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Technical note

Batch electrodialytic treatment of copper smelter wastewater

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ABSTRACT

In this paper, the electrodialysis technique is tested as a possible treatment of smelter wastewater containing mainly copper and arsenic. The results show that it is not feasible to treat the raw wastewater, because the highly acidic pH favours the proton electro migration compared to copper. However, when adjusting the pH of the wastewater to 2 and 3, the copper could be removed entirely into a copper concentration section. Less than 2.5% of the total arsenic migrated into the copper concentration section, indicating the possibility to separate copper from arsenic. At higher pH values and current density, copper is removed faster but at pH values greater than 3 precipitates start to form.

1. Introduction

During the smelting of copper sulphides and the subsequent gas treatment, considerable volumes of wastewater are generated containing mainly copper, arsenic and other inorganic species (such as heavy metals, H^+ and SO_4^{2-}) in concentrations that exceed the local legal threshold values (Chilean Republic, 2000). Actually, arsenic and heavy metals are removed by chemical precipitation with lime but this treatment results in large amounts of sludge, where important amounts of copper are lost.

This paper presents the electrodialysis (ED) technique as an alternative to the previous treatment, allowing separating (and recovering) copper from arsenic. Fig. 1 illustrates the principle in the suggested method. Cu^{2+} is transported to Section 2, and arsenic species (either negatively charge or with no electrical charge at low pH) remain in Section 3 or are transported into Section 4.

Earlier work has proven this separation but only from synthetic aqueous solutions and with high Cu-to-As ratios (Cifuentes et al., 2002). Other attempts have been done to separate As from Cu in earlier steps such as flotation (Long et al., 2014) or during the smelting process (Mihajlovic et al., 2007). In general it was concluded that it was difficult to separate Cu from As before or during smelting.

The objectives of this work were to study the feasibility of separating the copper present in an arsenic-rich mineral processing wastewater using ED, evaluate and quantify the separation of copper from arsenic by electrodialysis, to study the influence of current density and pH of the wastewater, and to analyse the current efficiency with respect to copper.

2. Experimental

The wastewater was sampled at the División Fundición Chagres copper smelter in V Region of Chile. Calcium hydroxide was added to adjust the pH of the wastewater to 1, 2 or 3.

Total As and Cu contents were determined by AAS according to the Official Chilean Standard NCh 2313/10 Of. 96. As(III) concentration was determined by quantitative Vogel analysis. As(V) concentration was determined by the difference between the total As and As(III).

Fig. 1 shows the cylindrical acrylic ED cell divided into 5 sections, separated by cation and anion exchange membranes. Sections 1, 2, 4 and 5 were filled initially with 0.1 M sulphuric acid. Section 3 was filled with wastewater. Stainless steel electrodes were placed in Section 1 (cathode) and Section 5 (anode). Ion exchange membranes were CMI-7000 and AMI-7001 from Membrane International Inc.

Table 1 illustrates the operating conditions and results for the experiments carried out. Each experiment was performed as a batch ED experiment at fixed times (1, 2, 3, 4 or 5 h). Preliminary studies were conducted (tests a to c) on raw wastewater to investigate the copper removal without pH adjustment. In experiment series (1)–(9) pH was adjusted before ED treatment. Experiment series (10) were performed to evaluated the separation of Cu from As.

3. Results and discussion

Table 1 illustrates the result that only a small amount of copper moved into Section 2. These results illustrate that electromigration depends mainly on specie concentration and specie ionic mobility. The molar ratio hydronium/copper is approximately 3.8 at pH 1. In the raw wastewater pH is lower than 1, which

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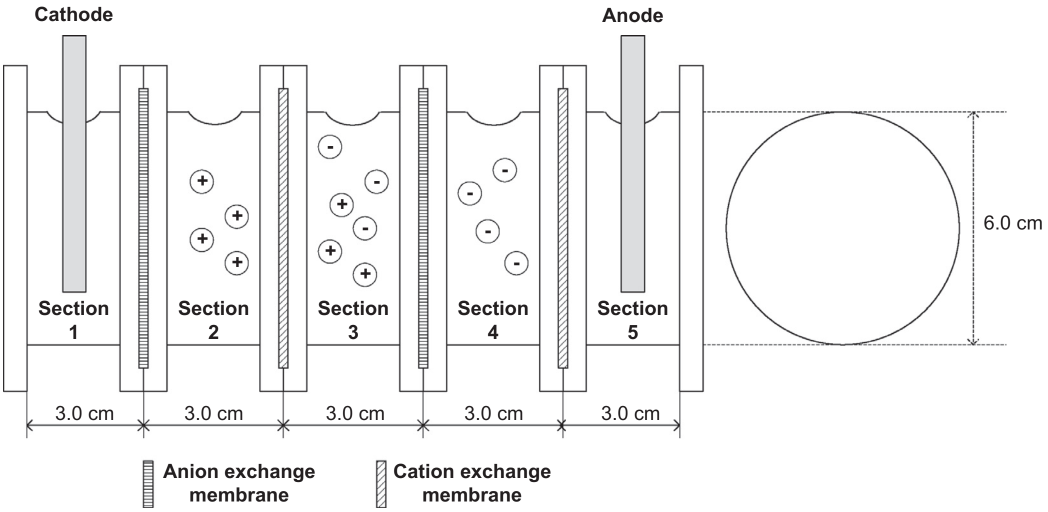

Fig. 1. Electrodialytic cell.

Table 1
Experimental plan and results from treatment of raw and pH adjusted copper smelter wastewater, for different pH, time and current densities.

Analysed element	Experiment series	Current density (A m^{-2})	Time (h)	Cu (mg L^{-1}) Section 3	Cu (mg L^{-1}) Section 2	Cu (mg L^{-1}) Section 4
Raw wastewater, pH < 1.0, initial concentration of Cu: 1652 mg L^{-1} (analysed element: Cu)						
Cu	a	150	4	1549	2.4	2.4
			5	1608	7.4	6.8
	b	225	4	1589	10.1	2.2
			5	1604	<1	5.0
	c	300	3	1556	15.6	1.1
			4	1549	18.5	2.0

Wastewater pH [–]	Experiment series	Current density (A m^2)	Section	Time 1 h Cu (mg L^{-1})	Time 2 h Cu (mg L^{-1})	Time 3 h Cu (mg L^{-1})	Time 4 h Cu (mg L^{-1})	Time 5 h Cu (mg L^{-1})
pH adjusted wastewater, initial concentration of Cu, Section 3: 639 mg L^{-1} (analysed element: Cu)								
1	1	300	3	552	492	442	358	212
			2	89	136	287	323	345
	2	225	3	575	536	454	456	319
			2	69	96	196	251	276
	3	150	3	582	549	504	515	423
			2	56	79	144	200	188
pH adjusted wastewater, initial concentration of Cu, Section 3: 489 mg L^{-1} (analysed element: Cu)								
2	4	300	3	295	156	13	0	–
			2	124	357	461	510	–
	5	225	3	358	282	157	32	0
			2	96	249	357	449	463
	6	150	3	407	334	246	162	126
			2	93	184	233	305	382
pH adjusted wastewater, initial concentration of Cu, Section 3: 498 mg L^{-1} (analysed element: Cu)								
3	7	300	3	222	81	0	–	–
			2	289	500	444	–	–
	8	225	3	298	165	107	0	–
			2	231	337	437	467	–
	9	150	3	313	245	201	145	92
			2	128	248	310	378	461

Experiment series	*t* (h)	Arsenic (mg L^{-1})			Copper (mg L^{-1})		
		Section 2	Section 3	Section 4	Section 2	Section 3	Section 4
pH adjusted wastewater, current density 225 A m^{-2}, pH: 2 (analysed elements: As and Cu)							
10	0	0	2154*	0	0	897	0
	1	6.5	1814	6.3	–	–	–
	2	27.7	1890	18.1	620	275	0.1
	3	42.9	1609	78.3	–	–	–
	4	54.8	1327	486	837	3	0.3

* In the initial sample both total As, As(III) and As(V) were analysed. The results showed that the sample had 2154 mg L^{-1} of As(III) and less than 1 mg L^{-1} of As(V). Therefore in the rest of the samples only total arsenic was measured – assuming presence of As(III) only.