ARSENIC'S BEHAVIOUR AND BENEFITS IN COPPER ELECTROREFINING

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ABSTRACT

The toxicity of arsenic is well known and documented. However, the presence of arsenic in copper electrorefining anodes and electrolyte is critically necessary to produce high quality cathode. Arsenic as well as antimony and bismuth concentrations vary depending on their relative concentration in the anode copper received from the smelter. This paper will discuss the behaviour and benefits of arsenic in copper electrorefining and the detrimental effects of antimony and bismuth on cathode quality and tankhouse performance. This will include the minimization and mitigation of problems associated with arsenic, antimony and bismuth including cathode contamination, floating slimes, scaling and anode passivation.

KEYWORDS

Copper electrorefining, lead, bismuth, antimony, arsenic

INTRODUCTION

In the production of copper from sulfidic ores, certain impurity elements are problematic either from an environmental or processing standpoint. Smelters assess penalties and maximum limits on such elements like arsenic, antimony and bismuth. Penalties and limits occur for a number of reasons such as ability to efficiently capture and stabilize these elements in the generated waste streams, compliance with environmental regulations and ability to meet anode specifications for refineries. In recent years, concerns about arsenic have gained new momentum due to:

(1) the gradual increase in the arsenic content of copper concentrates,
(2) increasing global copper demand,
(3) regulations introduced by China that ban the import of copper concentrates with arsenic content over 0.5% (Brook Hunt, 2010), and
(4) new regulations that will be implemented in Chile fixing the minimum arsenic capture at the smelters (Gobierno de Chile Ministerio del Medio Ambiente, 2013).

However, arsenic in copper electrorefining is critically needed to produce high quality cathode.

This paper is written in honor of Professor William Davenport who has spent his career educating engineers by helping them understand overall production processes of various metals and most especially copper. In the spirit of Prof. Davenport's work, we hope the reader will gain a better understanding of the role and behavior of arsenic in copper processing.

ARSENIC IN SMELTING

While arsenic is critical for the electrorefining process, it still must pass through a copper smelter. Thus, arsenic behavior in copper smelting is a relevant topic for this review. A substantial amount of fundamental knowledge has been generated regarding arsenic deportment in the smelting, converting, slag cleaning and refining processes over the last 30 years. This information is used to support technical decisions concerning the selection of adequate slag systems and associated smelting and slag cleaning processes in order to maximize arsenic removal and minimize waste streams generations (Chen & Jahanshani, 2010; Lynch, Akagi, & Davenport, 1991; Nagamori & Chaubal, 1982a; Nagamori & Chaubal, 1982b; Takeda, 1998; Takeda, Ishiwata, & Yazawa, 1983; Valenzuela, Fytas, & Sanchez, 2000).

The gradual increase of arsenic content in copper concentrates has being accompanied by increases in other minor elements such as lead, zinc, bismuth and antimony, especially in polymetallic copper concentrates generated in Peru and Chile. Therefore, attention needs to be given to the interaction between arsenic and these other elements, in the produced phases (solid, liquids, and gas), when examining pre-treatment (such as arsenic removal by roasting as practiced at Ministro Hales Mine in Chile) or direct smelting options of high arsenic concentrates. The removal of impurities generates waste streams that need to be treated to produce by-products or disposal compounds. Treatment of the waste streams often involves a combination of hydrometallurgical, pyrometallurgical and mineral processing techniques. Integration of knowledge from each discipline plays a key role in producing a suitable, cost effective and environmentally acceptable technical solution to the removal of impurities including arsenic.

Table 1 shows the deportment of arsenic, lead, zinc, bismuth and antimony in the Outokumpu flash smelting (Davenport, Jones, King, & Partelpoeg 2001) and ISASMELT™ processes (Fountain, Coultier & Edwards 1991; Alvear, Hunt & Zhang 2006). During pyrometallurgical processing, slag making and volatilization are the main mechanisms to remove these elements. As such, both mechanisms need to be analyzed when changes to pyrometallurgical processes are made. In this way, the detrimental impact of these elements on the quality of the product anodes and the performance of the refinery can be minimized. Davenport, King, Schlesinger, & Biswas (2002) also indicate the recycle of dusts, slag concentrates, reverts and sludges complicate the deportment of the impurity elements.

Table 1 – Deportment of As, Pb, Zn, Bi and Sb during Outokumpu flash smelting (Davenport et al., 2001)

Element	% to matte	% to slag	% to offgas
		Flash Smelting	
As	15-40	5-25	35-80
Pb	45-80	15-20	5-40
Zn	30-50	50-60	5-15
Bi	30-75	5-30	15-65
Sb	60-70	5-35	5-25
		ISASMELT™	
	% to matte	% to slag	% to offgas
As	6–10	4-8	82-90
Pb	60-65	15-20	15-25
Zn	25-30	60-70	5-10
Bi	14-25	1-2	75-85
Sb	20-40	30-40	17-45

A holistic approach to minimize waste generation and stabilize elements in the final waste stream can provide an alternative approach to directly treat complex concentrates. An example of such is being practiced at the Mount Isa Smelter. The smelter has combined a high efficiency arsenic removal smelting technology, ISASMELT, with a leaching process to treat smelter dust, acid plant weak acid and refinery effluent that ultimately stabilizes arsenic in an iron matrix (Alvear, Hourn, & Salas, 2013).

As Table 1 indicates, while the majority of arsenic can be removed during pyrometallurgical stages, the removal of bismuth and antimony is more difficult. In the future, multi-stage anode refining processes may be needed to eliminate, in a sequential mode, minor elements from the molten copper phase. For example, the production of low level arsenic- and antimony-containing anode copper could be generated by the use of sodium carbonate based slags. Sodium carbonate flux could reduce arsenic and antimony levels in the anode copper to levels under 0.01 and 15 ppm, respectively, if proper processing conditions are selected (Alvear, Tanaka, Fukuyama, Fujisawa, & Yamauchi, 1999).

Arsenic in Anodes

Following pyrometallurgical processing, the blister copper is cast into anodes. The concentration of arsenic in anodes varies widely depending on the copper source. The typical anode arsenic concentration reported by 35 copper refineries is presented in Figure 1 (Moats, Robinson, Wang, Filzwieser, Siegmund, & Davenport, 2013). Anode composition ranges from 7 to 1800 ppm with an average of 870. The average arsenic in anodes has increased from ~700 ppm to ~900 ppm from 1987 to 2013 according to Moats, Robinson and Wang (2014) indicating some of the arsenic in the concentrate is making its way through the smelter to the refinery

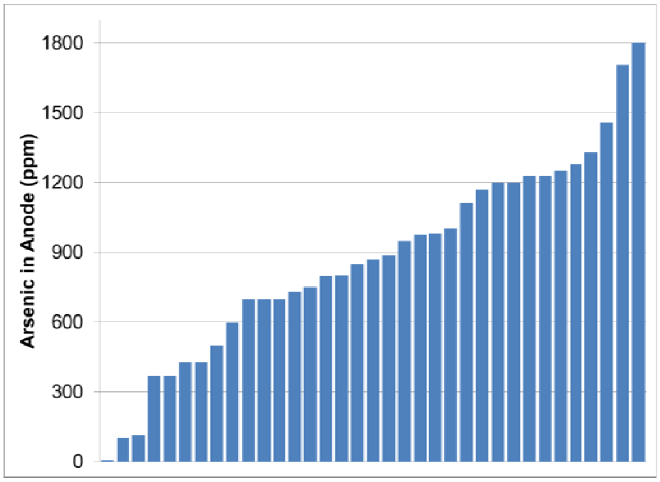

Figure 1 – Reported arsenic concentration in anodes from 35 copper refineries (Moats et al., 2013)

Arsenic in anodes can be found in solid solution with the copper and in secondary oxide particles. Chen and Dutrizac (1990, 1991, 1993, 2005) reported that 30-60% of the arsenic is found in solid solution. The remaining arsenic exists as arsenic oxide associated with complex lead-copper-oxide structures. In "high" arsenic anodes, the solid solution content is typically 30-35%. The Cu-As phase diagram indicates that up to 6% arsenic is soluble in oxygen-free copper, but the presence of many arsenic oxides indicate that in industrial practice arsenic, is more likely to react with oxygen then remain in solid solution with copper.

It has been known for many years that arsenic in copper electrorefining is beneficial. Arsenic is particularly helpful in mitigating problems associated with antimony and bismuth. Over time, refineries have determined that controlling the molar ratio of As/(Sb+Bi) is important in addition to having a minimum concentration of arsenic in the anode (irrespective of the ratio). A minimum arsenic in anode is generally targeted around 300 ppm. Wenzl (2008) summarizes the effects of low As/(Sb+Bi) ratio (< 2) in anodes from the publications of Krusmark, Young, & Faro (1995) and Noguchi, Itoh, & Nakamura (1995) as:

1. Increasing floating slimes/ cathode top nodulation/ decrease in cathode surface quality/ more short circuits/ decreased current efficiencies
2. Slimes that are thinner, denser, less cracked, more tenacious, more adherent during washing/ anode passivation/ more apparent gas evolution

The reasons behind these effects will be discussed in later sections.

Most refineries maintain the As/(Sb+Bi) ratio (Figure 2) in their anodes above 2 (Moats, et al., 2013). The median value of the data set is 4.35. However, 9 of the 34 refineries report using anodes with As/(Sb+Bi) ratio less than 2. An As/(Sb+Bi) ratio greater than two is achieved by controlling or blending of concentrates, recycling arsenic-containing dusts and/or arsenic from liberator cells and in some cases by adding speiss in the preceding pyrometallurgical processes.

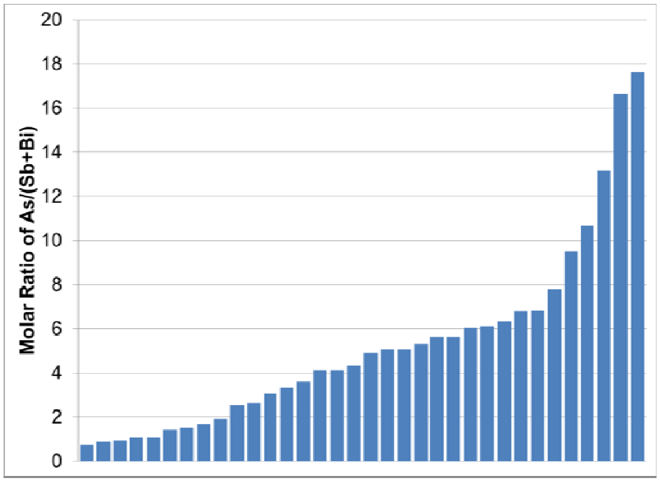

Figure 2 – Reported molar ratio of As/(Sb+Bi) in anodes from 34 copper refineries (Moats et al., 2013)

ARSENIC IN ELECTROREFINING

Arsenic Deportment – Solution vs. Slimes

Arsenic can report both to the slimes and the electrolyte (Larouche, 2001). Demaerel (1987) reported for anodes with Pb less than 4500 g/t and Sb less than 2300 g/t, the percent of arsenic reporting to the slimes varied from 100% at 0 g/t As to 10-20% for As contents between 3000-4000 g/t. Demaerel also showed that in high impurity anodes, increasing anode oxygen contents can decrease the percent of arsenic reporting to the slimes and the settling rate of the slime. These trends were also recently confirmed by Möller, Bayanmunkh, & Friedrich (2008) using specially cast anodes. Industrial survey data (Moats et al., 2013) does not support any correlation between arsenic content in the anode and percent of to the slimes. The industry data indicate less than 20% of the arsenic in the anode reports to the slimes in most refineries with a median value of 13.7%.

The behaviour of arsenic appears to depend on localized and bulk equilibriums along with kinetics. Solid solution arsenic is believed to dissolve readily into the electrolyte as As(III). Arsenic contained in complex oxides typically dissolves into the electrolyte. Some oxides, especially those in high-lead anodes or encapsulated in selenide, report directly to the slimes. Additionally, a complex amorphous "oxidative" phase forms by precipitation and consists of Cu-Ag-AsO_4-SO_4 and minor amounts of Pb, Sb, Se, Te, Bi and Cl. This oxidative phase is the "cement" that holds the slimes together. Krusmark, et al. (1995) reported that higher arsenic anodes (>300 ppm) had thicker, more porous slimes that were easier to wash off the anode surface, granular in nature and appearing more cracked. Lower arsenic anodes had slimes which were non-porous, oily and sleek in appearance. Interestingly, Krusmark et al. (1995) indicated that low arsenic anodes had more "cementate" in the slimes. Increasing arsenic content has also been shown to decrease slimes adhesion (Demaerel, 1987; Moats & Hiskey, 2006).

Bismuth and Antimony Control

Electrolyte Composition Control

As, Sb and Bi enter the electrolyte from an anode in the trivalent oxidation state. They can all be oxidized to pentavalent state by dissolved oxygen. It has been reported that Sb(V) is strongly associated with amorphous, poor-settling slimes which is harmful to cathode quality. As(III) suppresses the oxidation of Sb(III) to Sb(V) and therefore helps prevent float slimes; hence the importance of controlling minimum arsenic in anode and minimum As/(Sb+Bi) ratio. It is believed that As(III) oxidizes to As(V) faster than Sb(III) to Sb(V). The high level of As(V) in the electrolyte near the anode surface encourages precipitation of $BiAsO_4$ and $SbAsO_4$, which controlled the concentration of Bi and Sb in the electrolyte. Chen and Dutrizac (1990, 1991, 1993, 2005) have reported observing arsenates in the slimes of several refineries.

Thus, As(V) is allowed to accumulate in the electrolyte and has become a major control parameter to minimize antimony and bismuth in the electrolyte. Bismuth and antimony form arsenates, $BiAsO_4$ and $SbAsO_4$ respectively, by precipitation from the electrolyte and these report to the slimes if the precipitation occurs at the anode surface. Braun, Rawling, & Richards (1976) indicated that floating slimes form by precipitation away from the anode surface. In the electrolyte, they can float to the cathode where they can be entrapped, thus causing contamination.

The relationship between arsenic, bismuth and antimony in the electrolyte is complicated. It is influenced by many factors such as temperature, oxidation state, anode composition and bleed rate. Industrial electrolyte data (Moats et al., 2013) is summarized in Table 2 and indicates a wide range of concentrations are present in refineries.

Table 2 – Summary of industrial refinery electrolyte data (Moats et al., 2013)

	Minimum	Median	Maximum
As (g/L)	0.25	6	20
Sb (g/L)	0.06	0.32	0.7
Bi (g/L)	0.01	0.2	0.58
As*Sb (g^2/L^2)	0.11	1.7	14
As*Bi (g^2/L^2)	0.003	0.95	6

Since the precipitation of $SbAsO_4$ and $BiAsO_4$ is controlled by a solubility product, the As*Sb and As*Bi products indicate whether the electrolyte is saturated. Braun et al. (1976) indicate the solubility product should be 1.4 and 0.8 g^2/L^2 for As*Sb and As*Bi, respectively. The industrial data indicate median values close to these values, but many plants operate above and below them. Operating electrolyte data from Moats et al. (2013) were plotted on the same type of saturation plots generated by Braun et al. (1976) (Figure 3). The data indicates that most refineries still operate near or close to the predicted saturation level for arsenates, but most of the data indicate the electrolytes are probably supersaturated especially in bismuth.

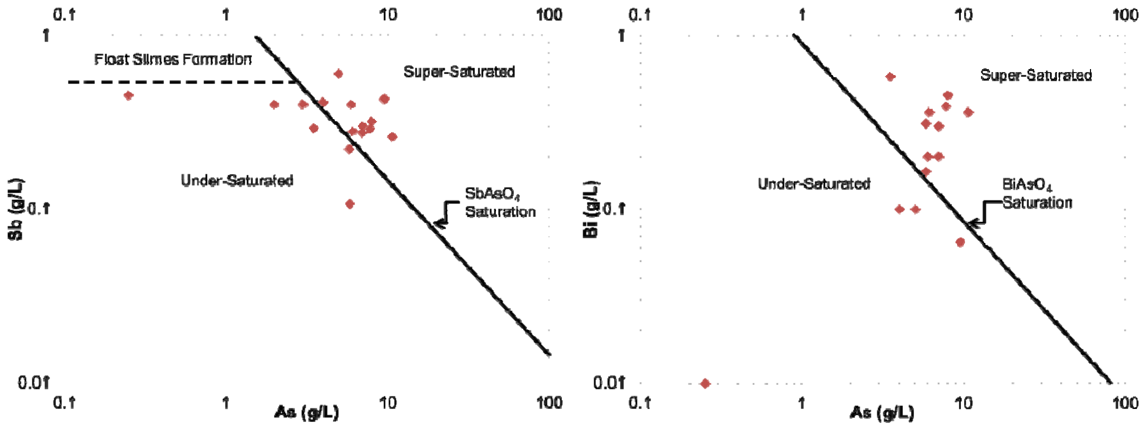

Figure 3 – As, Sb and Bi electrolyte concentrations reported by copper refineries in 2013 (Moats et al., 2013) plotted on saturation plots generated by Bruan et al. (1976)

Moats, Wang, & Kim (2012) showed for one electrolyte stream in one refinery, As*Sb and As*Bi ranged from 1.0-4.0 and 0.4-1.8 g^2/L^2, respectively, over a ten year period revealing an electrolyte evolution with time. Operational data from another refinery (Figure 4) show large variance in As*Sb and As*Bi solubility products over a 7 year period. Electrolyte fluctuates between equilibrium (saturated Sb, Bi) and super-saturated condition. Supersaturated electrolyte is unstable and leads to sudden precipitation of arsenates from electrolyte. Corresponding cathode quality (Figure 5) shows elevated As, Sb and Bi associated with these events. Secondary contamination can also occur where precipitation of arsenates causes rough, nodular cathode surface which leads to further contamination from electrolyte and slimes entrapment.

Scaling

Precipitation of Sb and Bi from saturated electrolyte (as arsenates or antimonates) results in the formation of scale accretions in pipelines, cells, filters and heat exchangers. This can have serious impact on cathode quality if electrolyte flows to the cells are impacted. Pipe cleaning / maintenance procedures are an important activity in all refineries. Operating with under-saturated electrolyte with respect to Sb and Bi helps to some extent, but precipitation will inevitably occur whenever electrolyte is exposed to cooler surfaces during and immediately after harvesting activities.

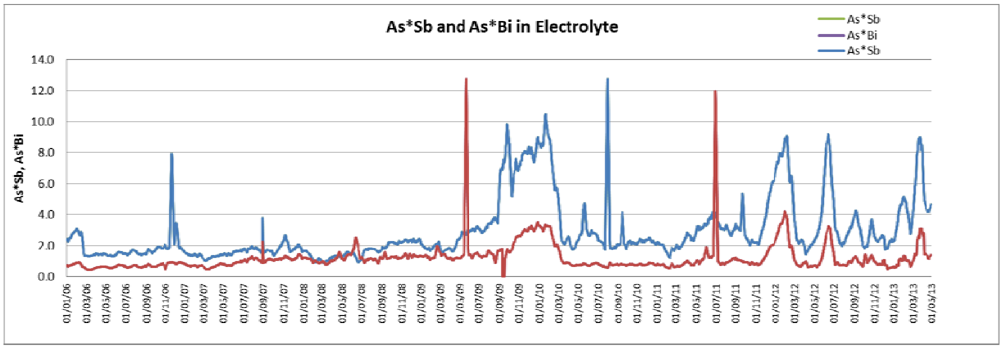

Figure 4 – As*Sb and As*Bi solubility trends from an operating copper refinery

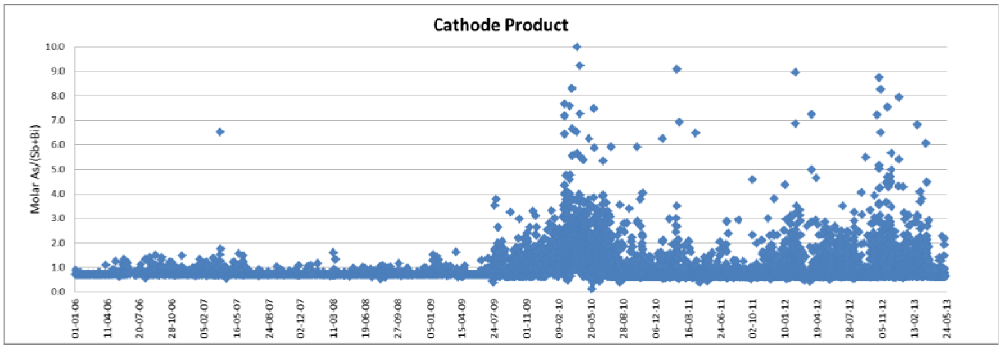

Figure 5 – As/(Sb+Bi) ratio in the cathode product from the same refinery

Inhibiting Anode Passivation

It has also been reported that anode passivation is mitigated by arsenic in the anode. Krusmark, et al. (1995) indicated that 300 ppm As was necessary to avoid passivation at the San Manuel refinery. Arsenic in the anode is the only known impurity that hinders passivation. This effect has been identified in the laboratory and in practice (Baltazar, Claessens, & Thiriar, 1987; Hiskey, Cheng, Moats, & Campin, 1996; Minotas, Djellab, & Ghali, 1989; Moats & Hiskey, 2006; Möller, Bayanmunkh, & Friedrich, 2008). Arsenic addition to the electrolyte does not inhibit passivation (Moats & Hiskey, 2007).

It has been proposed that arsenic inhibits passivation by one and/or two mechanism(s). Arsenic appears to assist in the formation of slimes that are less adherent (Demaeral, 1987; Moats, 1998) and/or porous (Krusmark, et al., 1995). Slimes from high arsenic anodes would not block the surface as readily or inhibit the diffusion of ions. It has also been proposed (Hiskey, et al., 1996) that arsenic generates acid at the anode surface under the slimes layer as its oxides dissolve through reaction (1). The generation of hydrogen ions can lower the pH at the anode surface and inhibit the formation of cuprous oxide.

$$As_2O_3 + 3H_2O \rightarrow H_2AsO_4 + 2H^+ + 2e \quad (1)$$

Arsenic at the Cathode

The mechanisms for cathode contamination are electrolytic co-deposition, slime occlusion, electrolyte occlusion or precipitation. Braun et al. (1976) indicate that co-deposition of arsenic in a commercial cell is unlikely and upon analysis of several “brands” of cathode concluded that slimes or electrolyte occlusion could not be the sole source of contamination based on a As/(Sb+Bi) molar ratio of near one in the cathodes. Hoffmann (2004) stated that arsenic contamination is likely caused by electrolyte entrapment. However, no correlation between the arsenic concentration of the electrolyte and arsenic in the cathode was reported in recent industrial data (Moats et al., 2013). The recent industrial data also indicate a wide range in the As/(Sb+Bi) molar ratios found in cathode (0.21 to 8.2, median 1.3). Electrolytic co-deposition of arsenic appears unlikely, except in rare incidents where flow to a cell is disrupted. Incorporation of arsenic into the cathode could occur by any of the other methods.

Arsenic in Liberators

While arsenic does not electrodeposit with copper in commercial electrorefining cells, it will if the copper concentration is low (e.g. liberator cells). Great care is needed in 3rd stage liberation as arsine gas generation is possible once copper is depleted from the electrolyte. To avoid arsine generation and maximize arsenic removal, Freeport-McMoRan’s El Paso refinery maintains the copper concentration between 2-4 g/L in their liberator cells to produce copper arsenide at the cathode (Wesstrom & Araujo, 2012).

CONCLUSIONS

Arsenic is a very important element in copper electrorefining. Its input is increasing to smelters from South American concentrates, which is causing concern. However, some arsenic is needed in anodes to produce high quality cathodes and reduce the effects of antimony and bismuth. It is generally accepted that a minimum arsenic concentration of 300 ppm and a As/(Sb+Bi) molar ratio of greater than 2 should be used in anodes. Arsenic is beneficial to the refinery by minimizing floating slimes, inhibiting anode passivation and controlling the concentrations of Sb and Bi in the electrolyte.

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