



## Assessment of the floatability of chalcopyrite, molybdenite and pyrite using biosolids and their main components as collectors for greening the froth flotation of copper sulphide ores



Lorenzo Reyes-Bozo <sup>a,\*</sup>, Pablo Higuera <sup>b</sup>, Alex Godoy-Faúndez <sup>c</sup>, Francisco Sobarzo <sup>a</sup>, César Sáez-Navarrete <sup>d</sup>, Jorge Vásquez-Bestagno <sup>e</sup>, Ronaldo Herrera-Urbina <sup>f</sup>

<sup>a</sup> Departamento de Ciencias de la Ingeniería, Facultad de Ingeniería, Universidad Andres Bello, Sazié 2315, Santiago, Chile

<sup>b</sup> Departamento de Ingeniería Geológica y Minera, Universidad de Castilla-La Mancha, Plaza M. Meca 1, 13400 Almadén, Ciudad Real, Spain

<sup>c</sup> Facultad de Ingeniería, Universidad del Desarrollo, Av. La Plaza 680, Santiago, Chile

<sup>d</sup> Departamento de Ingeniería Química y Bioprocesos, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Santiago, Chile

<sup>e</sup> Departamento de Desarrollo, Gerencia de Negocios y Servicios de Terceros, Essbio, Diagonal Pedro Aguirre Cerda 1129, Concepción, Chile

<sup>f</sup> Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo, Mexico

### ARTICLE INFO

#### Article history:

Received 28 January 2014

Accepted 2 April 2014

#### Keywords:

Froth flotation agents

Sulphide minerals

Biosolids

Humic acids

### ABSTRACT

Biosolids and representative compounds of their main components – humic acids, sugars, and proteins – have been tested as possible environment-friendly collectors and frothers for the flotation of copper sulphide ores. The floatability of chalcopyrite and molybdenite – both valuable sulphide minerals present in these ores – as well as non-valuable pyrite was assessed through Hallimond tube flotation tests. Humic acids exhibit similar collector ability for chalcopyrite and molybdenite as that of a commercial collector (Aero 6697 promoter). Biosolids show more affinity for pyrite. The copper recovery (85.9%) and copper grade (6.7%) of a rougher concentrate obtained using humic acids as main collector for the flotation of a copper sulphide ore from Chile, were very similar to those of a copper concentrate produced by froth flotation under the same conditions with a xanthate type commercial collector. This new and feasible end-use of biosolids and humic acids should be new environment-friendly organic froth flotation agents for greening the concentration of copper sulphide ore. Now, further research is needed in order to scale current laboratory assays to operational mining scales to determine efficiencies to industrial scale.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Chile bases its economic growth on natural resources exploitation, which makes it vulnerable to the impacts of climate change (ECLAC, 2010). Economic and industrial development has brought environmental and social consequences for communities inhabiting near industrial operating sites (Subramanian and Kawachi, 2004). A case of interest is the mineral processing industry, particularly the copper minerals industry.

Currently, both copper oxides and sulphide ores are actually being exploited in Chile, but sulphide ores predominate over the oxides (Bulatovic, 2007; Cochilco, 2012). Chalcopyrite ( $\text{CuFeS}_2$ ) is the main copper sulphide mineral in these ores, which also contain varying amounts of non-valuable and undesired pyrite ( $\text{FeS}_2$ ) (Bulatovic, 2007). Another mineral species associated with copper sulphide ores is molybdenite ( $\text{MoS}_2$ ), which has a high commercial

value. On an industrial scale, copper sulphide ores are concentrated via froth flotation processes (Ata, 2012; Farrokhpay, 2011; Rahman et al., 2013).

According to statistics from the Copper Chilean Commission (Cochilco, 2013), in the year 2012 Chilean copper industry had an annual handling capacity to concentrate around 450 million tonnes of copper sulphide ore by froth flotation, and produced 3.7 million tonnes of fine copper. It is expected that in 2021 the fine copper production will reach 6.8 million tonnes with an installed capacity projected to process 1200 million tonnes of copper sulphide ore. This enormous capacity of ore processing could potentially cause continuous environmental impacts, throughout the release of huge solid waste deposits such as tailings storage facilities, sterile piles, and lixiviation piles, among others. Based on copper cycle assessment all steps of mineral processing are highly energy-intensive and generate hazardous waste materials (McLellan and Corder, 2012; Mearns et al., 2012; Moors et al., 2005).

Different chemical reagents are nowadays required to concentrate copper sulphide ores by flotation. These chemicals include

\* Corresponding author. Tel.: +56 2 26618456; fax: +56 2 26615894.

E-mail address: [lreyes@unab.cl](mailto:lreyes@unab.cl) (L. Reyes-Bozo).

collectors, depressants, activators, modifiers and frothers, used in order to separate valuable copper-containing minerals from gangue minerals. Their properties allow the control of the wettability of solid surfaces, the electrochemistry of the solution, the dispersion and aggregation of solid particles, and also the generation of foam stability (Hadler et al., 2005; Herrera-Urbina, 2003). On the other hand, many of these chemicals are expensive, and some have been classified as hazardous materials because they may affect both the environment and health of humans, flora and fauna if improperly managed and disposed (Ralston, 2002; Thomas, 2010). Since copper production has been increasing lately as a driving economical force to achieve development, the copper mining sector is in a tipping point to achieve equilibrium between development and sustainable production, thus avoiding increasing levels of pollutant discharges towards the environment. Therefore, the mining industry needs new environment-friendly reagents for froth flotation and to use new strategies and concepts derived from industrial ecology, cleaner production, green chemistry and sustainable engineering.

A new and novel way of biosolids revalorization is described in the literature (Reyes-Bozo et al. 2011a, b, c), where the potential use of biosolids and humic substances – both environment-friendly compounds – as froth flotation reagents for the concentration of copper sulphide ores has been documented. The typical chemical composition of stabilized biosolids is highly diverse and varies according to geographic region, population consumption habits, degree of industrialization of cities, and the type of process applied by the wastewater treatment plant (Peppas et al., 2000). Despite this, as cited in specialized literature (Baham and Sposito, 1982; Eskicioglu et al., 2006; Parnaudeau and Dignac, 2007; Ras et al., 2008; Reyes-Bozo et al., 2011a) the main components of biosolids could be polysaccharides (sugars), proteins (aminoacids) and to a lesser extent humic substances (fulvic and humic acids), and nucleic acids. The main functional groups present in humic acids are carboxylic acids, alcohol, carbonyl, phosphates, sulphates, amides and sulphides, all of which are capable of interacting with metal species in solution (Baek and Yang, 2005).

In Chile, final disposal of biosolids is limited to landfills and monofills (SISS, 2010); however, under local regulation it is feasible to use biosolids in mining operations (Minsegespres, 2009). This option is considered to be the final disposal. Therefore, the use of biosolids in phytostabilization of tailings and the new use disclosed in our manuscript (use of biosolids in froth flotation processes) are feasible in Chile.

According to statistics and forecasting from Superintendencia de Servicios Sanitarios (Chilean Superintendency of Sanitary Services), biosolids generators are mainly located in the central and southern regions of Chile (SISS, 2010). In the central zone of Chile (Metropolitan Region and regions V and VIII), which is the most significant producer, 220,000 tonnes/year are produced. Then, biosolids will be inevitably generated and these wastes will be disposed in a safe way.

The aim of this research was to evaluate the possibility of using solid wastes generated in wastewater treatment plants as new environment-friendly froth flotation agents. In particular, biosolids and their main components were tested in modified Hallimond tubes as feasible collectors for chalcocopyrite, pyrite and molybdenite as well as the use of humic acids as main collector for the flotation of copper sulphide ores.

## 2. Materials and methods

### 2.1. Chalcocopyrite, pyrite, and molybdenite samples

Chalcocopyrite and pyrite samples were obtained from División Los Bronces (Anglo American, Chile), while molybdenite sample

was supplied by Molymet (Santiago, Chile). Samples of chalcocopyrite and pyrite were ground in an IKA MF 10 Basic Microfine Grinder apparatus. They were then sieved for 6 min on a Rotap (W.S. Tyler Model Number RX-29-10) to obtain 125–150 µm (–100 + 120 mesh) size fractions for microflotation tests in a modified Hallimond tube.

Mineralogical analyzes of these samples indicates that the chalcocopyrite sample contains 65.4% chalcocopyrite, 13.4% pyrite, 9.9% magnetite, and 10.2% nonmetallic gangue minerals. The purity of the pyrite sample was found to be 95.8%, with minor contents of chalcocopyrite (0.5%) and nonmetallic gangue (3.2%). The purity of the molybdenite sample was found to be 98.7%, with minor contents of chalcocopyrite (0.6%) and nonmetallic gangue (0.7%). Elemental chemical analyzes were also performed for each of these mineral samples. A portion of the sample was digested via microwave by using the Rock High Sulfide Method; once digestion was completed it was centrifuged and sent to an atomic absorption spectrometer (ICP-MS, Perkin Elmer ELAN 6100) for analysis. A nitrous-oxide/acetylene flame was used as the oxidant for quantification of molybdenum. Dumas combustion method was used to quantify sulphur contents. The elemental chemical composition of the chalcocopyrite, molybdenite and pyrite samples is given in Table 1.

### 2.2. Biosolid sample

Biosolids used in this study were obtained from a wastewater treatment plant (Essbio, Concepción, Chile). The biological removal of organic load was performed by using activated sludge technology. The samples were previously ground using mortars, homogenized and sieved to a fraction smaller than 1 mm. Biosolids samples were physically and chemically analyzed in certified laboratories (Análisis Ambientales and Laboratorio de Suelos y Análisis Foliar, PUCV). Biosolids, whose aqueous suspensions (1:2.5 solid:water ratio) have a pH of 7.8 and an electrical conductivity of 7.2 mS/cm, were found to contain 66.5% organic matter. The total content (in mg/kg) of Cu, Fe, Mo and P was 280.8; 5652.2; 2.6 and 13148.3, respectively. All metal content were determined by atomic absorption spectrophotometry with a Perkin Elmer Analyst 300 apparatus. The content of humic substances, quantified by standard method (Sadzawka et al., 2006), was 10.6% fulvic acid, 2.5% humic acids and 27.8% humins.

### 2.3. Microflotation tests in a modified Hallimond tube

Assessment of the collecting ability of biosolids and their main components was performed with a modified Hallimond tube. A commercial salt of humic acid (Aldrich) was used as representative of humic substances present in biosolids. According to Pandey et al. (1999), this humic acid has a characteristic composition of 44.67% organic carbon, 5.87% hydrogen, 4.88% total nitrogen, 43.9%

**Table 1**  
Elemental chemical composition of chalcocopyrite, pyrite and molybdenite samples.

Sample	Chemical composition (%)	Value
Chalcocopyrite	Total copper	21.5
	Total iron	30.2
	Total sulphur	26.2
	Total molybdenum	0.01
Pyrite	Total copper	0.2
	Total iron	46.8
	Total sulphur	47.5
	Total molybdenum	0.01
Molybdenite	Total copper	0.2
	Total iron	0.6
	Total sulphur	61.4
	Total molybdenum	37.7

oxygen, and 0.58% ash with a total acidity of 12.3 mol/kg. The concentration of functional groups such as -COOH and phenol (-OH) is 4.1 and 8.2 mol/kg, respectively.  $\alpha$ -D-glucose and bovine serum albumin (both from Aldrich) were used as representatives of sugars and proteins contained in biosolids.

The industrial collector, Aero 6697 promoter (Cytec), was used for comparison. This collector, an alkyl monothiophosphate, is a chemical reagent used in various operations of sulphide ore concentrations worldwide. Its specific gravity is 1.14 (@ 20 °C), pH > 13, viscosity of 15–35 (cps @ 20 °C), infinitely soluble in water. Cytec reports that a common dose of 5–100 g/t of Aero 6697 which is used to concentrate copper and precious metals (Thomas, 2010). No collector reagent was used in negative controls.

All mineral suspensions were prepared with 0.5 g of solids in 130 ml of 1.0 mM KNO<sub>3</sub> aqueous solution. These suspensions, whose pH was adjusted by adding small aliquots of either 0.1 M NaOH or HCl to achieve values of 4.0, 5.5, 7.0, 8.5 and 10.0, were agitated with a magnetic stirrer at 150 rpm. Then, the suspension was conditioned for five minutes before adding the biosolids or chemical reagents to be tested as collectors at a concentration of 50 g/t. Mineral suspensions were conditioned for another 5 min in the presence of collector.

At the end of the overall conditioning period, the pH was measured again, and this value is reported as final pH. The mineral suspension was then transferred into the Hallimond tube where the material was floated for two minutes with an air flow rate of 150 mL/min. The floated and non-floated fractions were recovered, filtered and dried at 40 °C. Finally, the floated fraction was weighed to obtain the percentage of recovered mineral.

No frother was used in Hallimond tube tests, and all experiments were performed in triplicate. Doubly distilled water was used for all the experiments, which were carried out open to the atmosphere at an average temperature of 20 ± 2 °C.

#### 2.4. Rougher froth flotation tests

Rougher flotation test were carried out at laboratory scale using copper sulphide ore. This ore sample had 0.94% copper grade and the mineralogical analysis was performed using standard methods according to Gaines et al. (1997). The copper sulphide ore contained chalcopyrite (0.65%), molybdenite (0.001%), pyrite (0.92%) and gangue minerals (98.4%).

The experimental procedure involved the following steps: conditioning of the copper sulphide ore with main collector (i.e. xanthates, dosage 38 g/t) in a ball mill; adding 1 kg of copper sulphide ore into a Wenco cell containing 2 L of fresh water; stirring the pulp at 1200 rpm; adjusting the pH to 10.0 with CaO solutions; adding the collector and frother (additional 10 g/t of main collector type xanthate and 12 g/t of frothers: DowFroth and methyl isobutyl Carbinol); conditioning the pulp and introducing fresh air; collecting the concentrates after 12 min of froth flotation; separating the solids from the liquids in the concentrates by filtration; and finally, quantifying the total copper by atomic absorption spectrophotometry with a Perkin Elmer Analyst 300 apparatus. Concentrate weight and assays were used to calculate copper recoveries and copper concentrate grade.

#### 2.5. Statistical analysis

Two-way ANOVA without interaction (Software Minitab 16<sup>®</sup>) was performed to determine the main factor (pH and/or collector type) in the mineral flotation yield by chalcopyrite, molybdenite and pyrite. Statistical significance was reported for *P* values <0.05. Normality of data was verified using asymmetry statistics and standardized kurtosis, and the homogeneity of variances using an F-test.

### 3. Results and discussion

#### 3.1. Chalcopyrite flotation

Fig. 1 presents the floatability of chalcopyrite in the absence and presence of various collectors at different pH values. In the absence of collectors, chalcopyrite floatability is almost negligible (less than 12.0%) at all pH values investigated. The chalcopyrite hydrophilic behaviour shows that mineral surfaces may be oxidized because grinding, sieving, conditioning and flotation were carried out open to the atmosphere. Additionally, this chalcopyrite sample contains about 10% magnetite (Fe<sub>3</sub>O<sub>4</sub>), a mineral species that exhibits a hydrophilic behaviour (Kirchberg et al., 2011; Potapova et al., 2012).

In the pH range from 4.0 to 10.0, and at the concentration of collector used, the industrial collector Aero 6697 gives the best flotation of chalcopyrite: about 50%. This low recovery may be due to the impurities present in the mineral sample, which contains magnetite and non-metallic gangue.

Humic acids exhibit a similar collector behaviour as that of Aero 6697. In both cases, chalcopyrite recovery increases at alkaline pHs reaching values close to 43.0%. This behaviour is consistent with previously reported results (Reyes-Bozo et al., 2011b, c) where humic acids were found to have collector properties for copper-containing species. Furthermore, as reported in our previous studies (Reyes-Bozo et al., 2011b), humic acids and conventional collectors can interact with surface of copper sulphide ore and sulphides minerals changing their isoelectric point.

Biosolids, humic acids and conventional collectors make the zeta potential of copper sulphide ores and sulphide minerals more electronegative. Humic acids interact with sulphides of copper through outer-sphere linkages, since humic substances may adsorb physically on chalcopyrite and pyrite through hydrogen bonds or Van der Waals forces. In the case of biosolids, this waste contains humic acid, phosphorus compounds and other components that can interact with copper sulphide ores and sulphide minerals surfaces through complex mechanisms involving both inner and outer-sphere linkages due to the diversity of functional groups presents in these wastes (i.e. carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulphates, amides, sulphides, among others).

The functional groups present in biosolids and humic acids could interact with mineral surfaces making them more hydrophobic. Depending on the pH evaluated, different flotation responses will be obtained from the Hallimond tests.

With  $\alpha$ -D-glucose, BSA and biosolids, chalcopyrite floatability ranges from 20% to 30% in the pH range investigated indicating that these compounds have the least collecting ability for chalcopyrite.

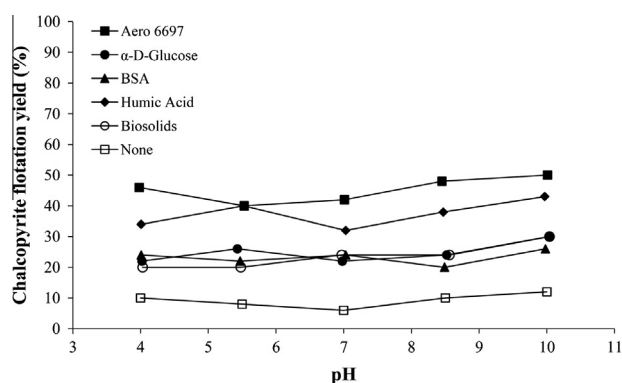


Fig. 1. Flotation response of chalcopyrite at different pH values in the absence and presence of various compounds tested as collectors, at a concentration of 50 g/t. BSA, bovine serum albumin.

The statistical analysis shows that the chalcopyrite flotation yield (%) varies significantly with the collector type (without collector, Cytec Aero 6697,  $\alpha$ -D-glucose, bovine serum albumin (BSA), humic acid sodium salt or biosolids) (two-way ANOVA,  $F = 124.49$ ,  $P < 0.05$ ) and also with the pH evaluated (4.0, 5.5, 7.0, 8.5 or 10.0) ( $F = 6.93$ ,  $P < 0.05$ ). The interaction between the factors (collector type and pH) could not be quantified. Therefore, the percentage of chalcopyrite recovered in the concentrate obtained in modified Hallimond tubes depends on the type of collector and the pH used.

### 3.2. Molybdenite flotation

Fig. 2 presents the flotation response of molybdenite at different pH values in the absence and presence of various compounds tested as collectors, at a concentration of 50 g/t. In the absence of a collector, molybdenite floatability is between 20% and 24% in the pH range from 4.0 to 10.0. These percentages are consistent with data reported in the literature (Ansari and Pawlik, 2007), where a natural floatability between 25% and 40% is reported.

The flotation response of molybdenite in the presence of the different compounds tested as collectors is significantly higher under acidic conditions and decreases as the pH increases. Chander and Fuerstenau (1972) have also reported that the flotation of molybdenite decreases with increasing pH. Although it has been reported that various polymeric additives such as polyacrylamide, dextrin and humic acids are known to be strong depressants of molybdenite (Ansari and Pawlik, 2007; Castro and Laskowski, 2004; Lai et al., 1984; Wie and Fuerstenau, 1974), the results presented in Fig. 2 show no depressant effect of sugars, proteins and humic acids, maybe because of the low concentration used (50 g/t) in this research work.

The statistical analysis shows that the molybdenite recoveries (%) varies significantly with the collector type (without collector, Cytec Aero 6697,  $\alpha$ -D-glucose, bovine serum albumin (BSA), humic acid sodium salt or biosolids) (two-way ANOVA,  $F = 13.11$ ,  $P < 0.05$ ), however the pH is not significant ( $F = 2.10$ ,  $P = 0.119 > 0.05$ ). Due to lack of freedom degree in model, the interaction between the factors (collector type and pH) could not be quantified. Therefore, the percentage of molybdenite recovered depends on the type of collector used.

### 3.3. Pyrite flotation

Fig. 3 describes pyrite floatability in the absence and presence of various collectors according to pH. In the absence of collectors, pyrite floatability is almost negligible (less than 14.0%) at pH 4.0–10.0. The hydrophilic behaviour of pyrite shows that mineral

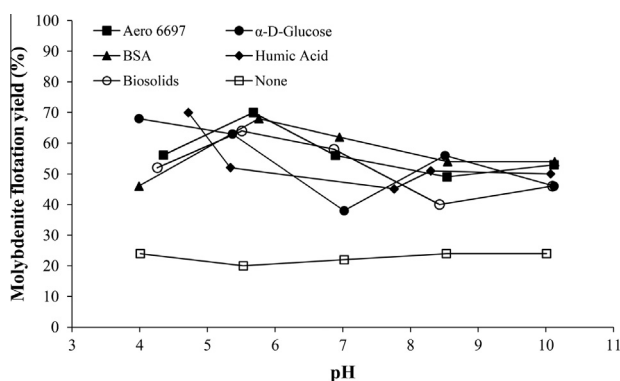


Fig. 2. Flotation response of molybdenite at different pH values in the absence and presence of various compounds tested as collectors, at a concentration of 50 g/t. BSA, bovine serum albumin.

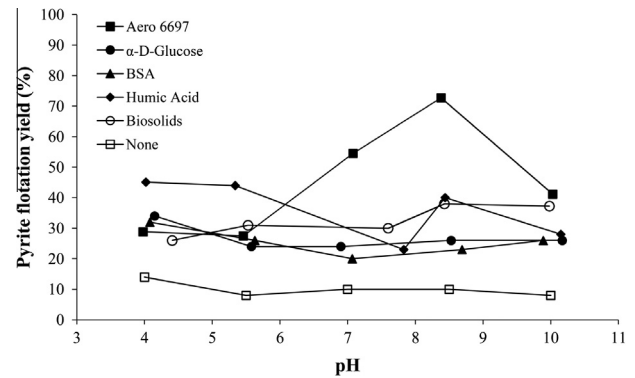


Fig. 3. Flotation response of pyrite at different pH values in the absence and presence of various compounds tested as collectors, at a concentration of 50 g/t. BSA, bovine serum albumin.

surface may be oxidized because grinding and sieving processes were carried out under atmospheric conditions, in the presence of ambient oxygen.

There are no extensive studies reporting on pyrite oxidation behaviour in air; however, the following oxidation values of mineralogical sulphide species have been documented:  $\text{FeAsS} > \text{FeS}_2 > \text{CuFeS}_2 > \text{ZnS} > \text{PbS} > \text{Cu}_2\text{S}$  (Steger and Desjardins, 1978; Sutherland and Wark, 1955). Therefore, this result reveals that pyrite and chalcopyrite tend to oxidize rapidly in air as compared to other sulphides, which could affect the natural floatability of these metal sulphides.

In acidic pH range a floatability of 30% is obtained with the industrial collector reagent Aero 6697, whereas for pH 8.5 over 70% flotation is achieved. This is consistent with manufacturer specifications, since the collector works properly in alkaline flotation processes. However, the reagent is not intended to concentrate iron, given that in industrial systems the reagent Aero 6697 has greater affinity for copper-containing species (Thomas, 2010). Previous studies (Reyes-Bozo et al., 2011b) show that industrial xanthate collectors cannot selectively interact with pyrite and chalcopyrite when both mineralogical species are studied in isolation. Collector Aero 6697 (alkyl monothiophosphate) also exhibits this non-selective behaviour.

Both  $\alpha$ -D-glucose and BSA slightly increase pyrite floatability. For pH values ranging from 4.0 to 10.0, both reagents enable flotation around 20% and 30% of the mineral species. This increase in floatability may be caused by the interaction of glucose and protein with impurities present in the pyrite. Sugars and proteins have been described as hydrophilic substances that have been used as dispersing reagents and/or depressants in metal sulphide concentration processes (Laskowski et al., 2007; Patra and Natarajan, 2006).

For acidic pHs (4.0–5.5), humic acids can float 45% of pyrite. A similar behaviour is observed at pH 8.5. This behaviour may be due to the presence of different functional groups in these substances. The main functional groups found in a sample of humic acids are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulphates, amides and sulphides, all of which are capable of interacting with metal species in solution (Baek and Yang, 2005; Stevenson, 1994; Schulten and Schnitzer, 1997). Therefore, depending on the pH various functional groups may interact with the pyrite surface.

The flotation response of pyrite with 50 g/t biosolids is about 40% between pH 8.0 and 10.0. When comparing recovered material at pH 10.0 it is seen that the biosolids and industrial collector float 40% of pyrite, whilst with humic acids the flotation response is only 28%. These results are consistent with previous results (Reyes-Bozo

et al., 2011b) that show that biosolids have higher affinity for Fe-containing species.

The statistical analysis shows that the pyrite flotation yield (%) varies significantly with the collector type (without collector, Cytec Aero 6697,  $\alpha$ -D-glucose, bovine serum albumin (BSA), humic acid sodium salt or biosolids) (two-way ANOVA,  $F = 7.57$ ,  $P < 0.05$ ), however the pH is not significant ( $F = 0.77$ ,  $P = 0.557 > 0.05$ ). The interaction between the factors (collector type and pH) could not be quantified. Therefore, the percentage of pyrite recovered in the concentrate obtained in modified Hallimond tubes depends on the type of collector used.

Our previous studies (Reyes-Bozo et al., 2011b, 2011c) as well as Hallimond tube flotation results have indicated the possibility of using humic acids and biosolids as collectors for the concentration of copper sulphide ores by froth flotation.

Additional rougher flotation tests were performed in Wemco cell at laboratory scale. In these tests, a copper sulphide ore from central-southern Chile was used. The mineral had a copper grade of 0.94% and its main mineral species were chalcopyrite (0.65%), molybdenite (0.001%), pyrite (0.92%), and non-metallic gangue (98.4%). Three experimental conditions were evaluated to investigate the effect of total (100%) or partial (50%) replacement of the main collector. The first experimental conditions involved using 38 g/t of the main collector (i.e., xanthate type), a second set of conditions involved using 19 g/t of the main collector (i.e., xanthate type) and 19 g/t of humic acids, while a third experimental setup involved using 38 g/t of humic acids.

The use of a xanthate type collector shows that the copper recovery and concentrate grade obtained were 90.4% and 5.8% Cu, respectively. When humic acids replace 50% of the main collector (19 g/t), similar results were obtained in the copper concentrate (recovery and grade). When humic acids replace 100% of the main collector (38 g/t), the copper recovery and concentrate grade obtained only with humic acids were 85.9% and 6.7% Cu, respectively.

The use of humic acids shows that the copper recovery is a bit lower (4.5%) and the copper concentrate grade is a little higher (0.9% Cu). These results show that the commercial collector increases the copper recovery with a decrease in copper grade. Then, the commercial collector may be less selective to float copper sulphide ore than the humic acids because more gangue minerals are also recovered in the concentrate. Therefore, these findings make it feasible the total or partial replacement of the existing chemical reagents used industrially for copper sulphide ore concentrations.

### 3.4. A sustainable froth flotation process

Since 2000, Chilean mining operations, and particularly the copper industry, has set a goal to achieve a sustainable management model in all its operations, including local communities in this challenge (Lostarnau et al., 2011; Prno, 2013; Urkidi, 2010). The industry realizes that its core business is associated with the exploitation of a nonrenewable resource with industrial processes generating high social, environmental and economic impacts (Newbold, 2006; Castro and Sanchez, 2003).

The first step emphasized the social dimension of sustainable development, through the adoption of strict rules on occupational safety and plant workers health in order to reduce risks faced by operators (Laurence, 2011). Subsequently, due to increased environmental conflicts derived from accumulation of environmental liabilities (i.e., tailings storage facilities, sterile heaps, and lixiviation piles, among others), and the high energy consumption of the different stages of both concentration and final product obtention processes (i.e., blister copper), the mining industry focused on the remediation (Godoy-Faúndez et al., 2008) and rehabilitation

(Santibañez et al., 2012) of such environmental liabilities through planning closure and abandonment of mines (Campusano, 2002). Lower environmental risks reduce economic impacts affecting the mining industry resulting from costs reduction of planning of hazardous landfills in mine closure operations. Additionally, efforts have been made to optimize the use of energy and water consumption by incorporating seawater in copper sulphide ore concentration processes.

Nevertheless, one of the unexplored challenges has been the gradual replacement of the use of chemical reagents in froth flotation and hydro-metallurgy processes. Currently, tools such as life cycle analysis and industrial ecology are being used for the gradual replacement of reagents posing high risk factors for health and population (Swart and Dewulf, 2013). Based on the results described above and findings already published by the authors (Reyes-Bozo et al., 2011a, 2011b, 2011c), it is possible to bring up the total or partial replacement of current chemical reagents used in copper sulphide ore concentration processes, which during their transport, storage and use constitute risk factors for plant operators as well as potential environmental effects. In both cases, the impact translates into high costs, either for the mining industry that increases costs in occupational health or for society in environmental terms.

Gradual replacement of traditional chemical reagents—collectors, frothers and modifiers – used for the concentration of copper sulphide ores would advance greening the froth flotation process. Incorporation of concepts associated with industrial ecology and green chemistry may in turn improve population quality of life by minimizing the environmental impacts through less chemical reagents consumption, reduction of hazardous wastes generation and conversion of these wastes into less dangerous materials. Total or partial replacement of conventional industrial flotation chemicals may also reduce environmental and social conflicts thus improving people's perception of mining industry performance, while building trust and confidence among stakeholders.

## 4. Conclusions

Microflotation tests – in a modified Hallimond tubes – show that the chalcopyrite recovery increases at alkaline pHs reaching values close to 45%. In this case, only humic acids exhibit a similar collector behaviour as that of a commercial collector evaluated (Aero 6697 promoter). The flotation response of molybdenite in the presence of the different compounds tested as collectors (Aero 6697 promoter, glucose, bovine serum albumin, humic acids and biosolids) is significantly higher under acidic conditions and decreases as the pH increases. The molybdenite flotation yield decreased from 65% (acid pH) to 50% (alkaline pH). The flotation response of pyrite shows that at pH 10 biosolids and Aero 6697 promoter float 40% of pyrite. Then, at alkaline pHs, biosolids have higher affinity for Fe-containing species.

Rougher froth flotation tests carried out with only humic acids (total replacement of the main collector) shows that the copper recovery and concentrate grade obtained were 85.9% and 6.7% Cu, respectively. The use of a commercial collector increases the copper recovery (90.4%) with a decrease in copper concentrate grade (5.8% Cu). Therefore, the results of this research work show that biosolids and their main components may be new environment-friendly froth flotation agents to concentrate copper sulphide ores. However, further research is needed to scale-up current laboratory results to industrial froth flotation stages.

## Acknowledgments

This research was partially funded by Chilés Conicyt program through the National Fund for Scientific and Technological

Research (Fondecyt) via No. 11121159 Project. Additional support came from a research Grant from Universidad Andres Bello, Project DI-20-12/R (L. Reyes-Bozo). Biosolids and industrial chemical collector were provided by Essbio (G. Wolf and J. Vásquez) and Cytec Chile (R. Capanema), respectively. Further, chalcocopyrite, pyrite and molybdenite samples were provided by Anglo American Chile and Molymet Chile (J. Gacitúa).

## References

- Ansari, A., Pawlik, M., 2007. Floatability of chalcocopyrite and molybdenite in the presence of lignosulfonates. Part II. Hallimond tube flotation. *Miner. Eng.* 20, 609–616.
- Ata, S., 2012. Phenomena in the froth phase of flotation – a review. *Int. J. Miner. Process.* 102–103, 1–12.
- Baek, K., Yang, J., 2005. Humic-substance-enhanced ultrafiltration for removal of heavy metals. *Sep. Sci. Technol.* 40 (1), 699–708.
- Baham, J., Sposito, G., 1982. Chemistry of water-soluble, metal-complexing ligands extracted from an anaerobically-digested sewage sludge. *J. Environ. Qual.* 12 (1), 96–100.
- Bulatovic, M., 2007. Handbook of flotation reagents: chemistry, theory and practice: volume 1: flotation of sulfide ores, first ed. Elsevier Science, The Netherlands.
- Campusano, R., 2002. Research on Mine Closure Policy, IIED/MMSD. Cochilco (Chilean Copper Commission). <<http://pubs.iied.org/pdfs/G00541.pdf>> (accessed 27 January).
- Castro, S.H., Laskowski, J.S., 2004. Molybdenite depression by shear degraded polyacrylamide solutions. In: Laskowski J.S. (Ed.), Particle Size Enlargement in Mineral Processing: Proceedings of the Fifth UBC-McGill Bi-Annual International Symposium on Fundamentals of Mineral Processing, Metallurgical Society of CIM, pp. 169–178.
- Castro, S., Sanchez, M., 2003. Environmental viewpoint on small-scale copper, gold and silver mining in Chile. *J. Clean. Prod.* 11 (2), 207–213.
- Chander, S., Fuerstenau, D.W., 1972. On the natural floatability of molybdenite. *Trans. AIME* 252, 62–68.
- Cochilco, Chilean Copper Commission, 2012. Yearbook: Copper and other mineral statistics 1993–2012, Santiago, Chile.
- Cochilco, Chilean Copper Commission, 2013. Inversión en la minería Chilena: Cartera de Proyectos 2013–2021 (Investment in the Chilean mining: Portfolio of Projects 2013–2021), Santiago, Chile.
- ECLAC, 2010. Economics of climate change in Latin America and the Caribbean. Summary 2010, UN ECLAC, p. 107.
- Eskicioglu, C., Kennedy, K.J., Droste, R.L., 2006. Characterization of soluble organic matter of waste activated sludge before and after thermal pretreatment. *Water Res.* 40, 3725–3736.
- Farrokhpay, S., 2011. The significance of froth stability in mineral flotation – a review. *Adv. Colloid Interface* 166, 1–7.
- Gaines, V.R., Skinner, W.C., Foord, E.E., Mason, B., Rosenzweig, A., 1997. Dana's New Mineralogy, eighth ed. John Wiley & Sons, Inc.
- Godoy-Faúndez, A., Antizar-Ladislao, B., Reyes-Bozo, L., Camaño, A., Sáez-Navarrete, C., 2008. Bioremediation of contaminated mixtures of desert mining soil and sawdust with fuel oils by aerated in-vessel composting in the Atacama Region (Chile). *J. Hazard. Mater.* 151 (2–3), 649–657.
- Hadler, K., Aktas, Z., Cilliers, J.J., 2005. The effects of frother and collector distribution on flotation performance. *Miner. Eng.* 18, 171–177.
- Herrera-Urbina, R., 2003. Recent developments and advances in formulations and applications of chemical reagents used in froth flotation. *Miner. Process. Extr. Metall. Rev.* 24, 139–182.
- Kirchberg, S., Abidin, Y., Ziegmann, G., 2011. Influence of particle shape and size on the wetting behavior of soft magnetic micropowders. *Powder Technol.* 207 (1–3), 311–317.
- Lai, R.W.M., Stone, L.C., Rimmasch, B.E., 1984. Effect of humus organics on the flotation recovery of molybdenite. *Int. J. Miner. Process.* 12, 163–172.
- Laskowski, J.S., Liu, Q., O'Connor, C.T., 2007. Current understanding of the mechanism of polysaccharide adsorption at the mineral/aqueous solution interface. *Int. J. Miner. Process.* 84, 59–68.
- Laurence, D., 2011. Establishing a sustainable mining operation: an overview. *J. Clean. Prod.* 19, 278–284.
- Lostarnau, C., Oyarzún, J., Maturana, H., Soto, G., Señoret, M., Soto, M., Rötting, T.S., Amezaga, J.M., Oyarzún, R., 2011. Stakeholder participation within the public environmental system in Chile: major gaps between theory and practice. *J. Environ. Manage.* 92 (10), 2470–2478.
- McLellan, B.C., Corder, G.D., 2012. Risk reduction through early assessment and integration of sustainability in design in the minerals industry. *J. Clean. Prod.* 53, 37–46.
- Memary, R., Giurco, D., Mudd, G., Mason, L., 2012. Life cycle assessment: a time-series analysis of copper. *J. Clean. Prod.* 33, 97–108.
- Minseggres, Ministerio Secretaría General de la Presidencia (Ministry General Secretariat of the Presidency), 2009. Decreto Supremo No. 4: Reglamento para el manejo de lodos generados en Plantas de Tratamiento de aguas servidas (Chilean regulation on handling sludge generated at wastewater treatment plants), Santiago, República de Chile.
- Moors, E.H.M., Mulder, K.F., Vergragt, P.J., 2005. Towards cleaner production: barriers and strategies in the base metals producing industry. *J. Clean. Prod.* 13, 657–668.
- Newbold, J., 2006. Chile's environmental momentum: ISO 14001 and the large-scale mining industry – case studies from the state and private sector. *J. Clean. Prod.* 14 (3–4), 248–261.
- Pandey, A.K., Pandey, S.D., Misra, V., Viswanathan, P.N., 1999. Formation of soluble complexes of metals with humic acid and its environmental significance. *Chem. Ecol.* 16 (4), 269–282.
- Patra, P., Natarajan, K.A., 2006. Surface chemical studies on selective separation of pyrite and galena in the presence of bacterial cells and metabolic products of *Paenibacillus polymyxa*. *J. Colloid Interface Sci.* 298, 720–729.
- Parnaudeau, V., Dignac, M.-F., 2007. The organic matter composition of various wastewater sludges and their neutral detergent fractions as revealed by pyrolysis-GC/MS. *J. Anal. Appl. Pyroly.* 78, 140–152.
- Peppas, A., Komnitsas, K., Halikias, I., 2000. Use of organic covers for acid mine drainage control. *Miner. Eng.* 13, 563–574.
- Potapova, E., Yang, X., Westerstrand, M., Grahn, M., Holmgren, A., Hedlund, J., 2012. Interfacial properties of natural magnetite particles compared with their synthetic analogue. *Miner. Eng.* 36–38, 187–194.
- Prno, J., 2013. An analysis of factors leading to the establishment of a social licence to operate in the mining industry. *Resour. Policy* 38 (4), 577–590.
- Rahman, R.M., Ata, S., Jameson, G.J., 2013. Froth recovery measurements in an industrial flotation cell. *Miner. Eng.* 53, 193–202.
- Ralston, I.D., 2002. The process, health, safety and engineering issues related to the storage and use of xanthates, ATD Report No. PRE-2002-003, Anglo American.
- Ras, M., Giralb-Neuhauser, E., Paul, E., Spérandio, M., Lefebvre, D., 2008. Protein extraction from activated sludge: an analytical approach. *Water Res.* 42, 1867–1878.
- Reyes-Bozo, L., Herrera-Urbina, R., Godoy-Faúndez, A., Sáez-Navarrete, C., Herrera, M., Ginocchio, R., 2011a. Use of biosolids as froth reagent in flotation process: chemical and physical characterization. *Dyna* 78 (167), 66–73.
- Reyes-Bozo, L., Herrera-Urbina, R., Escudey, M., Godoy-Faúndez, A., Sáez-Navarrete, C., Herrera, M., Ginocchio, R., 2011b. Role of biosolids on hydrophobic properties of sulfide ores. *Int. J. Miner. Process.* 100 (3–4), 124–129.
- Reyes-Bozo, L., Herrera-Urbina, R., Sáez-Navarrete, C., Otero, A.F., Godoy-Faúndez, A., Ginocchio, R., 2011c. Rougher flotation of copper sulphide ore using biosolids and humic acids. *Miner. Eng.* 24, 1603–1608.
- Sadzawka, A., Carrasco, M.A., Grez, R., Mora, M.L., Flores, H., Neaman, A., 2006. Métodos de análisis recomendados para los suelos de Chile (Recommended analytical methods for soils of Chile). Instituto de Investigaciones Agropecuarias (Chilean Agricultural Research Institute), Santiago, Chile.
- Santibañez, C., de la Fuente, L.M., Bustamante, E., Silva, S., León-Lobos, P., Ginocchio, R., 2012. Potential use of organic- and hard-rock-mine-wastes on aided phytostabilization of large-scale mine tailings under semiarid Mediterranean climatic conditions: short-term field study. *Appl. Environ. Soil Sci.* 2012.
- Schulten, H.R., Schnitzer, M., 1997. Chemical model structures for soil organic matter and soils. *Soil Sci.* 162, 115–130.
- SISS, Superintendencia de Servicios Sanitarios (Chilean Superintendency of Sanitary Services), 2010. Informe de gestión del sector sanitario 2010 (Management report of the sanitary sector 2010). SISS, Santiago, pp. 164.
- Steger, H.F., Desjardins, L.E., 1978. Oxidation of sulphide minerals, 4. pyrite, chalcocopyrite and pyrrhotite. *Chem. Geol.* 23, 225–237.
- Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reaction, second ed. John Wiley & Sons, Inc.
- Subramanian, S.V., Kawachi, I., 2004. Income inequality and health: what have we learned so far? *Epidemiol. Rev.* 26 (1), 78–91.
- Sutherland, K.L., Wark, I.W., 1955. Principles of Flotation. Australasian Institute of Mining and Metallurgy, Melbourne.
- Swart, P., Dewulf, J., 2013. Quantifying the impacts of primary metal resource use in life cycle assessment based on recent mining data. *Resour. Conserv. Recycl.* 73, 180–187.
- Thomas, W., 2010. Mining Chemical Handbook. Cytec Industries Inc., USA.
- Urkidi, L., 2010. A global environmental movement against gold mining: Pascua-Lama in Chile. *Ecol. Econ.* 70 (2), 219–227.
- Wie, J.M., Fuerstenau, D.W., 1974. The effect of dextrin on surface properties and the flotation of molybdenite. *Int. J. Miner. Process.* 1, 17–32.