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Thiocyanate hydrometallurgy for the recovery of gold. Part IV: Solvent extraction of gold with Alamine 336☆

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ABSTRACT

Solvent extraction with amines has been evaluated as a possible method to purify and concentrate gold from thiocyanate solutions. No significant difference was observed in gold extraction with commercially available tertiary amines (Alamine 336, Alamine 308, and Alamine 304–1). The effects of Alamine 336 and thiocyanate concentrations were examined for gold extraction. Gold extraction isotherms were established at different thiocyanate concentrations. The extraction and stripping of gold showed satisfactory results at an organic/aqueous (O/A) ratio of 1:5 for extraction (~100%) and 5:1 for stripping (~92%), in the presence of decanol. Possible solvent extraction reactions and stripping reactions with thiourea are discussed in order to better understand the system chemistry. Sodium hydroxide/thiocyanate, ammonium hydroxide, and acidic thiourea were examined for the stripping of gold from the loaded organic phase. Acidic thiourea gave the best results (with complete stripping of gold) under the conditions studied.

1. Introduction

Much has been written over the past years on the recovery of gold from thiourea (Li and Miller, 2006) and cyanide solutions (Marsden and House, 2006; Senanayake, 2005). However, the investigation of thiocyanate leaching and recovery of gold is more limited (Barbosa-Filho and Monhemius, 1989, 1994a, 1994b, 1994c; Broadhurst and Du Preez, 1993; Li et al., 2008; Monhemius and Ball, 1995).

Recovery of gold from thiocyanate solutions by activated carbon adsorption (Kholmogorov et al., 2002; Kononova et al., 2005; Monhemius and Ball, 1995), ion exchange (Fleming, 1986; Kholmogorov et al., 2002; Monhemius and Ball, 1995), cementation (Ravaglia and Barbosa-Filho, 2000, 2005; Wang et al., 2007; Yen et al., 1998) and reduction–precipitation with sodium borohydride (Awadalla and Ritcey, 1991) has been reported. According to these studies, activated carbon has strong adsorption properties for Au-SCN complexes for high gold recovery, and rapid kinetics, but lacks selectivity, and needs stripping at high temperatures (about 150 °C). Strong base ion exchange resin has similar properties to activated carbon. Medium base resin shows promising potential — high gold recovery and easy stripping conditions at room temperature. Sodium borohydride is not as effective for gold recovery from thiocyanate solution.

Gold forms anionic complexes in thiocyanate solutions (Li et al., 2008). In this regard it is expected that amine extractants may be suitable for gold extraction. There are four types of amines with different molecular structures, i.e. primary, secondary, tertiary, and quaternary amines. The thiocyanate solution for gold leaching is quite acidic and the pH is usually from pH 1 to 2 (Li et al., 2008). In contrast, cyanide solutions for gold leaching have a pH of about 10. Relatively weak alkyl amines should be considered for extraction from thiocyanate solutions since strong base amines would likely be difficult to strip (Ma et al., 2000; Mooiman and Miller, 1984, 1985). In fact, the gold cyanoanion is so difficult to strip from loaded quaternary amine that it has been incinerated in order to recover gold (Riveros, 1990). Thus, in this current research, tertiary amines were evaluated for gold recovery from acidic thiocyanate/ferric sulfate solutions.

2. Materials and methods

Three tertiary amines; i.e. Alamine 336 (trialkyl (C8–C10) amine), Alamine 308 (triiso-octyl amine), and Alamine 304–1 (tridodecyl amine), were obtained from Cognis Company and used as received. Decanol (Cognis Company) was added to improve the solubility of gold and ferric species in the organic phase and to mitigate the viscosity of the organic phase when loaded with ferric ion in some

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☆ This paper is an extension of the work presented and published in Hydrometallurgy 2008, 6th International Symposium, Phoenix, AZ, United States (Li et al., 2008).

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experiments. Hexane (Sigma-Aldrich Company) was employed as received for the dilution.

Sulfuric acid and sodium hydroxide (both AR, Mallinckrodt) were used to adjust pH. Ammonium hydroxide and thiourea (both AR, Mallinckrodt) were used for gold stripping. In all experiments, DI water was used to prepare the aqueous solutions.

For the purpose of comparing three amine extractants, experiments were performed in separatory funnels at a volumetric phase ratio of 1 (organic/aqueous: O/A) with a shaker (MAX^Q 2000, Barnstead/Lab-Line) for equilibration. However, this shaker was found to be inadequate for solvent extraction of gold at a high phase ratio and hence hand shaking was used for those experiments. Gold thiocyanate solutions were prepared and extracted with amine. Chemical analyses were performed using an ICP-OES.

3. Solvent extraction at low phase ratios

3.1. Scoping experiments

For the initial scoping experiments, pH was not controlled and thus the initial and final pHs were not the same. Comparison of the three tertiary amines was made with respect to their extraction of gold and thiocyanate as shown in Fig. 1. Gold-thiocyanate anionic complexes and free thiocyanate appear to be co-extracted into the organic phase. However, selectivity of the gold species over free thiocyanate appears to be possible by pH control.

Fig. 2 illustrates the relationship between the initial pH and final pH for these experiments. As tertiary amines have moderate alkalinity, it is expected that acid will be extracted from aqueous solutions which appears to be the case. These results suggest that the tertiary amines examined have similar properties under the conditions investigated. Alamine 336 was chosen for use in subsequent experiments due to its slightly better gold extraction curve.

3.2. The effect of ionic strength on the extraction of gold

The effect of ionic strength on gold extraction was studied by using aqueous solutions of varying Na_2SO_4 concentration. Two different Alamine 336 concentrations (4×10^{-4} and 4×10^{-2} M) were examined. pH was controlled at 1.8 throughout the experiments, which were performed at 23 °C, O/A of 1:2, and mixing time of 20 min. Fig. 3 reveals that ionic strength did not have a significant effect under the conditions studied. Therefore, an indifferent electrolyte was not added for control of ionic strength in subsequent experiments. Obviously, the concentration of the extractant will have an effect on gold extraction. According to Fig. 3, at a low concentration of Alamine 336 (4×10^{-4} M), the system is starved for extractant.

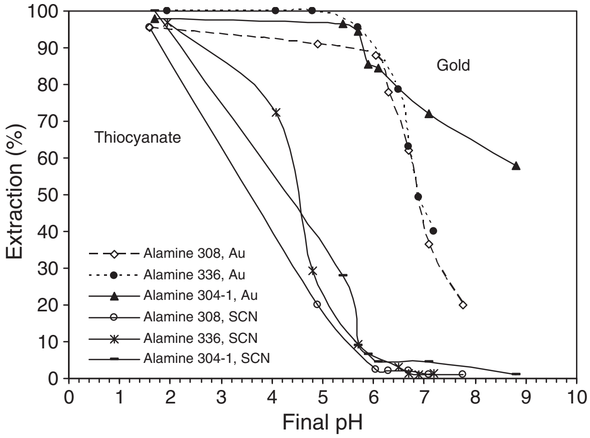

Fig. 1. The effect of final pH on the extraction of gold and thiocyante. Initial aqueous phase composition: SCN 0.1 M, Au 10 mg/L. Initial organic composition: Alamine 336, Alamine 308, or Alamine 304–1 0.1 M, using hexane as solvent/carrier at room temperature (~23 °C). O/A of 1 and mixing time of 20 min.

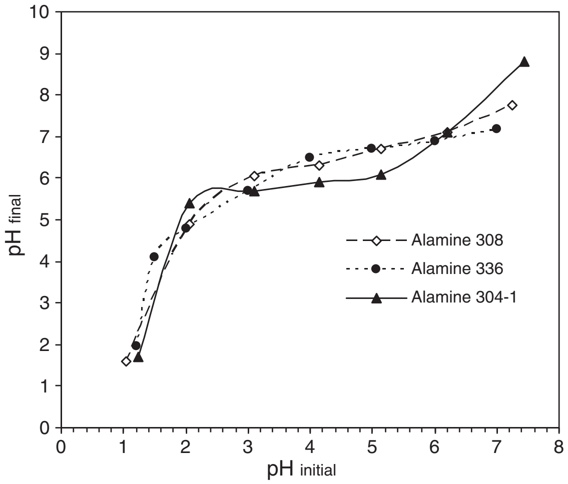

Fig. 2. Variation of pH before and after gold extraction by Alamine 336, Alamine 308, and Alamine 304. Initial aqueous phase composition: SCN 0.1 M, Au 10 mg/L. Initial organic composition: Alamine 336, Alamine 308, or Alamine 304–1 0.1 M, using hexane as solvent/carrier at room temperature (~23 °C). O/A of 1 and mixing time of 20 min.

3.3. The effect of Alamine 336 concentration on the extraction of gold

The effect of Alamine 336 concentration on gold extraction was more thoroughly examined as shown in Fig. 4. The results demonstrate that when the molar ratio of Alamine 336/gold is above 10, gold extraction at a high level (~98%) is achieved, and the effect of Alamine 336 concentration is negligible. For molar ratios less than 10, gold extraction increases with increasing Alamine 336 concentration.

3.4. The effect of thiocyanate concentration on the extraction of gold

As presented in Fig. 5, at a relatively high Alamine 336 concentration of 0.05 M, the variation of thiocyanate concentration from 0.01 to 0.2 M does not significantly affect the extraction of gold under the conditions employed.

However, at low Alamine 336 concentrations it can be seen that at equal molar Alamine 336 and gold concentrations the effect becomes

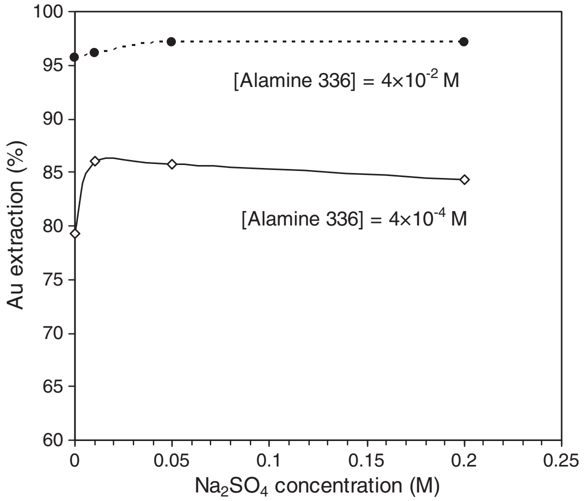

Fig. 3. The effect of ionic strength (I) on gold extraction by Alamine 336 (4×10^{-2} and 4×10^{-4} M) in hexane. Au 10 mg/L, SCN 0.1 M, pH 1.8, and 23 °C. Mixing time 20 min. and O/A of 1:2.