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Recovery of metals from chloride leach solutions of anode slimes by solvent extraction. Part II: Recovery of silver and copper with LIX 63 and Alamine 336

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ABSTRACT

In Part 1 of this paper, gold(III) and Sn(II) were recovered from the chloride leach solution of anode slimes by extraction with Cyanex 272 and stripping with $(NH_4)_2S_2O_3$ and NaOH solutions for gold(III) and Sn(II), sequentially. In this work, solvent extraction experiments were conducted to recover Ag(I) and Cu(II) from the Au (III) free raffinate containing Ni(II), Sn(II) and Zn(II) using two systems. In the first system, Cu(II) and Ag(I) were sequentially separated using LIX 63 and Alamine 336, respectively. Dilute HCl and NH_4SCN were used as the stripping agents for Cu(II) and Ag(I), respectively. In the second system, Cyanex 301 co-extracted Ag(I), Cu(II) and Sn(II) from the Au(III) free raffinate. Aqua regia at different dilutions stripped these three metal ions from the loaded Cyanex 301. First, Cu(II) was selectively stripped from the loaded Cyanex 301 by employing ten times diluted aqua regia. Second, most of Ag(I) was selectively stripped over Sn(II) by five times diluted aqua regia. A process flowsheet for the separation and recovery of noble and base metals from the chloride leach solution of anode slime using extraction and stripping has been proposed.

1. Introduction

Copper, gold and silver are valuable metals, which are widely used in electronics industries (Robinson, 2009; Xing and Lee, 2017). Anode slimes containing these valuable metals together with some platinum group metals (PGMs) are important secondary resources for these metals (Chen and Dutrizac, 2013; Liu et al., 2014; Widmer et al., 2005) and the development of an efficient process to recover the noble and base metals from the anode slimes is needed. In the conventional processes, the first step is to remove some base metals from the anode slimes by pretreatment like smelting and selective leaching. Then the enriched slimes are dissolved into various media (Bas et al., 2015; Li et al., 2015; Liu et al., 2014; Xu et al., 2014, 2016). Solvent extraction (Fouad, 2009; Laki et al., 2016; Papaiconomou et al., 2008; Xie and Lu, 2013), ion exchange (Liu et al., 2009; Mpinga et al., 2014; Nguyen et al., 2015; Ramesh et al., 2008) and bio-leaching and biosorption (Chi et al., 2011; Won et al., 2014) are generally employed to separate the metals in the leach liquor. Among these methods, solvent extraction has some advantages over ion exchange on the basis of capacity and selectivity (Laki et al., 2016).

In our previous work, Au(III) was successfully separated by Cyanex 272 and LIX 63 from the hydrochloric acid solution containing Pt(IV) and Pd(II) (Xing et al., 2018b). During our ongoing work on the recovery of gold from the chloride leach liquor of anode slime which contained copper, nickel, silver, tin and zinc, Au(III) was selectively recovered by solvent extraction with Cyanex 272 (Xing et al., 2018a). Further work is necessary to recover Ag(I) and Cu(II) present in the Au (III) free raffinate. Previous studies reported the extraction behavior of Ag(I) by various extractants from the media of nitric, thiocyanate, cyanide and thiourea (Arroyo et al., 2008; Ohto et al., 1997a; Sanuki et al., 2000; Zuo and Muhammed, 1990). In concentrated hydrochloric acid solution, most of Ag(I) precipitates as silver chloride but some of Ag(I) remained as the dissolved chloro-complexes. Since the concentration of Ag(I) in concentrated hydrochloric acid solutions is low, the solvent extraction of Ag(I) from hydrochloric acid solutions is a viable option (Mendoza et al., 1995; Ohto et al., 1997b; Sole et al., 1994; Zuo and Muhammed, 1990).

First, gold(III) and Sn(II) were recovered from the chloride leach solution of anode slimes by extraction with Cyanex 272, leaving Ag(I), Cu(II), Ni(II), and Zn(II) in the raffinate. Batch simulation experiments on the two stage counter-current extraction led to complete extraction of Au(III) and 98% extraction of Sn(II). Pure Au(III) solution was

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recovered from the loaded Cyanex 272 by selective stripping of Au(III) with $(NH_4)_2S_2O_3$, leaving most of Sn(II) in the stripped Cyanex 272 (Xing et al., 2018a). A solution of 2 M NaOH at an organic/aqueous phase ratio of unity stripped 80% of Sn(II) from the Au(III) free Cyanex 272/kerosene phase, which were in good agreement with the reported results on the stripping of Sn(II) (Swain et al., 2015; Zou et al., 2004).

In this work, separation of Ag(I) and Cu(II) was investigate from the Au(III) free raffinate using solvent extraction. For this purpose, the extraction behavior of Ag(I) in chloride solutions in the absence of other metal ions was investigated by employing several extractants. Two solvent extraction systems were tried in order to recover Ag(I) and Cu (II) from the Au(III) free raffinate. First, Cyanex 301 was used to study the separation behavior of Ag(I), Cu(II), Ni(II), Sn(II) and Zn(II) ions present in the Au(III) free raffinate. The co-extracted Ag(I), Cu(II) and Sn(II) into the Cyanex 301 were separated by selective stripping with diluted aqua regia. In the other system, Cu(II) was first separated by extraction with LIX 63 and then Ag(I) was extracted by Alamine 336. The stripping of Cu(II) and/or Ag(I) from the loaded organic was also investigated. By comparing these two extraction systems, a process has been proposed to recover Ag(I) and Cu(II) with high purity from the Au (III) free raffinate by extraction and stripping.

2. Experimental

2.1. Chemicals

The synthetic chloride leach solution of anode slime was prepared by dissolving a required amount of $HAuCl_4$ (30 wt% in dilute HCl, Sigma-Aldrich), $CuCl_2{\cdot}2H_2O$ (97%, Daejung Chemicals & Metals Co., Ltd., Korea), $SnCl_2{\cdot}H_2O$ (97%, Daejung Chemicals & Metals Co., Ltd., Korea) as well as $ZnCl_2$ (90%, Duksan Pure Chemicals Co., LTD, Korea) and $NiCl_2{\cdot}6H_2O$ (YAKURI Pure Chemicals CO., LTD, Japan, 96%) into 5 M HCl solution. During the preparation of the synthetic solution, a small amount of H_2O_2 (30%, DaeJung Chemical & Metals Co., Ltd.) was added to suppress the formation of grainy-like precipitates. In order to investigate the extraction behavior of silver(I) from hydrochloric acid solutions, pure silver(I) solutions were prepared by dissolving the required amount of AgCl (above 99.5%, Daejung Chemicals & Metals Co., Ltd., Korea) into hydrochloric acid solutions of different concentrations. The composition of the chloride leach solution of anode slime is shown in Table 1.

2.2. Reagents

The structures of all the organic reagents are shown in Appendix 1. Acidic extractants, like D2EHPA (95%), PC88A (95%) and Cyanex 301 (70%) were purchased from Daihachi Chem. Industries, Japan and Cytec Industries, Canada, respectively. Neutral extractants like TBP (98%), MIBK (98.5%), Cyanex 923 (92%), TOPO (99%) and TOP (99%) were purchased from Yakuri Pure Chemical Co., Ltd. Daejung Chemical & Metals Co., Ltd. and Samchun Pure Chemical Co. Ltd., respectively. As basic extractants (amines), Alamine 336 (95%, BASF Co., USA), Aliquat 336 (100%, BASF Co., USA), Alamine 300 (97%, Samchun Pure Chemical Co.) and Alamine 308 (95–100%, BASF Co., USA) were employed and kerosene was used as a diluent. All the reagents were employed in the experiments without further purification.

Table 1
Concentration of metal ions in synthetic anode slime leach solution.

Elements	Cu	Zn	Ni	Ag	Sn	Au
Concentration ($mg\,L^{-1}$)	2520	15.0	25.4	40.1	450	100

2.3. Solvent extraction procedure

In the extraction and stripping experiments, equal volumes (10 mL) of aqueous and organic phases (unless otherwise stated) were mixed in 50 mL bottle with screwed cap. In the extraction and most of the stripping experiments, the mixtures were shaken about 30 min (Xing et al., 2018b) by using a wrist action shaker (Burrel, USA) at ambient temperature. However, it was observed that stripping of the metals from the loaded Cyanex 301 by aqua regia took 2 h to reach equilibrium and thus 3 hour shaking time was employed in these stripping experiments. After equilibrium, the two phases were separated and the concentrations of metal ions present in the raffinate were measured by ICP-OES (Spectro arcos model). The concentrations of metal ions in the organic phase were calculated by mass balance.

3. Results and discussion

3.1. Sequential extraction of Cu(II) and Ag(I) from the Au(III) free raffinate

3.1.1. Separation of Cu(II) by extraction with LIX 63

Table 2 shows the composition of the raffinate obtained by batch simulation experiments after two stage counter current extraction with Cyanex 272. The separation of Cu(II) was tested by extraction with 0.2 M LIX 63 in the HCl concentration range of 0.5 M to 9 M. Fig. 1 shows that the extraction percentage of Cu(II) increased as HCl concentration increased from 0.5 to 5 M and then decreased to 50% as HCl concentration increased to 9 M. In contrast, the extraction of Sn(II) increased as HCl concentration increased from 0.5 to 1 M and then decreased significantly when HCl concentration was higher than 1 M. The extraction reaction of Cu(II) by LIX 63 can be represented by Eqs. (1) and (2), where HA refers to LIX 63. These two equations indicate that the increase in H^+ concentration has negative effect on the extraction of Cu(II).

$$Cu^{2+} + (HA)_{2,org} = CuA_{2,org} + 2H^+ \tag{1}$$

$$CuCl^+ + (HA)_{2,org} = HCuClA_{2,org} + H^+ \tag{2}$$

Equilibrium constant is a function of the activity of the species involved in a chemical reaction. Therefore, ionic strength of the solution and water activity affect the speciation of copper chloro-complexes in strong hydrochloric acid solution (Cote et al., 1994). When chloride ion concentration is low, Cu^{2+} is the predominant species of copper(II) and the mole fraction of $CuCl^+$ would increase as chloride ion concentration increases (Lee et al., 2008). With further increase of chloride ion concentration, $CuCl_2$ and subsequently anionic complexes like $CuCl_3^-$ and $CuCl_4^{2-}$ begin to form (Senanayake and Muir, 1988; Winand, 1991). Likewise, the reported distribution diagram of Sn(II)-chloride complexes shows that Sn^{2+} and $SnCl^+$ are the predominant species only at very low chloride concentrations (< 0.2 M), whereas $SnCl_2$, $SnCl_3^-$ and $SnCl_4^{2-}$ become predominant when chloride concentrations are higher than 0.4 M, 1.3 M and 2.4 M, respectively (House and Kelsall, 1984). Thus, high acidity and the formation of neutral or anionic chloro-complexes of Cu(II) and Sn(II) at higher concentrations of HCl prevents the extraction of these two metal ions by LIX 63.

The concentration of Cu(II) and Sn(II) in the Au(III) free raffinate was 2520 and 8.3 $mg\,L^{-1}$, respectively (Table 2). Therefore, the

Table 2
Concentration of metal ions in the raffinate after two stages of counter-current extraction of gold and tin by Cyanex 272.

Elements	Cu	Zn	Ni	Ag	Sn	Au
Concentration ($mg\,L^{-1}$)	2520	14.8	25.0	40.0	8.3	0.01

([Cyanex 272] = 0.2 M; [HCl] = 5 M; shaking time = 30 min; O/A = 1.)