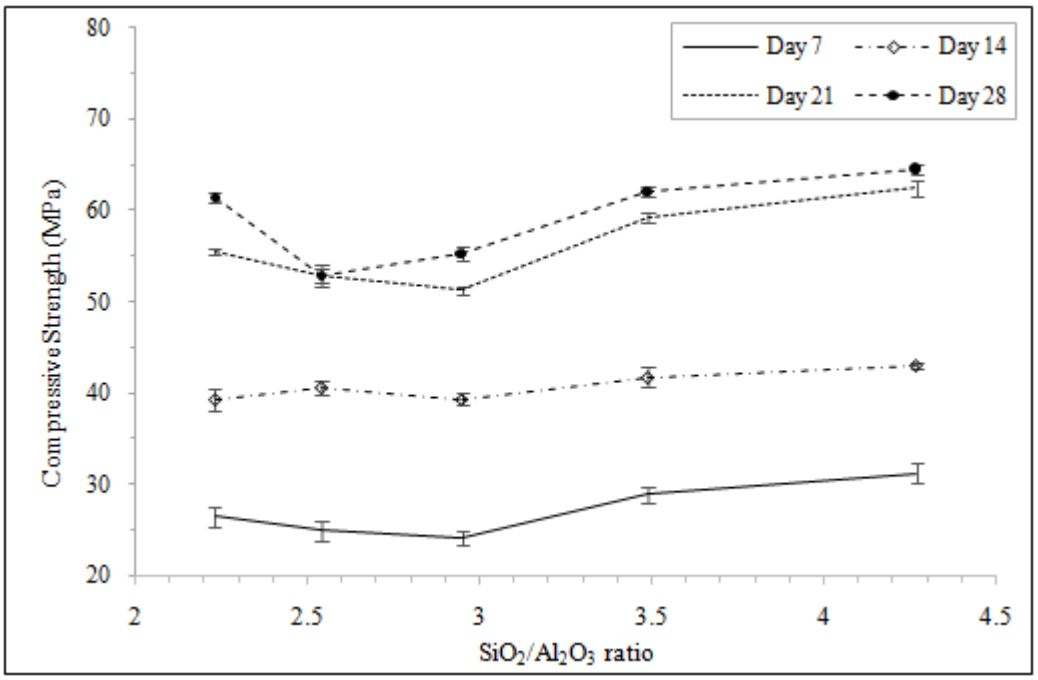


Figure 1: Mechanical stability of the slags geopolymers with variation of the SiO_2/Al_2O_3 ratio at different curing time

Table S1: Multiple means comparisons and ANOVA results of the compressive strength between slag geopolymers and curing times.

Curing time	Copper slag geopolymers					Sig.
	CSAA1	CSAA2	CSAA3	CSAA4	CSAA5	
7	abA	aA	aA	bcA	cA	0.0001***
14	aB	abB	aB	abB	bB	0.0040**
21	bC	aC	aC	cC	dC	0.0001***
28	cD	aC	bD	cD	dC	0.0001***
Sig.	0.0001***	0.0001***	0.0001***	0.0001***	0.0001***	

* For each curing time, values with the same lowercase letter are not statistically different between copper slag at 5%.
* For each copper slag, values with the same uppercase letter are not statistically different between curing time at 5%.

3.3 Stability

The chemical stability of the slag geopolymers was analysed through the attacks of the specimens with three different acids: sulfuric acid, chloric acid and ammonia. The Figs. 3a, 3b and 3c results display the weight losses trends of the submerged specimens in the sulfuric acid, chloric acid and ammonia solutions, respectively. The Figs. 3a and 3b showed that the weight loss decreased with both the increasing curing time and decreasing SiO_2/Al_2O_3 ratio.

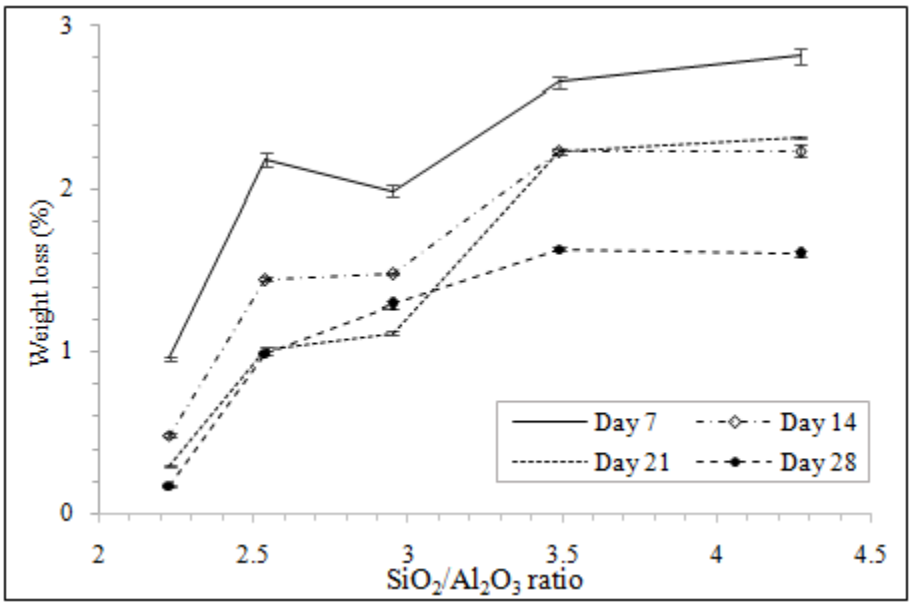
In sulfuric acid and chloric acid (Fig. 3a and 3b), only the specimens with SiO_2/Al_2O_3 value of 2.2 presented the weight losses less than 1% for all the curing times, suggesting a high amount of clay in the slags which promoted their long durability. However, for the SiO_2/Al_2O_3 value of 2.2, the best stabilities were found for the 28 days curing time with value of 0.2% per day in sulfuric acid and 0.1% per day in chloric acid. This finding was similar with those of in previous literature that suggests weight loss of (value) (Joseph, 2015). The observed low weight losses at 28 days curing day can be due to the increase of the geo-polymerization rate with the decreasing SiO_2/Al_2O_3 ratio (Joseph, 2015; Kabange, 2013; Zhang et al., 2018). At low SiO_2/Al_2O_3 ratios, a densification of the cement geopolymer microstructure occurs through the formation of geo-polymerization phases in the form of a gel in the hardened paste, which prevents the diffusion of the acidic solutions in the test specimens (Bilek et al., 2016; Dassekpo et al., 2017; Mo et al., 2014; Muñiz-Villarreal et al., 2011; Nath et al., 2014; Zhang et al., 2018).

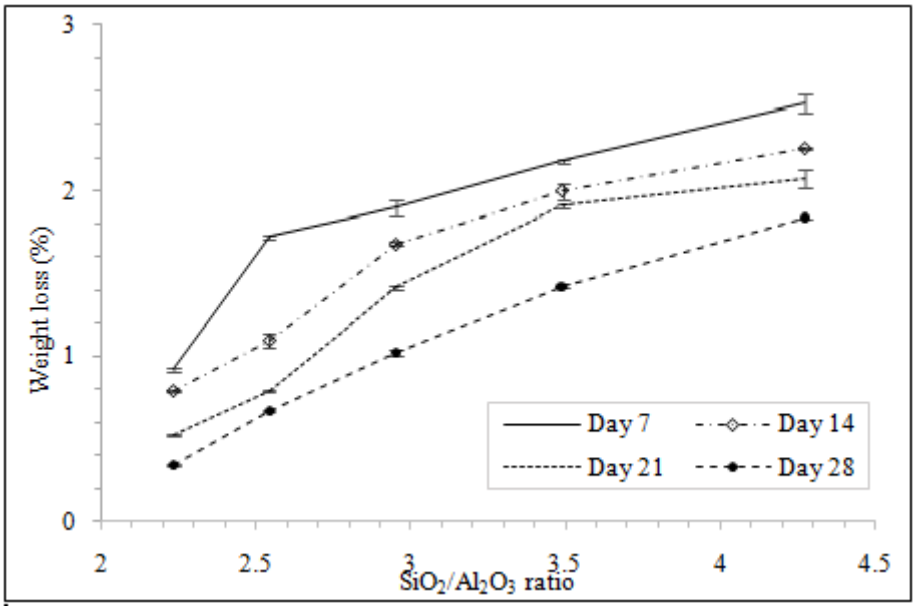
The specimens with SiO_2/Al_2O_3 ratio higher than 3 were less stable than those with SiO_2/Al_2O_3 ratio of 2.2 because: in a geopolymer cements, the formed phases are generally amorph or semi-amorph presenting chains of three-dimensional polysialates with very strong covalent Si-O-Al bonds (Joseph, 2015; Kabange, 2013), while (2) in activated cements, the reaction phases are C-S-H of type-I or C-A-S-H where some Ca^{2+} ions have been replaced by the Na^+ ions (C- (N)-S-H) or C- (N)-A-S-H when CaO is of high level (i.e. weak $(S_{tot}+A_{tot}+F)/(N+C+M+K)$index).These compounds (C- (N)-S-H) or C-(N)-A-S-H) have a high rate of crystallinity than the C-S-H et/ouC-A-S-H of Portland cement and geopolymer phases (Roy, 1999).

In the acidic environment, the hydrated phases of activated cements are subject of two processes attack. First, the cation exchange between the Na^+ and Ca^{2+} ions in the gel of the hydrated products and the proton H^+ of the acid, and

secondly the electrophile attack of the H^+ ions on the polymeric Si-O-Al bonds. The result is the ease decalcification of the hydrated phases when the acidity index of the cement is low, followed by the deposition of gypsum in the solution, and thus a significant weight loss of the hardened specimens.

Finally, in the ammonia solution, the weight losses should be nil or non-measurable (Joseph, 2015). The observed weight losses could indicate the presence of acidic phases that may react with ammonia, as all the formulated pastes, except the one containing 5% wt. of AA which has an acidity index greater than 1.Therefore, in these hardened pastes it can be concluded the presence salts of calcium and / or sodium hydrosilicates ($H_3SiO_4^-, H_2SiO_4^{2-}$-, …) (Kabange, 2013) acids, capable of reacting with the NH_3 and give soluble salts that induce weight loss.





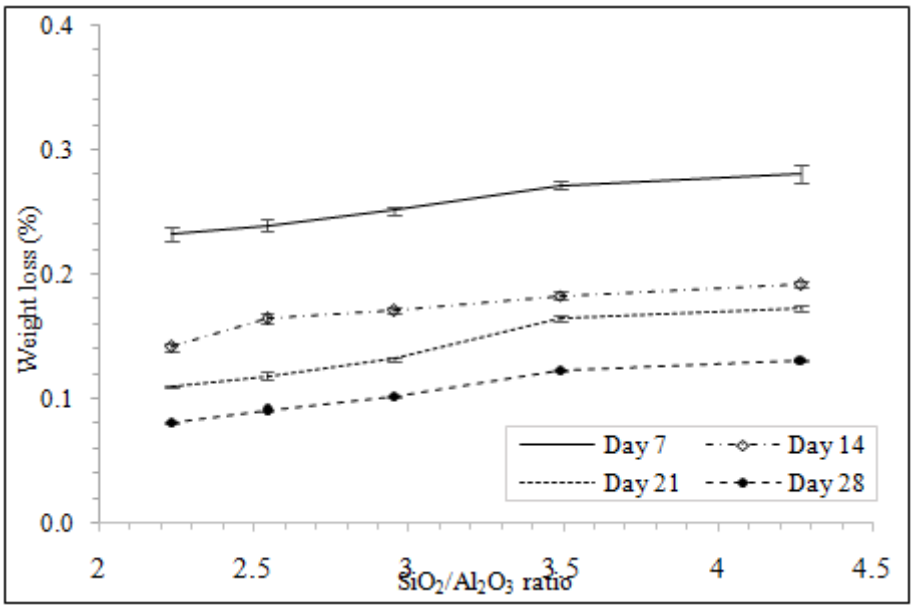


Figure 3: Weight loss of the slags geopolymers with variation of the scories level at different curing time after treatment in: a) H_2SO_4 10%, b) HCl 5%, and c) NH_3 10 %

Table S2: Multiple means comparisons and ANOVA results of the compressive strength between copper-clay mixtures and among curing times for H2SO4 10%, HCl 5% and NH3 10% treatments.

Solution	Curing time	Copper Slags					Sig.
		CSAA1	CSAA2	CSAA3	CSAA4	CSAA5	
H2SO4 10%	7	aA	bA	cA	dA	dA	0.0001***
	14	aB	bB	bB	cB	cB	0.0001***
	21	aC	bC	cC	dB	eB	0.0001***
	28	aD	bC	cD	dC	dD	0.0001***
	Sig.	0.0001***	0.0001***	0.0001***	0.0001***	0.0001***	
HCl 5%	7	aA	bA	cA	dA	eA	0.0001***
	14	aB	bB	cB	dB	eB	0.0001***
	21	aC	bC	cC	dB	eB	0.0001***
	28	aD	bD	cD	dC	eC	0.0001***
	Sig.	0.0001***	0.0001***	0.0001***	0.0001***	0.0001***	
NH3 10%	7	aA	aA	abA	bcA	cA	0.0010**
	14	aB	bB	bcB	cdB	dB	0.0001***
	21	aC	bC	cC	dC	dC	0.0001***
	28	aD	bD	cD	dD	eD	0.0001***
	Sig.	0.0001***	0.0001***	0.0001***	0.0001***	0.0001***	

*For each solution and curing time, values with the same lowercase letter are not statistically different between copper slag at 5%.

*For each solution and each copper slag, values with the same uppercase letter are not statistically different between curing time at 5%.

4. Conclusion

In the current research, binding geopolymer materials were synthetized at defined proportions of clay, copper slag and activation solutions. It was found that the greater clay content in the geopolymers (lower SiO_2/Al_2O_3 ratio) results to a low mechanical compression resistance and a high chemical stability of the hardened specimens in sulfuric acid and chloric acid solutions. The high chemical stability of the specimens was linked to the increased acidity index with the rising clay content. However, the studied specimens dissolved almost similarly in the ammoniac solution and independently to the SiO_2/Al_2O_3 ratio. The best geopolymer composition was observed for the SiO_2/Al_2O_3 ratio of 2.23 and an acidity index of 1.3, corresponding to the mixture of 25% clay:75% copper slag (w:w) geopolymer. This composition gave a cement geopolymer with the compressive strength of 62 MPa at 28 days, and better chemical stability in sulfuric and chloric acids solutions. For the other geopolymers with SiO_2/Al_2O_3 ratio greater than 3 (SC>75%) and the acidity index lower than 1.2, the obtained materials were similar to activated cement. Thus, they were less chemically stable although their compressive strength slightly higher than those of cement geopolymer. This research has a large environmental impact as it helps to valorise copper slags and immobilize their containing ETMs; therefore it also indirectly aids to reduce the energy use and direct CO2 emissions during the manufacture of ordinary Portland cement.

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