MILAF: INTEGRAL MANAGEMENT OF ARSENICAL SLUDGE, TREATMENT AND RECOVERY OF BY-PRODUCTS OF ACID WATERS FROM SMELTER PLANTS

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ABSTRACT

Currently, the copper mining industry produces high amounts of sulfuric acid with low purity and high concentrations of arsenic and other metals. Most of these acid waters are neutralized in the copper smelting plants by using lime to raise the pH from 1 to 12 generating high amounts of arsenical sludge that has to be disposed on safety landfills because of its high toxicity. This has forced the mining companies to pay large sums of money for the disposal of significant volume of solid waste. Each copper smelting plant produces in average during this specific process more than 18,000 tons of arsenical sludge yearly, spending on the treatment and disposal stage more than US 2.8 million dollars per year where a 70 % of this cost corresponds to the disposal costs of the solid waste [1,2,3].

Different technologies for treating these acid wastewaters have been developed and patented worldwide. However, these treatments have focused on obtaining the separation of the arsenic from the effluent through physical-chemical precipitation using different basic components and cations that reacts with the contaminants and then precipitates in the solution [4]. These technologies have not been able to solve the problem because they are expensive, complex, not always efficient and still generates high amounts of arsenical sludge requiring high disposal costs; hence, mining companies have not implement them.

The Environmental Program of Fundación Chile developed a unique treatment that combines two processes based on precipitation and selective removal of arsenic. The technology, named MILAF, was developed to minimize these costs by decreasing the volume of the arsenical sludge through the recovery of a by-product (gypsum) of commercial value.

The treatment was developed through a laboratory study and validated by a field test where two different methods, one based on an oxidation process and the second based on the MILAF process, were used to treat acid wastewater from a national copper smelting plant.

Prior application of the oxidation process at a copper smelter showed that it was difficult to operate and had a lower efficiency than expect. Hence, a study was performed by comparing the oxidation process with the MILAF to analyze the differences and advantages of the two methods.

According to the results obtained from the study, the MILAF presents comparative advantages over the oxidation process. Both treatment methods clearly showed comparative advantages to the current neutralization process used by copper smelters. The oxidation process achieved a 62 % of reduction of the current arsenical sludge generation while the rest of the sludge obtained showed the generation of a stabilized non- toxic sludge by the toxicity analysis of TCLP performed. The MILAF process resulted in a 90 % of reduction of the current arsenical sludge. The resulting arsenical sludge contained most of the arsenic and metals present in the wastewater. In addition, a pure by-product, CaSO4 * 2H2O was obtained generated, which can be sold to the gypsum distributors creating additional revenues for the mining companies. The MILAF process also decreased the consumption of calcium hydroxide, by a 20%.

1. INTRODUCTION

Copper can be produced either pyrometallurgically or hydrometallurgically. Different processes can be used for copper production. Wastewater from primary copper production contains dissolved and suspended solids that may include: copper, lead, cadmium, zinc, arsenic, mercury, and residues from mold release agents (lime or aluminum oxides). Fluoride may also be present and the effluent may have a low pH.

The pyrometallurgical process uses a smelting process to concentrate the copper into anodes with 99,5% copper, which then are refined in a electrolytic process. Liquid effluents from the smelter like cooling water; wastewaters originated in scrubbers (if used), wet electrostatic precipitators and acid wastewaters with high concentrations of metals and arsenic are generated [5].

Chile is the world’s biggest copper producer. This means that aside from all the benefits, large quantities of wastewaters with different physicochemical characteristics and different treatment needs are produced during the extraction and concentration process.

Around the world there are 124 copper smelting plants. Chile has seven copper smelters, four that are linked to primary producers (three owned by Codelco and one by Anglo American) and three custom smelters (two owned by Enami and one by Xstrata Noranda).

Wastewater treatment (i.e., bleed streams, filter backwash waters, boiler blowdown, and other streams) may require treatment by precipitation, filtration or other methods to reduce suspended and dissolved solids and heavy metals. Residues from treatment process are either sent for metal recovery or to sedimentation basins. Fundación Chile estimates that acid wastewaters generated at each copper smelter averages 3 million cubic meters per year. These acid wastewaters are currently treated by a neutralization process generating on average in each plant over 18,000 tons of arsenical sludge per year. In 2004, 70,931 tons of arsenical sludge were registered in Chile [6].

Different technologies for treating these acid wastewaters have been developed and patented worldwide. However, these treatments have focused on obtaining the separation of the arsenic from the effluent through physical-chemical precipitation using different basic components and cations that reacts with the contaminant and then precipitates in the solution. Treatments to generate stabilized and non toxic sludges by using cations, oxidant agents, high temperatures and sometimes even pressurized systems have been developed in order to precipitate a stable or non-leaching waste product that can be disposed in conventional landfills. The disadvantages of all these systems are that (a) they use high amounts of inputs, (b) they operate at high pH to precipitate all the arsenic, (c) they are expensive as they involve complex operations, and (d) they continuing to generate high volumes of arsenical sludge.

This paper addresses an existing problem concerning the arsenical sludge generation in the copper smelting industry. It compares the oxidation process with the MILAF process, a unique treatment that avoids substantial arsenical sludge generation that is currently produced in copper smelters from the neutralization of acid wastewater produced during sulfurous gas washing. This paper explains how MILAF minimizes the current disposal costs and how it creates a new business opportunity because of the generation of a commercial by-product (gypsum) within the treatment process.

2. EXPERIMENTAL METHOD

Laboratory Tests

Partial Precipitation:

A first test was performed to study the behavior of different compounds present in an acid wastewater sample taken from a copper smelter process when rising the pH through lime addition (partial precipitation step). A liquid solution of 13 %p/p prepared with calcium hydroxide P.A was added in small quantities to 2 L samples of acid wastewaters coming from a national copper smelting plant. The samples were mixed with a magnetic stirrer while the pH was constantly measured with a Hanna HI – 8417 instrument. Supernatant samples were taken in range between pH 0.37 and 12 for sulphate, arsenic, calcium and metal content analyses by gravimetric method, total arsenic content and ICP, respectively.

Arsenic Removal:

The supernatant samples of the treated water were treated by two different processes: a) advanced oxidation of the supernatant at pH 2 by hydroxide peroxide and ferrous salt addition and b) selective extraction of arsenic between pH 6 and 7 by pumping the water through packed columns containing arsenic adsorbing material followed by a precipitation step to reach pH 10 by adding a solution of 13 %p/p prepared with calcium hydroxide P.A. In both cases the volume and content of sulphate, arsenic, calcium and metals were analyzed by gravimetric method, total arsenic content and ICP, respectively.

Mass and content of sulphate, arsenic, calcium and metal in solid precipitates were analyzed in all the steps. Analysis of toxicity of the solid precipitate obtained from the advanced oxidation process was also performed through TCLP analysis (Toxicity Characteristic Leaching Procedure).

The process involving a first partial precipitation step, followed by a selective extraction of arsenic and final precipitation step has been named as the MILAF process.

Field Tests

A field test was performed at a National Copper smelter to analyze the first step of the partial precipitation process. The focus of this first field test was to validate the laboratory results from the first stage of the treatment process and to demonstrate the feasibility of separating pure gypsum from the heavy metals pollutants present in the acid wastewater. The field tests included the operation of reactors built inside the facilities of the copper smelting plant.

3. RESULTS AND DISCUSSION

The main purpose of this project was to develop an effective wastewater treatment for effluents generated from copper smelters. To achieve this objective, several tests were conducted using sequential steps of partial precipitation combined with 1) advanced oxidation and 2) MILAF (selective extraction of arsenic and heavy metals). The main results obtained from these feasibility studies would show the efficiencies and advantages of both treatments. Prior industrial testing showed that the oxidation process presents difficulties in the operation and efficiency. Hence, it was proposed to test both the oxidation process compared with the MILAF process developed by Fundación Chile.

The first treatment method performed had the focus of obtaining clean water and a stabilized and non- toxic sludge while the second treatment performed had the focus to generate clean water and very small amounts of arsenical sludge to dispose. In both cases the costs of the treatments were estimated.

Acid wastewater samples were taken from a National Copper smelting plant to be used for the experimental study. Table 1 shows the concentrations of different compounds present in the sample.

Table 1. Physicochemical analysis of acid wastewater from copper smelting plant

Element	Unit	Result
pH	-	0.37
Aluminum	mg/L	2.4
Arsenic	mg/L	557
Cadmium	mg/L	21.4
Calcium	mg/L	223
Copper	mg/L	208
Iron	mg/L	53.6
Magnesium	mg/L	61
Manganese	mg/L	0.76
Molybdenum	mg/L	0.67
Níquel	mg/L	1.26
Lead	mg/L	1.45
Sodium	mg/L	159
Sulphate	mg/L	63,710
Zinc	mg/L	126

Laboratory Tests

Partial Precipitation:

Solubility curves were generated when a liquid solution of 13 %p/p of calcium hydroxide P.A was added in small quantities to the acid wastewater. Supernatant samples and solid precipitates where analyzed in range between pH 0.37 and 12. Figure 1 and 2 shows the behavior of the different compounds present in the wastewater sample. Figure 3 shows the volume of sludge generated during the experiment.

It was possible to see from Figure 1 and 2 that arsenic and metals tended to remaining in the liquid phase when the pH was raised from 1 to around 4. In fact until pH 2, no precipitation of arsenic and metals occurred. However, the sulphate concentration in solution decreased from 63.7 g/L to around 7.3 g/L when reaching pH of 2 precipitating as di-hydrated calcium sulphate. Between pH around 4 and 10 all the metals precipitates with less than 0,3 mg/L in the liquid phase. At pH 10, a concentration of 11.45 mg/L arsenic remained in the liquid phase.

In Figure 3, it is possible to see that over a 60 % of the precipitate was generated between pH 0,37 and 2. Between pH 2 and 11 a 15 % of precipitate was generated and between 11 and 12 additional 25 % of sludge was generated.

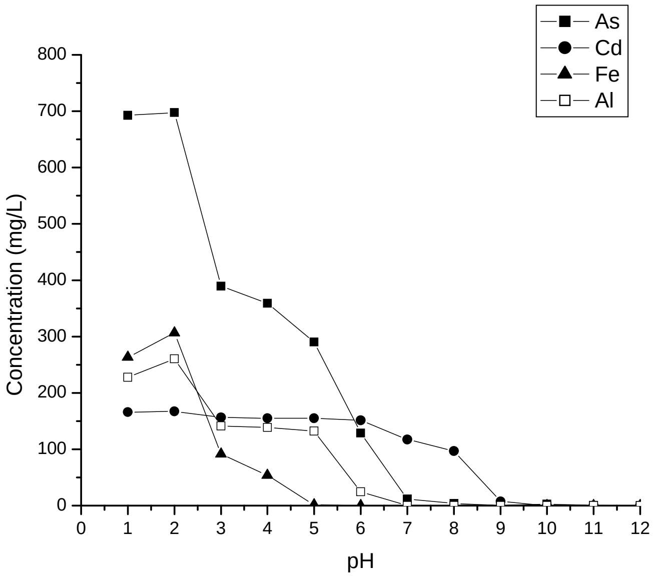


Figure 1. Solubility curves for arsenic, cadmium, iron and aluminum in the wastewaters from smelting plant

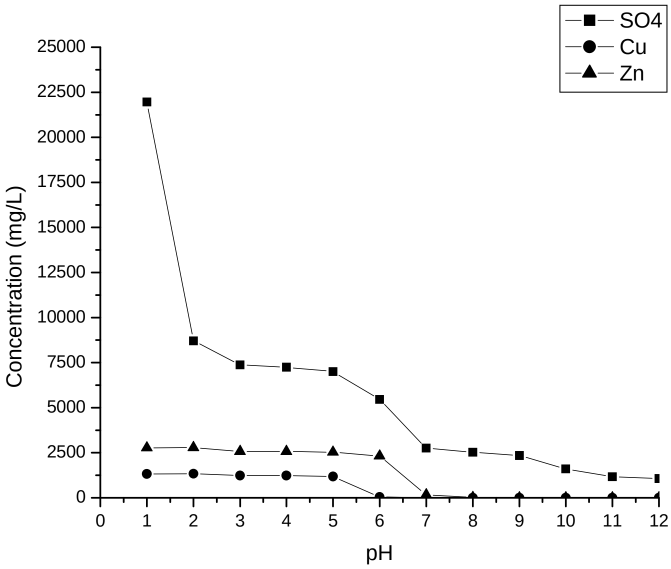


Figure 2. Solubility curves for sulphate, copper and zinc in the wastewaters from smelting plant

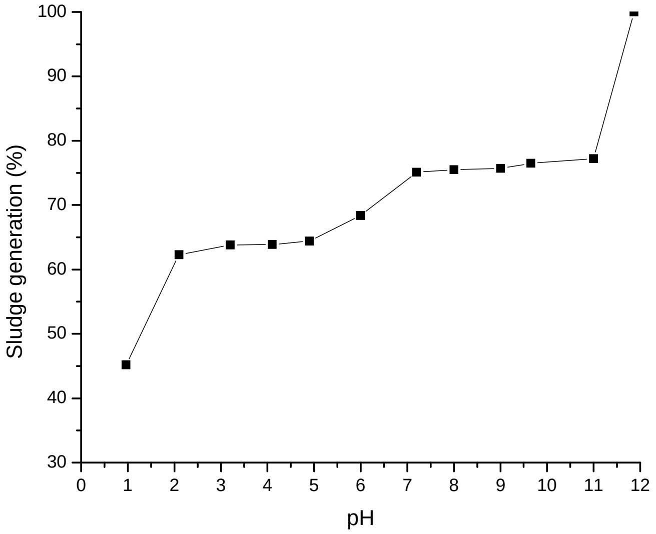


Figure 3. Percentage of sludge generation as a function of pH

According to the results obtained from the analysis of the supernatant and solid samples, it was possible to see that the major volume of precipitate (62 %) occurred when the pH rose between 0,37 and 2. On the other hand, this solid contained over a 99,5 % of di-hydrated calcium sulphate. Above a pH of 2, the metals and arsenic started to precipitate generating sludge that contained the majority of metals and arsenic remaining low concentrations of pollutants on the treated wastewater. This result confirmed the possibility of separating high volumes of pure di-hydrated calcium sulphate (gypsum) as a commercial by-product and confining the toxic compounds to a small volume of sludge.

Arsenic Removal

The supernatant of the treated water sample were subjected to two different processes: a) advanced oxidation of the supernatant at pH 2 by hydroxide peroxide and ferrous salt addition and b) selective extraction of arsenic between pH 6 and 7.

a) Advanced Oxidation

Hydrogen peroxide and ferrous salt were added to the supernatant samples at pH 2. This treatment was followed by addition of calcium hydroxide to reach pH 11. Different quantities of oxidant were used in order to study the behavior of arsenite oxidation. Analysis of arsenite and arsenate were performed before and after the oxidation process at an external laboratory. A 100 % of arsenic oxidation was reached when using a mass proportion of oxidant/arsenic equal to or greater than 10:1. Only 78% of the arsenic was oxidized when using a mass proportion of oxidant/arsenic of 4:1. Table 2 shows the concentration of the different pollutants in the treated wastewater after the oxidation and precipitation step at pH 11 when using a mass proportion of oxidant/arsenic 10:1 and 4:1 and a control sample where no oxidant were added. Table 3 shows the results of TCLP analysis of the solid samples generated from these experiments.

Table 2. Concentration of different compounds in the treated wastewater after the oxidation and precipitation step at pH 11

Element	Unit	oxidant/arsenic 10:1	oxidant/arsenic 4:1	Control sample
Aluminum Total	mg/L	0.2	0.1	0,3
Arsenic Total	mg/L	0.23	0.04	11.45
Cadmium Total	mg/L	<0.01	<0.01	<0.01
Calcium Total	mg/L	943	1025	1130
Copper Total	mg/L	<0.01	<0.01	0.02
Iron Total	mg/L	<0.05	<0.05	<0.05
Magnesium Total	mg/L	1.5	5.1	0.7
Manganese Total	mg/L	<0.01	<0.01	<0.01
Molybdenum Total	mg/L	0.28	0.84	0,07

Níquel Total	mg/L	<0.01	<0.01	<0.01
Lead Total	mg/L	<0.02	<0.02	<0.02
Sodium Total	mg/L	110	126	148
Zinc Total	mg/L	0.06	0.01	0.01

Table 3. TCLP analysis of the solid samples

Sample	**As**	**Se**	**Ba**	**Pb**	**Cd**	**Cr**	**Ag**	**Hg**
Unit	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Sludge oxidant/arsenic 10:1	0.5	< 0.5	< 0.5	< 0.2	0.04	< 0.05	< 0.02	0.084
Sludge oxidant/arsenic 4:1	1.3	< 0.5	< 0.5	< 0.2	0.66	< 0.05	< 0.02	0.28
Control Sample	7	<0.5	< 0.5	0.6	2.54	1.5	< 0.02	0.52
Regulated value in Chile D. S N° 148	5	1	100	5	1	5	5	0.2

Table 2 shows that oxidation reduces arsenic concentrations below 0.5 mg/L, whereas in the unoxidized control sample 11.45 mg/L of arsenic remained in the treated water. Table 3, shows that the sludge generated after oxidizing with the oxidant/arsenic ratio of 10:1 is not toxic base on the TCLP analysis. The sludge generated when using a mass proportion of oxidant/arsenic 4:1 is toxic because of the leaching of mercury. On the other hand, the control sample was toxic because of the leaching of arsenic, cadmium and mercury. The results obtained showed the importance of the oxidative process on the generation of stabilized and non-toxic sludge.

b) Selective Extraction of Arsenic, Milaf

Table 4 shows the composition of the precipitated di-hydrated calcium sulphate at pH 2. After this step a second precipitation was performed at pH 7 in order to generate a sludge that contained all the metals and arsenic present in the acid wastewater, Table 5 shows the composition of the arsenical sludge generated.

Table 4. Composition of di-hydrated calcium sulphate at pH 2, by -product

Parameter	**Unit**	**Pure Gypsum**	**Percentages (%)**
Aluminum	mg/Kg Al	346	0.04
Arsenic	mg/Kg As	160	0.02
Cadmiun	mg/Kg Cd	155	0.02
Calcium	mg/Kg Ca	139,000	17.49
Copper	mg/Kg Cu	1450	0.18
Iron	mg/Kg Fe	478	0.06
Manganese	mg/Kg Mn	53,3	0.01
Nickel	mg/L Ni	22.3	0.00
Lead	mg/L Pb	30	0.00
Sulphate	mg/Kg SO4	652,870	82.17

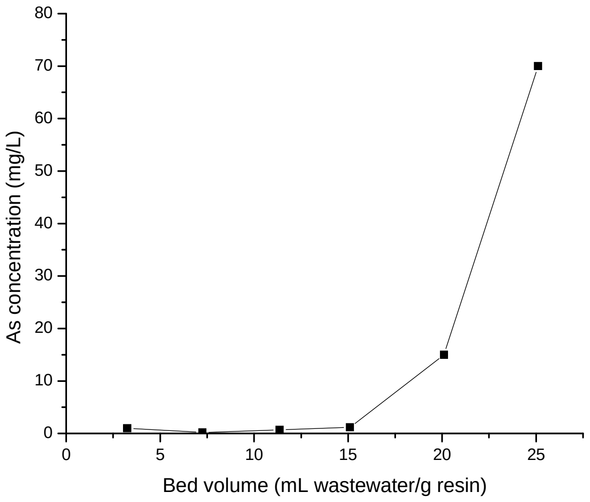
Table 5. Arsenic sludge composition at pH 7

Parameter	**Unit**	**Arsenical Sludge**	**Percentages (%)**
Aluminum	mg/Kg Al	12300	2,06
Arsenic	mg/Kg As	59600	9,98
Cadmiun	mg/Kg Cd	21900	3,67
Calcium	mg/Kg Ca	123000	20,60
Copper	mg/Kg Cu	126000	21,10
Iron	mg/Kg Fe	2330	0,39
Manganese	mg/Kg Mn	1310	0,22
Nickel	mg/L Ni	27100	4,54
Lead	mg/L Pb	1460	0,24
Sulphate	mg/Kg SO4	222060	37,19

The supernatant sample at pH 7 obtained from the second precipitation step, where metals and arsenic were precipitated and separated from the wastewater, was pumped through packed columns containing a specific ion exchanger for arsenic removal in order to remove the arsenic remaining in solution. The dissolved arsenic in this water contained between 15 and 70 mg/L arsenic in the different tests performed. Analysis of arsenic in the treated water was performed.

In table 6 it is possible to see that the capacity of the ion exchanger reached 1,05 mg As/g of resin when the initial concentration of arsenic was 70 mg/L and the treated water contained 1,2 mg/L. This result shows the possibility of removing arsenic from the water at pH 7 by using this treatment method. It also shows that the maximum capacity of the resin reached 1,32 mg/g.

Table 6. Capacity of the ion exchanger

Final concentration of Arsenic (mg/L)	**Capacity of ion exchanger (mg/g)**	
0,2	0,503	
0,7	0,788	
1,2	1,046	
15,0	1,321	
70,0	1,321	

After the selective extraction of the residual arsenic an additional neutralization step was performed in order to reach pH 11 and precipitate an additional 30 % of di-hydrated calcium sulphate with only small concentrations of metals.

Table 4 shows the contents of the generated pure by-product and Table 5 shows the contents of the sludge during the confinement of the metals and arsenic, “arsenical sludge”.

The process involving the first partial precipitation step, followed by the selective extraction of arsenic and final precipitation step has been named as the MILAF process.

Field Tests

The field test performed within the facilities of a National Copper smelting plant focused on the first step of the treatment concerning the partial precipitation process. The results obtained confirmed the laboratory results validating the possibility of separating a commercial gypsum by-product reducing the current arsenical waste sludge by a 60%.

4. CONCLUSIONS

According to the results obtained from the study, it was possible to see that the oxidation and the MILAF processes presented many advantages when comparing with the current neutralization process used by copper smelting plants. Table 5 shows some of the differences between these treatment methods.

Table 5. Differences between Neutralization, oxidation and MILAF process

Parameter	**Unit**	**Neutralization process**	**Oxidation Process**	**MILAF**
Reduction of arsenical sludge	%	0	62	90 – 94
Treatment costs	US/day	3433	5018	3465
Disposal costs	US/day	8797	50.48	833
Lifespan of a safety landfills	Years	2	Uses conventional landfills	20
Lime use	g/L	187	187	152
Technical complexity	-	low	high	medium
Revenues by gypsum selling	US/day	0	1096	1644

Comparing the three alternatives, The MILAF constitutes a cost-effective treatment that allows higher savings comparing to the oxidation process reaching a 40-50 % of savings over the current neutralization process when considering all associated operational costs. On the industrial level, the oxidation process presents many operational difficulties in generating a stable and non-toxic sludge causing limitations in its implementation. The MILAF process is a simpler treatment method based on precipitation and ion exchanging methods compared to the oxidation process, which requires complex control of a chemical reaction.

In general, the innovative MILAF process enabled the reduction of a 90 and 95 % of the arsenical sludge generation, separating an equal amount of by-product ($CaSO4 * 2H2O$) that exceeded the required pureness of 85 % established by the gypsum providers. The MILAF process also decreased the consumption of the main input currently used,, calcium hydroxide, by a 20%.

The reported results were based on the application of the treatment methods to 3 different matrixes of acid wastewaters. The selling of gypsum adds revenues of US 0.6 million dollars per year for each copper smelter. The reduction of arsenical sludge volume increases the life of the safety landfills up to 10 times, compared to current precipitation processes. It allows saving the land as an invaluable environmental benefit.

Today further studies are being performed using acid waters from other smelter plants in order to validate the technology for other effluents and smelter plants.

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