As, Sb And Aulfate Immobilization From Flotation Tailings Of An Intrusion-Related Gold Mineralization

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Abstract

The Salave Gold Prospect is the largest unexploited and well-known gold deposit in Spain. Gold occurs almost exclusively as refractory and invisible, within the arsenopyrite crystal structure. During the closure phase, it is expected that about 2 Mt of flotation tailings (~0.1% of sulfides) will have to be allocated in an isolated dam. To assess best option to stabilize these tailings in the long-term, some leaching tests have been performed over mixtures of tailings with different binding materials. The optimum behaviour in terms of contaminant immobilization was reached by the addition of 5%(wt) Portland cement, 5% quicklime and 1% limestone filler. The release of As and Sb decreased by 98.37% and 94.68%, respectively, while sulfate release is below 5 mg/L.

Keywords: Flotation tailings management, Arsenic, Antimony, Sulfate, Leachability.

Introduction

Most of the gold-bearing ores currently being mined must undergo -before hydrometallurgy- a mineral separation process called flotation. This process usually produces a sulfide-rich concentrate containing the gold and a tailings fraction composed of milled mineral particles of the host rock, typically silicates, carbonates, or a mixture of both. While the sulfide concentrates proceed to cyanide leaching, the tailings are usually stored in engineered tailings facilities, where they accumulate until mine closure or are repurposed for backfilling mine voids using cemented paste backfilling (CPB) technology. If reuse is not feasible, flotation tailings must be properly stabilized and neutralized to prevent long-term environmental impacts

Experimental studies on the stabilization of this type of tailings, based on published data (Choi *et al.* 2009; Coussy *et al.* 2011, 2012; Kiventera *et al.* 2018, 2019; Hamberg *et al.* 2015; Tariq and Yanful 2013, among others), suggest the use of various binding materials to effectively immobilize the elements of concern present in the tailings. Ordinary Portland cement, often combined with different additives, is the most used material. The recommendations for mine sludge management outlined by the European Commission in the Best Available Techniques (BATs, Garbarino *et al.* 2018) are aligned with the findings of these studies.

The tailings used in this study come from the pilot-scale froth flotation of gold ore from the Salave gold prospect. This mineralization is considered among the most important in Europe that has yet to be exploited (measured resources are more than 1 Moz Au at 4.6 g Au/tonne). Although numerous exploration campaigns have been conducted since the 1970s, scientific literature on this mineralization is scarce, being the work of Rodríguez-Terente *et al.*. 2018 the most valuable contribution. Gold-mineralization is hosted by a variscan subalkaline and hyperpotassic granodiorite (I type granite) affected by a late hydrothermal episode. This hydrothermal activity has intensely affected the host rock, resulting in significant albitization, chloritization, and sericitization. The paragenetic sequence of the mineralization is dominated by arsenopyrite and pyrite, with appreciable amounts of molybdenite and stibnite, and occasional presence of chalcopyrite, sphalerite, berthierite and rutile. Gold is essentially refractory and is associated with sulfides, primarily arsenopyrite.

Considering the above cited background, and as a first step in developing the most effective stabilization strategy for these tailings, several preliminary tests were conducted using different concentrations of Portland cement (PC, Portland cement without additives or CEM I), quicklime and blast furnace slag (BFS) as stabilizers. These initial mixtures were analysed for mechanical properties, permeability, and leaching behaviour.

Methods

The proportional distribution of the various mineral species, along with the chemical composition and the particle size distribution of the tailings must be thoroughly analysed to design a stable tailings storage facility for long-term storage of tailings.. Grain size distribution curves were obtained by Static Light Scattering with a Laser (λ=520 nm) Particle Sizer Analyssete 22 Nano Tec Plus (FRITSCH) following the standard ISO 13320. Major elements composition was determined by Wavelength-Dispersive X-Ray Fluorescence (WDS-XRF) with a Philips PW2404 spectrometer. Minor and trace elements of the solid tailings bulk sample were assessed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Agilent 5800 instrument). Mineralogical composition was evaluated by means of X-Ray Diffraction (XRD) using a Seifert XRD 3000 T/T Diffractometer. Energy-Dispersive X-Ray Fluorescence (ED-XRF, Inca Energy 350 module from Oxford) coupled to a Scanning Electron Microscope (SEM) was used for grain scale chemical analyses. Permeability determinations were carried out at PanTerra Geoconsultans using a digital nitrogen permeameter following the methodology described in Zhang *et al.* (2013). Leaching tests were performed according to European standards EN-12457:4 (dynamic leaching) and EN-15863 (static leaching). The filtrate resulting from these tests was analysed for the substances indicated in the Spanish Regulations for surface water quality (RD 817/2015): As, Sb, Ba, Cd, Cu, Cr, Sn, Mo, Ni, Pb, Se and Zn were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and SO_4^{2-}, F-and Cl- were analysed by Ionic Chromatography. Hg was quantified by Cold Vapour Atomic Absorption Spectrometry (CV-AAS).

Results and Discussion

Grain size distribution

As can be seen in Fig. 1, the frequency distribution of tailings particles sizes (diameters) indicates a trimodal set of measurements: there is a first mode at 10 µm, a second one at around 50 µm – which is the dominant particle size – and another one, less important, at 250 µm. D_{10} is 4.3 µm, D_{50} is 29.8 µm and D_{90} is 88.2 µm.

Chemical composition and mineralogy

XRD results show that, from a mineralogical point of view, the tailings are mainly composed by Na-rich plagioclase (albite-oligoclase) and muscovite, followed by moderate proportions of dolomite, quartz and orthoclase. Small amounts of clinochlore and sulfides can also be identified. As expected, major element composition is dominated by Si and Al. Among the alkalis, Ca and K are predominant. Calcium is primarily associated with dolomite and, to a lesser extent, with plagioclase, while K is almost entirely derived from K-feldspar. Magnesium concentrations are also high, largely due to dolomite. The predominance of muscovite among the micas contributes to relatively low Fe concentrations. Concerning trace elements, the micro-analyses carried out by ED-XRF coupled to a SEM pointed out that As and Sb appear in the form of very small particles (2-10 µm) of sulfides (stibnite and arsenopyrite) and sulfosalts.

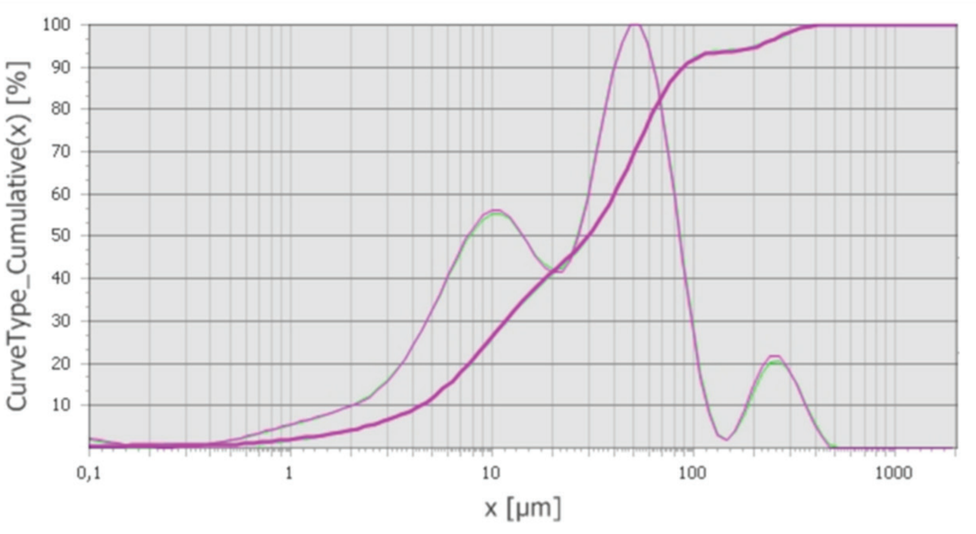

Figure 1 *Grain size distribution curve of the flotation tailings.*

Table 1 *Composition (major, minor and trace elements) of the flotation tailings.*

Oxides	Weight %	Element	mg/kg
SiO_2	54.16	As	1098
$Al2O_3$	18.38	Sb	83.6
$FeO+Fe_2O_3$	2.60	Cd	<5
MnO	0.10	Cu	32.2
MgO	3.49	Cr	11.9
CaO	4.70	Hg	<10
Na_2O	2.53	Mo	6.4
K_2O	4.41	Ni	<5
TiO_2	0.54	Pb	28.5
P_2O_5	0.20	Se	<10
Loss On Ignition	8.70	Zn	<50

Permeability and Leaching tests

Permeability and leaching tests are usually used to assess the behaviour of flotation/mine tailings that are going to be deposited in an on-land tailings impoundment after the closure of mining activities. The final disposal of this type of waste is typically achieved using a binding agent that, when properly dosed, ensures both physical and chemical stabilization of the tailings. A review of the existing scientific literature indicates that the most suitable binding agents include geopolymers, cement, quicklime and blast furnace slag. To evaluate the most suitable option among the available alternatives, a series of specimens (18 units, 160 × 40 × 40 mm) were initially prepared using Portland cement, lime and blast furnace slag as binders for the tailings, at dosages of 5% and 10% (dry weight), which are typical in such cases. The preparation of the test specimens was carried out in stainless steel molds with a longitudinal tolerance of 0.2 mm. In all cases, the specimens were demolded after 7 days of curing, with the specimens made with lime/quicklime being air-dried and those made with cement being cured in a humidity chamber at 25°C. The curing time to assess permeability in these mixtures was set at 28 days. The results are shown in Table 2 (air permeability for untreated tailings was not determined, as it depends on the degree of compaction):

As can be seen in Table 2, the reduction in water permeability – when comparing with the untreated tailings – is high in all cases, with the best values provided using PC as binding material. The reduction in permeability is not very significant (~1%, from 94.09 to 95.11) between a 5% and a 10% of PC dosage.

Leaching tests were conducted in dynamic mode (standards EN-12457:4 and

Table 2 *Results of the permeability tests conducted on the different binding materials considered.*

Sample(dosification)	**Air permeability** (mD)	**Water permeability (hydraulic conductivity, m/day)**	**Reduction (%)**
5% Quicklime	14.5	0.01064	82.26
10% Quicklime	6.95	0.00509	91.52
5% PC	4.84	0.00354	94.09
10% PC	4.00	0.00293	95.11
5% Lime+BFS	9.42	0.00689	88.51
10% Lime+BFS	10.6	0.00778	87.03
Tailings (without stabilization)		0.06	

Table 3 *Results of* ***the*** *dynamic leaching tests (DOC: Dissolved Organic Carbon; TDS: Total Dissolved Solids).*

Parameter	**Units**	**Tailings**	**7 d**	**28 d**	**Reduction (7 d)**	**Reduction (28 d)**	**Threshold**
pH (25C)		8.92	12.53	12.62			
Cl-	mg/L	<50	<50	<50.0			
F-	µg/L	<1.0	3.2	5.2			1500
Sulfate	mg/L	52.7	<5	<5	>90,51%	>90,51%	
COD	mg/L	<150	<150	<150			
TDS	mg/L	<1000	15890	15020			
Sb	µg/L	0.94	0.21	<0.05	77,66%	>94,68%	
As	µg/L	2.7	0.06	<0.05	97,77%	>98,14%	50
Ba	µg/L	<0.05	4.4	4.3			
Cd	µg/L	<0.01	<0.01	<0.01			
Cu	µg/L	<0.05	<0.05	<0.05			5
Cr	µg/L	<0.05	0.13	0.30			50
Sn	µg/L	<0.05	<0.05	<0.05			
Hg	µg/L	<0.0010	<0.0010	<0.0010			0.07
Mo	µg/L	0.16	0.28	<0.10		>37,5%	
Ni	µg/L	<0.05	<0.05	<0.05			20
Pb	µg/L	<0.05	0.09	0.06			7.2
Se	µg/L	<0.05	<0.05	<0.05			1
Zn	µg/L	<0.50	<0.50	<0.50			30

EN-15863, respectively), using the same mixtures evaluated in the permeability tests. The achieved reductions in the mobilization of As and Sb ranged between 80% and 95%, respectively, with PC being the most effective binding material for metals and metalloids. In contrast, quicklime demonstrated better performance in mitigating sulfate leaching. The reductions observed after 28 days of curing were consistently greater than those at 7 days, except in the case of Pb, where some tests showed higher reductions at 7 days.

Several studies have specifically investigated Pb immobilization in mining waste, concluding that its mobility can be minimized through calcium carbonate amendments (Martínez-Sánchez *et al.* 2014; Yun and Yu 2015) or treatment with H_3PO_4 (Navarro *et al.* 2011). Based on these findings, the proposed final mixture for large-scale implementation during mine closure consists of 5% PC, 5% quicklime and an additional 1% of limestone filler. This formulation combines the effectiveness of PC in immobilizing As and Sb with the sulfate-stabilizing properties of quicklime, while the limestone filler helps to improve the retention of Pb. The results obtained with this mixture are presented in Table 3, which includes data from untreated tailings, treated tailings at 7 and 28 days of curing, and the regulatory limit values established by Spanish legislation for these leachates. It is noteworthy that there are no threshold values for leachate pH. Nitrogen species are not considered, as the original material (flotation tailings) has not been subjected to cyanidation.

As observed in the previous Table (3), the proposed binding mixture (5% PC + 5% quicklime + 1% limestone filler) meets the environmental quality standards for surface water established in RD 817/2015 under the experimental conditions of the standard. The retention of As exceeds 98%, while that of Sb surpasses 94%. These values represent minimum estimates, considering that As and Sb were undetectable with the analytical technique used. Static leaching test (EN-15863) results, not presented here, are in no case worse than that of dynamic leaching test (EN-12457:4, Table 3). On the other hand, there are some elements whose mobility increases with the stabilization treatment. While the increases in pH and TDS can be easily explained by the binding material used and the conditions of the leaching test, there is no obvious explanation for the increase in Ba and Cr content in the leachates after applying the stabilizing agents to the tailings, as both elements are considered to be more mobile at low pH values.

PC, as a raw material, is cheaper than BSF or quicklime. From an environmental standpoint, the use of BSF would be more interesting since it is a recycled waste product. However, the better performance of PC in terms of stabilizing tailings should be a key selection criterion.

It is also important to highlight that the tailings, without any treatment (Table 3), meet the threshold values for surface water quality. In any case, the competent environmental authority points out the need to design, with proper justification, a stabilization treatment for the disposal of the tailings in a final storage facility. In the specialized literature, it is stated that, in general terms, the behavior of the tailings-PC or tailings-quicklime mixtures usually improves in the long term, concerning contaminant immobilization. In the Salave project, a long-term monitoring system will be implemented (starting from the beginning of the activity) to detect and address a potential increase in the levels of metals, metalloids, and sulfates in the leachates. The addition of the binder mix (PC + quicklime + limestone filler) to the tailings will be done at the end of the exploitation's life, and only if the tailings cannot be reused in any way

Conclusions

The tailings from the flotation process during the operational life of the Salave mine will consist of fine particles (90% smaller than 88.2 μm) and are expected to contain approximately 1000–1100 mg/kg of As and 80–90 mg/kg of Sb, in the form of arsenopyrite and stibnite, respectively.

To prevent the mobilization of these metalloids and the generation of sulfate-rich leachates at a future final disposal site, some leaching tests have been conducted using Portland cement (PC), quicklime and blast furnace slag (BFS) as binding materials. All these materials have shown good performance; however, PC exhibits the highest retention capacity for As and Sb, while quicklime is more effective in retaining sulfates. The most impermeable mixture is also achieved with PC. BFS provides the best mechanical properties, although in this case, they are of lower priority.

Using a mixture of 5% PC + 5% quicklime + 1% limestone filler, the reductions in sulfate, As, and Sb leaching exceed 90% after 28 days of curing. Additionally, the leachates obtained in the dynamic test EN-12457:4 comply with Spanish environmental quality standards for surface waters.

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