



## Thiosulphate leaching of silver from an arsenical refractory ore

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### ABSTRACT

Thiosulphate leaching has received particular attention in recent years as an environmentally benign alternative to cyanide leaching. In this study, thiosulphate leaching combined with ultra-fine grinding (UFG) was studied for silver extraction from an arsenical refractory ore. Direct cyanidation of the ore ( $d_{80}$ : 50  $\mu\text{m}$ ) led to a low silver extraction of  $\leq 70\%$  over 24 h. leaching period. Extraction of silver in cyanide leaching was improved to 85% after ultra-fine grinding. In comparison, up to 98% of silver extraction was achieved in thiosulphate leaching system after ultra-fine grinding of the ore down to 5  $\mu\text{m}$  ( $d_{80}$ ) in a stirred mill. Furthermore, thiosulphate leaching is more selective than cyanide leaching with only negligible leaching of arsenic, antimony and other metals observed in this study. This is of particular importance considering the environmental concern for the presence of arsenic in cyanide leaching solutions and effluents. Effects of thiosulphate (0.2–0.6 M  $\text{Na}_2\text{S}_2\text{O}_3$ ), ammonia (0.04–0.52 M  $\text{NH}_3$ ) and copper (0.02–0.11 M  $\text{CuSO}_4$ ) on the extraction of silver were investigated using a Box-Behnken design. Statistical analysis of the experimental data (%Ag extraction at 8 h.) confirmed that all the parameters have quadratic effects in that the extraction of silver tends to improve with increasing their concentration up to a critical level above which a reverse trend occurs. The addition of a small amount (0.1 M EDTA, 50 mg/L CMC) of ethylenediaminetetraacetic acid (EDTA) and carboxymethyl cellulose (CMC) improved (by  $\sim 20$ –30%) silver extraction and reduced thiosulphate consumption by  $\sim 20\%$ . Using nickel sulphate in place of  $\text{CuSO}_4$  also improved silver extraction with concurrent decrease in thiosulphate consumption. Recovery of silver from real pregnant leach solutions using sodium borohydride ( $\text{NaBH}_4$ ) as the precipitating agent was also investigated in detail. A high silver recovery of  $\geq 98\%$  was achieved under suitable conditions. These findings highlight that ammoniacal thiosulphate leaching in combination with ultra-fine grinding can be used as a suitable and environmentally sound alternative to cyanide leaching and the additives such as EDTA and CMC, and nickel in place of copper can improve the extraction of silver from refractory silver ores.

### 1. Introduction

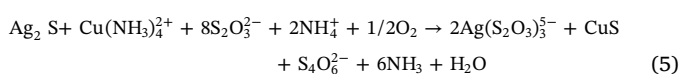
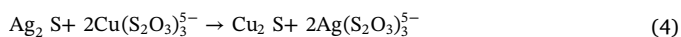
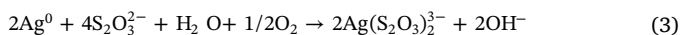
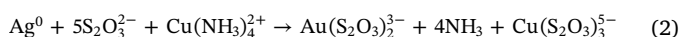
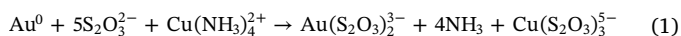
Cyanide is the most extensively used leaching agent for extraction of gold from ores since it forms strong complexes with gold (Marsden and House, 2006). Due to high toxicity of cyanide and, hence, stringent environmental regulations, there has been growing interest in alternative lixivants such as thiosulphate, thiourea, and bisulphide for leaching of gold (Hilson and Monhemius, 2006; Aylmore, 2016a,b). Thiosulphate is often regarded to be the most promising alternative to cyanide due to a number of attributes including its non-toxicity, fast leaching kinetics, relatively lower unit cost, higher selectivity and suitability for certain ores (e.g. preg-robbing ores and copper-rich ores) (Aylmore and Muir, 2000; Zhang and Senanayake, 2016). Thiosulphate leaching suffers from prohibitively high reagent consumption, complexity of reaction chemistry and difficulties in downstream purification and recovery have appeared to adversely affect its industrial

acceptance as an alternative even for those particular ores for which cyanide leaching is essentially unsuitable (Marsden and House, 2006; Grayson, 2007; Zhang and Senanayake, 2016). Notwithstanding this, Barrick has developed a proprietary thiosulphate process, which is currently exploited in a full-scale operation at Goldstrike Mine (Gorain et al., 2016).

Thiosulphate leaching of silver/gold is carried out in the presence of ammonia ( $\text{NH}_3$ ) and cupric copper ( $\text{Cu}^{2+}$ ) as catalyst (Zhang and Senanayake, 2016). Thiosulphate can form strong silver-thiosulphate complexes (e.g.  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ,  $\log K = 13.5$ ) in wide Eh-pH intervals (Muir and Aylmore, 2004). The role of ammonia is to stabilise copper (II) and minimise the decomposition of thiosulphate through the reduction of Cu(II) to Cu(I) (Muir and Aylmore, 2004; Zhang and Senanayake, 2016). The chemistry of the thiosulphate leaching is rather complex as the following reactions (Eqs. (1)–(5)) for the dissolution of gold and silver in ammoniacal copper-thiosulphate system has been

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proposed (Muir and Aylmore, 2004; Rivera et al., 2015):



The presence of some inorganic/organic additives in thiosulphate leaching including ethylenediaminetetraacetic acid (EDTA) (Feng and van Deventer, 2010; Celep et al., 2014; Puente-Siller et al., 2014), carboxymethyl cellulose (CMC) (Feng and van Deventer, 2011a; Xu et al., 2015), phosphate/polyphosphates (Feng and van Deventer, 2011b) and sodium citrate (Puente-Siller et al., 2014) have been tested to reduce the consumption of thiosulphate through complexation ability of these reagents with copper. Alternative leaching systems such as  $\text{O}_2$ - $\text{Na}_2\text{S}_2\text{O}_3$  (pressure leaching), Fe(III)-EDTA- $\text{Na}_2\text{S}_2\text{O}_3$ , Fe(III)-oxalate- $\text{Na}_2\text{S}_2\text{O}_3$ , Ni(II)/Co(II)- $(\text{NH}_4)_2\text{S}_2\text{O}_3$ - $\text{NH}_4$  were also evaluated in which copper was not included in the leaching system (Aylmore, 2016a,b; Deutsch and Dreisinger, 2013a; Gorain et al., 2016). These studies on the alternative reagent systems and additives have focused essentially on gold ores and, to a limited extent, silver sulphide (acanthite).

Refractoriness and treatment of silver ores have received no particular interest in that gold and gold/silver ores have become the focus of attention. Silver occurs in a variety of forms including native silver, sulphides, antimonides, sulphosalts and in solid solution within sulphide minerals (Gasparini, 1984; Samuel, 2002; Zhou et al., 2009; Celep et al., 2009; Zhou, 2010; Celep et al., 2015a, 2015b). This complexity of silver mineralogy complicates the treatment of silver and gold/silver ores (Zhou et al., 2009) with often poor silver extractions compared with gold (Celep et al., 2009, 2015a; Zhou, 2010). Although acanthite ( $\text{Ag}_2\text{S}$ ), the most common silver mineral, responds readily to cyanide leaching, others including pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), proustite ( $\text{Ag}_3\text{AsS}_3$ ) and stephanite ( $\text{Ag}_5\text{SbS}_4$ ) as well as silver bearing copper sulphides (tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ), tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) and enargite ( $\text{Cu}_3\text{AsS}_4$ ) are refractory in character with their markedly low rate and extent of dissolution in cyanide leaching (Samuel, 2002; Zhou, 2010). Zhou (2010) attributed the slow leaching of pyrargyrite to the formation and retarding effect of Ag-Sb or  $\text{Ag}_2\text{S}$  rims on the surface. Acanthite can also occur as finely grained and entirely encapsulated within sulphides (e.g. galena), iron oxides, barite, quartz or other minerals with concomitant low silver extractions (Deutsch, 2012; Celep et al., 2015a, 2015b). Such ores in which silver is locked up within iron oxide, barite or quartz are not particularly liable to chemical pretreatment for exposure of the locked-up silver phases. In this regard, ultra-fine grinding might allow exposure of the encapsulated grains and/or activate refractory silver phases, hence improving silver extraction from such ores (Davey, 2010; Celep et al., 2010; Celep et al., 2015a, 2015b).

The leaching of silver sulphide (refractory sulphides in particular) with thiosulphate solutions has not been researched extensively. Data on extractions from naturally occurring silver sulphide is limited. Recently, some researches have been performed on silver leaching by thiosulphate leaching system. The effects of ethylenediaminetetraacetic acid (EDTA) and ferric complexes such as ferric-EDTA, ferric-oxalate and ferric-citrate as alternatives to the cupric-ammonia catalysed thiosulphate system were studied to improve the silver extraction essentially from silver sulphide (Puente-Siller et al., 2013; Deutsch and Dreisinger, 2013a, 2013b).

One of the main obstacles for industrial exploitation of thiosulphate leaching is the technical problems encountered in solution purification and gold recovery stages (Dai et al., 2013). There have been several

methods suggested for downstream processing of pregnant leach solutions including ion exchange, reductive precipitation, cementation, sulphide precipitation, solvent extraction, electro-winning and ion flotation (Awadalla and Ritcey, 1991; O'Malley, 2002; Aylmore, 2016a,b; Adams, 2016). Although ion exchange appears to be the most promising method and hence, was adopted in a commercial application (Goldstrike mine, Barrick Gold), some technical difficulties associated with ion exchange process were reported (Braul, 2013; Adams, 2016). Therefore, a suitable metal recovery method from thiosulphate leach solutions should be also considered.

Thiosulphate leaching of silver appears to be limited essentially to silver sulphide with complex, refractory silver minerals having received less attention. This comprehensive study was designed to investigate various aspects of thiosulphate leaching of a refractory arsenical silver ore. The ore is essentially double refractory in character since silver occurs as both physically encapsulated silver sulphide and silver-bearing complex arsenic/antimony/base metal minerals/phases. Effect of ultra-fine grinding on the rate and extent of thiosulphate leaching of silver was demonstrated. Response surface methodology (i.e. Box-Behnken design) was adopted to investigate the main and interactive effects of  $\text{Na}_2\text{S}_2\text{O}_3$  (0.2–1 M),  $\text{CuSO}_4$  (0.02–0.2 M) and  $\text{NH}_3$  (0.04–1 M) concentrations on the silver extraction (%). The effects of CMC, EDTA and  $\text{NiSO}_4$  on thiosulphate leaching of silver ore were also investigated to further improve/maximise the extraction of silver. A comprehensive theoretical analysis of potential leaching reactions for those mineral phases identified in the ore was performed. Leaching behaviour of other elements such as As, Fe, Sb, Zn and Pb in the thiosulphate leaching was also demonstrated. Precipitation of silver from thiosulphate leach solutions using sodium borohydride ( $\text{NaBH}_4$ ) under different reaction periods (5–60 min) and  $\text{NaBH}_4$  concentrations (38–132 mM) was also investigated.

## 2. Material and methods

### 2.1. Ore sample

In this study, an arsenical silver ore sample from Turkey was used. The ore sample was subjected to size reduction through crushing in a jaw crusher (–4 mm) and then grinding in a rod mill (–100  $\mu\text{m}$ ). The chemical analysis of the sample (Table 1) was carried out using ICP-ES (Inductively Coupled Plasma-Emission Spectroscopy) after four acids ( $\text{HNO}_3 + \text{HCl} + \text{HF} + \text{HClO}_4$ ) digestion, fire assay (for silver) and X-ray fluorescence (XRF). The ore was determined to contain predominantly  $\text{SiO}_2$  (63.7%) with 1.31% As and 127 g/t Ag. The X-ray diffraction analysis of the sample using a Rigaku X-ray diffractometer (D/Max-IIIC), showed that quartz ( $\text{SiO}_2$ ) is the most abundant phase, followed by barite ( $\text{BaSO}_4$ ) and silicate minerals (Fig. 1).

Ultra-fine grinding of the ore was performed in a laboratory scale

**Table 1**  
Chemical composition of the ore sample used in this study.

Compound	Content (%)	Element	Content (ppm)
$\text{SiO}_2$	63.7	Ag	127
$\text{Al}_2\text{O}_3$	11.7	As	1.31%
$\text{BaSO}_4$	5.44	Zn	7182
$\text{Fe}_2\text{O}_3$	5.19	Pb	7252
CaO	0.73	Sr	491
MgO	0.69	Sb	699
$\text{Na}_2\text{O}$	0.2	Ni	245
$\text{K}_2\text{O}$	4.14	V	86
$\text{TiO}_2$	0.47	Zr	148
$\text{P}_2\text{O}_5$	0.16	U	8
MnO	0.2	Cd	103
$\text{Cr}_2\text{O}_3$	0.068	Ga	13.1
Tot. S	0.99	Tot. C	0.21
LOI	7		

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