



Modeling of selenium and tellurium removal from copper electrowinning solution



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ABSTRACT

In this study, the kinetics of selenium and tellurium reduction by cuprous ions were reviewed and a comprehensive model capable of predicting the rate constants for various Cu^{+2} - H_2SO_4 compositions and temperatures is presented. The rate constant data were fitted to the relationship: $\ln k_1 = (A + \frac{B}{T}) + (C + D \times \ln [\text{H}_2\text{SO}_4]) + (E + F \left(\frac{[\text{Cu}^{2+}]^{0.5}}{1 + [\text{Cu}^{2+}]^{0.5}} \right))$, where k_1 is in $\text{M}^{-1} \text{s}^{-1}$ and $[\text{Cu}^{2+}]$ and $[\text{H}_2\text{SO}_4]$ are in molar at temperature T (K), and A to F are empirical constants. The model was validated using different rate constant data points obtained during the reduction of Se^{VI} and Te^{VI} under different solution conditions. The rate constant k_1 given by the comprehensive model was within a $\pm 3.3\%$ for Se^{VI} and $\pm 5.1\%$ for Te^{VI} reduction reactions compared to the rate constant determined using the experimental data. The model was used to estimate the selenium and tellurium reduction reaction times under Vale's (Sudbury, Canada) Electrowinning Department (ED) plant conditions. As a result, potential factors that may affect the selenium and tellurium removal rate at the ED plant of Vale were proposed and discussed.

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1. Introduction

Dissemination of selenium and tellurium in pyritic ores and many other sulfide minerals results in downstream contamination of pregnant leach solutions and electrolytes in hydrometallurgical treatment of sulfide ores, concentrates and residues. The selenium and tellurium content dissolves in the form of $\text{Se}^{\text{IV/VI}}$ and $\text{Te}^{\text{IV/VI}}$ species during acid pressure oxidation leaching, resulting in a contaminated copper sulfate solution (Morrison, 1963; Qin, 2005). Selenium and tellurium must be removed from the leach solution before copper electrowinning to prevent contamination of the copper cathode (Cooper, 1985). In an effort to reduce the detrimental effects of selenium and tellurium, it has been of great interest to remove selenium and tellurium from contaminated solutions to lower levels than allowed in environmental regulations, product specifications or process requirements. Contamination of copper metal by selenium and tellurium adversely affects the annealability and the recrystallization temperature of electroplated copper. For instance, wire bars produced from cathodes with selenium content between 6 and 10 ppm contained cracks (Charles and Hannaert, 1970). Tellurium has a greater adverse effect on annealability of copper than selenium (Cooper, 1971). Therefore, the total combined concentration of tellurium, selenium and bismuth must be kept to less than 3 ppm in Grade 1 Electrolytic Copper Cathode (ASTM B115-00,

2004) and therefore must be maintained well below 1 mg/L in the electrowinning electrolyte to achieve this level of purity.

The selenium and tellurium content of the solution may be reduced into insoluble precipitates of copper selenides and tellurides using cuprous ion. Cuprous ion is used as a reducing agent in hydrometallurgical applications and can be specifically used to remove selenate (Se^{VI}), tellurate (Te^{VI}), selenite (Se^{IV}) and tellurite (Te^{IV}) from solutions containing cupric ion. In addition to cuprous ion, metals with reduction potentials below those of $\text{Se}^{\text{VI/IV}}$ and $\text{Te}^{\text{VI/IV}}$ or $\text{Se}^{\text{IV/0}}$ and $\text{Te}^{\text{IV/0}}$ couples may also have the thermodynamic possibility of reducing Se^{VI} , Se^{IV} , Te^{VI} and Te^{IV} to elemental selenium (Se^{0}) and elemental tellurium (Te^{0}) or selenide (Se^{2-}) and telluride (Te^{2-}). For example, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple can reduce $\text{Se}^{\text{VI}}/\text{Te}^{\text{VI}}$ to $\text{Se}^{\text{IV}}/\text{Te}^{\text{IV}}$. The couples Cu/Cu^{2+} , $\text{Cu}^{+}/\text{Cu}^{2+}$ and $\text{SO}_2/\text{HSO}_4^-$ have the thermodynamic ability to reduce selenate/selenite to elemental selenium and tellurate/tellurite to elemental tellurium, and the base metal couples of Fe/Fe^{2+} , Ni/Ni^{2+} and Zn/Zn^{2+} can further reduce elemental selenium or tellurium to hydrogen selenide or telluride, respectively. Nevertheless, in cupric-bearing solutions, couples with electrochemical potentials below that of the cupric-copper couple will cement elemental copper as well. Ladriere (1973) demonstrates that copper metal does not directly reduce Se^{VI} species to Se^{IV} while this reduction is possible with cuprous ion. The distinct advantage of using cuprous as a reducing agent rather than using metals such as Fe, Co, Ni and Zn is that cuprous ion adds no impurities to copper electrowinning electrolytes, which consists primarily of cupric cations, while other metals as reductants would dissolve to form their respective metal cations.

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Reduction of selenium and tellurium ions by sulfur dioxide gas is one alternative to using cuprous ion. However, the reduction of selenium and tellurium ions with cuprous is an environmentally cleaner process whereas SO_2 gas poses a hazard in the workplace. The precipitation of Se^{VI} and Te^{VI} with sulfur dioxide requires an autoclave and is favored at low acidity, while $\text{Se}^{\text{IV/VI}}$ and $\text{Te}^{\text{IV/VI}}$ reduction reactions are favored at high acidities (Stewart et al., 1985). In contrast with SO_2 gas, the reduction reaction with cuprous ions occurs effectively at low pH, allowing the refined solution to be transferred to the copper electro-winning tankhouse without further pH adjustment and at atmospheric pressure and temperatures near 100°C .

The disadvantages of using cuprous ions as the reductant are the slow reaction kinetics for the reduction of Se^{VI} and Te^{VI} with cuprous ions, the high air sensitivity of cuprous ions and the low saturated concentrations of cuprous ions in solution. Vale's Electrowinning Department (ED) plant in Sudbury, Canada (Stewart et al., 1985), Naoshima's smelter and refinery in Kagawa, Japan (Shibasaki et al., 1992), Freeport's refinery in El Paso, USA (Wang et al., 2003) and the Luilu metallurgical plant in Katanga, Congo (Charles and Hannaert, 1970) are examples of industrial plants where a process for selenium and tellurium removal in the presence of copper metal (cuprous ion) from acidic copper sulfate solution is practiced. The Luilu plant (Katanga Mining), as the world's largest cobalt producer, was the first operating plant to use cuprous ions to remove selenium and tellurium from copper electrolyte solution (Charles and Hannaert, 1970). Considering the advantages of cuprous ions and the lower reagent costs associated with it, sulfur dioxide has been replaced with cuprous in the selenium and tellurium removal circuit at the ED plant of Vale (Canada) since 1976. Since then, Vale has used cuprous sulfate to remove selenium and tellurium impurities from copper sulfate-sulfuric acid electrolyte prior to electro-winning (Stewart et al., 1985). In this plant, selenium and tellurium are dissolved during high pressure oxidative leaching of a copper sulfide residue to give $\text{Se}^{\text{IV/VI}}$ and $\text{Te}^{\text{IV/VI}}$ species into the electrolyte (Qin, 2005). The $\text{Se}^{\text{IV/VI}}$ and $\text{Te}^{\text{IV/VI}}$ species are reduced in the presence of copper metal and copper sulfate solution, which forms cuprous sulfate, to form insoluble copper selenides/tellurides. A long reaction time was reported as the main drawback of the process. Further details of the Vale (Canada) selenium and tellurium removal circuit are discussed in Section 2.3.

1.1. Research objectives

Selenium and tellurium rates of removal are a function of the selenium and tellurium concentration, cuprous concentration, solution acidity, temperature and cupric concentration (Mokmeli et al., 2013, 2014a). Accordingly, the objective of this study is to predict the removal rates of selenium and tellurium under different solution conditions. This will be accomplished by suggesting a comprehensive model capable of predicting the rate constants for various Cu^{+2} - H_2SO_4 compositions and temperatures. Subsequently, the model will be validated using several experimental rate constants obtained during the reduction of Se^{VI} and Te^{VI} with cuprous under different solution conditions. By knowing the rate constant k_1 under different acidities, temperatures and cupric concentrations it becomes possible to estimate the residence time needed for the removal of the selenium and tellurium using the integrated form of the rate laws (see Section 2.2.2, Eqs. (7) and (8)).

2. Theoretical background

2.1. Thermodynamics of selenium and tellurium removal

Superimposed Eh–pH diagrams of Se–Cu– H_2O and Te–Cu– H_2O at 100°C in acidic solution, ($\text{Se} = 10^{-3}$ and $\text{Te} = 3 \times 10^{-4}$ molar scale) are depicted in Fig. 1. Selenium and tellurium activities for these diagrams were chosen to simulate a typical impure copper electro-winning solution composition. Dashed lines and italic fonts are used to represent the selenium species while solid lines and regular fonts are used for the tellurium species.

According to the diagram, in highly acidic solutions ($0 < \text{pH} < 2$), inorganic Se^{VI} , Se^{IV} , Te^{VI} and Te^{IV} mainly exist as biselenate (HSeO_4^-), selenious acid (H_2SeO_3), telluric acid (H_6TeO_6) and telluryl ion ($\text{TeO}(\text{OH})^+$), respectively. From this diagram, a plausible reduction sequence for selenate by cuprous ion in a pH range of 0 to 1 likely has the order: $\text{HSeO}_4^- \rightarrow \text{H}_2\text{SeO}_3 \rightarrow \text{Se} \rightarrow \text{CuSe} \rightarrow \text{Cu}_2\text{Se}$. Similarly, the sequence for the reduction of tellurate at low pH and $T = 100^\circ\text{C}$ is likely: $\text{H}_6\text{TeO}_6 \rightarrow \text{TeO}(\text{OH})^+ \rightarrow \text{Cu}_2\text{Te}$. The mechanism of the Se^{VI} and Te^{VI} reduction to lower oxidation states may consist of a number of electron transfer steps to form short lived intermediate species. At higher pH, the reduction sequence of tellurate may occur through reduction of $\text{TeO}_2(\text{s})$.

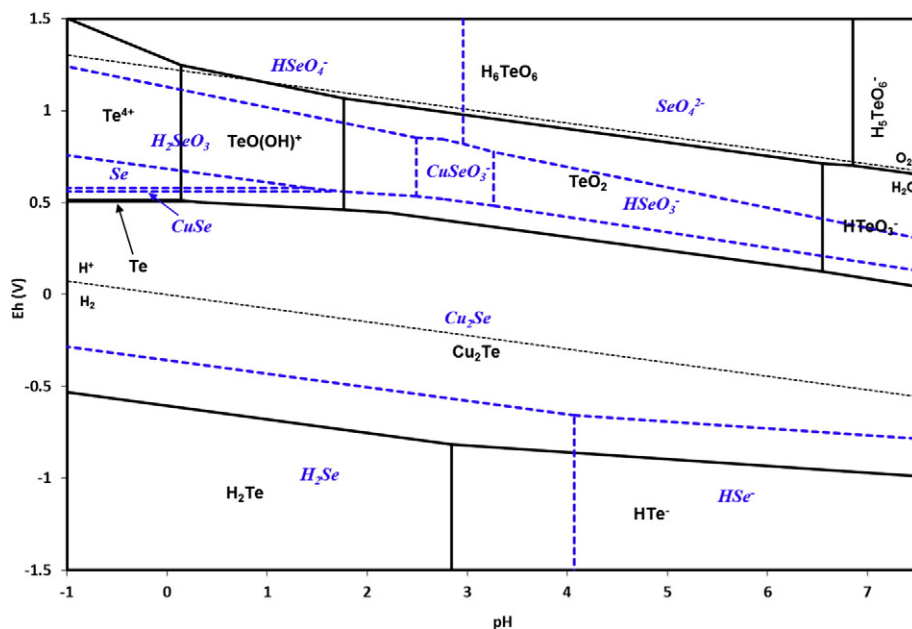


Fig. 1. Superimposed Eh–pH diagrams of Se–Cu– H_2O and Te–Cu– H_2O at 100°C and ionic activities of $\text{Se} = 10^{-3}$ M, $\text{Te} = 3 \times 10^{-4}$ M, Cu ions = 0.8 M.

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