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Thermodynamics and kinetics study of tellurium removal with cuprous ion

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ABSTRACT

The chemistry and kinetics of the removal of tellurium from copper sulphate-sulphuric acid solution by cuprous ion reduction and precipitation were studied. The Te^{VI} reduction reaction order with respect to cuprous and tellurium concentration was investigated at an acidity range of 10–100 g/L H_2SO_4 and at temperatures of 75 °C–95 °C. The reduction reaction mechanism, a suggested rate determining step and a rate law were offered accordingly for reduction of Te^{VI} with cuprous. The kinetics fit the simple rate equation of $\frac{-dTe^{VI}}{dt} = k_1[Cu^+][Te^{VI}]$. A plausible Te^{VI} reduction with cuprous was suggested via slow reduction of H_6TeO_6 to $TeO(OH)^+$ followed by faster reduction of $TeO(OH)^+$ to lower tellurium oxidation states. The rate constant k_1 was calculated at different sulphuric acid concentrations (10, 15, 50, 75, 100 g/L) at T = 95.2 °C. Increasing solution acidity significantly increased the tellurium reduction reaction rate. An empirical correlation of $k_1 = 0.0297 \times [H_2SO_4]^{1.35}$ was found between the rate constants and the sulphuric acid concentration over the range of $10\ g/L < [H_2SO_4] < 100\ g/L$. An activation energy of 70.9 kJ/mol for k_1 was calculated by varying the temperature from 75 to 95 °C.

1. Introduction

The presence of tellurium in copper–sulphide ores and concentrates results in down-stream contamination of leach solutions and electrolytes in hydrometallurgical treatment of copper minerals, copper sulphide residues and copper anode slimes. It was reported that 30–40 percent of the tellurium in copper matte smelting finds its way into the blister copper and finally to the copper anode slimes (Cooper, 1971). Anode slimes usually contain copper, nickel, selenium, tellurium, gold, silver and trace amounts of platinum group metals. The copper and tellurium content of the slime may vary from 3 to 35 percent and 0.5 to 8 percent respectively (Morrison, 1963). Copper, selenium and tellurium need to be separated from the slimes prior to precious metal extraction. In most cases, copper and nickel are removed by oxidation and sulphuric acid leaching (Morrison, 1963). The tellurium content of the copper sulphide residues and copper anode slimes dissolves in the form of $Te^{IV/VI}$ species during acid pressure oxidation leaching resulting in a contaminated copper sulphate solution (Morrison, 1963; Qin, 2005). Tellurium must be removed from the leach solution before copper electrowinning to prevent contamination of the copper cathode.

As a practical example, at Vale's Copper Cliff Nickel Refinery, nickel is recovered from nickel matte using the INCO Pressure Carbonyl (ICP) process. The resulting ICP residue which contains copper (55–60%), nickel (6–10%), cobalt (4–8%), selenium (0.06–0.1%), tellurium (0.06–0.1%) and precious metals (41 tons/day) is pressure leached in two stages. In the first stage nickel, cobalt and iron are leached under non-oxidative conditions at 150 °C, 100–200 g/L H_2SO_4 and 5.6 kg/cm^2 steam pressure. In the second stage copper, selenium and tellurium are oxidatively dissolved from the first stage leach residue. After solid/liquid separation, the solution is forwarded to the selenium and tellurium removal circuit. The solution passing to the removal circuit has a typical composition of 100 g/L copper sulphate, 125 g/L sulphuric acid, 10 g/L Ni, 8 g/L Co, 7 g/L Fe and 40–100 ppm Se and 20–60 ppm tellurium (Stewart et al., 1985). The $Te^{IV/VI}$ species are reduced in the presence of copper metal to form insoluble copper tellurides. Black particles of copper telluride (as well as copper selenide) are settled and collected in the bottoms of the ageing towers and the purified copper sulphate solution (low in selenium and tellurium) enters the electrowinning circuit to produce copper cathode.

Cathode contamination is the principal factor affecting the quality of copper. Contamination of copper metal by tellurium adversely affects the physical properties of electroplated copper such as annealability. The detrimental effect on the annealability of copper metal is increasingly affected by the following elements in the order of: tellurium > selenium > bismuth > antimony > arsenic (Cooper, 1985). 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

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accordingly must be maintained much lower than 1 mg/L in the electrowinning electrolyte. In addition to being harmful impurities in copper cathode, tellurium is a valuable by-product of electrolytic copper refining and anode slimes that may be recovered. It is thus of interest to investigate effective methods to extract tellurium from the copper bearing solutions prior to copper metal recovery.

Copper metal or cuprous ion may be used to remove tellurium ion species in cupric-bearing solutions. Vale's CRED 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 of tellurium and selenium removal in the presence of copper metal (cuprous ion) from acidic copper sulphate solution are practised. It is well known that under these conditions, copper metal and cupric sulphate react to form cuprous sulphate solutions (Mokmeli et al., 2012). Pressure reduction of tellurium ions with sulphur dioxide is also practised (Western Platinium Ltd, South Africa) to separate tellurium from the copper-tellurium acid leach solution (Lottering et al., 2012). Sulphur dioxide may be used to remove impurities in higher oxidation states such as selenate and selenite and tellurate and tellurite from solutions containing cupric ions. It was shown by Hamada (1961) that H^+ ions act as a negative catalyst in the reduction of tellurious acid in a sulphuric acid medium. Hence, tellurite may be reduced by sulphur dioxide in very weak acid solutions. Morrison (1963) showed that the reduction of Te^{IV} and Te^{VI} with sulphur dioxide is inhibited by adding sulphuric acid such that precipitated tellurium percentage decreased from almost 100% at $pH = 6$–20% at $pH = 0.5$. The precipitation of Te^{VI} with sulphur dioxide requires an autoclave. A partial pressure of 45–50 psi SO_2 and a temperature of 105–120 °C can precipitate tellurium as Cu_2Te at low concentration of sulphuric acid (Jennings et al., 1969; Morrison, 1963). The mechanism for the reduction of tellurium with sulphur dioxide in the presence of cupric ion is not clearly understood. The precipitate appeared to be cuprous telluride with a minor amount of metallic copper (Morrison, 1963). Based on observations of produced copper metal, it was suggested by Wang et al. (2003), that it is probable that the SO_2 reduced the cupric to cuprous and then the cuprous disproportionated to copper metal and cupric. Subsequently, the tellurium would be cemented on to the surface of the fine copper particles. However, this mechanism wasn't proven and a more likely mechanism involves the reduction and precipitation of tellurium species with the cuprous ions followed by direct reduction of cupric and cuprous to copper metal by SO_2 gas. Direct reduction of $Te^{VI/IV}$ and $Se^{IV/VI}$ with cuprous rather than sulphurous acid was also suggested by Newman et al. (2004) in the selenium and tellurium removal circuit of Stillwater. For the Stillwater base metal refinery process, selenium and tellurium are removed by pressure feeding of the sulphurous acid (mixture of SO_2 gas and water) into a reactor containing a copper pregnant leach solution with selenium and tellurium ions.

The reduction of tellurium ions with cuprous is an environmentally clean process whereas SO_2 gas may result in contamination of the workplace caused by piping leaks (Stewart et al., 1985), the reduction reaction effectively occurs at low pH (refined solution may transfer to copper electrowinning tank house without further acidity adjustment), atmospheric pressure and low temperature.

The kinetics of reduction of Te^{VI} and Te^{IV} in the presence of copper metal and with cuprous is not well understood. Few studies are referenced (Jennings et al., 1969; Shibasaki et al., 1992) on the kinetics of reduction of tellurate in the presence of copper metal, but as will be shown, similar to selenate, tellurate reduction most likely occurs homogeneously by reacting with cuprous ion rather than reacting directly on the surface of the copper metal. It appears that there are no studies on the mechanism and kinetics of the tellurate reduction reaction with cuprous ion. It is therefore an objective of this research to investigate the Te^{VI} and Te^{IV} reduction reaction kinetics with cuprous ion in acidic solution and identify factors enhancing the removal rate. In this study, the chemistry and kinetics of tellurium removal by cuprous ion precipitation and the effects of acidity and temperature on the removal rate were investigated.

1.1. Tellurium chemistry

Tellurium, a silvery-white semimetal, bears a definite resemblance to selenium and sulphur in many of its properties. Tellurium, like sulphur and selenium, readily forms oxides which can be hydrolyzed to produce oxyacids (Dutton and Cooper, 1966).

Tellurium has several oxidation states: telluride (Te^{2-}), Te^-, elemental tellurium, Te^{II}, Te^{IV}, Te^V and Te^{VI}; Te^{II} and Te^V are unstable states. In addition, however, tellurium can exist in the oxidation states of I and III, as well as fractional oxidation states but there are uncertainties regarding the existence and the thermodynamic stability of these species (Holleman and Wiberg, 2005).

The differing properties of selenium and tellurium in aqueous solution are based on differences in the relative ease of oxidation and reduction of their various valence states, their stability and differences in the solubility of their respective oxides, oxyacids and salts. For instance, in aqueous solution, tetravalent tellurium passes through a minimum solubility in water at pH 4.5 (solubility 6.3×10^{-6} mol/L TeO_2 at 25 °C) whilst tetravalent selenium is freely soluble throughout the pH range 0–14. Te^{IV} is relatively soluble in acid media, sparingly soluble in neutral media, and soluble in alkaline media. Tellurium is soluble as tellurite and bitellurite ions in alkaline media but hydrolyzes and precipitates as tellurium dioxide or its hydrated form, H_2TeO_3 on acidification.

Most tellurium-selenium separation processes are based on this property (Dutton, 1971). If the neutralisation of sodium tellurite is carried out near the boiling point, a cruddy precipitate of tellurous acid, H_2TeO_3, is first formed; this soon changes to crystalline tellurium dioxide. The product is white when it is pure. At lower temperatures, transformation from tellurous acid to tellurium dioxide may not take place (Dutton, 1971)

There have been disputes over the aqueous chemistry of tellurium since tellurium speciation has been investigated. Deltombe et al. (1956) were the first to publish an Eh-pH diagram for the system Te-H_2O at 25 °C. Aqueous species present in the Deltombe diagram included H_2TeO_4, $HTeO_4^-$, TeO_4^{2-}, Te^{4+}, $HTeO_2^+$, $HTeO_3^-$, TeO_3^{2-}, Te_2^{2-}, H_2Te, HTe^- and Te^{2-}. It was found later that the known Te^{VI} species are not H_2TeO_4, $HTeO_4^-$ and TeO_4^{2-} and simple tetrahedral telluric acid or simple tetrahedral tellurate anions do not exist. Andersson et al. (1981) confirmed the octahedral, monomeric structure of telluric acid in the crystal form and aqueous solution. The Te-OH distance found in solution is somewhat longer than those in crystals, which indicates that Te-OH bond is slightly weaker in solution than in the solid state (Andersson et al., 1981). In other words, Te^{VI} does not form a simple tetrahedral MO_4^{2-} ion in contrast with selenic and sulphuric acid which exist only in the tetrahedral form. Telluric acid formulas, then, may be written as H_6TeO_6 or $Te(OH)_6$. Telluric acid is very soluble in water (about 2 mol/L) (Deltombe et al., 1956). Only the first three dissociation constants of the acid are known. The values recommended for the first three dissociation constants of telluric acid have been estimated as: $K_1 = 2 \times 10^{-8}$, $K_2 = 1 \times 10^{-11}$, and $K_3 = 3 \times 10^{-15}$ (Dutton and Cooper, 1966).

Tellurium(V) species are very short lived intermediate species. Four different Te^V oxoradicals are formed in aqueous solution: $H_2TeO_4^-$, TeO_3^-, $HTeO_4^{2-}$ and TeO_4^{3-} (Klaening and Sehested, 2001). Te^V species may be formed by reduction of telluric acid, bitellurate and tellurate or oxidation of bitellurite and tellurite. For instance, TeO_3^-, $HTeO_4^{2-}$ and TeO_4^{3-} are formed by reduction of H_6TeO_6, $H_5TeO_6^-$ and $H_4TeO_6^{2-}$ respectively. $HTeO_4^{2-}$ and TeO_4^{3-} are the dominant species in strongly alkaline solutions.

Te^{+4}, $TeO(OH)^+$ or $H_3TeO_3^+$, TeO_2, H_2TeO_3, $HTeO_3^-$ and TeO_3^{2-} are the main Te^{IV} species in aqueous solution (McPhail, 1995). Te^{4+} is limited to very low pH (depending on the differences at $\Delta G^0{}_f$ it may