



Silver sulfide leaching with thiosulfate in the presence of additives Part II: Ferric complexes and the application to silver sulfide ore



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ABSTRACT

Ferric complex alternatives to the cupric-ammonia catalyzed thiosulfate system including ferric-EDTA, ferric-oxalate and ferric-citrate were studied with a silver sulfide rotating disk. Of these complexes, ferric-EDTA and ferric-oxalate were the most promising alternatives. All ferric complexes tested were unreactive towards thiosulfate, but are reduced by sulfides present in the ore. When leaching a silver sulfide ore, the most effective lixivants were ferric-EDTA and the cupric-ammonia thiosulfate systems. None of the thiosulfate alternatives were able to recover as much silver as cyanide leaching, likely due to the presence of other silver minerals which may not be amenable to thiosulfate leaching. Although less silver was recovered, less than 1% of mercury in the ore was leached by thiosulfate complexes compared to 50% mercury recovery by cyanide.

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1. Introduction

The use of thiosulfate leaching processes is very promising for the treatment of silver ores; however the difficulties associated with the cupric-tetraammine additive including excessive thiosulfate oxidation and high reagent costs has led to the proposal of alternative additives such as ferric complexes. In this second part of a study on thiosulfate leaching of silver sulfide, alternatives to cupric-tetraammine are investigated including ferric-EDTA, ferric-oxalate and ferric-citrate. Of these alternatives, ferric-oxalate and ferric-EDTA are the most promising alternatives although both require a higher molar concentration than the cupric complex to achieve reasonable leaching rates. The results of the pure silver sulfide leaching studies from Part I of this work (<http://dx.doi.org/10.1016/j.hydromet.2013.03.012>) with cupric-tetraammine complexes and this study with ferric alternatives are then applied to leaching a silver sulfide ore from Yanacocha.

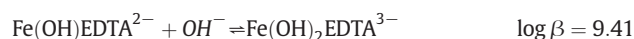
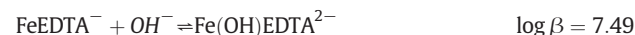
2. Background and literature review

Multiple additives and complexing agents were considered for use with the thiosulfate leaching of silver sulfide. Before discussing the application of these chemicals to silver leaching, the chemistry of these reagents will be briefly reviewed.

2.1. Ferric-EDTA

Ethylenediaminetetraacetic acid (EDTA, IUPAC: 2,2',2'',2'''-(Ethane-1,2-diylidinitrilo)tetraacetic acid, C₁₀H₁₆N₂O₈ or C₁₀H₁₂N₂O₈⁴⁻) has been suggested both as an additive to the cupric-ammonia thiosulfate system (Feng and van Deventer, 2010b) and as a complexing agent for ferric (Heath et al., 2008; Zhang et al., 2005). EDTA can complex most multivalent heavy metal ions as a hexadentate ligand (Feng and van Deventer, 2010b). Ferric-EDTA and cupric-EDTA are both stable complexes.

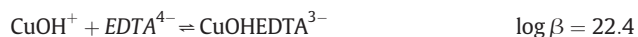
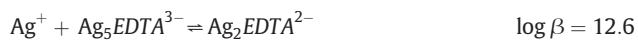
Depending on the pH, the dominant ferric-EDTA complex may be FeEDTA⁻, Fe(OH)EDTA²⁻ or Fe(OH)₂EDTA³⁻ (Hutchison and Cheng, 2004). Near pH values of 7.5–9.5, Fe(OH)EDTA²⁻ will dominate while increasing the pH past 9.5 will increase the prevalence of Fe(OH)₂EDTA³⁻. The reactions for the complexation of iron by EDTA are (stability constants from (Martell and Smith, 1989)):



The mixed potential of solution will decrease as the pH increases and hydroxides are added to the ferric-EDTA complex. Increasing the pH too much will result in the precipitation of iron hydroxides. Other relevant complexation reactions for silver and copper with EDTA are (Anderegg, 1992; Martell and Smith, 1989):



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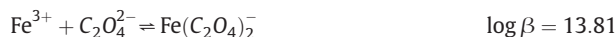


Copper–EDTA complexes are very stable, so there is potential for excess EDTA in solution to leach copper contained in the ore. The dissolution of oxidation products from sulfide minerals by EDTA has been previously observed (Feng and van Deventer, 2010a). Depending on the recovery step (electrowinning, cementation or ion exchange) implemented after leaching, this may or may not be a concern (Abbruzzese et al., 1995). Silver–EDTA complexes are less stable than silver thiosulfate complexes, and there is a large amount of thiosulfate in solution, so thiosulfate complexes are thermodynamically expected as discussed in Part I of this work.

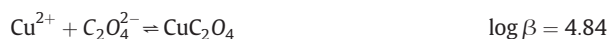
2.2. Ferric–oxalate

Oxalate (IUPAC: ethanedioate, $\text{C}_2\text{O}_4^{2-}$) is another ligand that has been proposed for the complexation of ferric in solution (Chandra and Jeffrey, 2005). The oxalate complex acts as a bidentate ligand complexing ferric in one of three forms: $\text{Fe}(\text{C}_2\text{O}_4)^+$, $\text{Fe}(\text{C}_2\text{O}_4)_2$ or $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. Based on the work of Chandra and Jeffrey, the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ complex is stable in the thiosulfate solution and minimizes the concentration of ferrous in solution. This complex is the dominant complex at a molar ratio of 3 oxalate molecules to 1 ferric in solution.

The complexation of oxalate with ferric reduces the activity of ferric and its tendency to oxidize thiosulfate in solution (Chandra and Jeffrey, 2005). The reactions for the complexation of iron by oxalate are (stability constants from Chandra and Jeffrey):



Other relevant reactions for the complexation of silver and copper by oxalate are (stability constants from (Martell and Smith, 1989)):



From the stability constants, it can be seen that silver and copper–oxalate complexes are not as stable as iron oxalate complexes (Martell and Smith, 1989; Yadava et al., 1976). The trioxalate–ferric complex is very stable, so a molar ratio of 3 oxalate to 1 ferric was used for leaching experiments. Chandra and Jeffrey (2005) also observed that ferric–oxalate is relatively stable in thiosulfate solutions. The reason for the stability of ferric–oxalate in thiosulfate solutions was proposed to be due to the kinetically slow reactivity of ferric–oxalate, even in the presence of dissolved oxygen.

2.3. Ferric–citrate

Citrate (IUPAC: 2-hydroxypropane-1,2,3-tricarboxylic acid, $\text{C}_6\text{H}_5\text{O}_3^{3-}$) is another iron complexing agent that can stabilize ferric in solution (Silva et al., 2009). Although published information on the use of EDTA and oxalate for the stabilization of ferric in gold/silver leaching solutions

was found, no information on the use of citrate was available. The ferric–citrate complexes can take many forms depending on the ratio of ferric to citrate and solution pH; however the most common species exist in a stoichiometric ratio of 1:1 (Silva et al., 2009). For ferric to citrate ratios in the range of 1:1 to 1:2, Silva et al. determined the dominant ferric–citrate complex using electrospray ionization mass spectrometry. In this case, the dominant complex was the trinuclear $[\text{Fe}_3\text{O}(\text{C}_6\text{H}_4\text{O}_7)_3\text{H}_3]^{2-}$ complex; other researchers have found the mononuclear ferric complex predominant (Martell and Smith, 1989).

Relevant complexation reactions for iron, copper and silver with citrate are complicated by the potential for citric acid to act as up to a tetrabasic complex (Silva et al., 2009). In acidic solutions with comparable amounts of citrate to ferric, it is reasonable to treat citrate as a tribasic ligand. Complexation reactions and stability constants are included for mononuclear complexes assuming that the citrate ligand is a tribasic complex (Martell and Smith, 1989). Silver citrate is only soluble in concentrated citric acid solutions (and can precipitate out over time), so is not included in the list (Djokić, 2008).



Pyrophosphate ($\text{P}_2\text{O}_4^{4-}$) was another complexing agent considered for the stabilization of ferric in solution as it is often grouped with citrate, oxalate and EDTA. However, initial tests demonstrated that ferric–pyrophosphate is not soluble at a pH where thiosulfate is stable so this ligand was not used in further tests.

2.4. Application of ferric complexes to thiosulfate leaching

The use of ferric–EDTA to treat gold/silver ores has been proposed by a number of researchers with the primary advantage being slower thiosulfate degradation compared to the cupric–ammonia system (Heath et al., 2008; Zhang et al., 2005). In the study by Heath et al., ferric–EDTA leaching was carried out at pH 7 with 50 mM ammonium thiosulfate (ATS) and between 1 and 10 mM ferric–EDTA. Zhang et al. used 0.3 M sodium thiosulfate with 10 mM thiourea and 2–3 mM ferric–EDTA at a pH between 6 and 7. Gold recoveries using ferric–EDTA exceeded 90% after 8 h or less. In the study by Heath et al., the addition of sulfide minerals (pyrite and pyrrhotite) decreased gold leaching rate for both ferric–EDTA and ferric–oxalate.

Ferric–oxalate is another potential oxidant that has been suggested to replace the cupric–ammonia system due to decreased reactivity with thiosulfate (Chandra and Jeffrey, 2005; Heath et al., 2008). Using ferric–oxalate with a molar ratio of 1 ferric to 2.5–3 oxalate, gold was leached effectively with only limited thiosulfate consumption (less than 2% after 5 h).

The possibility of ferrous oxalate dihydrate precipitation in a reductive environment was pointed out by Chandra and Jeffrey (2005). Increasing the amount of oxalate to a molar ratio of 1:10 was enough to prevent this occurrence. In this case, the ferrous oxalate complex was re-oxidized by air to form the ferric–oxalate complex, although this reaction was slow. As ferric–oxalate was shown to be relatively unreactive towards thiosulfate, using this excessive amount of oxalate would likely only be necessary for highly reductive ores (Chandra and Jeffrey, 2005).

When equivalent molarities of ferric–EDTA and ferric–oxalate were used to leach metallic gold by Heath et al. (2008), ferric–oxalate initially leached gold faster than ferric–EDTA. This was observed even under comparable solution potentials. At very long run times in excess of 48 h, ferric–EDTA was sometimes more effective than ferric–oxalate. Optimizing the amount of ferric species, ATS, thiourea additions and pH seem critical to the effective leaching gold using both ferric–EDTA and ferric–oxalate.

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