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# International Congress of Science and Technology of Metallurgy and Materials, SAM -CONAMET 2013 Characterization of Slags Produced During Gold Melting Process

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# Abstract

In the extractive metallurgy of gold ores the cyanidation and melting processes are generally applied. These processes allow obtaining the "dore". The slag generated during the melting process presents various characteristics, depending on the mineral source and the type of flux used. The literature information on this pyrometallurgical process at high temperature is very poor. For this reason this paper is focused on the characterization of three synthetic slags. The main objective of the study is to characterize the slags: a) improve the melting process operation, b) to analyze the environmental impact, c) to determine the possibility of slags being recycled.

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# 1. Introduction

The increased demand for gold leads to an increased number of explorations that include cheaper deposits, and also to move forward to production efficiency. Depending on the grade of the ore, different processing methods are applied. High-grade ores are pulverized and treated in terms of inherent characteristics: minerals consisting of oxides are incorporated to the leaching circuit; refractory gold ores containing carbonaceous ligands are treated by roasting at 500°C in order to finally obtain oxides; sulfated minerals without C are oxidized in autoclave to separate

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gold from sulfides which are then incorporated to the cyanidation circuit. Gold is extracted from the cyanide-bearing solution by means of activated carbon [F. Reith et al (2012)].

Cyanidation is one of the most frequently applied processes; the wastes derived from this process may contain hematite, cupric ferrite, fine metals such as Au, Ag, etc [I. Wilkomirsky et al (2010)].

Another source of gold are slags that are generated during the pyrometallurgical treatment of mineral concentrates, which represent a high percentage of the mining industry residues. In many cases, these slags may contain metals which may be of interest such as Au, Ag y Cu depending on the source ore they come from and on the pre-treatment conducted. Additionally, in such cases, the concentrations in which these ores occur may be higher than those of many metal ores. Identification of the constituting elements and contents of these residues allows on the one hand to evaluate and optimize pyrometallurgical processes themselves and on the other hand, to improve the operation of the furnaces. Moreover, this identification makes possible to design extraction processes of the metallic residues, to analyze possibilities for slag recycling or decontamination and to remove toxic substances.

As a consequence, this represents an advance towards a more favorable environmental impact of the processes. Many research workers have developed a number of studies to find out new uses for the various types of slag generated by pyrometallurgical processes. In the case of the steel industry, slags produced during steel-making are recycled in various industrial processes or used in Portland cement making, ceramics, etc. To a lesser degree, slags from copper pyrometallurgy are applied to similar uses or in reprocessing for metallic recovery [A. Acosta et al (2001), X. Elias (2009), A. Muller et al (2002), K. Mills (2011), N. Kanari et al (1999) and S. Orizola (2009)].

However, there are few records of studies of gold slags and their reprocessing for other uses. In designing and developing pyrometallurgical processes, it is necessary to consider beforehand aspects of metallic recovery and slag recycling in order to foresee from the start the attainment of environmental and economic benefits.

This leads to the "Development of sustainable processes" in order to seek generating welfare for present day generations without compromising the future generations' welfare. This work presents a characterization of three slags obtained from melting processes of minerals from the area of the province of San Juan. Consideration is given to determination of the chemical and mineralogical composition, the melting process behavior and to the structural characterization of the slags through optical microscopy and scanning electron microscopy (SEM).

#### 2. Experimental procedure

### 2.1. Melting process

First, 3 slag samples are obtained by melting mineral concentrates, using  $PbO_2$  as a flux in the melting process. Melting is carried out in a Lindberg furnace at 1000°C during 1 h. The  $PbO_2$  is reduced to a metallic Pb, which collects the precious metal. When the melted mixture is cooled down, the lead bearing the precious remains at the bottom of the crucible covered by a glassy slag with an approximate density of 2,53 gr/cm3 that remains on top [V.A. Shvetsov and N. V. Adel'shina (2009)]. Once the slags generated out of the 3 samples of different minerals are obtained, their characterization starts.

#### 2.2. Characterization of the slags

When characterizing slags, determination is made of their chemical composition through application of various chemical analysis techniques, namely, determination of substances (precious metals) present through "fire assay", minority elements through acid digestion and subsequent reading by means of ICP "inductively coupled plasma-atomic emission spectrometry".

The mineralogical composition is determined through X-ray diffraction by using a PhillipsX'Pert equipment and the interpretation software Match. Determination of the melting behavior is performed through hot-stage microscopy (HSM). The structural study includes optical microscopy techniques in white and polarized light modes using an Olympus GX 51 microscope and an image analyzer Leco IA 32. In addition, observation is made and a semi-

quantitative chemical analysis performed of the phases present by using a scanning electron microscope (FEI Quanta 200) that is able to perform analyses through the EDS (energy dispersive spectrometry) technique.

# 3. Results and discussion

## 3.1. Determination of the chemical composition

The analysis procedure includes attack with acid digestion to solubilise the sample. Then, the sample volume is leveled up to be incorporated into the ICP equipment. The determination of the substances concentrations obtained is presented in Table 1.

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Sample	Ca	Mg	Na	Κ	Si	Pb	Cu	Fe	Al	Ag	
	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	(ug/g)	
E1	878,8	918,2	152720	2220	18590	361000	39,2	5496	4908	9,8	
E2	742,4	1577,2	155200	7302	4880	343800	23,8	3030	9586	25,6	
E3	354,2	2624	173380	9428	6706	1399,2	25,3	6088	17958	64	•
	<i>,</i>										
Sample/cont	Cr	Sn	Мо	Ni	Tl	V	Mn	Zn	Р	Ва	As
Sample/cont.	Cr (ug/g)	Sn (ug/g)	Mo (ug/g)	Ni (ug/g)	Tl (ug/g)	V (ug/g)	Mn (ug/g)	Zn (ug/g)	P (ug/g)	Ba (ug/g)	As (ug/g)
Sample/cont.	Cr (ug/g) 95,4	Sn (ug/g) -	Mo (ug/g) 0,4	Ni (ug/g) -	Tl (ug/g) 62	V (ug/g) 14,6	Mn (ug/g) 30,6	Zn (ug/g)	P (ug/g) -	Ba (ug/g) 1187	As (ug/g) 151,8
Sample/cont. E1 E2	Cr (ug/g) 95,4 194,8	Sn (ug/g) -	Mo (ug/g) 0,4 6,4	Ni (ug/g) - 90,4	Tl (ug/g) 62 52	V (ug/g) 14,6 15,2	Mn (ug/g) 30,6 521,2	Zn (ug/g) - 16,8	P (ug/g) - N/D	Ba (ug/g) 1187 136	As (ug/g) 151,8 9,6

Table 1. Composition of the slag samples from the gold melting process

# 3.2. X-ray diffraction.

X-ray diffraction is performed over the three slag samples. Results are shown in Figure 1 (a-c). As shown in the pictures, all of the slags are totally glassy.



Fig. 1. Results from the X-Ray diffraction obtained from the slag samples.

#### 3.3. Hot Stage Microscopy (HSM)

The slags melting behavior and critical temperatures are determined through hot stage microscopy (HSM). The results obtained are shown in Table 2. During the melting process, cyclic expansions and contractions of the cakes were observed, which subsequently stabilized and melted. This was apparently due to a high removal of volatile

particles. This phenomenon was more noticeable in slags E1 y E2 than in E3 at temperatures ranging from 300°C y 590°C, See Figure 2.



Table 2. Results of critical temperatures obtained with hot stage microscopy (HSM)

If a comparison is made of the melting behavior of each of the slags, similarities may be found to exist as to the melting range of slags E1 and E2 (650°C-700°C). Slag 3 has considerably higher critical temperatures (> 750°C). Figura 3



Fig. 2.Expansion and contraction cycles undergone by slag E1 on account of gas elimination.



Fig. 3. Comparing the melting behavior of the three slags

### 3.4. Structural study

Observation of the slag samples is performed by means of optical microscopy applying white and polarized light and also electronic SEM over samples in receptive state. Results obtained by means of optical microscopy are first shown in detail. Both E1 and E2 samples were found to be composed of very large, sharp, glassy and homogeneous fragments. In sample E1, greenish particles with variable transparency are identified. Figure 4.

In slag E2, large glassy particles are also present, some greenish and other brownish in color (See Figure 5). With bigger amplifications, internal veins may be observed with precipitated phase appearance. Sample E3 is made up of glassy particles smaller in size and with a varying morphology which includes sharp-edged particles, rod-shaped particles and irregularly shaped particles. The larger ones have an average size of 274  $\mu$ m. The characteristics described may be noted in Figure 6. Slag E1 presents a homogeneous green color and high transparency when observed with polarized light under the same condition and with amplifications of 100, (Figure 7).

In slag E2 particles with various colors such as pink, bluish and greenish are identified. In the interior part of some of them, it is possible to visualize bubbles, spherical particles and crystals that are pink in color and have a polygonal morphology. Figure 8 shows one of the particles with bubbles in. In slag E3, most of the particles are also bluish or greenish in color. However, pink and amber particles may be identified to a lesser degree. Figure 9 shows the physical appearance of some particles from such slag.



Fig.4. Appearance of a homogeneous glassy particle in slag E1.



Fig.5. Large glassy particles in sample E2



Fig.6. Particles with varying morphologies in

slag E3



Fig 7. Appearance of sample E1 observed with polarized light.



Fig.8. Particles having spherical nuclei in slag E2.



Fig.9. Particles in slag E3. In pink particles, blue spheres may be identified

Observation made with scanning electronic microscopy (SEM) made it possible to verify the homogeneous and glassy appearance of particles in the three of the slags. The (semiquantitative) chemical composition of the particles in the slag may be determined by means of EDS. All of the slags have contents of SiO<sub>2</sub>, Na<sub>2</sub>O y FeO. Slug E1 (see Table 3) has also a PbO<sub>2</sub> content of of ~ 48,31%. Globular particles with Pb can also be identified that are accumulated in localized zones of the sample (shown squared in Figure 10).

Using the same method, the various particles of slag E2 are analyzed (Table 3). In this case, it is shown that these have PbO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO (~ 49,50 %) and traces of Pt. In the case of slag E3 (Table 3), a content of PbO<sub>2</sub> (~39,06 %) and CaO is verified. Inside the particles, globular inclusions and spherical particles with Cu-Ni were identified that contain Pb exploded on account of the incidence of the beam of electrons, Figures 11 and 12.



Fig. 10. Appearance of the Pb spherical particles present in slag E1.

Table 3. Chemical composition of the slags

Slag	%FeO	%Na <sub>2</sub> O	% SiO <sub>2</sub>	%PbO <sub>2</sub>	%MgO	%Al <sub>2</sub> O <sub>3</sub>	%CaO
E1	2,47	16,82	32,39	48,31	-	-	-
E2	0,93	11,70	31,76	49,50	0,95	5,13	-
E3	0,91	37,44	18,10	39,06	-	2,83	1,63



Fig12. Spherical particle with Pb that explodes when impinged by the beam of electrons.

Based on the results from the chemical composition of the slags and when the contents of FeO,  $Na_2O$  y  $SiO_2$  are taken to a 100%, such chemical compositions are located in the ternary diagram FeO- $Na_2O$ - $SiO_2$  [Ficha Sal de Plomo II,(2005)] that partially represents the slags under study, see figure 13. From this analysis, it may be verified that the E1 slag is on the coexistence line of sodium silicate ( $Na_2O$ . $SiO_2$ ) and sodium disilicate( $Na_2O$ . $2SiO_2$ ), which during cooling could turn into sodium metasilicate. Slag E2 has a chemical composition in the stability field of the sodium disilicate ( $Na_2O$ . $2SiO_2$ ) and during cooling will also form sodium

metasilicate. This reasoning may account for the similar melting behavior found through hot stage microscopy although the slight differences in critical temperatures indicate the impact of the MgO y  $Al_2O_3$  contents.

Slag E3 is located on the stability field of the disodium silicate  $(2Na_2O.SiO_2)$  and, through cooling, would turn into sodium ortosilicate. Differences in the chemical composition of this slag and, in particular, the CaO y  $Al_2O_3$  contents present would be responsible for the increased critical temperatures observed in the melting behavior of the slag.



Fig. 13. FeO-Na2O-SiO2 system

Also, based on the results of the chemical composition of the slags, it may be concluded that the recovery of Cu, Ag y Pt in the pyrometallurgical process is acceptable. It may be noted that toxic elements such as Cr, Pb are present in various proportions. This leads to thinking on the possibility that certain compounds may be formed that could undergo accumulation of the food chain. Alert should be given that in case they are in too low doses in the environment, they may get concentrated in plants or animals and cause health damage. Recommendation should be given for a later reprocessing of the slags so as to mitigate the presence both of these metals and of the PbO<sub>2</sub> that turns out to be considerably high in these three slags.

From the chemical composition and the behavior determined during the EDS analysis and from the release of gases visualized through hot stage microscopy, it may be deduced that the substance constituting the spherical particle with Pb content could be lead carbonate (PbCO<sub>3</sub>).

As reported by the International Chemical Safety Cards ICSC 0999, this substance is decomposed by heating it at  $315^{\circ}$ C, producing toxic fumes of PbO<sub>2</sub> which are highly dangerous since high exposure to them could cause serious health problems. Thinking on a possible application of recycled E3 slag, the CaO and Al<sub>2</sub>O<sub>3</sub> contents could give rise to the presence of phases such as: calcium silicates, calcium ferrosilicate or tricalcium aluminates. In particular, calcium ferrosilicate could be generated in E2 slag due to its MgO content [M. Kowalski et al (1995) and J.F. Schairer et al (1995)]. Portland cement has composition characteristics that could make possible its incorporation to the production chain. As a global analysis of the foregoing, it is estimated that despite the fact that slag production in gold industry is not as big compared with steel and copper industries, these slags could be recycled provided the level of toxic elements in them, mainly PbO<sub>2</sub>, is eliminated by previously treating it through some metallurgic extraction process.

# 4. Conclusions

Based on the results obtained it may be concluded that:

- Advances were made as to knowledge and characterization of Au slags, demonstrating that they are mostly composed of SiO<sub>2</sub>, FeO y Na<sub>2</sub>O. Some slags may contain Al<sub>2</sub>O<sub>3</sub>, CaO y MgO. These slags have a fully glassy structure, with an approximate density of 2,53 gr/cm3. Their melting behavior is determined by their chemical composition and it develops within the range of 650°C y 850°C. The insights provided are regarded relevant for Au extractive metallurgy. However, further studies of such systems should be required to determine additional physical properties at high temperature that would allow better adjustments of the metallurgic processes as well as a better understanding of the behavior of these slags.
- The slags show a good metallurgical efficiency of the metals, which are of specific interest since they do not bear Au. Only slag E2 has traces of Pt, and slag E3 has scanty inclusions of Cu-Ni.
- It was determined that in the 3 slags studied there exists a considerable concentration of compounds harmful both to the environment and the human health. This shows that special attention should be given to the area where these wastes are stored, a post-treatment being required to mitigate harmful elements so as to prevent environmental pollution.
- As to slag recycling in terms both of their chemical composition and of the results obtained from thermodynamic study through application of equilibrium diagrams of related systems, Portland cement industry could be thought of as a possible integration in the case of E3 slag. However, in order to confirm this, specific physical, chemical, and mechanical studies should be carried out that are beyond the scope of this article.

# References

- Reith F., Zammit C.M., Rogers S.L., 2012. Potential utilization of microorganism in gold processing: a review, Mineral Processing and Extractive Metallurgy, 121,4, pp. 251-260.
- Wilkomirsky I., Rojas N., Balladares E., 2010. Gold and Silver Cyanidation from a residue produced byleaching dead copper-roasted white metal, Canadian Metallurgical Quarterly, 49, 1, pp. 29-38.
- Acosta A., Aineto M., Iglesias I. 2001. Physico-chemical characterization of slag waste coming from IGCCthermal power plant, Materials Letters, 50, pp. 246-250.

Muller A., BlachnikR.2002.Reactivity in the system copper-arsenic-sulfurI. The formation of Cu<sub>3</sub>AsS<sub>4</sub>, enargite. Thermochimica Acta 387, pp153-171

Mills K.2011, The estimation of slag properties. Southern African Pyrometallurgy 2011

Kanari N. E., I. Allair, , A Gaballah. F. García. 1999. Caracterización de elementos contaminantes en escorias procedentes de laincineración de residuos de laindustria química y metalúrgica. Rev. Metal Madrid, 35 (1), pp:3-10

Orizola S.. 2006. Uso de escoria de cobre encementos . Memoria de titulo. Universidad de Chile.

Elias, X. 2009 Los Residuos mineros, Reciclaje de residuos industriales, 2ºEdición, Ed.: Diaz de Santos .

Shvetsov V. A. and Adel'shina N. V. 2004 .A Study of the Process of Gold Recovery from a Slag Meltinto the Bottom Phase in Fire Assay. Journal of AnalyticalChemistry, Vol. 59, No. 7, pp. 628–632

Ficha Sal de Plomo II, 2005, carbonato de Pb II, Fichas Internacionales de Seguridad Química ICSC 0999 - CE IPCS

Kowalski M., Spencer P.J. and Neuschutz D., 1995. Phase Diagrams, Slag Atlas, 2º Edición, VerlagStahleisen GmbH, pp 148-154.

Schairer J.F. and Yagi K., 1995The system FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Slag Atlas, 2º Edición, VerlagStahleisen GmbH, pp 148-154