

Flotation of Sulphide Minerals Using Organosolv Lignin as Collector—Pilot-Scale Trials [†]

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Abstract: The use of toxic chemicals as flotation reagents raises concerns about the sustainability of the process and its environmental impact. Xanthates are a family of efficient collectors that find application in the selective recovery of lead, gold and zinc ores, but they are toxic, with the majority of them being imported from eastern countries. Recently, organosolv lignin (OLN) micro- and nanoparticles have been produced and tested as collectors in the flotation of Cu minerals with positive results. The material is attractive because it is natural, biodegradable, and possesses a low carbon footprint compared to the conventional reagents. A mixed sulphide ore deposit in Halkidiki, Greece, is operated by Hellas Gold S.A., a subsidiary of Eldorado Gold. The company produces galena (PbS), sphalerite (ZnS) and Au bearing pyrite/arsenopyrite (FeS₂/FeAsS) concentrates by applying consecutive froth flotation stages. Our previous laboratory studies have shown that the partial substitution of sodium isopropyl xanthate (SIPX) with OLN is possible, without worsening the flotation performance or downgrading the concentrates' quality. This study presents the findings of 3-stage pilot-scale flotation tests using OLN as a partial substituent of the SIPX collector on sphalerite and pyrite/arsenopyrite circuits. In the sphalerite recovery circuit, the partial replacement of SIPX with OLN (25 and 50%) resulted in an increase in Zn grade and a similar recovery compared to the standard case, while better selectivity was achieved since the Au recovery in the Zn concentrate was lower. Similarly, with the pyrite/arsenopyrite flotation circuit, the replacement of SIPX with OLN resulted in an increase in gold recovery with a parallel reduction in Pb recovery. It appears that OLN can efficiently replace part of the SIPX collector in Zn and Au flotation, producing concentrates of similar to better purity, in terms of grade and recovery of valuable metals, because of the improved selectivity of the mixed collector. The introduction of OLN in the collector mixture and the parallel reduction of SIPX drastically reduce the environmental footprint of the process.

Keywords: sphalerite; pyrite; arsenopyrite; flotation; lignin; collector; selectivity; xanthate



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1. Introduction

The Hellas Gold plant is located at Olympias, Halkidiki, Greece. It employs sulphide mineral processing in consecutive flotation steps leading to the production of galena (PbS)-silver (Ag) concentrate (Pb: 63% grade and 85% recovery, Ag: 1850 g/t grade and 85% recovery), sphalerite concentrate (ZnS) (Zn: 50% grade and 85% recovery) and gold concentrate (Au) (Au: 20 g/t grade and 85% recovery) primarily composed of pyrite/arsenopyrite (FeS₂/FeAsS). The tailings are used for backfilling purposes. As for the sphalerite, its floatability is greatly enhanced by the exchange of Zn ions with metal ions of the pulp,

acting as active sites to react with the collector, while long-chain xanthates are often chosen as collectors [1]. Concerning pyrite/arsenopyrite flotation, although both ferrous minerals are readily floatable with several types of collectors (xanthates, dithiophosphates and fatty acids), sodium isopropyl xanthate (SIPX) is chosen due to its high efficiency [2]. However, xanthates have a negative environmental impact because they degrade easily, producing toxic compounds like carbon disulfide (CS_2), with decomposition kinetics affected by pH and temperature [3]. Furthermore, xanthates present moderate stability, causing quality deviations, with an unexpected impact on the flotation performance [4]. As a consequence of the aforementioned concerns, there is an increasing trend in the replacement of xanthates with safe and eco-friendly chemicals in the flotation process [5,6].

Lignin is an abundant and low-cost material obtained from forest residues and side streams of the pulp industry. Recent research has shown that lignin micro- and nanoparticles can be used as collectors in copper recovery using froth flotation [7]. Also, lab-scale trials have shown that OLN can replace a considerable fraction of xanthates in the collector mixture in the flotation of Zn and Fe sulphide ores [8,9]. In the current study, we investigate the use of OLN as collectors in sphalerite, pyrite and arsenopyrite flotation, aiming for the partial replacement of xanthates on a pilot scale. In this respect, pure SIPX and SIPX/OLN mixtures of different proportions were prepared and used as collectors in the flotation of sphalerite and pyrite/arsenopyrite from mixed sulphide ore. The composition of the concentrates obtained using either pure SIPX or the SIPX/OLN mixture was determined to evaluate their performance as flotation collectors and their selectivity.

2. Materials and Methods

2.1. Ore Properties and Pretreatment

The ore was obtained from Hellas Gold feeding stream, and prior to any treatment it was subjected to grinding in a ball mill, producing fine grade with $d_{80} = 193 \mu\text{m}$. For the chemical analysis of the sample, the following methods were employed: LECO for S and C with a detection limit of 0.05%; fire assaying for Au and Ag; and ICP for the remaining elements, with a detection limit down to 1 ppb. Table 1 presents the chemical analysis of the sphalerite feed expressed in oxides. As observed, the Fe_2O_3 and ZnO content is approximately 17.81 wt.% and 4.33 wt.%, respectively. Minor amounts of Na_2O , P_2O_5 , TiO_2 , SrO , and Ta_2O_5 were identified. The LOI content of the sample was found to be 12.86%.

Table 1. Chemical analysis of the feed material.

Oxide	Content (wt.%)
PbO	0.69
ZnO	4.33
Fe_2O_3	17.81
As_2O_3	5.25
S	16.26
Sb	0.03
CuO	0.05
C	4.02
MgO	2.04
Al_2O_3	5.25
SiO_2	22.12
K_2O	1.14
CaO	16.27
MnO	1.15
Other	3.59

A modal analysis was conducted by chemically balancing the elements to their corresponding minerals, and it is presented in Table 2. Specifically, the Pb, Zn, Fe and As contents of the sample were considered in the analysis for the estimation of galena, sphalerite, pyrite and arsenopyrite, respectively.

Table 2. Modal analysis of the feed.

Ore	Content (wt.%)
Galena (PbS)	0.74
Sphalerite (ZnS)	5.18
Pyrite (FeS)	14.09
Arsenopyrite (FeAsS)	6.04

2.2. Lignin Production

A novel process was applied to the production of lignin micro- and nanoparticles using birch and spruce wood chips as the lignin source [10,11]. The production steps included the following:

- (i) Wood chip pretreatment through fractionation with ethanol to separate lignocellulosic biomass into the three main fractions of cellulose, hemicellulose and lignin from wood. Lignin and hemicellulose liquid was obtained through pressure filtration.
- (ii) Ethanol removal using evaporation and lignin recovery.

Subsequently, nano- and microparticles were obtained using the solvent exchange method, according to the following steps:

- (iii) Lignin dissolution in ethanol/water solution;
- (iv) Pressure homogenization of ethanol/water solution at 750 b;
- (v) Dilution of homogenized lignin with deionized water, causing nanoparticle development;
- (vi) Freeze-drying to obtain nanoparticles as a dry powder.

2.3. Flotation Conditions

Figure 1a presents the flowsheet of the flotation process applied, consisting of one rougher and two scavenger flotation steps on the sphalerite circuit, followed by one rougher and one scavenger flotation step on the pyrite/arsenopyrite circuit. Figure 1b depicts the flotation cell used for that purpose. The tests were carried out on a Tankcell Metso cell, with a 30 L capacity, adding 8 kg of dry ground ore. Table 3 tabulates the parameters during pilot scale trials, including reagents used and dosages, conditioning and flotation duration, pH and air feeding rate.

Table 3. Reagent dosages, pH and duration of conditioning and flotations (rougher and scavenger) in both sphalerite and pyrite/arsenopyrite circuits. Different colours in the collector dosage are used to easily distinguish between the base case (black) and the two alternative scenarios of SIPX replacement with OLN (25 wt.% replacement: green, 50 wt.% replacement: blue).

Stage	Reagents in g/t					Time (min)	pH	Air (L/min)
	CuSO ₄	Collector SIPX:OLN Ratio= 100:0, 75:25, 50:50	DF250	CaO	H ₂ SO ₄			
ZnS Conditioning	200	25:0 18.75:6.25 12.5:12.5	+	+		5	10.5–11	0
ZnS Rougher		-		+		3		
ZnS Scavenger 1		2.5:0 1.9:0.6 1.25:1.25		+		2		15
ZnS Scavenger 2		1.5:0 1.1:0.4 0.75:0.75		+		1		
AsPy Conditioning	200	100:0 75:25 50:50	+		+	10	6.5–7	0
AsPy Rougher					+	3		
AsPy Scavenger	40	30:0 22.5:7.5 15:15			+	2		15

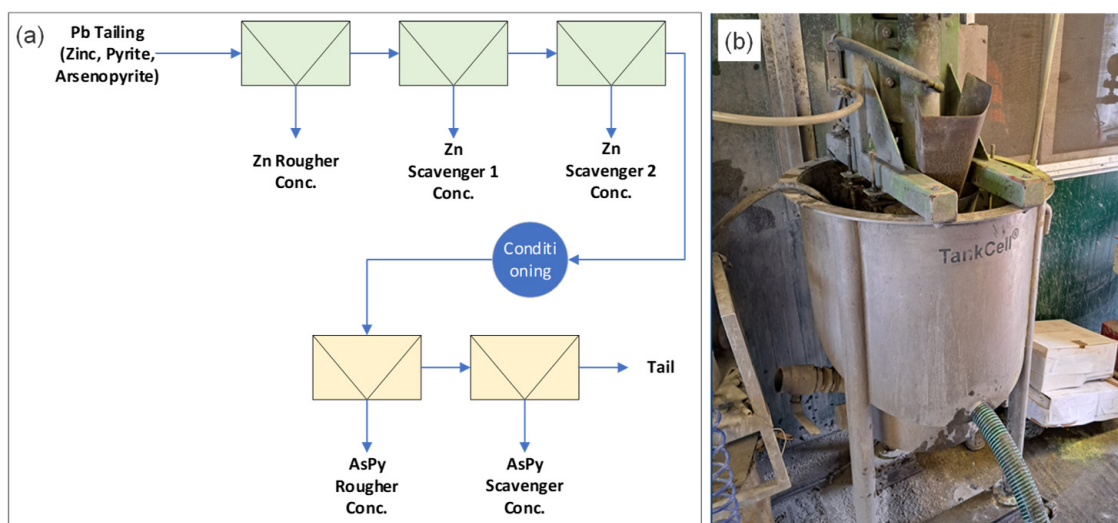


Figure 1. Flowchart of the pilot-scale flotation experiment procedure (a) and photo of the Tankcell Metso cell used in the experiments (b).

3. Results and Discussion

During experimentation on the sphalerite circuit, we explored the potential of the partial replacement of the chemical collector SIPX with lignin, at (a) 25 and (b) 50 wt.%. Figure 2a,b depict the observed Zn grade and recovery, and Figure 2c,d show the Au grade and recovery in Zn concentrate for the two experimental sphalerite flotation rounds with 25 and 50% OLN. The use of the mixed collector led to a better grade of sphalerite in the final concentrate. Whereas for pure SIPX, the Zn grade reached 18.7%, for the 25 and 50% replacement with OLN, the Zn grade reached 29.4 and 28.1%, respectively. Furthermore, the observed Au recovery was considerably lower when OLN substituted part of the SIPX; this suggests that OLN, when combined with SIPX, enhanced the selectivity of the extraction process, resulting in a lower loss of valuable gold-bearing ores in the Zn concentrate. Also, the recovery of sphalerite was slightly decreased. Nonetheless, the reduction in gangue material (pyrite and arsenopyrite) is beneficial, leading to an improvement of the overall quality of the final product.

Tailings from the Zn flotation circuit were further treated to recover pyrite/arsenopyrite and hosted Au. In addition to SIPX, two other collector combinations were applied, consisting of OLN by 25 and 50%. The Au (valuable) grade and recovery in the concentrates obtained using collectors of different compositions are depicted in Figure 3a,b, while the Pb (gangue) grade and recovery of the concentrates are depicted in Figure 3c,d, respectively. The results reveal the significant advantages of the mixed collector approach. The highest Au grade was observed in the concentrates when a mixed collector was used. Subsequently, the higher pyrite/arsenopyrite grade in these flotation rounds was associated with a considerable increase in Au recovery (from 50.5% with pure SIPX, to 74.6 and 76.3% for the 25 and 50% replacement with OLN, respectively). The good selectivity of OLN in this flotation circuit was demonstrated by the fact that the adverse Pb recovery in the Au concentrates was significantly lower when mixed collectors were used (from 32.3% with pure SIPX, to 12.9% and 15.1% for the 25 and 50% replacement with OLN, respectively). These observations are of paramount importance, with implications for the production of a concentrate of higher purity and improved quality.

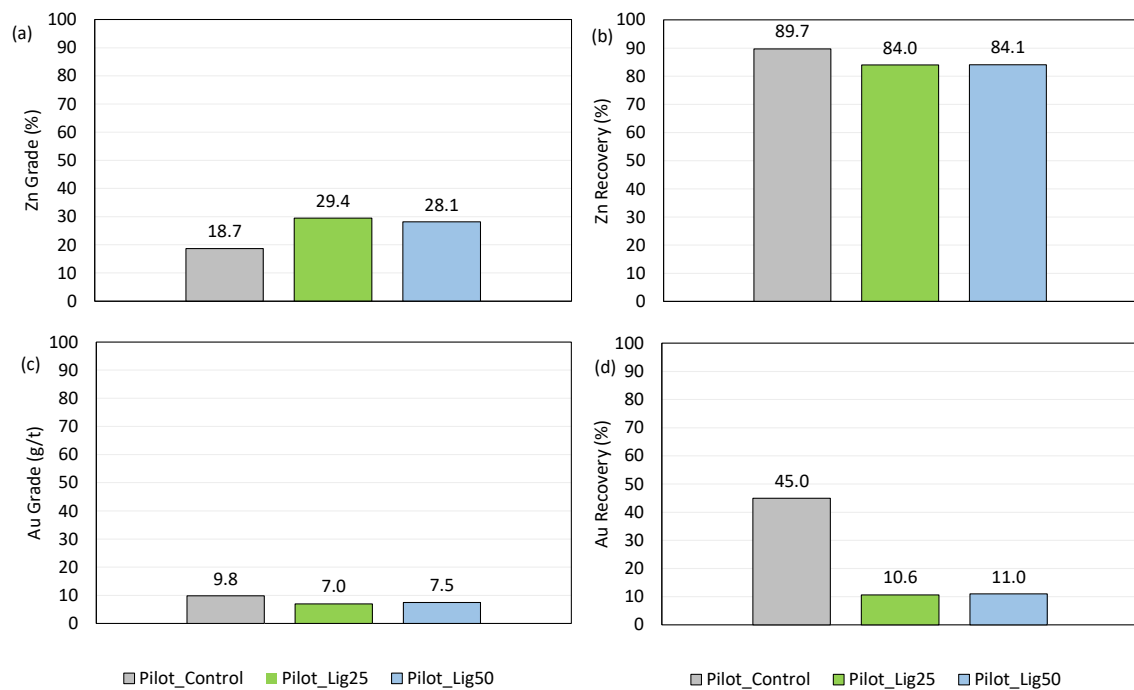


Figure 2. Zn grade (a) and recovery (b) of the concentrates obtained in the ZnS flotation circuit in terms of the collector composition (Pilot_Control: 100% SIPX, Pilot_Lig25: SIPX/OLN 75%/25%, Pilot_Lig50: SIPX/OLN 50%/50%). The Au grade (c) and recovery (d) for the same collector compositions are also presented.

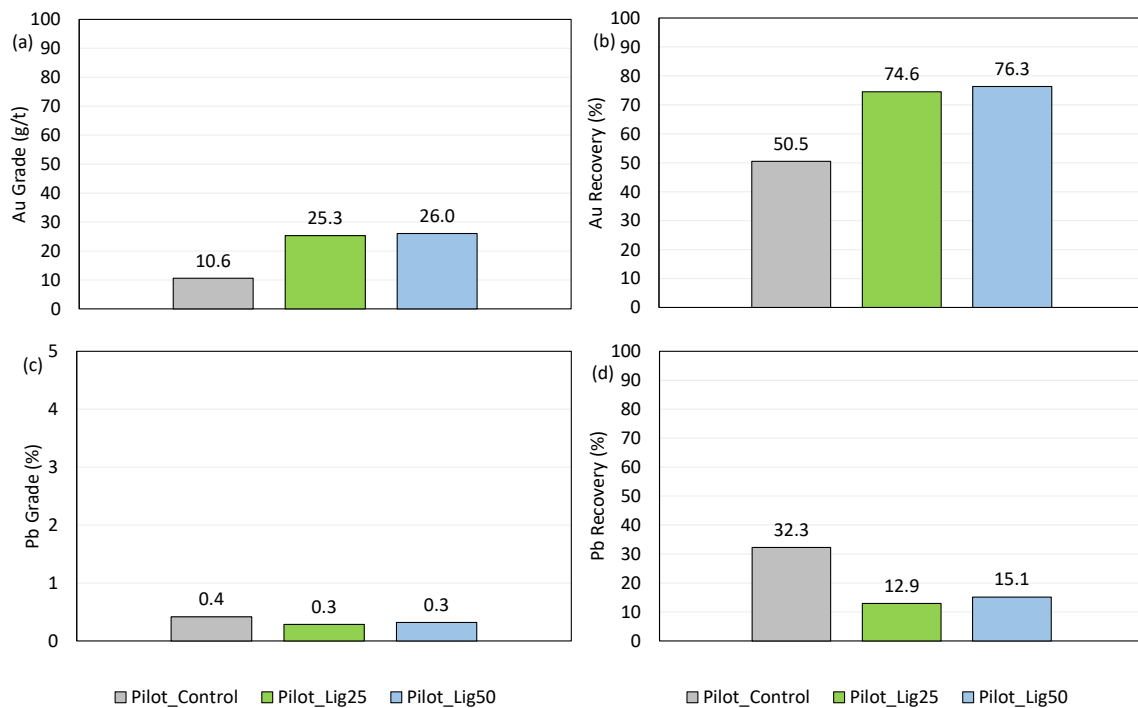


Figure 3. Au grade (a) and recovery (b) of the concentrates obtained in pyrite/arsenopyrite flotation in terms of the collector composition (Pilot_Control: 100% SIPX, Pilot_Lig25: SIPX/OLN 75%/25%, Pilot_Lig50: SIPX/OLN 50%/50%). The Pb grade (c) and recovery (d) for the same collector compositions are also depicted.

It appears that there was a synergistic effect when both lignin and xanthate were brought together in the flotation cell under the conditions applied in the current study and for the specific ores. The partial replacement of SIPX with OLN did not deteriorate the collector performance in terms of the obtained concentrates' quality or the flotation efficiency. On the contrary, better selectivity was achieved since the gangue presence in the concentrates reduced constantly. Lignin is a natural multipolar polymer, representing an extremely complex mixture of monomeric cyclic species with polymers which are both two- and three-dimensional in character [12]. Lignin has many chemical functional groups, mainly hydroxyl, methoxyl, carbonyl and carboxylic groups. It is possible that such functional groups provide linking points between the minerals and the xanthate molecules, or may adsorb on the minerals' surface, rendering them hydrophobic. However, none of these claims can be supported by the findings of the current study, and they all need further investigation.

4. Conclusions

This study investigates the performance of OLN as substitute collectors in the flotation of sphalerite, pyrite and arsenopyrite, through the 25% and 50% replacement of SIPX in pilot-scale tests.

In the sphalerite flotation circuit, the application of a mixed collector led to the following observations:

- A significant increase in Zn grade, as the Zn grade increased from 18.7% for pure SIPX to 29.4 and 28.1% for the 25 and 50% SIPX replacement with OLN. The Zn recovery reduced by approx. 5% when a mixed collector was applied, from 89.7% for pure SIPX to 84% and 84.1% for the 25 and 50% SIPX replacement with OLN, respectively.
- The produced concentrates contained much lower pyrite/arsenopyrite as revealed by their Au content. From an original 45% Au recovery using pure SIPX, it was reduced to 10.6% and 11.0% for the 25 and 50% SIPX replacement with OLN, respectively.

In the pyrite/arsenopyrite flotation circuit, the same ratios of SIPX replacement with OLN were applied, and the major conclusions are as follows:

- A significant increase of Au grade in concentrates, from 10.5 g/t for pure SIPX to 25.3 g/t and 26 g/t Au (for of the 25 and 50% SIPX replacement with OLN, respectively) was identified by applying a mixed collector. A sharp increase in Au recovery was also identified, from 50.5% for pure SIPX to 74.6 and 76.3% Au recovery for of the 25 and 50% SIPX replacement with OLN, respectively.
- A significant reduction of Pb grade was identified, implying better selectivity, from a Pb recovery of 32.3% for pure SIPX to 12.9% and 15.12% for the 25 and 50% SIPX replacement with OLN, respectively.

The findings highlight the considerable benefits of incorporating organosolv lignin nanoparticles in the collector mixture through the partial replacement of xanthate collector, in both sphalerite and pyrite/arsenopyrite circuits. In addition to the qualitative improvement of the produced concentrates and the reduction in value losses in tailings, a direct reduction of the environmental footprint of the process due to the eco-friendly, biodegradable nature of lignin is achieved.

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