



## Influence of potassium hydroxide pretreatment on the extraction of gold and silver from a refractory ore



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### ARTICLE INFO

#### Article history:

Received 12 July 2013

Received in revised form 4 March 2014

Accepted 7 March 2014

Available online 28 March 2014

#### Keywords:

Gold

Silver

Refractory ores

Alkaline pretreatment

Cyanidation

### ABSTRACT

Potassium hydroxide alkaline pretreatment of a refractory gold–silver ore containing 20 g/t Au and 220 g/t Ag was investigated with the purpose to evaluate its effectiveness on the extraction of gold and silver. The presence of antimony minerals such as stibnite ( $\text{Sb}_2\text{S}_3$ ), zinkenite ( $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$ ) and andorite ( $\text{Sb}_3\text{PbAgS}_6$ ) is the main reason for the refractory nature of the ore. Silver occurs as andorite, a Au–Ag alloy, tetrahedrite [ $(\text{Cu},\text{Fe},\text{Zn},\text{Ag})_{12}\text{Sb}_4\text{S}_{13}$ ] and in minor amounts in zinkenite whereas gold is associated with quartz and the antimony minerals. Cyanidation tests of the as-received ore show that the extraction of gold and silver is consistently low (i.e.  $\leq 49.3\%$  and  $\leq 18.7\%$ , respectively) over the leaching period of 24 h. The effects of potassium hydroxide concentrations (0.5–5 mol/L), temperature (20–80 °C) and particle size (5–50  $\mu\text{m}$ ) on the removal efficiency of antimony were investigated. Accompanying the removal of antimony, gold and silver recoveries improved with increases in the KOH concentrations (5 mol/L) and temperature (80 °C), and a decrease in the particle size (5  $\mu\text{m}$ ). Gold and silver extractions during subsequent cyanidation were improved to 87.6% and 94.5%, respectively, corresponding to 85.5% Sb removal by alkaline pretreatment. The antimony removal is also evidenced by the disappearance of stibnite, zinkenite and andorite which formed 4.57 wt.% of the original ore. The residual amount of antimony is due to the presence of unreactive Sb oxide and Pb–Sb sulphate minerals, sphalerite and tetrahedrite in the ore and Sb-bearing Pb sulphate compound(s) that formed during pretreatment. These findings indicate that potassium alkaline leaching can be an effective pretreatment method for refractory antimonial gold–silver ores.

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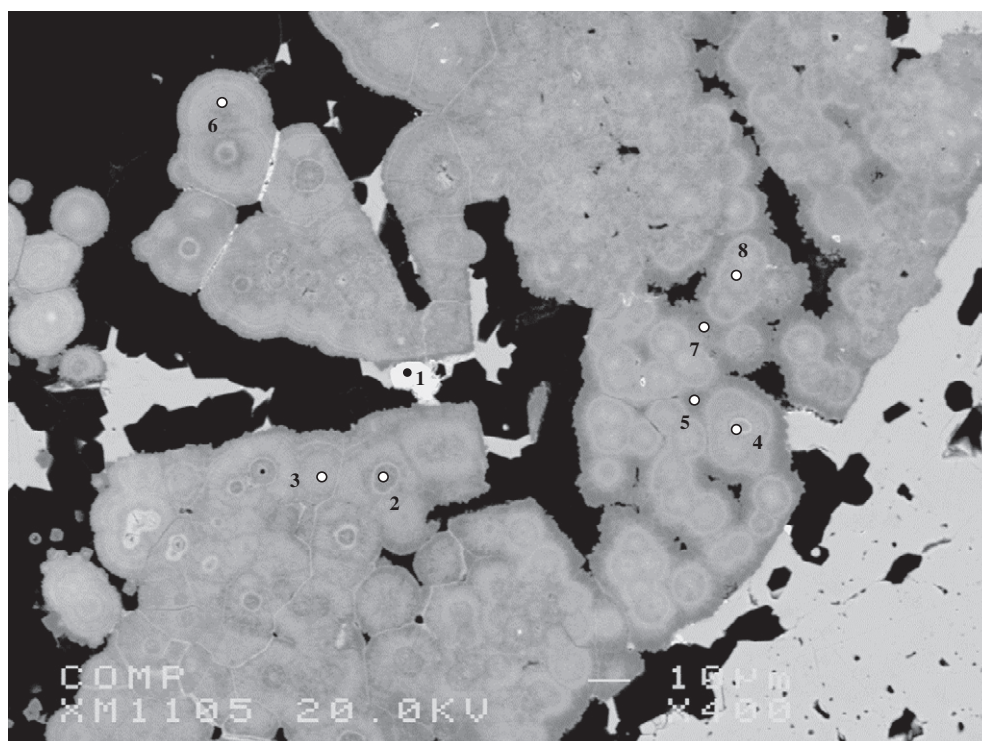
## 1. Introduction

Refractory gold ores which do not respond to direct cyanidation require pretreatment to liberate the contained gold and silver prior to cyanidation so that gold and silver extractions can be improved (La Brooy et al., 1994). Roasting (Dunn and Chamberlain, 1997), pressure oxidation (Gunyanga et al., 1999), biooxidation (Ciftci and Akcil, 2010; Iglesias and Carranza, 1994) and ultrafine grinding (Corrans and Angove, 1991) have been commercially practised to enhance gold recoveries from refractory ores. Another technique is CANMET's Enhanced Leach Process (CELP) developed to treat silver-rich gold ores (Rajala et al., 2011). In this technique, increased gold and silver recoveries are achieved through pre-aeration with lime and lead nitrate addition in order to passivate pyrite. Deschênes et al. (2009) claimed that gold can be effectively extracted from an ore containing aurostibite, several antimony

minerals and pyrrhotite at low cyanide concentrations with the addition of lead nitrate.

An additional practice has been the use of alkaline sulphide leaching as a pretreatment step for the recovery of silver as well as the removal of the hazardous or penalty elements such as As and Sb from the ores and concentrates (Awe and Sandström, 2010; Awe et al., 2010; Baláž and Achimovičová, 2006; Curreli et al., 2009; Ubaldini et al., 2000). We have shown that alkaline sulphide leaching is an effective pretreatment method ahead of cyanide leaching for the extraction of gold and silver from antimonial refractory ores containing sulphide minerals such as zinkenite ( $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$ ) and andorite ( $\text{Sb}_3\text{PbAgS}_6$ ) (Alp et al., 2010; Celep et al., 2011a). In addition, as reported by Anderson and Krys (1993), Ubaldini et al. (2000), Sminčáková and Komorová (2005) and Sminčáková (2009), sodium hydroxide can dissolve antimony from Sb-bearing minerals such as stibnite. Furthermore, Raschman and Sminčáková (2011) studied the kinetics of the reaction between stibnite and  $\text{Na}_2\text{S} + \text{NaOH}$  solutions. Baláž (2000) mentioned that some sulphide minerals such as proustite ( $\text{Ag}_3\text{AsS}_3$ ) and pyrargrite ( $\text{Ag}_3\text{SbS}_3$ ) can be decomposed during the alkaline leach, which makes high silver recovery possible during subsequent cyanidation. Recent

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**Fig. 1.** Backscattered electron image showing a native Au particle (white) measuring about 10  $\mu\text{m}$  in quartz (black) and barite (light grey) matrix with framboidal pyrite (grey) showing concentric zoning due to the presence of Sb. The numbers refer to electron microprobe analyses in Table 1.

studies demonstrated that sodium hydroxide pretreatment is a viable extractive metallurgy technique for the processing of refractory antimonial gold and silver ores containing zinkenite and andorite minerals (Celep et al., 2011b).

Potassium hydroxide (KOH) is the most vigorous alkaline reagent among reagents such as  $\text{NH}_2\text{OH}$ ,  $\text{NaCO}_3$  and  $\text{NaOH}$  (Gupta and Mukherjee, 1990). Although the dissolution behaviour of a low-grade niobium–tantalum ore in a highly concentrated KOH solution to benefit the formation of soluble potassium hexaniobate (Zhou et al., 2005) and the leaching of titanium from ilmenite ore by concentrated KOH solution under atmospheric pressure has been investigated (Liu et al., 2006), no such studies on potassium alkaline pretreatment of antimonial ores containing andorite and zinkenite as the main silver bearing minerals have been reported in the literature.

The Akoluk ore deposit with approximately 1 million tonnes of estimated reserves (Anon, 1993) is located near Ordu in northeastern Turkey. The deposit, hosted by volcanic-sedimentary rocks of the Eastern Pontides, was studied by Tüysüz and Akçay (2000), Yaylalı-Abanuz and Tüysüz (2010) and Ciftci (2000) for its geological and mineralogical characteristics and by Celep et al. (2009) and Alp et al. (2010) for developing optimum metallurgical processing options. Cyanide leaching of the ore consistently resulted in low extraction of gold (49%) and silver (18%) confirming the refractory nature of the ore (Celep et al., 2006). Cyanidation with lead nitrate following ultrafine grinding or roasting of the ore was ineffective in the recovery of gold and silver (Celep et al., 2010a,b,c). It was demonstrated by Celep et al. (2011a,b) that the ore has refractory characteristics due to the association of gold and silver with antimony minerals which necessitated a pretreatment method for improving the gold and silver recoveries.

This study was designed to evaluate alkaline leaching using potassium hydroxide as an alternate pretreatment process to alkaline sulphide or sodium hydroxide leaching techniques. The effect of potassium hydroxide concentrations, temperature and particle size on antimony removal and the gold and silver recoveries were investigated.

## 2. Experimental

### 2.1. Material

The antimony-rich refractory gold–silver ore consisted predominantly of quartz, the illite/kaolinite group of clay minerals and barite with lesser amounts of pyrite, stibnite, sphalerite, zinkenite and andorite (Celep et al., 2009). The antimony sulphides such as andorite ( $\text{Sb}_3\text{PbAgS}_6$ ) and zinkenite ( $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$ ) were some silver and gold carriers (Alp et al., 2010; Celep et al., 2011a).

The samples were crushed and ground by a rod mill. Fine grinding (80% passing size,  $d_{80} = 5 \mu\text{m}$ ) was performed by a laboratory-scale stirred media mill. A Malvern Mastersizer 2000 model laser analyser was used for the particle size analysis. The earlier chemical and mineralogical studies indicated that ore is high grade with 220 g/t Ag and 20 g/t Au (Celep et al., 2009) and contained 52.2%  $\text{SiO}_2$ , 17.1% Ba, 4.7%  $\text{Al}_2\text{O}_3$ , 6.9% S, 1.6% Sb, 1.5% Zn, 1.3%  $\text{Fe}_2\text{O}_3$ , 0.4% Pb, 0.02% As and 0.04% Cu (all in weight percent). Celep et al. (2006, 2009) reported that gold occurring in association with sulphide minerals and quartz had a variable particle size from 1 to 88  $\mu\text{m}$  with the majority being smaller than 3  $\mu\text{m}$ .

### 2.2. Method

The ground samples ( $d_{80} \leq 50 \mu\text{m}$ ) were leached in a 1-L beaker submerged in a water bath to control the leaching temperature (20–80  $^\circ\text{C}$ ) within  $\pm 2 \text{ }^\circ\text{C}$ . The beaker with 200-mL leach solution (KOH) and 70 g ore sample (solids 35% w/vol) was continuously stirred for 2 h. Variable amounts of potassium hydroxide additions in the 0.5–5 mol/L range were tested. Solution samples of 10 mL were taken at regular time intervals and analysed for their Sb contents. At the end of the leaching period after 120 min, solid and liquid phases were separated by filtration and the filtrates were analysed for Sb, Au, Ag, Pb, Zn, Cu and Fe. The residues were air-dried, and analysed to determine the metal recoveries.

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