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REMOVAL OF ANTIMONY AND BISMUTH FROM COPPER ELECTROREFINING ELECTROLYTE BY TWO PROPRIETARY SOLVENT EXTRACTION EXTRACTANTS

by

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PUBLICATION THESIS OPTION

This thesis consists of the following three articles formatted in the style used by the Missouri University of Science and Technology:

Paper I and II: pages 2-24 and 25-43, respectively, were published in JOM.

Paper III: pages 44-61 has been accepted to the Copper 2019 conference proceedings.

ABSTRACT

Antimony and bismuth are two of the most problematic impurities in copper electrorefining (ER). Because of this, much research has been done investigating the ways to remove them. Processes that are currently being used industrially include anode additions, liberators, ion exchange (IX), and solvent extraction (SX). Of these, liberators and anode additions are the most common while SX is the least, mostly being used for arsenic removal. There are other methods that have been evaluated, but are not in commercial use. These include the use of various electrolyte additives, and adsorbents such as bentonite clay and heavy metal sulfates.

Two proprietary phosphonic acid ester extractants (REX-1 and REX-2) were examined for the removal of antimony and bismuth from copper ER electrolytes. Experimentation included shakeout and break tests to determine the basic parameters for the extractants in terms of maximum loading, break times, and extraction and stripping efficiency as well as a laboratory-scale test using a mini-pilot plant to examine effectiveness under commercial conditions.

The shakeout tests found that REX-2 was able to extract Sb and Bi from the electrolyte, but required some mixture with REX-1 to better facilitate stripping with 400 g/L sulfuric acid. Phase break times revealed that glue in the ER electrolyte caused a statistically significant decrease in the disengagement times. In the mini-pilot plant, only REX-2 was used. Antimony and bismuth were both extracted effectively, and Bi was effectively stripped with 400 g/L sulfuric acid. Unfortunately, most of the extracted Sb remained in the organic phase. A conceptual flowchart to make a Bi product was created.

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SECTION

1. INTRODUCTION

1.1 OBJECTIVES

The main goal of this thesis was to determine the effectiveness of two solvent extraction extractants, REX-1 and REX-2, in removing Sb and Bi from Cu electrorefining (ER) electrolyte. However, this project was also used as an opportunity to research an additional production opportunity for Sb and Bi that is currently being overlooked.

1.2 PAPERS

This thesis is prepared using three individual papers that were previously published in journals or conference proceedings. Paper I and II (pp. 2-24 and pp. 25-43, respectively) were formatted for and published as a two-part paper in volume 70 of the peer-reviewed journal “JOM”. Paper III (pp. 44-61) was formatted for and submitted for approval to the Copper 2019 conference and will likely be presented in August 2019 in Vancouver, Canada.

PAPER

I. REMOVAL OF ANTIMONY AND BISMUTH FROM COPPER ELECTROREFINING ELECTROLYTE PART I – A REVIEW

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Reprinted by permission from RightsLink: Springer JOM Removal of Antimony and Bismuth from Copper Electrorefining Electrolyte Part I – A Review, Andrew Artzer, Michael Moats, and Jack Bender, 2018

ABSTRACT

Antimony and bismuth are two of the most problematic impurities in copper electrorefining. Because of this, much research has been done investigating the ways to remove them. Processes that are currently being used industrially include anode additions, liberators, ion exchange (IX), and solvent extraction (SX). Of these, liberators and anode additions are the most common while SX is the least, mostly being used for arsenic removal. There are other methods that have been evaluated, but are not in commercial use. These include the use of various electrolyte additives, and adsorbents such as bentonite clay and heavy metal sulfates.

1. INTRODUCTION

During the electrorefining of copper, anodes of, typically, 98-99% copper are dissolved into an electrolyte consisting of 130-220 g/L H_2SO_4 then plated onto a cathode (either a copper starter sheet or some other non-reactive metal like stainless steel or titanium) as a 99.99+% pure product. This cathode copper is typically used to produce rod and eventually wiring for electrical applications. However, some impurities even at ppm levels can ruin the drawing ability of the copper.

Throughout history, antimony and bismuth have been some of the most problematic impurities, as noted in this 1934 paper; "antimony is one of the most troublesome impurities with which the refiner has to contend" (Bardwell and Lapee, 1934) [1]. They precipitate at the grain boundaries of the copper and melt as the copper is heated during drawing, ruining the strength of the copper and making it very hard to draw. Antimony also causes considerable roughening of the surface of the copper cathode at 0.02-0.1 g/L [2], and has been known to precipitate within the cell and cause build-ups and eventual clogging of pipes and cells, anode passivation, and a drop in current efficiency [3].

Antimony and bismuth typically enter the electrolyte system via the anode. As shown in Figure 1, the concentrations of antimony and bismuth in anodes have been increasing steadily for several decades. Though many impurities precipitate at the anode and become trapped in the anode slimes, some impurities dissolve into the electrolyte, meaning an increase in anode impurities leads to an increase in electrolyte impurities.

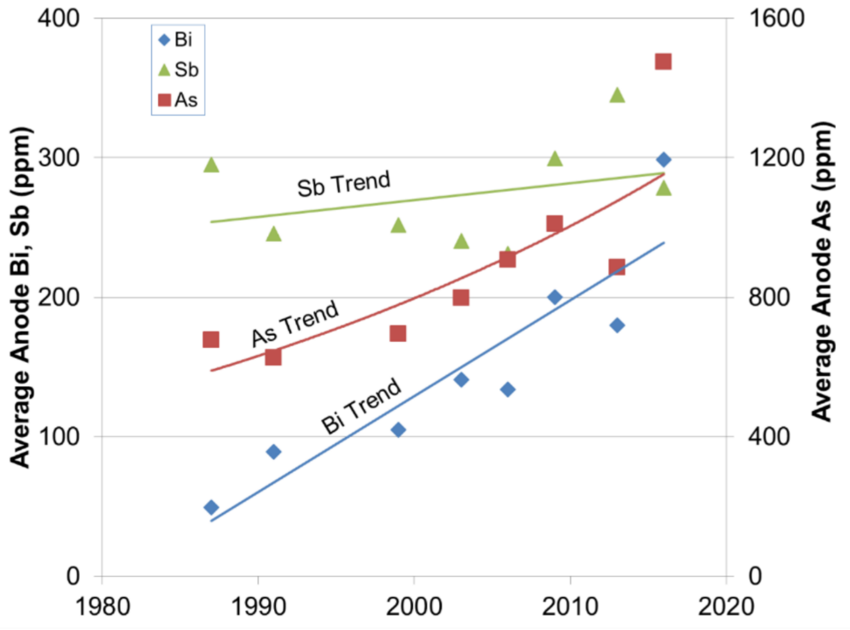

Figure 1. Impurity trends in copper electrorefining anodes over the last 30 years. Data published in copper refinery world surveys.

In the electrolyte, antimony and bismuth exist mainly as complex cations (SbO^+ and BiO^+) [4]. These ions can precipitate as arsenates or remain as ions in the electrolyte. Precipitates from the anode surface and the electrolyte can then become entrapped in the surface of the cathode and lead to contamination [3].

Since antimony and bismuth are problematic to copper electrorefining, control of their concentrations in the electrolyte is considered at all refineries. Thus, a review of the various methods available to remove antimony and bismuth from copper electrorefining electrolyte is useful for those working and studying in the field. The methods discussed will include; liberator cells [4-10], bleeding [11], doping and electrolyte additives [12-21], solvent extraction (SX) [2,7,22,23], activated carbon [24-27], molecular recognition technology (MRT) [28-31], ion exchange (IX) [3,7,10,11,26,27,32-40], and various other adsorption techniques [26,36,41-45].

2. ELECTROWINNING OR LIBERATOR CELLS

Electrowinning or liberator cells are what is referred to as the “conventional process” for antimony and bismuth removal from electrorefining electrolyte. It is one of the older practices used to purify the electrolyte, and is still in use at many refineries today. This technique involves the processing of a bleed stream from the refining cells in an up to three stage electrowinning process. To remove antimony and bismuth effectively, copper must first be plated from the electrolyte to lower its concentration, as it has the highest reduction potential and will plate preferentially to antimony and bismuth. This is shown in Figure 2 [5], where the impurity concentrations remain constant until a critical copper concentration is reached.

In the first stage of liberation, the copper concentration is often reduced from the operating concentration of ~45 g/L to 15-20 g/L [6]. The copper that plates on the cathode in this step is generally pure and can be used to produce copper rod. In second stage liberation, the copper concentration is further reduced to ~8 g/L. This step results in an impure copper cathode since copper co-deposits impurities such as arsenic and bismuth in very small amounts. The impurities mainly deposit on the cathode by entrapment of slimes and electrolyte. Second stage liberator cathode cannot be sold and is recycled back to the smelter or anode shaft furnace. Unfortunately, this means some of the impurities are returned to the refinery in the anodes [6,7]. Third stage liberation is used to further decopperize the solution to less than 1 g/L. This cathode is very high in arsenic and bismuth and is either used for arsenic manufacturing or simply recycled back to the smelter. Third stage liberation is not always performed due to potential production of extremely toxic arsine gas, but generally this will not be a problem above 0.5 g/L copper [6]. Modern refineries utilize arsine detectors in the areas around the liberator cells to stop the rectifiers if arsine is detected.

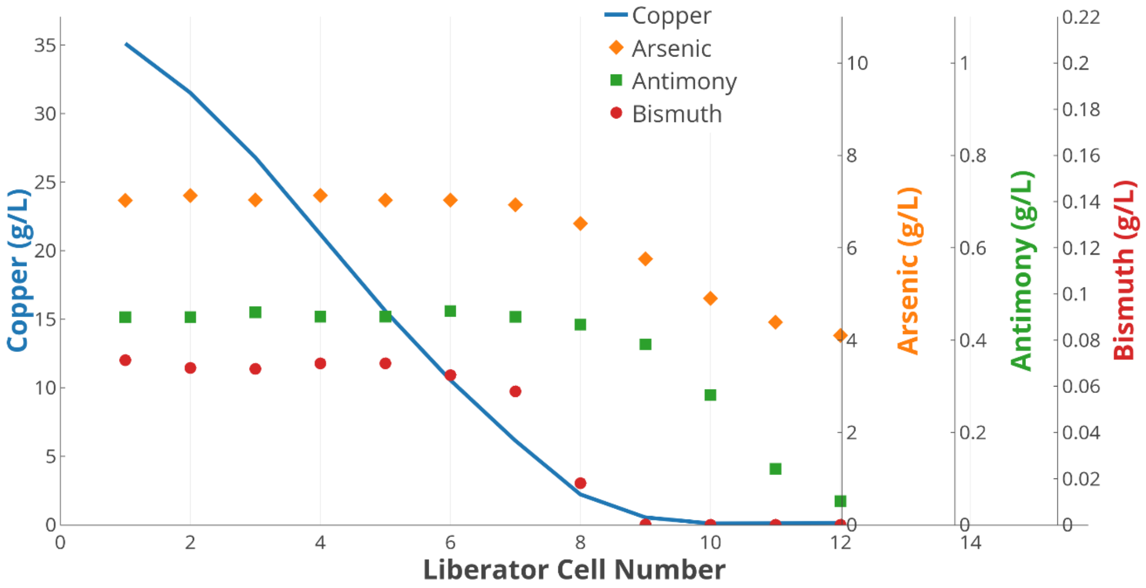

Figure 2. Trends of copper and impurity concentrations during liberator processing (data taken from Shibata et al. [5]).

Liberators are typically run to very low concentrations of copper in order to remove as many impurities as possible [8,9]. One refinery uses a cascading liberator set-up where the end electrolyte from the last cell is constantly recirculated back to the beginning of the liberator process to maintain a level of about 2-5 g/L copper, where the impurity removal efficiency is highest. The voltage in the cells is monitored so that when it begins to drop due to a decrease in copper concentration, pumps are activated to pump fresh electrolyte (from the electrorefining cells, ~45 g/L Cu) into the liberator cells, using a separate pump for each cell. Not only does controlling the concentration of copper to 2-5 g/L increase the liberator efficiency, but it also helps to decrease the chance of forming arsine gas [9].

Liberators are also used as a final purification step in some other processes. Ando et al. reported a way to extract antimony and bismuth using IX resins, then strip the elements from that, and electrowin the eluate [10]. A two-stage elution system, which will be discussed in detail later, was designed to selectively elute the antimony and bismuth, separately, from the resin. This eluant was composed mostly of H_2SO_4, and became the anolyte after desorption; it is separated from the catholyte by a cation-exchange membrane. This process was able to proceed even at very low concentrations of metal and gave about 99.5% recovery for bismuth. However, efficiency decreased greatly below 0.1 g/L Bi. The antimony process was able to go from an initial concentration of 3.5 g/L Sb to about 0.07 g/L Sb and keep the current efficiency much higher than that in conventional liberator processing [10].

There are several problems with liberator processing that have caused some refineries to abandon it in favor of newer processes, like IX columns or even carbon adsorption. Liberators have a relatively high cost and low efficiency, which becomes an increasing problem as the copper ore around the world becomes more and more dirty (Figure 1). This means the process will cost more to perform and generate comparatively less saleable product while only recycling the impurities back into the anode instead of removing them from the process completely [4,10]. Another problem is that the copper concentration in the electrolyte must be dropped very low in order to remove large amounts of impurities. Some refineries use a process that removes copper from the electrolyte as copper sulfate before the liberators. However, this process is hard to adopt for plants not designed around it and expensive to implement and operate [5].

3. BLEEDING

Bleeding is the process of removing a small volume of solution from the tankhouse electrolyte. Normally, bleeding is done to get electrolyte from the electrorefining process to the impurity removal operation, such as liberators or IX. However, some plants send their bleed to another facility for copper recovery and solution disposal. Examples include sending bleed solution to a SX/electrowinning plant where copper is recovered and the impurities will report to the raffinate and eventually precipitate or adsorb on ore particles within the heap [11].

4. ANODE DOPING AND ELECTROLYTE ADDITIONS

Doping is the addition of impurities to the anode in the hope that they will remove more impurities. This is practiced by many refineries through the addition of arsenic at the smelter. Lead can also be added. Electrolyte additions can also be made through the addition of arsenite. Oxide and carbonate additions to the electrolyte have also been studied. Smooth cathodes should always be a priority when doping or making electrolyte additions since precipitation may be high [12].

4.1 ARSENIC

Arsenic is used in most refineries as the main control method for Sb and Bi. This is done by controlling the molar fraction ratio (As/(Sb+Bi)) to a value between 2.9 and 3.3. At these compositions, most of the Sb and Bi from the anode will form insoluble products at the surface of the anode and report to the slimes [13].

Typically, arsenic dissolves from the anode in the trivalent state then quickly oxidizes to become pentavalent. This pentavalent arsenic will react with some of the antimony and bismuth to form a slime on the surface of the anode that easily falls off and sinks to the bottom of the cell [3]. Keeping the molar fraction ratio above 2 ensures that the solution near the anode is supersaturated and that most of the antimony and bismuth will precipitate as arsenates into the slimes.

The arsenic concentration in the electrolyte, which usually controls the antimony and bismuth concentration, is typically controlled by altering the arsenic concentration of the anode, but it is possible to add arsenic directly to the electrolyte [14]. This could be used as a way to more quickly reduce a large build-up of impurities in the electrolyte, instead of waiting for the anode composition to alter it. These additions must be made using copper arsenite or some other As(III) bearing compound. When As(III) is added to the electrolyte, the removal rate of antimony and bismuth greatly increases, while As(V) compounds have been shown to have lower removal rates [15].

A research group from China has published a series of papers related to the formation antimony arsantimonates, and arsenato antimonic acids (AAAc). They claim the variation in removal rates is most likely due to the partial oxidation of As(III) to As(V). When As(III) reacts in the electrolyte it has been reported to form antimony arsantimonates, and when As(V) reacts it forms AAAc. Antimony arsantimonates are typically composed of Sb(V), As(III), and Sb(III), while AAAc are complex compounds that form through a series of Sb-O-Sb and As-O-Sb bonds [13,16]. When arsenic dissolves from the anode, or is added in the trivalent state, both AAAc and antimony arsantimonates are formed. However, when additions of As(V) are made, only the AAAc compounds form [17].

Formation of AAAc requires a molar ratio of As(V):Sb(V) of greater than 1:1, though the precipitation relies much more on antimony than arsenic; tests showed that without Sb(V) there was no precipitation. Once this ratio is achieved, the acid will form and then change to arsenato antimonate precipitates when it comes into contact with Bi(III), As(III), and Sb(III). These precipitates will settle to the bottom of the cell and be removed with the slimes [16]. However, AAAc is one of the main components of floating slimes. To prevent their formation, the concentrations of Bi(III), As(III), and Sb(III) need to be high enough to ensure the AAAc will convert to arsenato antimonates [18]. They developed a process to create copper arsenite and optimized its addition in copper electrolyte. According to the study, the purification of the electrolyte increases with increasing copper arsenite up to 20 g/L, with removal rates maxing out at 53.85% for antimony and 53.33% for bismuth [19]. In this particular experiment, three precipitates were found, which appear to be an antimony arsantimonate and two arsenato antimonates.

Very similar results were gathered from another experiment. In the latter experiment, the maximum copper arsenite concentration was 18 g/L and the amount of bismuth extraction was slightly higher (58.67%) [14].

One comprehensive study, conducted by Kamath et al. (2003), detailed what occurred in the electrolyte while a copper refinery attempted to reduce its electrolyte impurities (very low As and very high Bi and Sb) using arsenic additions. They observed three distinct conditions: (1) having under-saturated antimony and bismuth without suitable amounts of arsenic caused more and more impurities to build up in the electrolyte, leading to impure cathodes; (2) having a fully saturated solution of Sb and Bi with some arsenic caused a large amount of precipitation to occur, leading to floating slime formation and impure cathodes but also greatly decreasing the concentration of antimony and bismuth in the electrolyte; and (3) further increasing the arsenic concentration led to lower concentrations of antimony and bismuth in the electrolyte until the system reached an equilibrium point. At equilibrium, mainly arsenic gets dissolved from the anode and the antimony and bismuth concentrations remain under-saturated [20].

4.2 LEAD

In a recent paper by Zeng, Wang, and Free, lead anode additions were shown to aid in the formation of sinking slimes. At a lead-arsenic ratio of 1.5 or greater, the slimes easily agglomerate and adhere to the surface of the anode [21]. Without a certain level of sintering or adhesion to the anode, the tiny floating particles would become entrapped in the cathode, resulting in bismuth contamination of the cathode. Thus, added lead to the anode resulted in more bismuth reporting to the slimes.

5. SOLVENT EXTRACTION

SX has been examined to remove antimony and bismuth from copper electrorefining electrolyte. Those that have implemented SX usually use it for arsenic removal, instead of antimony and bismuth. The reasons it has been studied so heavily are that it drastically reduces the power usage from liberator cells and is very fast compared to other operations such as adsorption.

Bis(2-ethylhexyl)phosphoric acid (DEHPA) along with mono-2-ethylhexylphosphoric acid (MEHPA), have been investigated. A mixture of DEHPA and MEHPA performed better than the extractants individually [22]. Selective stripping of antimony and bismuth was demonstrated [22]. A mixture of Kelex 100 and DEHPA was also reportedly able to extract antimony from copper electrolyte efficiently [23]. The major problem with these chemicals is that they have poor stability and quickly lose their antimony extraction ability [22].

An extractant called DS 5834, which contains mono(isooctadecyl)phosphoric acid, has also been suggested for use. The chemical is more stable in electrorefining solutions than MEHPA. It is capable of both Bi(III) and Sb(III) extraction with no loss of strength after six full cycles [7]. DS 5834 can be stripped with 6M HCl, but stripping is more effective when using diluted HCl with alkaline or alkaline earth metal chlorides. This will maintain a high concentration of chloride ions, which is the main factor in the stripping of the metals [7,22]. The strip solution can be treated by diluting the solution with water or by neutralizing it with sodium hydroxide. The solids formed from this process will be bismuth oxychloride and antimony oxychloride [7].

Alkyl phosphonic acid esters, alkyl phosphinic acid esters, and trialkylphosphine oxide, are also possibilities for Sb(III) and As(III) extraction. These chemicals can be used together in two different ways; either extracting arsenic and antimony together or selectively extracting antimony [22].

Co-extraction of As and Sb can also be achieved with a mixture of alkylated 8-hydroxyquinoline, phosphonic acid ester, and an inert diluent pretreated with 200 g/L H_2SO_4. Isodecanol can also help when used as a modifier. Using this method, almost 100% of the total arsenic and antimony can be extracted, though small amounts of copper will also be lost from the electrolyte. Each of these materials can then be selectively stripped from the organic; arsenic strips with 40 g/L H_2SO_4, antimony with NaOH, and copper with 200 g/L H_2SO_4 [22].

Various hydroxamic acids are also capable of extracting Sb and Bi. However, they are not selective. LIX 1104, for example, is capable of removing arsenic, antimony, bismuth, and iron. There is no modifier required for this process, and it is very stable at high acids. Antimony, bismuth, and iron extraction is rapid, while arsenic extraction typically takes 10s of minutes. Arsenic and bismuth can be stripped using sulfuric acid or other alkali metal sulfides [22]. Another method to strip the metals is 8M HCl. Sulfuric acid is not capable of stripping the antimony, but with the HCl and low O:A ratios, 90% of antimony was able to be stripped. Much of the iron and arsenic is left in the organic with this strip, though. Sulfuric acid can then be used to remove the arsenic and some iron. Sb_2S_3 can be precipitated from the stripping solution by mixing it with NaHS [23].

Another process that has been proposed is the use of a quaternary ammonium chloride (Aliquat 336) and alcohol (2-ethylhexanol) for the extraction of arsenic and antimony. The two metals can be selectively stripped using 0.5M H_2SO_4 for arsenic and aqueous NH_4OH for antimony. The ammonia stripping step will also strip arsenic, though, so it must be done last. The removed ions can be recovered as tetracupric arsenate and antimony trioxide [22].

Bender and Emmerich [2] examined two proprietary extractants, REX-1 and REX-2, a 1:1 mixture of REX-1 and REX-2 and a 1:1:1 solution of REX-2, tridecanol (TDA) and, tributyl phosphate on the extraction and strippability of antimony, bismuth, tin, iron, and arsenic using a 400 g/L H_2SO_4 strip. The results of their study [2] demonstrate the wide variety of situations that can be adapted to by altering the mixture of the reagents and modifiers. These reagents can offer the potential for selective extraction of antimony or bismuth or used to remove both the impurities at once. No research was done on selectively stripping the elements [2].

6. ADSORPTION

Adsorption processes that have been examined include activated carbon, IX, and MRT. All of these function off the same principle, but have different options for selectivity. Most use geometry, size, charge, stereochemistry, etc. Some are very selective and use many of these criteria to specify one ion from a solution of many.

6.1 ACTIVATED CARBON

Activated carbon has been employed by a select few copper refineries in order to remove antimony from electrolyte. This process is mainly applicable for high concentrations and typically is not used in strong acid solutions [24]. Though it can be made quick and efficient under the proper conditions, this process tends to have lower loading capacity than IX and slower kinetics than SX [24,25].

In a set of experiments performed by Toyabe et al., the removal efficiency of activated carbon was tested using a packed column that was bottom fed with copper electrolyte. The carbon was able to selectively adsorb bismuth, antimony and arsenic from the electrolyte, though antimony was removed with much higher selectivity and efficiency than arsenic and bismuth. However, as additional bed volumes (BV) were passed, the carbon became decreasingly selective for antimony [24].

In a second test, activated carbon was mixed with a liter of electrolyte for 60 minutes to examine the effect of arsenic concentration. The experiments revealed that the presence of arsenic in solution was necessary for antimony to absorb onto the activated carbon. This suggested that the antimony adsorbed as an Sb-As complex rather than an antimony ion. The average extraction efficiencies from this experiment were 12.1% Sb, 1.32% Bi, and 6.85% As, with less than 1% copper and nickel [24].

Gabai et al. produced similar results [26]. They found that there was about a 50% reduction in antimony after 4 hours of agitated contact with electrolyte. However, it took nearly four days to reach 90% extraction. Increasing solid/liquid ratios helped to increase extraction values, but the reaction rate was still very slow compared to other adsorption processes.

From a study by Ruiz et al., extraction using activated carbon showed asymptotic behavior; the highest retention that it seemed possible to achieve was around 85% [27]. This could explain the four days that it took Gabai et al. to reach 90% extraction.

Very little was discussed as far as the stripping or recovery of metal from the activated carbon, but one paper suggested using the loaded carbon as a reducing agent in a silver plant furnace [24].

6.2 MOLECULAR RECOGNITION TECHNOLOGY

MRT is a process that has been utilized by a few refineries to control the bismuth concentration in the copper electrolyte. This process is not suitable for antimony removal due to irreversible resin poisoning [28]. MRT is a highly selective process that employs specially designed ligands (crown ether molecules) that can be used at very low concentrations of impurities and very high acid levels [29,30].

This process involves passing electrolyte through a column filled with MRT material to extract bismuth. The elution of the bismuth is accomplished using a 9 M sulfuric acid solution [29]. In a study by Bruening et al., it was shown that the elution of bismuth from MRT resin was completed after one BV of heated sulfuric acid was used, even when 40 BV of electrolyte had been loaded onto it. This means that the resulting eluate is very concentrated with bismuth, as well as the material costs for the process being relatively low [30]. This eluate forms bismuth bisulfate spontaneously as it is cooled, which can be sold for value. The remaining solution is disposed. However, a Cu-Bi product could be obtained by electrolysis [31].

6.3 ION EXCHANGE RESINS

IX resins are any of a large group of styrene-divinylbenzene copolymers with functional groups attached, used to selectively extract particles from a solution by adsorption. Some resins perform an ion-exchange reaction, while others utilize chelation. Chelating resins are typically used for copper electrolytes; in the removal of bismuth and antimony, aminophosphonic acid or aminomethylenephosphonic acid functional groups are most common [32,33].

Eporus MX-2 resin has been employed industrially to remove antimony at the Hitachi and Saganoseki refineries [34,35]. This resin is characterized by a high adsorption capacity for antimony, high selectivity for antimony over copper, and good stability in high sulfuric acid solutions. The resin capacity is about 20 grams of antimony per liter of resin. Antimony can be eluted using 4-6 M hydrochloric acid. Elution is mostly complete after 2.5 BV, at which point, any additional acid that is passed through the column is recycled for use in the next elution run. Antimony is recovered from the eluate as Sb_2O_3 by neutralizing with lime and sold for use in fire retardants [34,35].

Unicellex UR-3300 and Duolite C-467 are two other resins that are commonly used in research for antimony and bismuth extraction, though UR-3300 was also employed in the Tamano refinery [36]. MX-2 has high selectivity for antimony, UR-3300 seems to adsorb both antimony and bismuth very well, and C-467 adsorbs arsenic as well as the other two impurities [7]. All of these resins (UR-3300, C-467, and MX-2) use functional groups that are within the aminophosphonic acid group, e.g. UR-3300 uses imino-bis(methylene-phosphonic acid) [36]. It is understandable, then, that several studies have been dedicated to comparing the efficiencies, capacities, selectivity, etc. of these resins, some of which will be summarized below.

Tadao Nagai compared the MX-2 and UR-3300 resins. He showed that for both resins, Bi tended to be replaced by ferric and antimony ions, indicating the resins are more selective for both antimony and ferric over bismuth. The study revealed the adsorption capacity of UR-3300 was about half that of the MX-2 resin. This is probably due to the fact that the matrixes of the resins are different; the UR-3300 has a phenolic support matrix, while the MX-2 uses di-vinyl benzene which has 2 times as many functional sites. MX-2, however, had a slower rate of elution, and a much harder time eluting ferric [35].

Ando and Tsuchida compared the capacities of C-467 and MX-2 [10]. C-467 appears to have slightly higher capacity for antimony and bismuth, while neither adsorbed a large amount of iron. It is possible the iron was in the ferrous state in this experiment.

A comprehensive study of MX-2, C-467, and a modified version of UR-3300 resin, called UR-3300S, by Cifuentes et al. [37] determined that for antimony extraction, the order of performance (worst to best) was MX-2, C-467, then UR-3300S. MX-2 seemed to have faster kinetics, but as more BVs of electrolyte were passed through the columns, the concentration of antimony in the effluent remained consistently low for only UR-3300S. This is due to the UR-3300S resin having less resistance to matter transfer and higher antimony capacity [37].

Finally, in a study by Gabai et al. [26], the kinetics of UR-3300S and MX-2 were shown to be almost the same. However, this test was performed using finite bath analysis opposed to column testing, which could explain the difference between their findings and those of Cifuentes et al. [3].

The stripping solution used for MX-2, UR-3300, and C-467 is generally an HCl acid solution around 6-9 M. This process may be improved by the addition of a chloride salt. Described by Ando and Tsuchida [10], this process selectively strips antimony and bismuth using a solution of HCl and chloride salts. It was found that the stripping of bismuth relies almost entirely on the chloride concentration in the eluant, while the antimony stripping relies on the acid concentration. This is used to devise a two-phase stripping procedure using a solution of sulfuric acid and sodium chloride where bismuth is removed in the first step with a low sulfuric acid solution and then antimony is removed by increasing the concentration of sulfuric acid [10].

Another elution process using a solution of chloride salts and hydrochloric acid was also examined [38]. This process will strip both the antimony and bismuth simultaneously and can be neutralized with NaOH to precipitate the antimony and bismuth as salts. This cake of antimony and bismuth salts can be sold, and the barren eluate can be reused by simply adding back the acid.

A common problem with chelating resins is poisoning by ferric ion. A way to prevent this is to run the solution through a bed of copper chips or past a copper wire before it enters the IX column. This will reduce the ferric to ferrous, keeping it from adsorbing onto the resin, and also reduce pentavalent antimony to its trivalent state [11].

Pre-reduction can also reduce adsorbed Sb(V) to Sb(III) and improve elution. Sluggish elution can lead to impartial stripping of the resin and decreased adsorption efficiencies over time. This problem can potentially be alleviated by the addition of thiourea to a 5-7 M HCl eluate [39].

Additionally, hydrochloric acid is sometimes needed to elute the resin, which requires precautions be taken to ensure the eluant does not enter the electrolyte stream. Using the previously suggested H_2SO_4-NaCl solution may solve this problem [40].

Another potential problem is solids precipitation during the regeneration of the resin. Precipitation can cause a sharp decrease in the capacity of the resin due to bad diffusion during adsorption. Precipitates can be removed by using sulfuric acid instead of hot water during the washing step after loading, as will monitoring the concentration of the elution acid in order to keep it constant at around 15-20% HCl [27].

6.4 OTHER ADSORBENTS

Other adsorbents have been investigated to remove Sb and/or Bi. These include zeolites [26,41], phyllosilicate clay [42], in-situ formed barium, strontium or lead sulfates [43,44], stannic acid [36] and a synthesized adsorbent called ICAA-PPG [45].

7. SUMMARY

Clearly, all of the processes reviewed have been shown to extract antimony and bismuth impurities from copper electrolytes. The advantages and disadvantages of each removal process is summarized in Table 2. The use of multiple processes have been shown to be able to remove significant quantities of antimony and bismuth [5].

Table 1. Comparison of impurity removal processes most often studied or used in industry.

	Advantages	Disadvantages
Liberators	● High removal rates of bismuth and arsenic ● Can produce saleable copper in initial stages	● Copper concentration must be greatly reduced. ● High energy consumption ● Off-spec copper returned to smelter ● Potential generation of hazardous gas
Bleeding	● Easy and inexpensive for refinery	● Location dependent ● Transfers impurities to another location ● Requires separate copper recovery step
Electrolyte Doping/Anode Composition	● Low energy input ● Minimal equipment at refinery	● Can lead to entrainment of impurities in cathode ● Impurities report to slimes ● Arsenic addition at the smelter
Solvent Extraction	● Low energy input ● Potential to produce salable product	● Potential problems with organic ● May contaminate electrolyte with strip or regeneration chemicals
Activated Carbon	● Removes Bi, As, and Sb ● Can be used as a reducing agent	● Low kinetics and loading capacity ● Very low Bi and As adsorption ● Carbon cannot be re-used
Molecular Recognition Technology	● Highly selective for Bi ● Salable product produced	● Only used for Bi extraction ● Expensive resin
Ion Exchange	● Recovers Sb and Bi with high efficiency ● Can produce saleable product ● Most widely used process in industry	● Product is typically not saleable ● Resin can be “poisoned” and lose efficiency ● Often requires use of HCl for elution

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II. REMOVAL OF ANTIMONY AND BISMUTH FROM COPPER ELECTROREFINING ELECTROLYTE: PART II – AN INVESTIGATION OF TWO PROPRIETARY SOLVENT EXTRACTION EXTRACTANTS

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Reprinted by permission from RightsLink: Springer, JOM, Removal of Antimony and Bismuth from Copper Electrorefining Electrolyte Part II – An Investigation of Two Proprietary Solvent Extraction Extractants, Andrew Artzer, Michael Moats, and Jack Bender, 2018

ABSTRACT

Antimony and bismuth recovery from copper electrorefining electrolyte could reduce the impacts of these problem elements and produce a new primary source for these elements. Two proprietary phosphonic acid ester extractants were examined (REX-1 and REX-2) for the removal of antimony and bismuth from copper electrorefining electrolytes. Experimentation included shakeout and break tests to determine the basic parameters for the extractants in terms of maximum loading, break times, and extraction and stripping efficiency. Five permutations of extractant mixtures (100 wt.-% REX-1, and 25, 50, 75 and 100 wt.-% REX-2) were studied. It was found that REX-2 was able to extract Sb and Bi from the electrolyte, but required some mixture with REX-1 to better facilitate stripping with 400 g/L sulfuric acid. Phase break times revealed that glue in the electrorefining electrolyte caused a statistically significant decrease in the disengagement times.

1. INTRODUCTION

As discussed in our review, antimony and bismuth in copper electrorefining electrolyte can cause problems [1]. The traditional method for removing antimony and bismuth involves putting a bleed-stream of electrolyte through liberator cells (or electrowinning cells). Liberators can remove most of the antimony and bismuth by electrodeposition; however, this process has several drawbacks. The copper electrodeposits produced during antimony and bismuth removal will contain arsenic, making the material hazardous. The deposits are recycled back to a smelter with the majority of the group 15 elements eventually returning to the refinery in future anodes. Liberators are costly to operate due to labor requirements and high electrical energy consumption, and can produce hazardous gases [2, 3, 4].

Because of these drawbacks, many refineries have examined alternative ways to remove antimony and bismuth from electrolyte. Solvent extraction (SX) [1, 5, 6], molecular recognition technology [7, 8], carbon adsorption [9, 10], and ion exchange (IX) [11, 12] have been the most researched processes. IX columns have been installed at several copper electrorefineries. IX is typically preferred over SX when the ion concentration to be removed is less than 0.5 g/L in the aqueous phase (as is the case for Sb and Bi in commercial electrolytes) [11, 13]. Refineries, however, use HCl to elute antimony and bismuth from the resins [11, 13], which can potentially cause electrolyte upsets if the high chloride content solutions enter the electrorefining solutions. Furthermore, most refineries do not recover Sb and Bi as a salable product. Therefore, a method that removes Sb and Bi from electrolyte, uses a sulfuric acid stripping agent and produces a salable product could be useful to copper electrorefineries.

BASF has recently developed a set of SX extractants designed for antimony and bismuth in electrolytes that can be stripped using sulfuric acid without regeneration [1]. The proprietary reagents (REX-1 and REX-2) are phosphonic acid esters that extract by forming ionic complexes with the ions of interest. Phosphonic acid is characterized by a phosphorus atom with one organic bond, two hydroxides, and one double-bonded oxygen (Figure 1). The phosphonic acid functional group was described by Sevrain et al. [14]. Phosphonic acid ester extractants have previously been examined in the removal of Co, Ni, and Mn from sulfate solutions [15, 16]. If these reagents could be used to recover bismuth and antimony as salable products, they could assist in improving the sustainability of the bismuth and antimony supply chains.

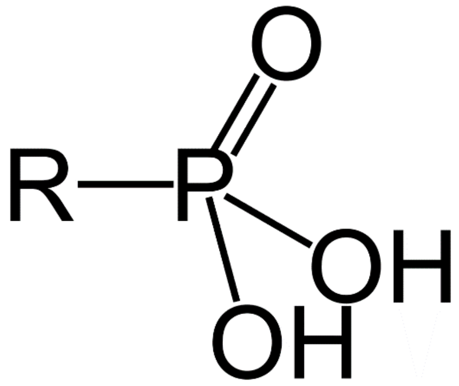

Figure 1. The structure of a phosphonic acid functional group.

2. PROCEDURE

2.1 ORGANIC SOLUTION

Two phosphonic acid ester extractants (REX-1 and REX-2) were provided by BASF Mining Chemicals. Five mixtures of the extractants were examined (100 wt.-% REX-1 and 25, 50, 75, and 100 wt.-% REX-2). Organic solutions used for solvent extraction experiments were created by mixing 100 g/L of the extractant mixture into Orfom SX-12 diluent (A Chevron Phillips product).

2.2 AQUEOUS SOLUTION

The aqueous solutions used in most of the solvent extraction experiments were electrolyte samples collected from a lab-scale copper electrorefining cell. The cell was operated in a manner similar to a stripper cell (a.k.a. produced starter sheets) in an industrial operation, including the addition of glue. The anodes were commercial copper anode samples from a North American refinery. Details about the lab-scale electrorefining cell and its operation were presented by Laforest [17]. Electrolyte samples from a laboratory electrorefining cell were used to more accurately reflect the performance of the extractants in an electrorefining plant. For convenience, these electrolyte samples, used within an hour of collection, will be referred to as “live” electrolyte for the remainder of this manuscript. Each individual “live” sample is denoted with the day of operation that it was collected on. The day number refers to the number of days after a new set of commercial anode samples were inserted into the laboratory cell. Electrolyte samples used after being stored about a month at room temperature will be referred to as “aged” electrolyte. The storage of electrolyte can fundamentally change the electrolyte (decomposition of glue, precipitation of copper or other species), so its use is noted for clarity.

Finally, synthetic electrolytes made from reagent grade chemicals were used for selected experiments. Extraction isotherms were created using synthetic electrolytes containing only sulfuric acid, copper and antimony or bismuth. To examine the effect of organics on phase disengagement time, an electrolyte (synthetic – break) was created of similar composition to the “live” electrolyte tested.

Compositions of each electrolyte used in this study are listed in Table 1. The original source chemicals were potassium antimony tartrate trihydrate for antimony, BiCl3 for bismuth, CuSO4·5H2O for copper, and As2O3 for arsenic. A commercial glue provided by a North American refinery was added to the lab-scale refinery cell at a rate of 2.16 mg glue per liter of electrolyte per day. In these tests, Avitone A was added to the refinery cell, but thiourea was not.

Table 1. Composition of the electrolytes used in the following experiments.

Electrolyte	Copper (g/L)	Antimony (g/L)	Bismuth (g/L)	Arsenic (g/L)	Acid (g/L)	Glue (mg/L/day)
Aged	51.0	0.098	0.009	5.35	147	2.16
Live (day 4)	40.8	0.193	0.078	7.89	158.4	2.16
Live (day 14)	45.6	0.179	0.119	7.88	140.7	2.16
Live (day 24)	40.3	0.157	0.159	7.27	160.5	2.16
Live (day 25)	40.2	0.17	0.16	7.44	160	2.16
Synthetic (Bi)	43.9	0	0.049	0	170	0
Synthetic (Sb)	42.3	0.178	0	0	170	0
Synthetic (break)	37.7	0.122	0.228	5.38	160	0

2.3 SHAKEOUT TESTS

Shakeout tests were performed to examine extraction and stripping efficiency. A Barrell model 75 wrist action shaker with amplitude set to 7.5 was used. 15 mL of organic and 15 mL of electrolyte were placed in 30 mL separatory funnels attached to the shaker. The funnels were rotated so they were parallel to the ground to ensure no unmixed organic or aqueous material remained at the tips of the funnels. The two phases were shaken for 30 minutes to reach equilibrium. After visual confirmation of phase disengagement, the raffinate was drained from the separatory funnel and passed through a Whattman 4 filter paper to remove organic entrainment. Organic material collected on the filter paper was returned to the funnel.

Following the extraction test, 15 mL of 400 g/L sulfuric acid was added to each separatory funnel containing loaded organic. The funnel was again shaken for 30 minutes. The aqueous strip product solution was collected in the same way as the raffinate in the previous step.

Shakeout tests were conducted with various electrolyte samples (“aged” or “live”) and one of the five organic solutions. All the electrolyte samples were allowed to cool to room temperature before shaking in order to guarantee consistent temperature between tests. Fresh organic solution was used in each test.

The collected samples of raffinate and strip product were diluted with deionized (DI) water and analyzed using an iCE3300 FL atomic absorbance (AA) system. The specific dilutions were 10000:1 for copper, 16:1 for antimony and bismuth, and 150:1 for arsenic. Due to manual dilutions, the AA measurements were found to return measurements with 1-4% error for synthetic solutions of known concentration. This error occasionally resulted in calculated raffinate concentrations being slightly (no greater than 4%) greater than those of the original electrolyte. Since fresh organic solutions were used in all experiments, it was assumed that the raffinate concentrations in these cases were equal to the original electrolyte. Otherwise, the concentrations reported are the average value for two experiments.

2.4 ISOTHERMS

Extraction isotherms for bismuth and antimony were created using the shake out procedure. Isotherms were only made for 100 wt% REX-1, 100 wt% REX-2, and the 50/50 blend. The extractants were dissolved in Orfom SX-12 at concentrations of 100 g/L. All the extractants were tested with 1:2, 1:1, 2:1, 4:1, 7:1, 10:1, and 20:1 A/O ratios. However, due to the higher loading capacity of REX-2 and the 50/50 blend, they were also tested at 40:1, 60:1, 80:1, and 100:1.

The aqueous solutions used were two simplified synthetic electrolytes that were made to resemble electrorefining electrolyte in terms of copper and acid concentrations but simplified in order to isolate antimony or bismuth extraction. One synthetic electrolyte contained H_2SO_4, copper, and antimony, while the other had H_2SO_4, copper, and bismuth. These electrolytes are named “synthetic (Sb)” and “synthetic (Bi)”, respectively, and their compositions are listed in Table 1.

2.5 PHASE BREAK TESTS

Phase break experiments were conducted due to previous literature indicating that glue can cause phase separation issues [18, 19]. Glue is added during electrorefining as a cathode leveling agent and was present in the “live” electrolytes. Therefore, break times were compared between “live” electrolyte and a synthetic electrolyte which did not contain glue. Both extraction and stripping break tests were performed, so the aqueous material consisted of an electrolyte (Table 1) or a 400 g/L H_2SO_4 stripping solution (for extraction and stripping, respectively). Disengagement times were determined for organic solutions with only REX-1 or REX-2. Emulsion phase continuity was also examined.

These experiments were conducted in a 1000 mL glass beaker with stainless steel baffles. 200 mL of aqueous and 200 mL of organic were mixed together using a Cole-Parmer Ultra-compact Digital Mixer (model # 50006-01) with a 1.25 in. diameter plastic impeller at 1750 rpm. The emulsion was mixed for 30 seconds after the mixer reached full speed. The impeller was removed after it had completely stopped. Disengagement time was measured from when the mixer was turned off until a clear visual boundary had formed between the two phases. The reported values are the average of two experiments.

3. RESULTS AND DISCUSSION

3.1 EXTRACTION AND STRIPPING EFFICIENCIES

Extraction efficiencies for Bi, Sb, Cu and As using fresh organic and an A/O ratio of 1:1 are shown in Figure 2. These data indicate that increasing the percentage of REX-2 in the extractant mixture increased the percentage of antimony and bismuth extracted. The 100 wt% REX-2 extractant removed 85-95% of the antimony and 60-70% of the bismuth in the “live” electrolyte samples. Thus, REX-2 appears to be a better extractant than REX-1 for antimony and bismuth. No synergistic effect was observed between REX-1 and REX-

2 on extraction efficiency. While extraction of Cu and As were small in terms of percentages (generally less than 10%), the starting concentrations of these elements are one or two orders of magnitude higher than Sb and Bi. Therefore, their extraction is not insignificant. As the aged electrolyte produced similar results as the "live" electrolyte, it appears that electrolyte can be stored and treated as needed.

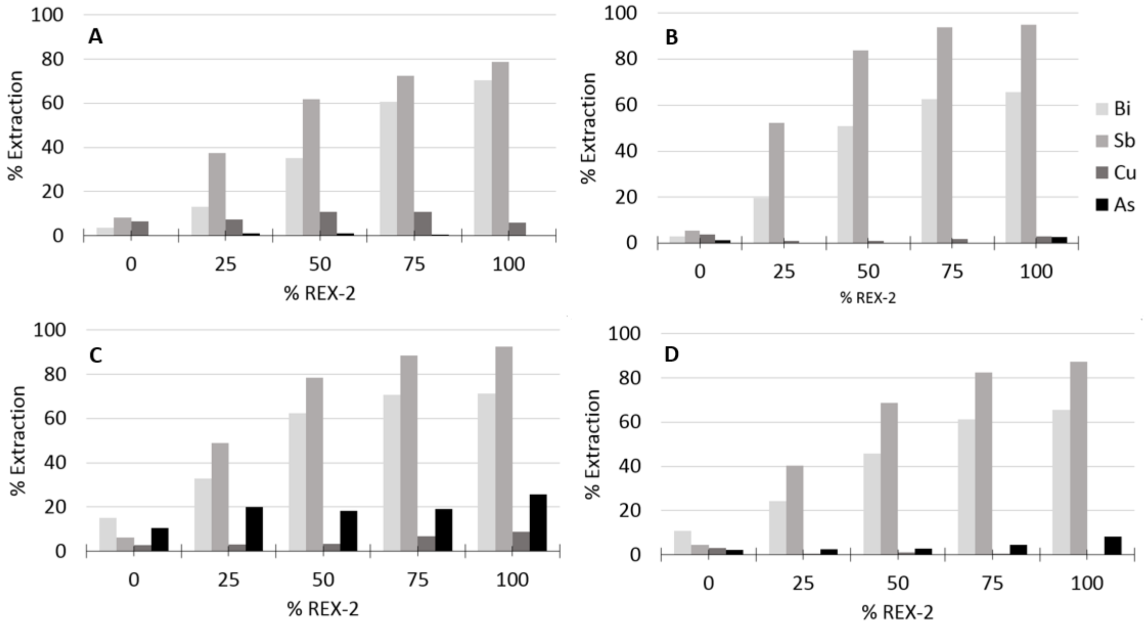

Figure 2. Extraction efficiency for REX-1 and REX-2 mixtures. Tested in (a) aged electrolyte, (b) live day 4 electrolyte, (c) live day 14 electrolyte, (d) live day 24 electrolyte. See Table 1 for electrolyte compositions. A:O ratio = 1:1 for all experiments.

Stripping efficiencies for the loaded organics produced in the extraction efficiency experiments are shown in Figure 3a-d. The stripping data in terms of percentages are more variable than the extraction data because of the smaller concentrations involved and the accuracy of the analysis method used (manual dilution + AA). Even so, a synergistic effect of REX-1 on the ability to strip Sb from REX-2 is indicated. The presence of REX-1 allowed for a higher percentage of the loaded Sb to be stripped with 400 g/L sulfuric acid. Bi stripping was also improved by the addition of REX-1 to REX-2. The stripping efficiencies indicate that some Sb and Bi remain on the extractant after stripping. The stripping efficiencies for Cu and As were extremely variable. This variation cannot be explained at this time, but may be related to the large dilution factors used prior to analysis.

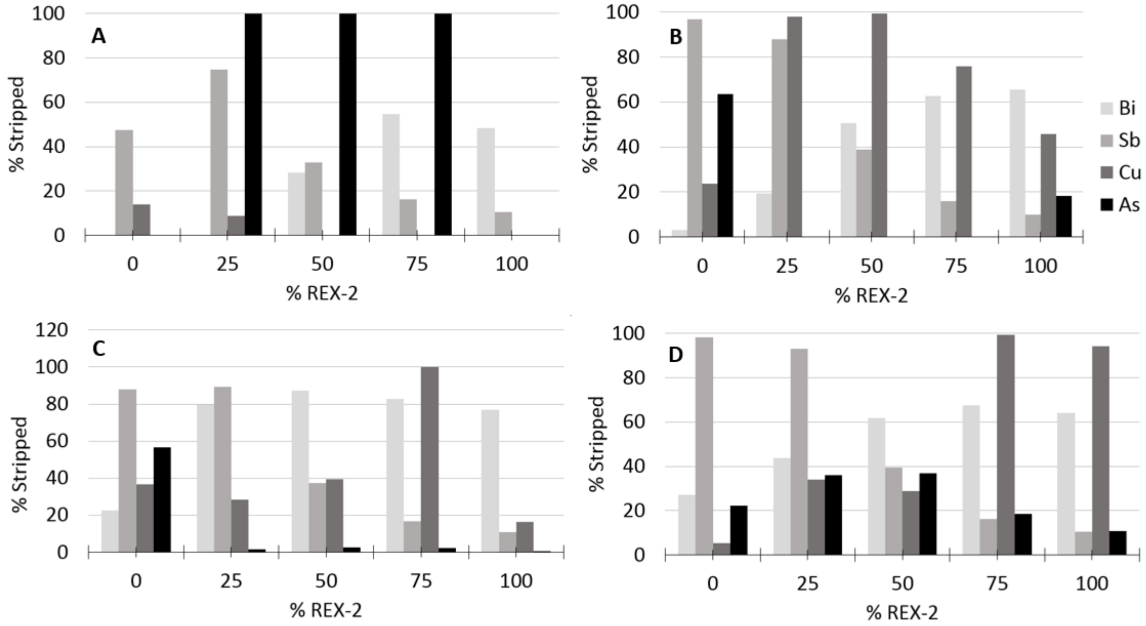

Figure 3. Stripping efficiency of the tested solvents. Tested in (a) aged electrolyte, (b) live day 4 electrolyte, (c) live day 14 electrolyte, (d) live day 24 electrolyte. (d) was performed for 24 hours. See Table 1 for electrolyte compositions. A:O ratio = 1:1 for all experiments.

Combining the extraction and stripping data, the overall removal efficiency for each shake out test was calculated (Figure 4a-d). For antimony, the higher percentage REX-2 solutions exhibited superior extraction efficiency, but poor stripping efficiencies. Thus, the antimony removal efficiencies for 75 wt% and 100 wt% REX-2 solutions were less than 15%. The 25 wt% REX-2 solution demonstrated the highest Sb removal efficiency because of its better stripping efficiency. Thus, a mixture of REX-1 and REX-2 provides synergistic behavior by REX-1 improving strippability and REX-2 increasing extraction.

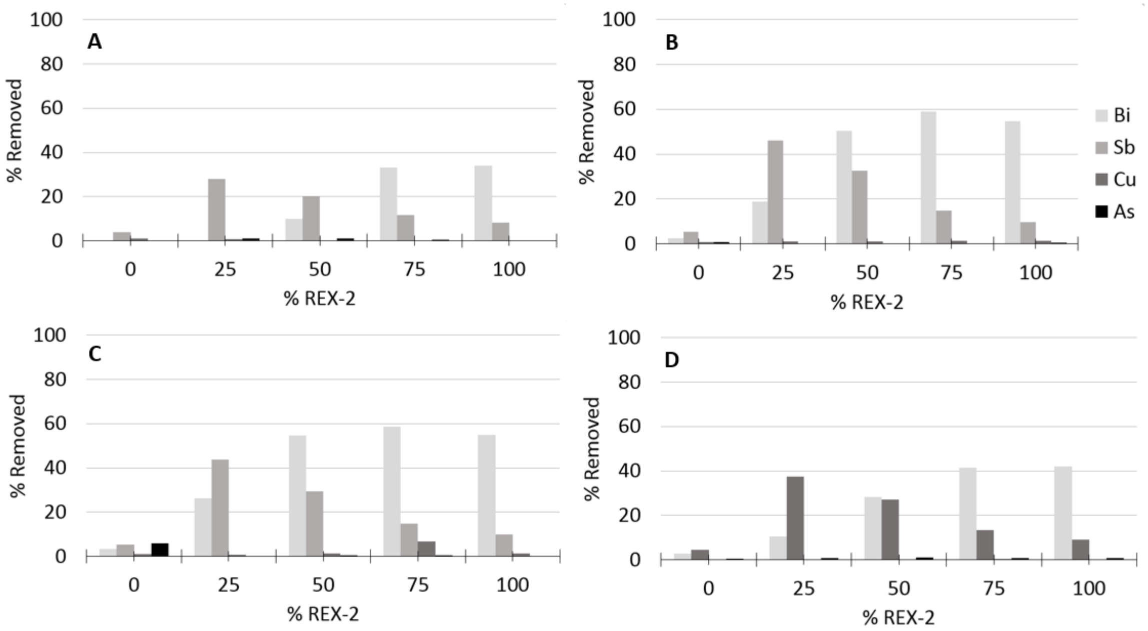

Figure 4. Removal percentages of the tested solvents. Tested in (a) aged electrolyte, (b) live day 4 electrolyte, (c) live day 14 electrolyte, (d) live day 24 electrolyte. See Table 1 for electrolyte compositions.

The removal efficiency for bismuth presents a different scenario. Bismuth removal is maximized at high wt% REX-2 solutions. The addition of small amounts of REX-1 may improve removal efficiency, but high concentrations of REX-1 appear to be detrimental to bismuth removal.

The ability to tailor the performance of the mixed extractant system to preferentially remove more Sb or Bi could be utilized by copper refineries. For example, a 25/75 REX-1/REX-2 mixture could be preferred by a refinery with high Sb, low Bi anodes. On the other hand, a 75/25 REX-1/REX-2 mixture might be favored for anodes with high Bi and low Sb.

Typically, high removal efficiencies are desired for solvent extraction systems. With the current extractant system, high removal rates are unnecessary. The purpose of the proposed system is to remove impurities from electrolyte. Thus, small removal efficiencies can be designed into a potentially effective bleed treatment system.

The removal efficiencies for copper and arsenic were low with all values less than 10%. This is a highly encouraging result as it indicates the potential to produce a strip product with low concentrations of copper and arsenic. Obviously more testing is needed and a mini-lab-scale-pilot plant test is planned for the near future.

3.2 ISOTHERMS

To understand further the loading capabilities of these extractants, extraction isotherms for Sb and Bi on 100 wt% REX-1, 50 wt% REX-2 and 100 wt% REX-2 were generated using synthetic electrolytes and different A/O ratios. The extraction isotherms for Bi are presented in Figure 5. As expected from the shake-out experiments, REX-1 alone does not extract bismuth to any appreciable extent. REX-2 alone demonstrated the ability to extract Bi. A maximum loading of 0.25 g Bi/L for 100 g REX-2 per liter in the organic phase was maybe reached at an A/O ratio of 100:1 (0.05 g/L Bi in the feed aqueous phase). The 50 wt% REX-2 achieved a maximum loading around 0.2 g Bi/L, showing that addition of REX-1 decreases Bi extraction.

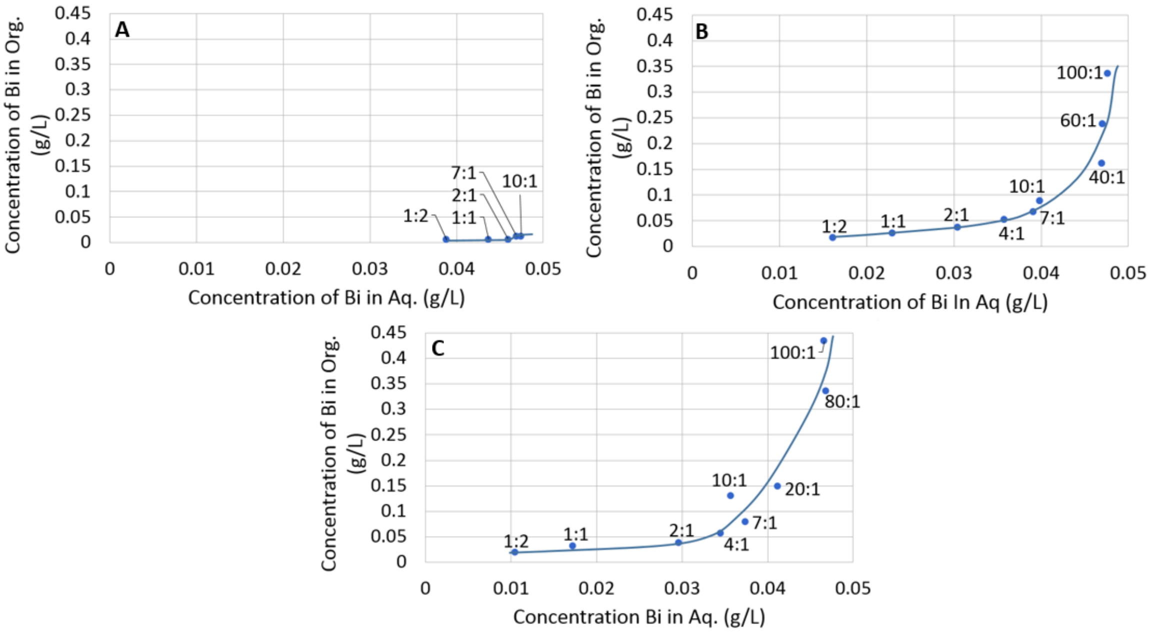

Figure 5. Extraction isotherms for antimony in (a) REX-1, (b) 50 wt.-% REX-2, and (c) REX-2. Performed with Synthetic (Sb) electrolyte. See Table 1 for electrolyte compositions.

The antimony extraction isotherms also revealed that REX-1 did not extract Sb significantly. Sb maximum loading for 50 wt% and 100 wt% REX-2 mixtures (Figure 6b-c) was substantially higher than those seen for Bi. The 100 g/L 100 wt% REX-2 solution appears to have a maximum loading near 7.1 g-Sb/L-organic. The 50 wt% REX-2 solution exhibited a maximum concentration of 1.6 g-Sb/L-organic.

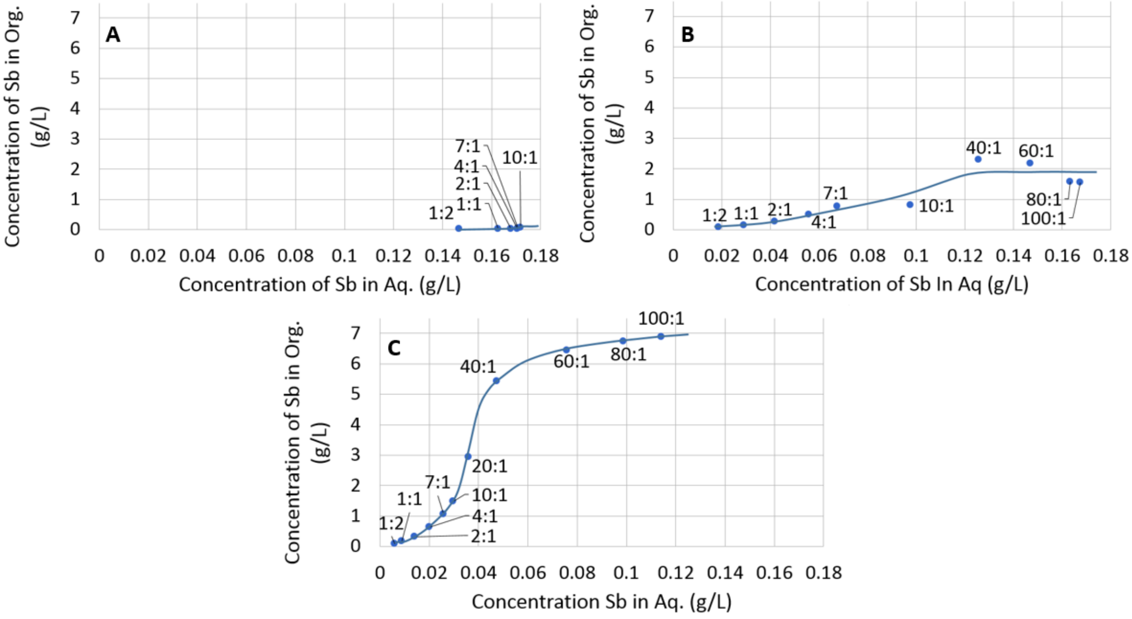

Figure 6. Extraction isotherms for bismuth in (a) REX-1, (b) 50 wt% REX-2, and (c) REX-2 Performed with Synthetic (Bi) electrolyte. See Table 1 for electrolyte compositions.

3.3 PHASE BREAK TIME

The final part of this investigation was to examine phase disengagement times. Based on previous literature [18,19], the effect of glue in electrolyte on solvent extraction was concerning. The results of the aqueous and organic continuous phase break tests are shown in Table 2. The results were analyzed by examining the differences in mean for each parameter in the factorial design and examining the p-values for the main parameters

(Table 3). Phase continuity (organic or aqueous), stage (extraction or stripping), and electrolyte type ("live" or synthetic) all affected the mean time for phase disengagement based on p-values <0.05 as shown in Table 3. The stripping step (using 400 g/L H2SO4) had a longer break time than extraction (with 180 g/L H_2SO_4) which was likely caused by the increasing in the viscosity of the aqueous phase. Organic continuity produced longer separation times than aqueous continuity. Finally, synthetic electrolyte (without glue) had longer disengagement times than "live" electrolyte (with glue).

Table 2. Average break times for aqueous and organic continuous phases. Performed with live (day 25) electrolyte (Table 1).

	Aqueous Continuous		Organic Continuous	
Extractant Percentage	"Live" Electrolyte (s)	Synthetic Electrolyte (s)	"Live" Electrolyte (s)	Synthetic Electrolyte (s)
100% REX-1 - Extract	59	69	71	94
100% REX-1 - Strip	123	113	164	236
100% REX-2 - Extract	53	50	104	221
100% REX-2 - Strip	66	77	87	199

While the presence of glue in the “live” electrolyte did have a statistical effect, the effect was the opposite of what was expected based on previous reports [18,19]. Glue was not the only organic in the solution at the time of testing (Avitone A and tartrate were also present in the “live” and synthetic electrolytes, respectively), which could be a reason for the discrepancy. Additionally, chemicals were not purified before testing and organic impurities could have also been present in the synthetic solutions. There is a plan for further testing of these extractants in a lab-scale extraction circuit. Break times and crud formation will continue to be monitored in order to verify these results.

Interactions between parameters were examined. From a statistical standpoint, two interactions (1 - phase continuity and electrolyte type; 2 – Stage and REX) were found to be as significant as electrolyte type. The authors are not sure if they believe these interactions are real or are an artifact of the testing and data analysis.

Table 3. The structure and results for the fractional factorial statistical analysis performed on the phase break data.

Factor	A	B	C	D
Parameter	Continuity	Electrolyte	Stage	REX
Low Value	Aqueous	“Live”	Strip	1
High Value	Organic	Synthetic	Extract	2
$\bar{y}$ (low)	80.7	96.7	149	119
$\bar{y}$ (high)	148	131	89.9	109
$\lvert\Delta\rvert$	67.1	34.3	59.1	10
p	<0.001	0.009	0.003	0.416

4. CONCLUSIONS

This investigation of two proprietary phosphonic acid ester extractants for the recovery of antimony and bismuth from copper electrorefining electrolyte revealed:

1. Extraction of Sb and Bi increased with increasing weight percent of REX-2 in the organic solution. REX-1 exhibited only a small ability to extract Sb and Bi by itself.
2. Stripping of Sb and Bi from REX-2 was assisted by the addition of REX-1.
3. The highest removal efficiencies were achieved with mixtures of REX-1 and REX-2. Higher REX-2 content mixtures exhibited the highest removal efficiencies for bismuth. Lower REX-2 content mixtures demonstrated larger removals of antimony.
4. Phase disengagement times were influenced by phase continuity, electrolyte used ("live" vs. synthetic) and the stage (extraction vs. stripping). The effect of glue in the live electrolyte was statistically significant, but showed a reduced phase separation time, which was not expected. All of the phase disengagement data indicate that phase separation will occur in a standard commercial SX settler.

While these extractants are fully capable of removing Sb and Bi from copper electrorefining electrolytes, they also extract small percentages of Cu and As. Though the percentages are small, the concentrations of Cu and As in the electrolyte are much higher than Bi and Sb. If Sb and Bi are wanted as a saleable product, additional purification steps or possibly organic scrubbing will be needed to separate Sb and Bi from Cu and As. If not, all the elements could be precipitated together and returned to the smelter. While returning the materials to the smelter would eliminate the possibility of Bi and Sb recovery, removal of Bi and Sb from the refinery without the use of liberator cells or IX with HCl elution would be advantageous.

Additional batch tests and a lab-scale solvent extraction circuit will be operated to understand better the removal and recovery of antimony and bismuth from copper electrorefining electrolyte. Special attention will be paid to the deportment of copper and arsenic, phase disengagement and the formation of any crud or stable emulsions.

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III.LABORATORY SCALE EXTRACTION OF BISMUTH AND ANTIMONY FROM A COPPER ELECTROREFINING ELECTROLYTE USING A PROPRIETARY PHOSPHONIC ACID ESTER EXTRACTANT

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ABSTRACT

Antimony and bismuth in copper electrorefining electrolytes can cause cathode contamination, leading to the careful control of their concentrations. This study examined the laboratory scale removal of bismuth and antimony from an electrorefining electrolyte using a solvent extraction mini-pilot plant. The ability of a proprietary phosphonic acid ester extractant (REX-2) in a commercial diluent was studied in a simulated commercial setting. Antimony and bismuth were both extracted effectively from the electrolyte (72% Bi and 70% Sb removed) and Bi was effectively stripped (92% Bi recovered) with 400 g/L sulfuric acid. A final strip solution was obtained from the SX circuit containing 0.36 g/L Bi, 0.043 g/L Sb, 1.3 g/L Cu, and 0.18 g/L As. Unfortunately, most of the extracted Sb remained in the organic phase. Following the pilot study, experiments were performed to examine the precipitation of bismuth from the aqueous strip phase and the removal of antimony loaded on to REX-2.

Keywords: Antimony, Bismuth, Copper, Electrorefining, Impurity removal, Solution purification, Solvent extraction

1. INTRODUCTION

For many years, antimony and bismuth have been some of the most problematic impurities in copper electrorefining (ER) (Bardwell & Lapee, 1933). Along with surface roughening, high concentrations of Sb and Bi can contaminate the copper cathode and precipitate at the copper grain boundaries. This drastically reduces the drawing ability of the metal (Bender & Emmerich, 2016). For these reasons, it is necessary to control Sb and Bi concentration in the cathode, which is done by controlling their concentration in the electrolyte.

Conventionally, Sb and Bi concentrations are controlled by maintaining a proper As/(Sb+Bi) molar ratio in the anode and arsenic concentration in the electrolyte. Antimony and bismuth are removed during electrolyte purification using liberators (electrowinning cells) and/or ion exchange.

Liberators treat an electrolyte bleed stream from the ER circuit and electrodeposit increasingly impure copper as the copper concentration of the solution decreases. Traditionally, first stage liberators reduce the copper concentration from ~45 g/L to ~15 g/L and produce saleable copper. Second stage liberators decrease the copper concentration to ~8 g/L (Biswas & Davenport, 1980) which results in contaminated cathode that is returned to anode production (Biswas & Davenport, 1980; Wang, 2004). Further electrolyte purification is not always required but third stage liberators can be used to reduce copper concentration below 2 g/L which results in significant removal of As, Sb and Bi and very impure deposits which are recycled to a smelter or used for As production. However, liberators do not have very high energy efficiency (Acharya, 2014; Ando & Tsuchida, 1997) and below 0.5 g/L copper, highly toxic arsine gas may form (Biswas & Davenport, 1980).

Ion exchange (IX) and molecular recognition technology (MRT) are also used for Sb and/or Bi removal. IX uses organic resin beads to remove impurities from an electrolyte bleed. MRT is a specialized form of IX that has been used specifically for Bi extraction. Using an engineered resin with crown ether functional groups, a high selectivity for Bi is achieved. Both these processes are capable of very high removal efficiencies. While IX and MRT systems have been installed commercially for Sb and Bi removal in Japan, Europe and the Americas, HCl is required for elution and the eluate contains Sb and Bi which makes recovery difficult. MRT uses a sulfuric acid eluant but is costly and unsuitable for Sb extraction due to irreversible resin poisoning.

In an attempt to solve the problems associated with liberators and IX columns, BASF has synthesized two solvent extraction (SX) reagents that can remove Sb and Bi from Cu ER electrolyte and be stripped with sulfuric acid. The two reagents, dubbed REX-1 and REX-2, are proprietary phosphonic acid esters that extract Sb and Bi by forming ionic complexes. The phosphonic acid functional group has been detailed by Sevrain, Berchel, Couthon, and Jaffrès (2017) and is characterized by a single phosphorous atom bonded to two hydroxides, with one double-bonded oxygen and one organic bond (Figure 1). Phosphonic acid ester extractants have been documented to be effective at removing Co, Ni, and Mn from sulfate solutions (Preston, 1982; Tsakiridis & Agatzini-Leonardou, 2005), and an article by the current authors demonstrated REX-1 and REX-2 to be effective at removing Sb and Bi from Cu ER electrolyte in batch tests (Artzer, Moats, & Bender, 2018). The purpose of this paper is to discuss the efficacy of REX-2 in a lab-scale pilot SX circuit working in conjunction with a lab-scale Cu ER cell.

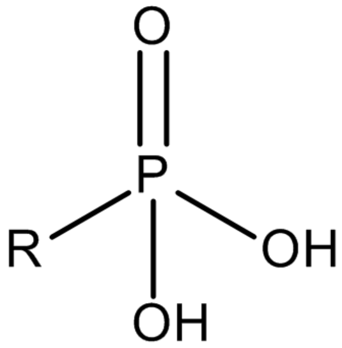


Figure 1. Atomic structure of the phosphonic acid functional group.

2. PROCEDURE

2.1 ORGANIC SOLUTION

The solvent extraction organic that was used for this experiment was made by mixing 100 g/L of REX-2 (BASF) into Orfom SX-12 diluent (Chevron Phillips). The organic used in the SX circuit was preloaded by mixing with the same electrolyte and strip solution that was to be used in the experiment. REX-1 (BASF) was not used in this research to determine if REX-2 could be used to produce a concentrated bismuth stream with minimal antimony contamination. However, BASF recommends that the two extractants always be used in a mixture. A similar test involving a combination of REX-1 and REX-2 is presently planned.

2.2 AQUEOUS SOLUTION

The electrolyte for this experiment was generated by running a laboratory Cu ER cell for 3 months prior to the start of this experiment. The anode composition used in the ER cell is shown in Table 1. The general operation of the cell is detailed in LaForrest (2015). A synthetic electrolyte with similar concentrations of Sb, Bi, As, and Cu was then added to the original electrolyte to increase volume when the SX circuit was connected. The total volume of electrolyte used was 24 L; five of which were synthetic electrolyte. These electrolytes mixed for 24 hours before the pilot plant began operating. The starting and ending compositions of the ER electrolyte are given in Table 2.

Table 1. Composition of anode used in ER cell.

Element	Bi	Ag	As	Fe	Ni	Pb	Sb	Te	O	Cu
Composition (ppm)	635	408	1939	13	301	4076	24	161	1332	Remainder

All solutions in this experiment were originally created using reagent-grade chemicals; potassium antimony tartrate trihydrate for antimony, $BiCl_3$ for bismuth, $CuSO_4 \cdot 5H_2O$ for copper, and As_2O_3 for arsenic. In addition, while running the ER cell, a commercial glue and thiourea were added at a rate of 2.12 mg per liter of electrolyte per day. Avitone A was also added to the ER cell at a rate of 0.237 mg per liter of electrolyte per day. Acid was added to the synthetic electrolyte and stripping solution as 99.8% H_2SO_4.

Table 2. Concentrations of various electrolytes used in this experiment.

Electrolyte	Cu (g/L)	Bi (g/L)	Sb (g/L)	As (g/L)	Acid (g/L)
Starting	46	0.045	0.056	5.4	130
Ending	45	0.013	0.017	5.6	120
Preg	1.4	0.35	0.043	0.17	400

2.3 CIRCUIT OPERATION

Operation details for the ER cell (Figure 2a) are given in LaForrest (2015) and simulate starter sheet production at a commercial refinery. The solvent extraction circuit (Figure 2b) consisted of three mixer settler stages - two extraction and one stripping. The two extraction stages were connected in series so that the fresh electrolyte flows into the first stage, then from the first stage to the second stage, and from the second stage back to the ER cell. The freshly stripped organic moves from the stripping stage to the second stage of extraction, then from the second stage to the first stage, and from the first stage back to stripping. The stripping solution was pumped from a storage drum into the stripping stage and back into the drum, constantly recycling it through the stage to produce a concentrated solution of Bi and Sb ions. Each mixer and settler was a jacketed glass reactor for temperature control. Each mixer had a volume of 0.4 L; while the settlers had volumes of 1.7 L.

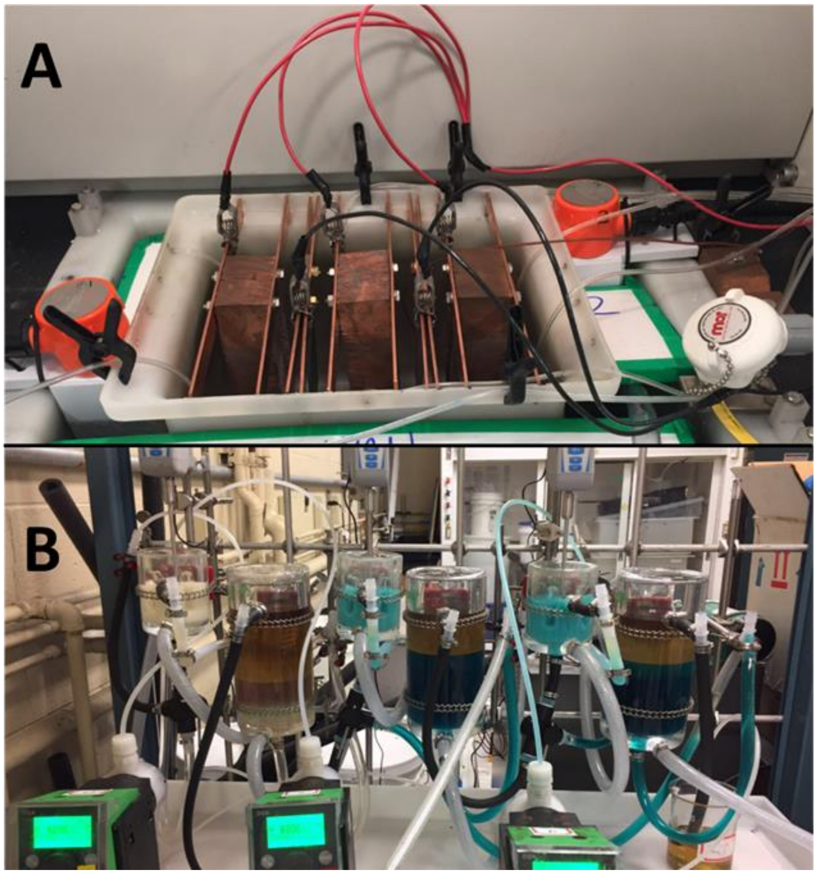


Figure 2. Construction of the laboratory-scale ER cell (a) and SX circuit (b).

The extraction stages used organic to aqueous (O:A) ratios of 1:2, while the stripping stage used an O:A of 2:1. These ratios were used to facilitate phase separation while also producing a reasonably concentrated strip solution. Flow rates were 1.62 L/hr for electrolyte, 0.78 L/hr for organic, and 0.36 L/hr for the strip solution. At day 19, all flow rates were decreased by about 25% to reduce organic entrainment back into the ER cell.

Various tubing materials were used in the circuit. Tygon was employed for the transport of acids. Viton was used for the organic solvents. PTFE carried the organic and aqueous emulsion. PVC was utilized for hot water circulation. All tubing was laboratory-grade.

The SX circuit was not operated every day as it was oversized compared to the ER cell. The ER cell was run for 21 hours every day (simulating a starter sheet production circuit) for 28 days. The SX circuit operated for only four hours on 3 days per week (e.g. the cell ran without the SX circuit on days 1–4, then for the first four hours of operation on days 5–7).

The SX circuit and ER cell were maintained at 60°C using a water heater/circulator. The temperatures were maintained to avoid unwanted precipitation in the SX circuit. Volume losses due to evaporation and sampling were replaced by adding de-ionized (DI) water and/or sulfuric acid.

Average daily sampling of electrolyte from the ER cell was about 125 mL. This included a daily sample of 50 mL from the cell, and 15 mL samples from each stage of the SX circuit (including the ER cell) once per hour while the circuit was in operation. Samples were also taken from the stripping stage and the stripping solution reservoir (referred to as the pregnant solution or Preg). Organic also needed occasional replacement due to entrainment into the ER cell.

Once samples were collected, both electrolyte and stripping solutions were diluted and analyzed in an iCE3300 FL atomic absorbance (AA) system to determine As, Bi, Cu, and Sb concentrations. The exact dilutions that were used for each element were 150:1 for As, 16:1 for Bi and Sb, and 10000:1 for Cu. Due to manual dilutions, the AA measurements were found to contain 1–4% error for synthetic solutions of known concentration.

2.4 ANTIMONY SPECIATION

A procedure provided by a research sponsor was used to measure the concentrations of Sb(III) and Sb(V) in the aqueous samples. 22.22 mL of the sample were mixed with 2.73 mL of 12 N HCl and then heated to 50°C. The solution was then passed through a bed of 50 mL of Dowex 1x8 IX resin. The IX resin captures the Sb(III). The resin bed was flushed with 100 mL of 1.5 N HCl and added to the raffinate. The solution was then then diluted and analyzed by AA. The resulting concentration was considered to be the concentration of Sb(V) while the difference between total Sb and Sb(V) was the concentration of Sb(III). The IX resin was stripped after every sample using about 50 mL of 12 N HCl, then rinsed with 100 mL of DI water. Then the IX resin was regenerated using a solution of 100 mL of DI water and 100 mL of 1.5 N HCl.

2.5 PREGNANT SOLUTION PRECIPITATION

To examine the recovery of Bi and Sb by precipitation from the Preg, a synthetic solution was prepared with the same concentration as the final Preg solution (see Table 2 for composition) from the SX circuit. Precipitation was achieved by neutralizing the solution. The pH was rapidly raised to 3–4 by the addition of 8 M NaOH. Then pH was further increased by the addition of 1 M NaOH to slowly approach the precipitation pH around 4.5. Once precipitation was observed, the solution was centrifuged to remove the solids and a small sample of the solution was analyzed by AA.

2.6 ANTIMONY STRIPPING

A mass balance of the system indicated that Sb had accumulated in the organic phase during SX circuit operation with only REX-2. Antimony removal from a synthetic Sb loaded REX-2 organic phase was attempted using 0.5 to 2 M NaOH, and 1 M NaOH with 10 g/L Na_2S. A synthetic electrolyte with 0.3 g/L Sb(III) was used to achieve 0.27 g/L Sb(III) in the organic; the concentration calculated to be retained by the organic at the end of the run.

3. RESULTS AND DISCUSSION

3.1 SB AND BI REMOVAL

The main goal of this study was to examine the removal and potential recovery of bismuth and antimony from a copper electrorefining circuit using REX-2. In Figure 3a, the concentrations of bismuth and antimony in the ER electrolyte versus operational time are presented. The decrease in both concentrations at the end of weeks 1 and 2 when the SX circuit was operating indicate that REX-2 was removing Bi and Sb from the electrolyte. During weeks 3 and 4, the removal rates appear to match the dissolution rates from the anodes in the ER cell. The Bi and Sb concentration trends are very similar indicating a similar extraction behavior. For both, as the concentration in the cell decreased, so too did the amount of Sb or Bi extracted, though this is to be expected based on isotherms generated in a previous paper (Artzer et al., 2018).

Copper and arsenic concentrations in the ER electrolyte are plotted versus time in Figure 3b. There is a slight decrease with time for both of these elements. The decline is the result of solution removal for sampling and some extraction by the SX circuit.

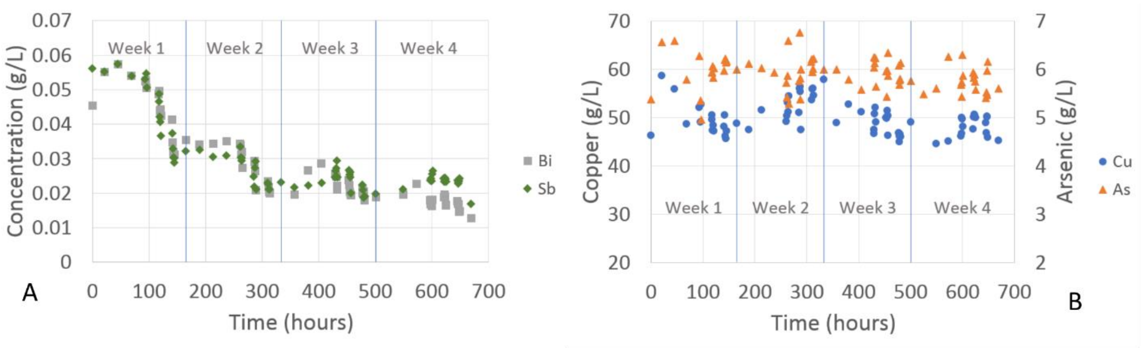


Figure 3. Graphs of the concentration of Bi and Sb (a) and Cu and As (b) as a function of cell run-time.

The concentrations of copper, arsenic, bismuth and antimony in the Preg versus time are shown in Figure 4. The final Preg solution had concentrations of 0.36 g/L Bi, 0.043 g/L Sb, 1.3 g/L Cu, and 0.18 g/L As. While Bi and Sb load similarly onto REX-2, their stripping behavior is quite different. The data for the entire campaign indicate ~92% of the Bi that was extracted was stripped from the organic, while only ~14% of the extracted Sb was stripped. A mass balance calculation for antimony infers that about 0.27 g/L of Sb remained in the organic phase at the end of the experiment. Since extraction was so similar between Sb and Bi, the accumulation of Sb on the organic is due to the poor stripping efficiency of Sb for REX-2. The mass balance calculation indicates the final concentration of Bi in the barren organic was ~0.04 g/L. The potential to preferentially strip bismuth from REX-2 was the reason the single extractant was used in this study instead of a combination of REX-1 and REX-2; an attempt to separate Bi and Sb to produce salable products.

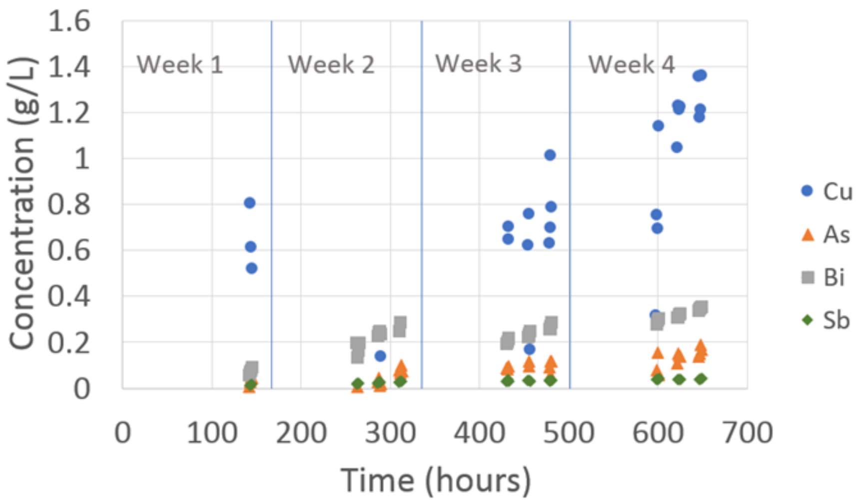


Figure 4. Concentrations of Cu, As, Sb, and Bi in the Preg solution as a function of cell run-time.

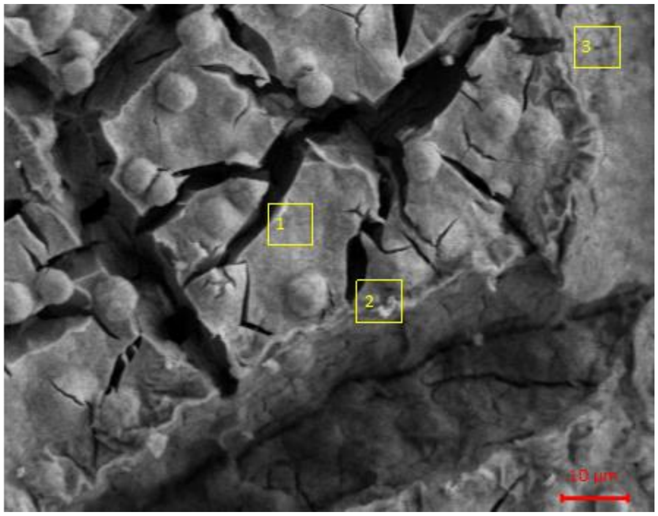
Figure 4 also shows the stripping patterns of Cu and As. The Cu in the Preg in Week 1 was due to a small amount of electrolyte flowing back into the stripping stage when the circuit was initially turned on. In Week 2, Cu may have back extracted and minimal As was extracted into the Preg. In Week 3, Cu and As stripping increased which coincided with low net extraction of Sb and Bi due to electrolyte concentrations depleting. This may indicate that Cu and As are not extracted or stripped in significant quantities at higher concentrations of Bi and Sb in the electrolyte. Furthermore, the initial electrolyte concentrations of Sb and Bi in this experiment were much lower than the 0.2 g/L Bi and Sb that are typically found in commercial Cu ER operations.

Oxidation states of antimony were also analyzed to determine if REX-2 preferentially extracts Sb(III) or Sb(V). The concentrations of Sb^{3+} and Sb^{5+} were determined for the incoming electrolyte, the SX system's raffinate, the eluent (strip), and the eluate (Preg). In the fresh electrolyte at the beginning of the experiment, ~55% of the antimony was Sb^{5+}. From analysis of the extraction and stripping results, it appears that stripping and extraction of Sb(V) was very low. Sb(III) was preferentially removed from the electrolyte leading to a higher percentage of Sb^{5+} in the ER electrolyte, ending at ~70% of the total Sb. Thus, it appears that Sb(III) was being extracted preferentially, but it was difficult to strip from REX-2 with 400 g/L H_2SO_4.

3.2 PREGNANT SOLUTION PRECIPITATION

While the Preg solution contained only traces of Sb, it also contained Cu and As. It may be that organic scrubbing could remove these elements from the loaded organic prior to the stripping stage. Even so, separation of Bi from the other elements was attempted by step-wise precipitation.

For a synthetic Preg solution of 0.36 g/L Bi, 0.043 g/L Sb, 1.3 g/L Cu, 0.18 g/L As and 400 g/L H_2SO_4, NaOH was added to a pH of 4.5 to create a precipitate. Based on EDS analysis (Figure 5), this precipitate may be a Na-Bi-oxy-sulfate. While no Cu was detected by EDS, analysis of the solution indicates copper precipitation likely occurred.



Element	1 (wt%)	2 (wt%)	3 (wt%)
Bi	64.5	39.2	34.3
Na	4.1	12.0	19.4
S	7.2	8.6	12.8
O	12.5	22.7	27.3
As	2.2	1.4	0.6
Sb	5.0	12.0	3.6

Figure 5. EDS results from analysis of the Preg solution precipitate.

While the results of this study did not produce a pure bismuth product, it is envisioned that SX removal of bismuth could be implemented in conjunction with other commercial operations for solution purification at copper electrorefinieries. A conceptual flowsheet using solvent extraction is provided in Figure 6. It is proposed that an electrolyte bleed is fed to solvent extraction using REX-2 and/or a combination of REX-1 and REX-2. The raffinate from SX is returned to the electrolyte circuit. The strip solution is sent to a short-bed ion exchange unit to remove acid including arsenic acid prior to bismuth recovery. Sheedy, Pajunen, and Westrom (2007) gives an example of this acid removal process at copper electrorefinery. The lower acidity Bi-bearing solution could then be sent to a liberation system using emew© technology that can electrodeposit copper and bismuth as either Cu-Bi and/or Bi powders (Jin, LaForest, Luyima, Read, Navarro, & Moats, 2015). Finally, a precipitation system could be used to produce a Bi and/or Bi/Sb product. This flowsheet could potential turn current wastes into salable product and provide critical materials to the marketplace.

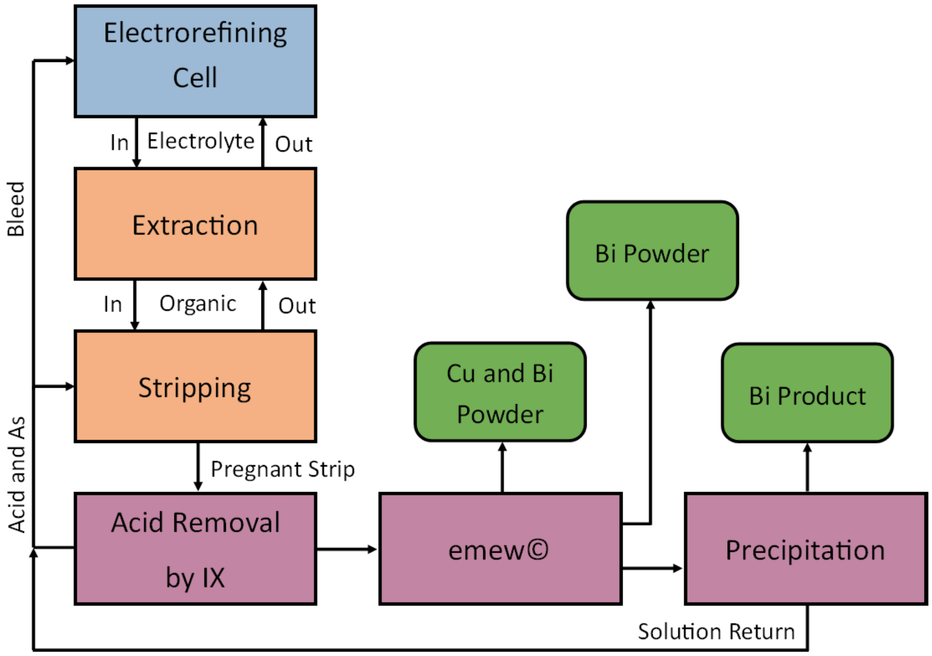


Figure 6. Conceptual flow sheet for precipitation of Bi product. Also shows alternate path to produce Cu and Bi cathode without removing acid.

3.3 ANTIMONY STRIPPING

Synthetic Sb(III) loaded REX-2/diluent (0.27 g/L Sb) was created to examine if Sb could be stripped using other reagents than H_2SO_4. BASF advised that stronger acids could degrade the extractant, so these were avoided. NaOH (0.5–2 M) was found to remove Sb from the organic, but resulted in immediate precipitation and a three-phase system was created. In the case of 0.5 M NaOH, a stable emulsion formed. While this could be implemented, operating continually with a third phase is not desirable. Based on literature (Nordwick & Anderson, 1993; Anderson, Nordwick, & Krys, 1994) a caustic solution with sodium sulfide should be capable of complexing Sb. However, when a solution of 1 M NaOH with 10 g/L reagent-grade Na_2S was used, precipitation still occurred. It may be that polysulfides and/or thiosulfate are needed to solubilize Sb.

3.4 CATHODE QUALITY

During this study, organic solution became entrained in the raffinate stream that was returned to the ER cell. The organic liquid created a film on top of the ER cell similar to what can be found in commercial in copper electrowinning operations. Unfortunately the organic film lead to the contamination of the titanium mother blanks during cell insertion. This led to incomplete starter sheet formation during the 21 hour plating cycle. This phenomenon is well known in electrowinning operations. To combat this problem, sand filters, after settlers, and/or coalescers would be needed to ensure organic does not return to the ER tankhouse.

4. CONCLUSIONS

A proprietary reagent, REX-2, was operated in a laboratory scale mini-pilot plant to examine the removal and recovery of bismuth and antimony from copper electrorefining circuits. The 28 day integrated experiment revealed that REX-2 is effective in removing both Bi and Sb(III), but not Sb(V) from the electrolyte. It was determined that 400 g/L H_2SO_4 is an effective stripping agent for bismuth, but not Sb. A conceptual flow sheet has been developed that utilizes solvent extraction along with electrowinning and/or precipitation that would produce bismuth containing products. Care must be given to reduce organic entrainment into the refinery electrolyte system.

While Sb removal from REX-2 was achieved by precipitation, this is not viewed as a potentially viable process. Thus, further investigation is warranted to evaluate the combination of REX-1 and REX-2 at the mini-pilot plant scale along with a more effective form of stripping Sb from REX-2.

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SECTION

2. CONCLUSION

There are several methods of removing Sb and Bi from Cu ER electrolyte that are currently implemented in commercial operations, such as IX and liberator processing. Though SX has never been used in a refinery, the proprietary extractants that BASF has created, REX-1 and REX-2, are capable of being stripped with sulfuric acid and possibly creating Bi and Sb products, both of which are improvements over the previously mentioned processes.

Conducting shakeout tests using various combinations of REX-1 and REX-2 showed that REX-2 is very capable of extracting both Sb and Bi, while REX-1 has very little extraction of either. However, as the percentage of REX-1 in the extractant mixture increases, the stripping efficiencies of Sb and Bi increase. Combined, this shows that REX-1 and REX-2 have the best complete removal efficiencies between 50% and 75% REX-2.

Phase break tests were analyzed to evaluate the effect of glue on phase break times. Glue was expected to significantly lengthen the times for phases to separate, but based on a statistical analysis, was shown to decrease them. Disengagement times were also affected by the phase continuity and stage (extraction vs stripping).

These tests showed that REX-1 and REX-2 could be used in commercial settings, based on their ability to extract Sb and Bi well, and their acceptable break times. They also suggested the possibility of creating a pure bismuth product using only REX-2.

Lab-scale pilot plant testing of the REX-2 extractant revealed that it is effective at removing Bi and Sb(III), but not Sb(V) from the electrolyte. It was determined that 400g/L H_2SO_4 was an effective stripping agent for Bi, but not Sb. Additionally, a conceptual flowsheet for producing a Bi product is given.

Though the extraction of Bi and Sb was successful, using REX-2 alone in a commercial setting is not seen as potentially viable, therefore additional testing is warranted to evaluate improved stripping using a combination of REX-1 and REX-2, as well as developing a way to strip Sb from REX-2.

VITA

Andrew Joseph Artzer was born to David and Victoria Artzer. He attended Blue Valley Northwest high school where he was a member of the marching and concert bands all four years.

After graduating, he began his college career at the Missouri University of Science and Technology. There he nurtured his love for chemistry and math in the Metallurgical Engineering department where he had undergraduate research positions under both Dr. Ron O’Malley and Dr. Von Richards.

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