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Leaching of Germanium from the Slag of the GECAMINES Factories in Lubumbashi by Oxalic and Sulfuric Acids

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ABSTRACT

The objective of this study is to contribute to the study of the purification of germanium in the slag of the pyrometallurgy of the GCM factories of Lubumbashi. To do this, a pre-treatment of the slag was done by drying at 105°C for 24 hours and a grindability study using a sieve whose mesh was 75µm maximum for 90 minutes. The moisture content was 0.52%, the grinding time 90 minutes to obtain 89% of passers-by. Initially, the slag assayed 0.02% Ge; 0.008% Ga; 5.4% Cu; 0.21% Co; 10.40% Zn; 10.30% Fe and 10.30% Si.

Our concern to recover the germanium from the slag with the other accompanying metals was to carry out the tests for dissolving the slag with oxalic and sulfuric acids after having characterized it. This slag was shown to be acidic and without a defined crystalline structure. The various dissolution tests were carried out by varying the quantity of oxalic acid for the preparation of the oxalic acid solution (100 to 150g/L), the leaching time (1h to 4h). The ratio between the amount of slag and the acid solvent was 1÷10 respectively. At this stage of our study, the optimal conditions for the dissolution of germanium were 4 hours of leaching at 40°C with one liter of acid solution of 125g/L for 100g of slag to obtain a yield of 98% of the Ge and a low yield of 42% Cu, 41% Co and 11% Zn. The low leaching yield observed for the other metals is explained by the high silica content of 10.30%. Indeed, the silica leads to a gel trapping the metals and preventing them from going into solution.

This is how we considered the elimination of silica by choosing the procedure using citric acid by varying the concentration in g/L of acid and the leaching time.

The optimal conditions were the use of one liter of aqueous citric acid solution consisting of 75g/L for 30 minutes of agitation in contact with 100g of slag to eliminate up to 99% of the silica. This process was followed by sulfuric acid leaching tests. The optimal conditions set was the preparation of one liter of acid solution of 122g of sulfuric acid to leach, in 2 hours, 150g of slag, i.e. a solid-liquid ratio of 15÷100. Leach results were 94% Ge, 91% Cu, 85% Co and 91% Zn.

Keywords: elimination, leaching, silica, germanium, metal refining, Lubumbashi slag

INTRODUCTION

During the pyrometallurgical processing of copper ores, blister copper is obtained. However, several metals are often entrained in the slag, as is the case in the Lubumbashi factories; which makes this slag heap a reserve of metals with high economic potential, in particular germanium, copper, cobalt and zinc (Tshibanda, 2012). On the other hand, the exploitation of this slag heap only produces the white alloy without declaring the fate of the other precious metals contained. When the last block of this white alloy leaves the factory, no one will be able to say where the valuable metals reported in the various GCM analysis reports have gone.

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Elements such as germanium, gallium and cobalt are part of strategic metals following their different applications in various high-tech industries (Petkof, 1985; Llewellyn, 1989; Boldrini, 2017). Germanium is typically used in the production of intrinsic semiconductors, polymerization catalysts, fiber optic components, and other applications. Cobalt is used in aircraft construction and electric batteries (Christman, 2010; Schimmel et al., 2001; Fujiwara et al., 2003; Depuydt et al., 2006).

The recovery of metals trapped in the silicate network by the hydrometallurgical route (Arroyo and Fernandez, 2008) has been the subject of several studies in recent years. A first study made on the oxidative leaching of the slag from the Lubumbashi Plants with sulfuric acid gave metal solution treatment yields of 94% for copper, 90% cobalt and 91% zinc after a time of 2 hours of leaching (Banza et al., 2002). Another study on the chelating leaching of metals (Cu, Co and Ni) with organic acids such as citric and oxalic acids gave solutionization yields using citric acid of 98% for copper, 87% for Ni and 98% for Co and good solution yields using oxalic acid of 99% for germanium and 97% for gallium (Meshram et al., 2020).

The present study based on the dissolution of germanium and the metals contained in the slag revealed that the slag had an acid character (I=1.4) which is due to the presence of network-forming metals. This acid character makes it insoluble in inorganic acids, which justifies the use of organic acids. The latter modify the silicate network by putting the silica in solution in the form of a hydrated gel and by concentrating the metals in the solid (Banza et al., 2002).

Thus the objective of this study is to contribute to the purification of the germanium contained in the slag. To achieve this, we will first proceed with the pretreatment and chemical analysis of the sample followed by the first test of dissolution of germanium and gallium with oxalic acid and secondly by the test of elimination of silica with citric acid to finish with the sulfuric acid leaching tests of the concentrate obtained after elimination of the silica.

METHODOLOGY

These will be different approaches that were used to produce the results presented in this study. After sampling, our procedure consisted first of a pre-treatment of the slag before dissolving the germanium in oxalic acid. The slag was bagged at 105°C before dry ball milling for 90 minutes passing through a 75 µm sieve. Secondly in a removal of the silica with citric acid followed by leaching with sulfuric acid.

The solid samples were analyzed using an X-ray fluorescence spectrophotometer (Rouessac et al., 2004). The analysis method for liquid samples is atomic emission spectrophotometry and atomic absorption spectrophotometry, which was carried out at the laboratories of OCC Lubumbashi and Gécamines Kipushi.

RESULTS AND DISCUSSION

Chemical Analysis of Slag

Chemical analysis allowed us to quantitatively determine the following elements: zinc, copper, cobalt, germanium, gallium, iron, aluminum, magnesium and silicon. The results obtained are shown in the tables below.

Table 1. Chemical characterization of UL slag

Elements	**Si**	**Fe**	**Zn**	**Cu**	**Co**	**Ge**	**Ga**	**Al**	**Mg**
%	10.300	20.010	10.400	5.381	0.210	0.020	0.008	3.970	3.171

Table 1 shows us that our sample of UL slag is concentrated in iron by 20.01% followed by zinc and silicon respectively by 10.40% and 10.30%. The other elements are also concentrated there at 5.38% copper, 3.97% aluminum, 3.17% magnesium, 0.21% cobalt, 0.02% germanium and 0.008% gallium. These results are part of the statistical average of the Gécamines team from the year 1935-1967 indicated by Tshibanda 2012.

Oxide Content of Slag UL

It is customary to express the chemical composition of rocks as a percentage of the weight of metal oxides present. The chemical analyzes carried out by XRF made it possible to determine the contents of the major elements as a percentage of the oxides. These analyzes were performed on the sample from the furnace in order to calculate the loss on ignition (P.F).

Table 2. Oxide contents

Oxyde	**ZnO**	**CuO**	**GeO**	**CoO**	**GaO**	**SiO_2**	**FeO**	**CaO**	**MgO**	**AlO**	**P.F**
%	8.650	2.800	0.029	1.700	0.026	32.690	15.630	12.170	11.030	11.100	

The slag obtained during the pyrometallurgical treatment can be described as a solution of oxides. In the case of ore with siliceous gangue, the main oxides are: SiO_2, FeO and Fe_2O_3. When SiO_2 is not present in the initially treated ore, it can be added to achieve a fluxing effect. Slag sometimes contains minor oxides, Al_2O_3, CaO, MgO, and other impurities. It is on the basis of the chemical composition of slag that metallurgists have been able to determine its acidity and basicity. A slag very rich in network-forming cations is said to be acidic, and the more the network is depolymerized by the presence of modifying cations, the more the basicity of the slag increases. However, in the case of copper metallurgy, the slag is acidic (Elamari, 1993). The sample on which we worked was the rejection of copper ore metallurgy from the Kipushi mine, we confirmed the acidity of the slag, by determining the acid-base index.

The acid-base index calculation gives (I) = 32.6912/23.20 = 1.41. We observe that the value of the acido-basicity found is greater than 1, which allows us to say that the sample of slag that we have for our study has an acid character. Elamari (1993) defined the acid-basicity of slag from copper pyrometallurgy as acidic when the acid-basicity index is higher while the opposite allows us to conclude that the slag is Basque. Results confirmed by other researchers on UL slag (Tshibanda, 2012; Banza, 2002), with an acid-base index of 1.4 and 1.32 respectively.

Characteristic Analysis of Slag

The data obtained by electron microscopy on the slag therefore makes it possible to see the different forms of the seeds of the slag. But these data are still insufficient and could be supplemented by those of the DRX.

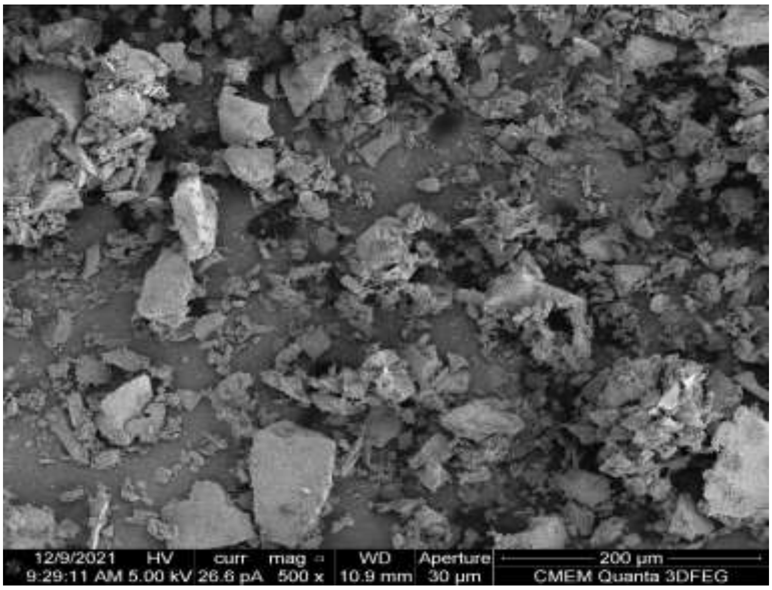

Figure 1. Characterization of slag under the scanning electron microscope

From the analysis of the image of the electronic gap in Figure 1, it appears that the slag of the ULs has a phase which is not homogeneous. UL slag is therefore an amorphous slag, it has not crystallized.

Mineralogical Analyzes of UL Slag

Petrographic studies of slag constitute a very important approach for reconstructing the processes, because they provide access to numerous clues: the nature and distribution of the crystallized phases, their elementary composition as well as their morphological texture. For our study, after several X-ray diffraction (XRD) analysis tests, the device only gave the background noise bands, no band appeared indicating the presence of a crystalline structure.

Dissolution of Germanium with Oxalic Acid

After grinding the slag, it was put into solution with oxalic acid in a stirred tank, varying various parameters such as time and concentration, at a solid/liquid ratio of 1/10 and a temperature of 40°C.

Influence of Oxalic Acid Concentration on Leaching Yield

The leaching agent used was oxalic acid in the presence of hydrogen peroxide (H_2O_2= 2mL). Metal leaching is carried out in oxalic acid at different concentrations of 100g/L; 125g/L and 150g/L. The leaching test yields are shown in the various tables and figures below.

Table 3. Leaching yield of Ge, Cu, Co, Zn and Fe as a function of concentration

$[C]_{Ox}$ (g/L)	Fe (%)	Cu (%)	Co (%)	Ge (%)	Zn (%)
100	9.47	46.65	44.44	58.38	5.22
125	12.02	46.84	51.22	63.33	6.07
150	12.49	27.14	49.41	40.52	6.93

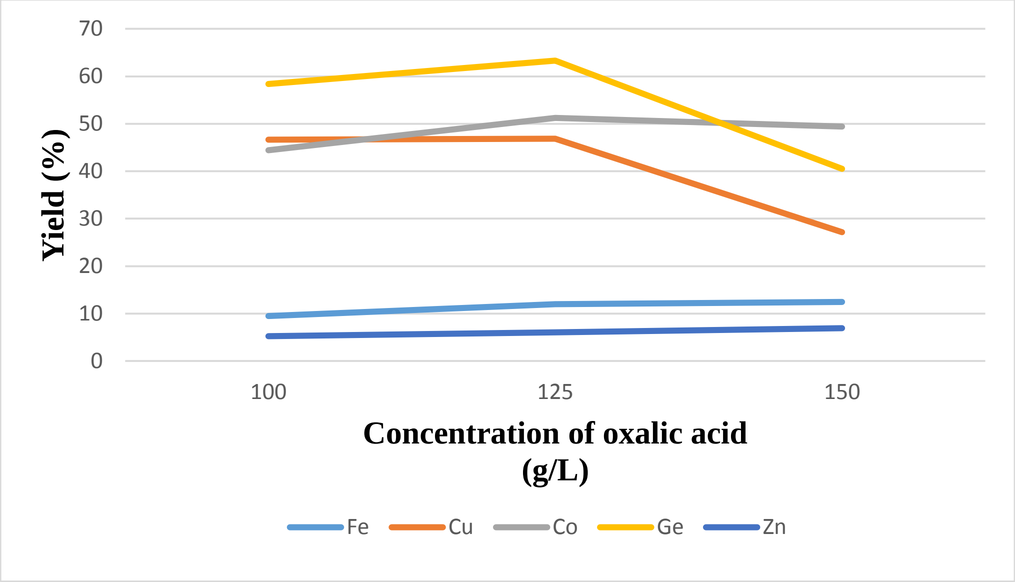

Figure 2. Influence of oxalic acid concentration on leaching yield at t = 1h and T = 313K

The effects of the concentration of oxalic acid on the leaching of germanium, copper, cobalt, zinc as well as iron, were examined with an S/L ratio of 1÷10 and a temperature of 40°C, the results are presented in Table 3.

- The germanium dissolution yield reaches its plateau at 125g/L of the acid concentration and above this the germanium yield decreases. This justifies that the oxalic acid complex Ge(IV), $Ge(OH)_2(C_2O_4)_{22}$- is stable in the range of pH 3-6 and at a high concentration the complex becomes unstable according to Pokrovski and Schott (1998);
- However for the other metals Cu, Co, Zn and Fe, this parameter does not influence their yields, they reach yields of less than 55%, at 125g/L concentration of oxalic acid.

Influence of Time on Oxalic Acid Leaching Yield

Table 4. Leaching yield of Ge, Cu, Co, Zn and Fe for 125g/L as a function of time

Time	Fe%	Cu%	Co%	Ge%	Zn%
1H	12.02	46.84	51.22	63.33	6.07
2H	14.62	48.32	56.52	79.54	10.53
3H	15.19	50.56	49.78	96.90	15.19
4H	8.89	41.82	41.17	98.37	11.29

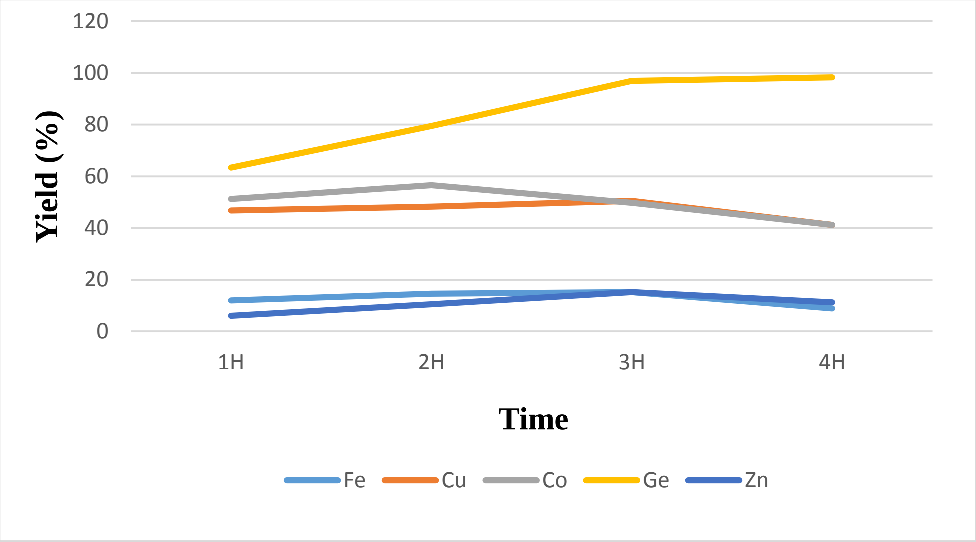

Figure 3. Influence of time on leaching yield at a concentration of 125g/L

Taking into account the variation of the leaching time and the concentration of oxalic acid in the presence of hydrogen peroxide, we found that the highest leaching efficiency was noted in the case of germanium at 98%. According to Heberlein et al. (1950), there is a formation of a water-soluble complex $[Ge(OH)_2(C_2O_4)^{-2}]$ at a pH lower than 6. The yield of the other metals was noticeably low because these metals have forms that are insoluble in slightly acidic solutions. As the leaching time increased, germanium leaching also increased up to a yield of 98.47% after 4 hours. The increase in the leaching time results in the formation of a silica gel according to the results of Matthew et al. (1977); He et al. (2010) and Xu et al. (2010).

Silica Removal

The purpose of this test was to determine the optimum conditions for removing silica from the slag before the sulfuric acid leaching tests. To do this, we varied three parameters including the citric acid concentration and time.

Influence of Citric Acid Concentration on Silica Removal Efficiency

These tests were carried out by varying the acid concentration from 0 to 100g/L with a step of 25, maintaining the time at 30 minutes. The test was carried out with 100 g of slag. The results obtained are shown in Table 5.

Table 5. Silica removal efficiency at different concentrations of citric acid at 30 minutes

g/L	**Element content in tailings (%)**					**Elimination yield (%)**				
	Cu	Co	Zn	Ge	Si	Cu	Co	Zn	Ge	Si
0	5.38	0.20	10.54	0.02	**10.34**	0.00	0 .00	0,00	0.00	0.00
25	3.04	0.41	10.10	0.01	**0.201**	61.72	25.66	13.18	59.40	**98.65**
50	4.78	0.38	9.40	0.0106	**0.200**	30.23	10.49	10.66	52.31	**98.94**
75	5.79	0.46	9.10	0.016	**0.196**	4.26	8.00	4.17	10.00	**99.22**
100	**Gelation of the mixture (paste)**									

The data in this table allowed us to draw the following graph:

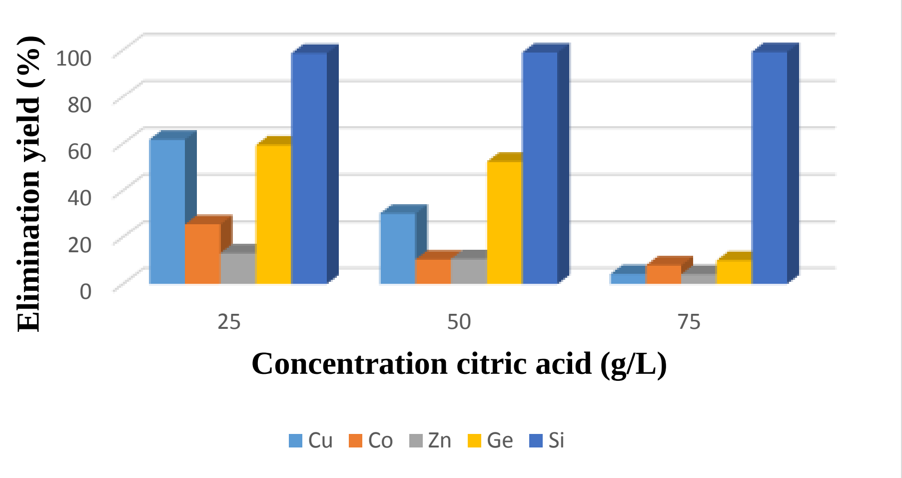

Figure 4. Influence of citric acid concentration on silicon removal efficiency

By maintaining the time at 30 minutes and by varying the concentration of citric acid from 0 to 100g/L, we observed that the silica was eliminated at 98.65% with 25g/L of citric acid, at 99. 22% with 75g/L citric acid. We also observed that the entrainment of other useful metals was greater at 25g/L citric acid and it decreased with increasing citric acid concentration. However, during this test, we observed that at 100g/L of citric acid that the mixture gelled (a paste). By varying the exposure time to citric acid from 60 to 90 minutes, we obtained 3.83 to 2.07 g of residues respectively. We observed that the mass of these residues decreased with the increase in the concentration of the acid used. Furthermore, at 120 minutes, the mixture had completely gelled. This is why we have chosen the time of 30 minutes and the citric acid concentration of 75g/L, as the optimum condition for the elimination of silica from the UL slag. Ambient temperature was also retained as the optimal condition for the elimination of silica in the slag because the rise in temperature led to a gelation of the slag and citric acid mixture.

Sulfuric Acid Leaching Results

The residues obtained after elimination of the silica in the slag in the presence of citric acid at a concentration of 75g/L for 30 minutes are then leached in sulfuric acid. Given that some of the metals sought have a low content in the concentrates, such as cobalt, germanium and gallium, we considered dissolving with sulfuric acid at a concentration of 120g/L, to make a total solution of metals. The parameters retained for the leaching are the solid-liquid ratio and the leaching time while the temperature and the acid concentration remained constant.

Influence of Solid-Liquid Ratio on Leaching Yield

To see the effect of the solid to liquid ratio on the leaching yield, we varied the ratio to 5, 10 and 15%. The time was maintained at 60 minutes for sulfuric acid leaching with a concentration of 122g/L, at T=313K. The results obtained are shown in Table 6 and Figure 5.

Table 6. Yield of leaching at 60 minutes

Ratio (%)	Content of metals in concentrates (mg/mL)				Metal leaching yield (%)			
	Cu	**Co**	**Zn**	**Ge**	**Cu**	**Co**	**Zn**	**Ge**
5	382.04	26.72	630.29	0.68	65.99	56.52	69.33	42.50
10	410.50	27.45	652.73	0.87	70.85	59.67	71.73	54.38
15	430.20	29.93	687.22	1.08	74.34	63.89	75.50	67.29

The solid/liquid ratio of this chart helped us plot the graph in the figure below.

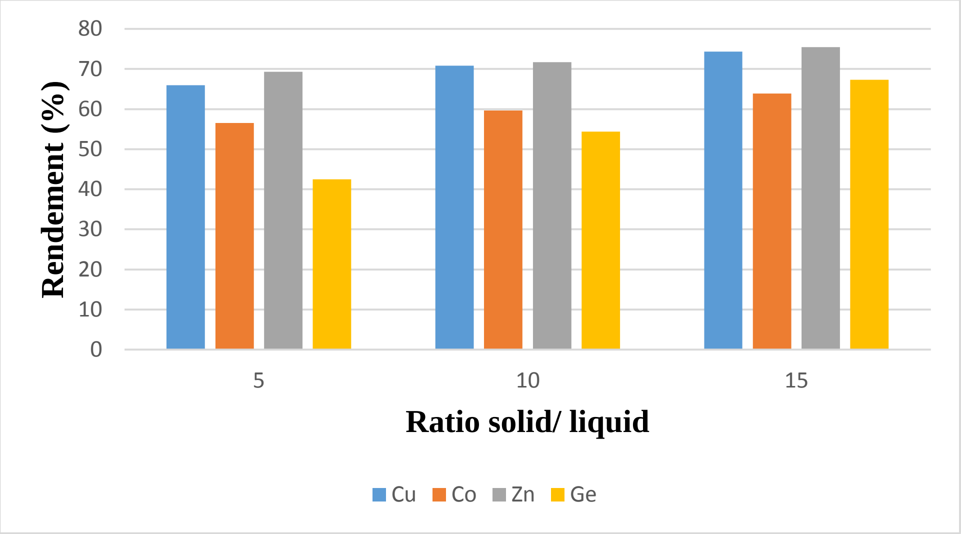

Figure 5. Influence of the ratio on the leach yield at 60 minutes

By maintaining the time at 60 minutes, we observed that the yield increased with a ratio of 15% i.e. a yield of 74.34% for copper, 63.89% for cobalt, 75, 50% for zinc and 67.29% for germanium. This is the best yield with this ratio of 15% for copper (74.34%), for cobalt 63.89%, for zinc 75.50% and germanium (67.29%). The effects of the liquid-solid ratio on the leaching of germanium and other metals were studied at an H_2SO_4 concentration of 120g/L, at a temperature of 313K and for 1h. The results are in Table 5. We observed that the more the liquid-solid ratio increased the leaching efficiency became more important, with as a consequence the increase in the leaching of silicon, which facilitates the production of a silica gel especially in a concentrated acid medium (Hua et al., 2002; Harbuck, 1993; Bodas, 1996). At the end of these tests, we retained the liquid to solid ratio of 15% as the optimum value for the rest of our experiments in the laboratory. At this report, we obtained good yields which allowed us to move on to another parameter.

Influence of Time on Sulfuric Acid Leaching Yield

To evaluate the influence of time on the leaching yields, we varied this parameter by keeping the solid-liquid ratio constant.

Table 7. Yield obtained as a function of time at a ratio of 15%

Time (min)	**Content of metals in concentrates (mg/mL)**				**Metal leaching yield (%)**			
	Cu	**Co**	**Zn**	**Ge**	**Cu**	**Co**	**Zn**	**Ge**
30	347.44	22.09	672.33	0.62	60.03	47.92	73.85	38.96
60	4 30.20	29.93	687.22	1.08	74.34	63.89	75.50	67.29
90	518.02	38.54	761.60	1.45	89.46	83.64	83.60	90.70
120	528.80	39.83	824.03	1.51	91.19	85.19	90.63	93.98
150	51921	39.54	786.41	1.46	89.67	85.96	86.42	91.25

The results of this table helped us plot Chart 19.

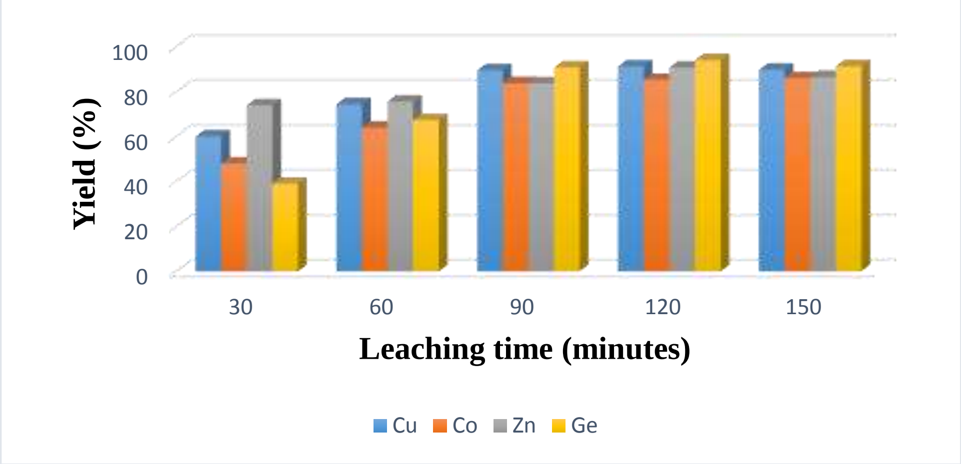

Figure 6. Results of the influence of time on yield at the 15% ratio

The effects of time on leaching showed that as time increased, the leaching of germanium, copper, cobalt as well as zinc increased up to 93.98% Ge, 91.19% Cu, 85.19% Co and 90 .63% Zn at 120 minutes. The increase in the leaching time favored the formation of a gel. This shows that silica polymerization is favorable with increasing leaching time (Matthew et al., 1977; He et al., 2010; Xu et al., 2010).

CONCLUSION

Our study is a contribution to the purification of germanium from the pyrometallurgical slag of the GCM factories in Lubumbashi. To do this, an application of the pre-treatment processes of these slags was made through drying at 105°C for 24 hours and grinding at 75μm for 90 minutes. This was followed by dissolution, firstly by attack with oxalic acid and secondly with sulfuric acid after having eliminated the silica.

The slag studied consisted mainly of gangue metals including iron (20.010%) and silicon (10.34%). The useful elements identified are germanium (0.02%), cobalt (0.22%), zinc (10.54%), copper (5.38%), gallium (0.008%) and silver (0.001%). This study looked at germanium, zinc, copper and cobalt.

To optimize the dissolution of the germanium, the process was started by leaching with oxalic acid carried out after 4 hours at 40°C with a yield of 98% of the Ge and a low yield of 42% of the Cu, 41% Co and 11% Zn. The gelling silica preventing the dissolution of the other metallic elements was eliminated by attack with citric acid at 125g/L for 30 minutes with a maximum yield of 99% before carrying out the sulfuric acid leaching tests. Following this process, the optimal conditions for leaching with sulfuric acid at a concentration of 2.5N, at room temperature, at a solid-liquid ratio of 1.5/10 and after 2 hours made it possible to 94% Ge solution as well as other metals including: 91% Cu, 85% Co and 91% Zn. Increasing the time beyond 2 h resulted in the formation of a gel.

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