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Optimization of the Geopolymer Obtaining Process to Immobilize Mercury and Its Mechanical Evaluation

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Abstract: The objective of this work was to form a geopolymer based on pumice stone and kaolin treated thermally, basic activating solution with sodium silicate solution ($Na_2SiO_3.nH_2O$) in order to immobilize solid mining waste (SMW). The influence of various physical factors during its elaboration and the response of the formed Geopolymer with the SMW previously stabilized were determined. The predominant physical factor evaluated was the resistance to compression, according to ASTM C-1157 method, which is a determining factor in the durability of the formed geopolymers. The results show a maximum of 34.70 MPa in a randomized treatment with levels (1:1, 8 and 60) of the studied factors and a minimum of 12.49 MPa with the factors (3:1, 4 and 20). The percentage ratio of the optimal geopolymerizing material formed to immobilize mercury present in the residue was 55% pumice stone, 45% metakaolin with a liquid/solid ratio of 0.4 and 10 Molar concentration of basic solution. This aluminosilicate synthetic material could well replace other materials. A complete factorial design with three central tests was used, applying the Statigraphics Centurion XVI software.

Key words: geopolymer, mercury, pumice stone, mining waste, compressive strength

1. Introduction

The southern middle region of Perú that comprises regions of Ica and Arequipa have polymetallic mining wealth exploited on a large, medium and small scale, being the small gold and artisanal mining, which predominates in the coastal area of this part of the country dedicated to the exploitation of gold. The technology used is the amalgamation process with mercury and in others through cyanidation [1] which when used and handled improperly; generate solid mining waste (SMW) with a high content of mercury and other toxic metals, causing serious damage to health and the environment irreversibly [2, 3].

Mercury is currently considered one of the global pollutants, a very dangerous toxic element that has no borders because it is transported by the wind hundreds of kilometers from the point of release due to its very peculiar physical and chemical properties compared to other dangerous and radioactive toxic elements [4]. Geopolymers are called green cement [5, 6] for their properties (high mechanical strength, fire resistance, acid resistance, low thermal conductivity and fast setting times [7] and low environmental impact by using raw materials such as industrial by-products, thermally treated natural clays, volcanic rocks [8, 9] and other materials that are available on a large scale and with CO_2 gas emissions close to 0.184 tons, which is the sixth part of what emit other industries such as cement plants [10]. Geopolymers act similarly to cement binder in terms of encapsulation; however, the physical and chemical properties of the product may be

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much higher and better than those treated with traditional cementitious materials [11] because properties of geopolymer have high resistance to mechanical compression, resistance to acid attack (high solubility of heavy metals at low pH), low permeability and high durability [12]. The objective of the present study was to evaluate the performance in terms of compressive strength of the geopolymeric material formed from pumice stone and metakaolin in the encapsulation [13] of the previously characterized [14] and stabilized Solid Mineral Residues (SMW).

2. Experimental Work

2.1 Method

The present study had two phases; the first was to find the optimal formulation of the geopolymer by varying two parameters: the percentage ratio of metakaolin (MK) with respect to pumice stone (PS) as raw materials and the concentration of basic solution.

We used as a base material of the geopolymer: PS whose chemical composition was determined by the test method 592 for alkaline fusion rocks, MK was achieved after subjecting a thermic treatment the kaolin for four hours, with a specific chemical composition by X-ray Fluorescence (ARL-dry base), (Table 1). For the activating solution, a basic solution of 98.3% purity, commercial sodium silicate solution and 55% H_2O was used with a volume ratio of sodium silicate/basic solution equal to 1. Then four formulations of raw material were prepared with different percentage compositions of PS and MK (45/55, 55/45, 65/35, 75/25) using basic solutions at different concentrations: 1 M, 3 M, 5 M, 7 M and 10 M to determine the optimal formulation for the procedure of the synthesis of the geopolymer. The mixing time was 10 minutes, stirring speed from 1500 to 2000 rpm, curing time for 28 days under ambient temperature conditions (23 ± 2°C) and relative humidity of 60%.

In the second phase after determining the optimal formulation of the geopolymer, the previously stabilized solid mining waste (SMW-S) was incorporated according to a factorial experimental design with three central points to achieve the immobilization of the mercury present in the residue.

The characteristic toxicity leaching procedure (TCLP, EPA, 1311) is a method of extracting soil samples and also applicable to solid waste for chemical analysis used as an analytical method to simulate leaching. TCLP toxicological tests of both the mining waste and the product obtained were performed to see if the degree of toxicity decreases after the treatments.

The evaluation test on resistance to mechanical compression was evaluated at 28 days of age (ASTM C-1157), with a constant load of 0.024 in/min using the NTP 334.051: 2013 test method and as reference the standard ASTM C-109. For the data analysis the Statigraphics Centurion XVI software was used.

3. Results and Discussion

3.1 Chemical characterization of Pumice Stone and Metakaolin

The results that show the previous Table 1 of the chemical analysis to the pumice stone and the metakaolin demonstrate that they are suitable materials to form geopolymers, considering that the percentage of alumina and silica add up to more than 70% of the total.

3.2 Geopolymer Training and Optimization

In the geopolymer formation process, tests were

Table 1 Chemical composition (% by weight) of the base materials for the formation of the Geopolymerv.

Chemical compound	Molecular formular	Meta kaolin	Pumice Stone
Silicon oxide	SiO_2	76.92	63.58
Aluminum oxide	Al_2O_3	21.82	10.50
Iron Oxide	Fe_2O_3	0.31	2.66
Calcium oxide	CaO	0.01	1.72
Magnesium oxide	MgO	0.02	0.69
Manganese oxide	Mn_2O_3	0.18	0.26
Sodium Oxide	Na_2O	0.09	9.43
Potassium Oxide	K_2O	0.24	2.92
LOI	LOI	0.17	4.70

previously carried out to obtain the optimal parameters and their performance was evaluated by means of compression resistance (RC) measurements. Table 2 shows the results of the RC varying the percentage composition of pumice stone with respect to metakaolin ranging from 45 to 75% for the first and 55% to 25% for the second, in order to achieve a formulation with one more RC high, for this, the concentration of basic solution was equal to 10 M for all treatments is taken as a reference, value referenced and recommended by Barbosa [15] as well as Hardjito [16] who obtained high values of resistance to compression of geopolymers in a range of 8 to 20 M basic solution. The molar ratios of the main oxides varied as shown in Table 2 due to the variation of the composition, while the liquid/solid ratio (L/S) remains constant at 0.374. As a result, the highest compression resistance value of 41.67 MPa was obtained in the 2B treatment with a formulation of the Na2O/SiO2, SiO2/Al2O3 and H_2O/Na_2O molar ratios at (0.24, 5.82 and 8.78) respectively and that it corresponds to a percentage composition of 55% pumice stone and 45% metakaolin, while the other treatments were not very encouraging. Once the optimum composition of the base raw material is achieved, it is necessary to confirm that the concentration of basic solution is as indicated so we did.

Table 2 Compressive strength of geopolymer formed with different percentages of pumice stone and metakaolin, with basic solution 10M.

Treatment	%(PP +MK)	Ratio Molar			Compression Resistance (MPa)
		$Na_2O/Si0_2$	SiO_2/Al_2O_3	H_2O/Na_2O	
1B	45+55	0.17	7.00	9.25	24.71
2B	55+45	0.24	5.82	8.78	41.67
3B	65+35	0.25	6.64	8.34	19.61
4B	75+25	0.26	7.69	7.95	5.3

Table 3 presents the compressive strengths for the five treatments, keeping the SiO_2/Al_2O_3 molar ratio constant at 5.83 and the sodium silicate content with a volume ratio of 1: 1; the Liquid/Solid (L/S) ratio at 0.374 and the other molar ratios of Na_2O/SiO_2 and H_2O/Na_2O vary in treatments depending on the concentration of the basic solution directly for Na_2O/SiO_2 and inversely for H_2O/Na_2O treatment five (T5), achieved the best compressive strength of 23.2 MPa corresponding to the 10 M concentration with molar ratios of Na_2O/SiO_2 equal to 0.25 and H_2O/Na_2O equal to 8.78, a result that is a function of the composition optimum of the geopolymer made as shown in Table 2 corresponding to treatment 2B, where a high value of mechanical compression was also obtained.

With these five treatments it is shown that the initially tested base concentration of 10M achieves the best response to mechanical compression, as mentioned by different authors [15, 17, 18].

Table 3 Compressive strength of geopolymer* by varying the concentrations of the basic solution and keeping the SiO2/Al2O3 molar concentration constant at 5.83.

Treatment	Base (M)	Ratio Molar		(CR) (MPa)
		Na_2O/SiO_2	**H2O/Na2O**	
T1	1M	0.15	14.83	0.3
T2	3M	0.17	13.01	1.3
T3	5M	0.19	11.58	3.9
T4	7M	0.22	10.35	10.0
T5	10M	0.25	8.78	23.2

*55% PP y 45 % MK

3.3 Immobilization of Mercury in Stabilized Mining Residue Sample with Geopolymer Formed

Once the formulation of the raw material (55% of PP and 45% of MK) was optimized, concentration of the activating solution (10 M), sodium silicate and L/S

ratio of 0.374 for the formation of the geopolymer was carried out immobilization of RSM-E, 2C following the same methodology of the geopolymer formation process according to the mix design and established process conditions, as shown in Table 4 for the 11 treatments. The last three are central treatments according to factorial design.

After obtaining the Geopolymer containing SMW-S for the eleven treatments, treatment seven was selected because it had a higher mechanical compression response compared to the other treatments. The toxicity was evaluated after 28 days of curing by means of the TCLP test method (EPA-1311 method), resulting in a decrease of the content of the mercury metal in the mining residue from 90% to 95%, as can be observe in Table 5. The result obtained compared to the National and International regulations, in the process of immobilization of the mine waste with the geopolymer formed, indicates that the mercury contaminant is immobilized.

Table 4 Mix design and process conditions of the Geopolymer formation with RSM-E and basic solution in 40.0 y 60.0 g.

Treatment	SMW-S (g) 2C*	Pumice stone (g)	Metakaolin (g)	Sodium silicate (g)
1	256	35.2	28.8	58.52
2	256	35.2	28.8	60.80
3	256	35.2	28.8	63.08
4	256	35.2	28.8	64.60
5	128	105.6	86.4	95.00
6	128	105.6	86.4	87.40
7	128	105.6	86.4	79.80
8	128	105.6	86.4	76.00
1-C	192	70.40	57.60	68.40
2-C	192	70.40	57.60	68.40
3-C	192	70.40	57.60	68.40

Table 5 Comparison of the result of the concentration of Hg in leachate with the national and international regulations.

Elemento contaminante	Mercurio en Residuo 2C* (mg/Kg)	ECA Perú suelos según D.S. 002-2013-MINAM (zona industrial)	Normativa Internacional (USEPA, 2012b)				TCLP en geopolímero con RSM-E	Observación
			Solido general		Solido restringido			
			CCS (mg/Kg)	TCLP (mg/L)	CCS (mg/Kg)	TCLP (mg/L)		
Mercurio (Hg)	>225	24	50	0.2	200	0.8	< 0.001	Cumple normativa (N-I)**

*Sample of the area of Secocha- Camaná -Arequipa

** National and International Regulations

3.4 Mechanical Compression Resistance Analysis

The eleven values of Compressive Strength (MPa), shown in Table 6, obtained according to the mix design of Table 4, show three blocks of differentiated values that are somehow associated with the percentage ratio of geopolymeric material with respect to stabilized mining solid residue, SMW-S; treatments 1 to 4 with an average value of 13.63 MPa, the second block corresponding to treatments 5 to 8 with an average value of 31.37 MPa, value twice as high as the first block, result associated with the content of geopolymerizing material in the proportion of 60/40, where there is a greater amount of geopolymerizing material with respect to the SMW-S, the third block presents values of the central points with an average value of 27.37 MPa, it can be concluded that the best values are in the specimens with the highest content of geopolymerizing material, as seen in Fig. 1.

Fig. 2 shows the standardized Pareto chart to see which factor has the greatest impact, as the only factor that has an important impact is the variable C (ratio of geopolymerizing material (MG) and SMW-S) that has an effect of 17.45 MPa and that positively affects maximizing CR. This analysis is corroborated with the statistical analysis applied, as shown in Table 7 regarding the participation of the three factors studied that influence the performance of this property.

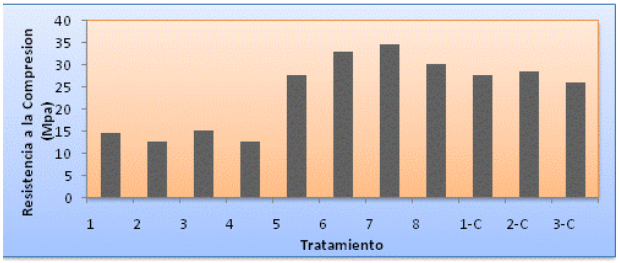

Fig. 1 Compressive strength (MPa) of monoliths.

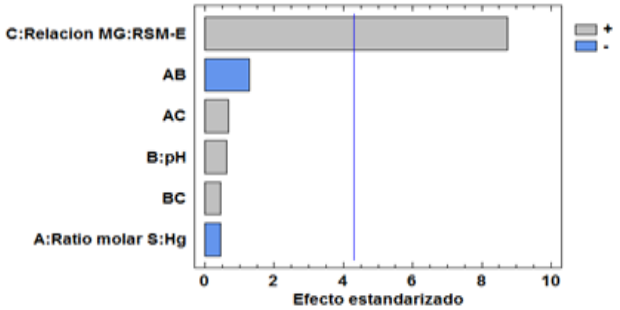

Fig. 2 Standardized pareto diagram for compression resistance.

Table 6 Factorial design matrix 23 with 3 central replicas and variable compression resistance response in (MPa).

N° Trat.	Factor real*			Factores de Diseño							Resistencia Compresión
	Z_1	Z_2	Z_3	A	B	C	AB	AC	BC	ABC	
1	1:1	4	20	-1	-1	-1	+1	+1	+1	+1	14.41
2	3:1	4	20	+1	-1	-1	-1	-1	+1	+1	12.49
3	1:1	8	20	-1	+1	-1	-1	+1	-1	+1	15.12
4	3:1	8	20	+1	+1	-1	+1	-1	-1	-1	12.49
5	1:1	4	60	-1	-1	+1	+1	-1	-1	+1	27.58
6	3:1	4	60	+1	-1	+1	-1	+1	-1	-1	32.92
7	1:1	8	60	-1	+1	+1	-1	-1	+1	-1	34.70
8	3:1	8	60	+1	+1	+1	+1	+1	+1	+1	30.29
1-C	2:1	6	40	0	0	0					27.65
2-C	2:1	6	40	0	0	0					28.48
3-C	2:1	6	40	0	0	0					25.98

Z1 (Ratio molar: stabilizing reagent: Hg en SMW), Z2 (pH) y Z3 (Dose in % weight geopolymerizer); A= Z1, B = Z2 y C = Z3

Table 7 Analysis of ANOVA variance of compressive strength in the process of immobilization of SMW containing mercury.

Source of variation	Sum of square	**GI**	Middle square	Reason-F	Value-P
A:Ratio molar S:Hg	1.63805	1	1.63805	0.2	0.6997
B:pH	3.38	1	3.38	0.41	0.588
C: relationship MG:RSM-E	629.77	1	629.77	76.19	0.0129
AB	13.6765	1	13.6765	1.65	0.3271
AC	3.7538	1	3.7538	0.45	0.5698
BC	1.78605	1	1.78605	0.22	0.6877
Lack of adjustment	26.4364	2	13.2182	1.6	0.3847
Pure error	16.5313	2	8.26563		
Total (corr.)	696.972	10			

The improved ANOVA variance analysis (ABC interaction is excluded) individually analyzes the Compression Resistance variability for each of the effects. The ANOVA tests the statistical significance of each effect by comparing its mean square against an estimate of the experimental error, the variable C has a P-value (0.0129) less than 0.05, with a confidence level of 95.0%, therefore it is concluded that factor C is statistically significant, while the other factors are not statistically significant.

This result confirms the preliminary analyzes performed, also in the same table it is noted that the

lack of adjustment has a value of 0.3847 above 0.05, being non-significant therefore does not present curvature and the model has a linear behavior.

3.5 Prediction

To predict the compressive strengths in the best treatment obtained (A ±, B + and C +) or in any other treatment that is to be checked, the regression model adjusted to the best ANOVA in table 7 is obtained and is given by Eq. (1):

$$\hat{Y} = 23.24 + 8.87\ C \quad (1)$$

The regression model associated with the analysis of improved variance interprets according to the coefficient of determination R2aj 84.58% of the variability in maximizing the compressive strength of the specimen formed, this quite optimal R2aj value allows us to have good quality of prediction.

It is necessary before validating the conclusions of the analysis to verify the assumptions for the model of Ec 1 that corresponds to the best ANOVA that assumes that the residues are distributed normal, independent and with constant variance; failure to comply with any of these assumptions leads to erroneous conclusions. In Fig. 3a the predicted against the residuals are plotted, there it is observed that the points randomly fall vertically within a horizontal band, this behavior validates the assumption of constant variance, Fig. 3b the points of the execution number are plotted against the residues, here there is no trend in the points, then it is indicative that this assumption is fulfilled therefore it is concluded that there is independence of the residues and finally in Fig. 3c, the residuals are plotted on normal probabilistic paper can be observed that the points to some extent adhere to a line placed visually (it is not a regression line), it concludes that the model meets the assumption of normality of the wastes; In conclusion, the model meets the assumptions of normality, independence and constant variance of the wastes, so the conclusions reached regarding the optimum levels are correct and adequate for obtaining maximum compressive strength.

Fig. 4a shows the response surface plot as a result of adjusting the model of Eq. (1) to a set of points in the experimental zone, where you can observe the points to achieve the minimums (A ±, B- and C-) and maximums (A ±, B + and C +) coincide with the results of the optimal levels found with the previous analyzes. While Figure 4b shows the three-dimensional graph as a function of the three factors and the regions where it is possible to perform optimization treatments, finally the optimal points that maximizes compressive strength are: geopolymerizing material (MG) ratio with stabilized mining solid residue (SMW-S) by 60%, taking into account stabilization factors such as pH and molar ratio of stabilizer.

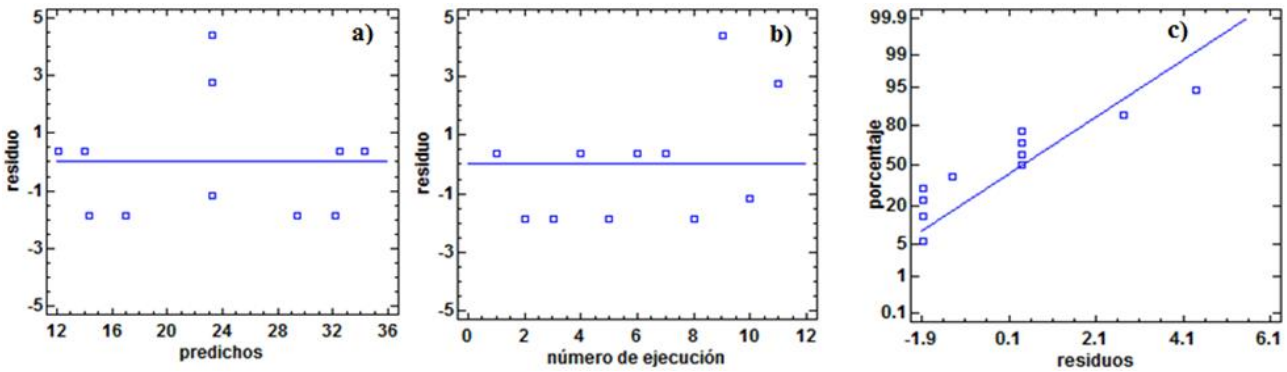

Fig. 3 Graphs of verification of assumptions a) constant variance of waste, b) independence of waste and c) normality of waste.

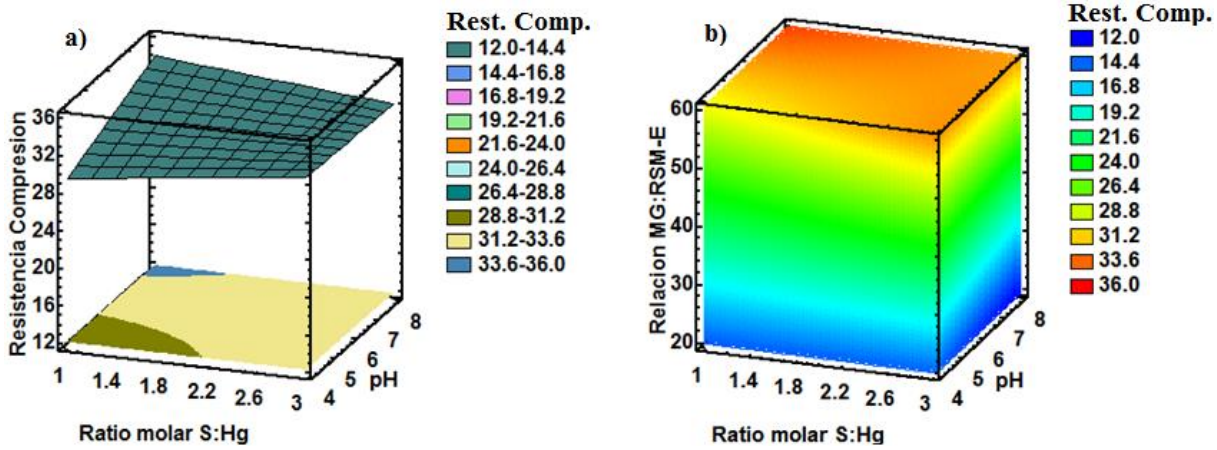

Fig. 4 Response Surface Graph for compressive strength at a MG: SMW-S ratio equal to 60%.

4. Conclusions

In the first phase of optimization of the geopolymer formulation with the raw material of 55% pumice stone and 45% metacaolin, a compressive strength of 41.67 MPa is achieved. Of the five concentrations evaluated for the alkaline solution, the 10M concentration proved to be adequate, resulting in a mechanical compression of 23.2MPa and with a molar ratio of Na2O/SiO2, SiO2/Al2O3 and H2O/Na2O at 0.24, 5.82 and 8.78 respectively. With this optimal geopolymeric composition, the stabilized mining solid waste from the Arequipa Region was immobilized. Of the eleven treatments performed, it turned out to be treatment seven that reached a value of 34.70MPa of mechanical compression at 28 days of cure, with the levels randomly designed according to factorial design (1: 1, 8 and 60) and the lowest values were in treatments 2 and 4, both with a value of 12.49 MPa. The optimum level determined was, in addition to the stabilized mining residue, the geopolymerizing material: stabilized mining residue (MG: SMW-S) ratio equal to 60%.

The variable that has a positive and important effect is the percentage of geopolymerizing material on SMW-S stabilized mining solid waste, reaching a value of 17.74 MPa with a percentage contribution of 70.83% followed by the interaction between AB variables with a percentage contribution of 10.79% negatively on the performance of compressive strength. It is concluded that the resistance to mechanical compression is governed by the percentage factor of geopolymerizing material, with respect to the mining waste, ratified by the ANOVA, with an R2 equal to 93.83 percent and an adjusted R2 of 84.58 percent indicating that the Model adequately explains the behavior of the data in the response variable. The variance analysis model meets the assumptions of verification of constant variance, independence and normality of the residues, so it adequately describes the hardening process measured by this property through compression resistance.

The concentration of mercury present in the mining waste of the Arequipa Region before the treatment was >225 and after the treatment with the geopolymer was < 0.001 in the TCLP test, a value that is below the national and international regulations. The heat treated materials are a source of aluminosilicates and in the presence of the alkaline activator, base with sodium silicate, gives a basic pH to the specimen formed with the mine residue, this basic pH is also responsible for this immobilization as well as the characteristics of the geopolymer formed, resulting very suitable for waste containing mercury, hazardous waste, such as solid mining waste, toxic waste considered harmful to human health and the environment

References

[1] S. Palacios, P. Alfonso, J. Yañez and P. Higueras, Evaluación de la Contaminación de mercurio en la cuenca

del río Ocoña, Perú, in: *III Congreso Internacional de Geología y Minería Ambiental para el Ordenamiento Territorial y el Desarrollo*, Catalunya 2013, pp. 241-248.

[2] S. Mendioroz, Mercurio, Instituto de Catálisis y Petroleoquímica del CSIC Canto blanco- Madrid España, 28049. 200, pp. 1-94.

[3] Huamán Paredes Flora E. et al., Efecto tóxico y ecotoxicológico de arenas negras de la minería artesanal en Madre de Dios, *Revista de la Sociedad Química del Perú* 83 (2017) (4) 403- 411.

[4] D. Y. Wang, X. Shi and S. Wei, Accumulation and transformation of atmospheric mercury in soil, *Sci. Total Environ.* 304 (2003) 209-214.

[5] F. Pacheco-Torgal, J. A. Labrincha, C. Leonelli, A. Palomo and P. Chindaparasirt, *Handbook of Alkali-activated Cements, Mortars and Concretes*, Sawston, Cambridge UK: Woodhead Publishing Ltd, 2014, p. 852.

[6] A. Palomo, M. W. Grutzeck and M. T. Blanco, Alkali –activated fly ashes A cement for the future, *Cem. Concr. Res*. 29 (1999).

[7] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo and J. S. J. Van Deventer,. Geopolymer technology: the current state of the art, *Journal of Materials Science* 42 (2007) (3) 2917-2933.

[8] Huamán Paredes Flora E. Caracterización de puzolana natural con potencial uso en encapsulamiento de residuos mineros. 1er Congreso Internacional de Residuos sólidos. Minimización, valorización y disposición final, in: *VI Congreso de Residuos sólidos en el Perú*, Lima Perú, 2017, p. 34.

[9] R. Castro, Diana Catalina, Tesis de grado. Obtención y Caracterización de Geopolímeros sintetizados a partir de ceniza volante y piedra pómez, utilizados para el desarrollo y mejoramiento del concreto, 2010, Universidad Industrial de Santander Bucaramanga-Colombia.

[10] J. G. S. van Jaarsveld, J. S. J. van Deventer and L. Lorenzen, The potential use of geopolymeric materials to immobilize toxic metals: part 1. Theory and applications, *Minerals Engineering* (10) 659-669.

[11] A. Palomo and M. Palacios, Alkali-activated cementitious materials: Alternative matrices for the immobilization of hazardous wastes Part II. Stabilization of chromium and lead, *Cement and Concrete Research* 33 (2003) 289-295, doi: 10.1016/s0008-8846(02)00964-x

[12] B. C. Mc Lellan, R. P. Williams, J. Lay, A. van Riessen and G. D. Corder, Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement, *J. Clean. Prod.* 19 (2011) 1080-1090.

[13] P. Randall and S. Chattopadhyay, Advances in encapsulation technologies for the management of mercury-contaminated hazardous wastes, *Journal of Hazardous Materials* 114 (2004) (1-3) 211-223.

[14] Huamán Paredes Flora E. Caracterización Mineralógica de residuos de minería aluvial en la Región Madre de Dios–Perú, in: *33° Latin-American Congress of Chemistry (33-CLAQ). X Congress of Chemical Sciences, Technology and innovation (QUIMICUBA 2018*), La Habana–Cuba, available online at: https://drive.google.com/file/d/1tQHEi__y16Q-vPaCl4cXERVWVVNFGZlZ/view

[15] V. F. F. Barbosa, K. J. D. MacKenzie and C. Thaumaturgo, Synthesis and characterization of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers, *International Journal of Inorganic Materials* 2 (2000) (4) 309-317.

[16] D. Hardjito and B. V. Rangan, Development and Properties of Low Calcium Fly Ash Based Geopolymer Concrete, Research Report GC1, Faculty of Engineering, Curtin University.

[17] J. Davidovits. Chemistry of geopolymeric systems, terminology, in: Joseph Davidovits, R. Davidovits & C. James (Eds.), *Proceedings of 99 International Conference*, France, 1999.

[18] A. V. Kirschner and H. Harmuth, Investigation of geopolymer binders with respect to their application for building materials, *Ceramics–Silikaty* 48 (2004) (3) 117-120.