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Speciation of the H_2SO_4–$Fe_2(SO_4)_3$–$FeSO_4$–H_2O system and development of an expression to predict the redox potential of the Fe^{3+}/Fe^{2+} couple up to 150 °C

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ABSTRACT

A thermodynamic model is developed and shown to reliably simulate the speciation of the quaternary H_2SO_4–$Fe_2(SO_4)_3$–$FeSO_4$–H_2O system through a wide range of solution compositions and temperatures (25 °C–150 °C). The main species involved (including H^+, Fe^{2+}, Fe^{3+}, SO_4^{2-}, HSO_4^-, $FeHSO_4^+$, $FeSO_4°$, $FeHSO_4^{2+}$, $Fe(SO_4)_2^-$, $FeSO_4^+$, Fe_2O_3 and H_2O) were investigated, and their thermodynamic data were collected and critically assessed to evaluate their activity coefficients and equilibrium constants. Results show that the species distribution depends highly on the initial total amount of iron, acidity, nominal Fe^{3+}/Fe^{2+} ratio and temperature. Modeling results also reveal that most of the Fe(III) is distributed as complexes or precipitates and the free Fe^{3+} accounts for only a minor percentage, whereas a large amount of Fe(II) exists in the form of free Fe^{2+}, with the rest dissolved as complexes. Moreover, based on the model results, the temperature dependence of the real Fe^{3+}/Fe^{2+} ratios and their activity coefficient ratios was subsequently obtained and employed to systematically study the redox potential of the Fe^{3+}/Fe^{2+} couple. The redox potentials predicted by the model increase with the nominal Fe^{3+}/Fe^{2+} ratio and temperature when the nominal Fe^{3+}/Fe^{2+} ratios are 10:1, 100:1 and 1000:1, with its values in the range of 736–956 mV (all potentials in the present study are quoted with respect to the Standard Hydrogen Electrode at 25 °C) from 25 °C to 150 °C in the studied acidic iron sulfate solutions. At a nominal Fe^{3+}/Fe^{2+} ratio of 1:1, the predicted potentials are relatively stable with respect to temperature, typically between 671 mV and 679 mV, because the real Fe^{3+}/Fe^{2+} ratio in solution is much lower for such a condition. The speciation model explains the change of redox potential with temperature for all nominal Fe^{3+}/Fe^{2+} ratios. An expression is also developed to calculate the redox potential and is supported by experimental results from the literature. It appears that the redox potential can be easily and accurately determined only based on the variables of temperature and nominal Fe^{3+}/Fe^{2+} ratio, independent of the nominal concentrations of H_2SO_4 and Fe^{3+}. Moreover, this expression is probably applicable to more general cases at or around room temperature. The proposed model was validated by reliable prediction of measured redox potential from 25 °C to 150 °C. Comparison of previously published results of ferric solubility, together with an analysis of the calculated pH and ionic strength, provides additional justification for the model developed herein. These findings contribute to the research on aqueous speciation of acid iron sulfate solutions, the reduction kinetics of the Fe^{3+}/Fe^{2+} couple, as well as the mechanistic analysis in industrial leaching processes of chalcopyrite and other sulfide minerals.

1. Introduction

It is well known that the largest preponderance of Cu is in sulfide porphyry deposits which consist largely of chalcopyrite (Gerst, 2008; Mudd et al., 2013). In recent years, the metallurgical industry has been searching for a hydrometallurgical process as an alternative to pyrometallurgical treatment due to some inherent advantages associated with hydrometallurgical processing, such as the possibility of treating low-grade ores (increasingly more abundant in the case of copper) and easier control of waste (Córdoba et al., 2008a). Most of the currently proposed processes are based on sulfuric acid with ferric ions and/or dissolved oxygen as oxidants. Some of them have been piloted or demonstrated in attempts to implement these technologies on an industrial scale; these have been reviewed by Dreisinger (2006), including Activox, Nenatech, Dynatec, AAC/UBC, Total Pressure Oxidation, and CESL.

Essentially, these processes can be regarded as electrochemical processes with cathodic reduction of the oxidant (ferric regenerated by oxygen) and anodic oxidation of chalcopyrite. To date, much effort has been devoted to understanding the kinetics and mechanisms of the oxidative processes (Córdoba et al., 2008b, 2009; Ghahremaninezhad

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et al., 2010; Hirato et al., 1987; Hiroyoshi et al., 2004) or the cathodic reduction reactions of chalcopyrite itself (Arce and González, 2002; Nava et al., 2008), by chemical or electrochemical methods. However, there is a lack of published reports describing the cathodic reduction of ferric ions or dissolved oxygen as well as their kinetics (McMillan et al., 1982; Parker et al., 1981; Tshilombo et al., 2002) (not to mention a comprehensive study and comparison of reduction kinetics at different temperatures). This is in spite of the fact that, as the most important cathodic processes in chalcopyrite leaching systems, they can affect the overall leaching rate as predicted by mixed potential theory. Dixon et al. have even assumed that it is the cathodic half-cell reaction (i.e. ferric reduction) that limits the overall leaching rate (Dixon et al., 2008).

In order to study the reduction behavior of ferric ions and further obtain its influence on the leaching rate, the true ferric concentration/activity in the leaching solution is required. In addition, despite the fact that ferric plays a central role in the oxidation of chalcopyrite, it has been reported that the reversible/redox potential of the Fe^{3+}/Fe^{2+} couple, determined by the Fe^{3+}/Fe^{2+} concentration ratio, also has a predominant effect on chalcopyrite leaching and passivation behavior (Córdoba et al., 2008b; Hiroyoshi et al., 2002, 2008; Kametani and Aoki, 1985; Vilcáez et al., 2009). For example, Kametani and Aoki (1985) found that ferric concentration had little effect on the oxidation rate of chalcopyrite and copper extraction was mainly controlled by the redox potential of the solution (a function of the Fe^{3+}/Fe^{2+} ratio). It is clear that a more efficient leaching process, therefore, requires an understanding of the factors affecting the true redox potential in leaching solutions. However, due to the fact that ferric and ferrous ions readily form complexes in acidic iron sulfate solutions, to date it has been difficult to accurately invoke the Nernst equation, where concentrations of free ferric and ferrous ions in the acidic iron sulfate solution are required to obtain the redox potential for the solution according to the published results (Dry and Bryson, 1988; Sapieszko et al., 1977; Stipp, 1990), and other basic electrochemical kinetic equations (Butler–Volmer equation and its extensions). Accurate speciation of this system is thus essential to obtain information relevant to the mechanism of industrial leaching process. For example, the Nernst equation can be used to distinguish which half reaction, cathodic or anodic, may govern the overall reaction rate (Jones, 1974; Li et al., 1992; Paramguru, 2002; Paramguru and Ray, 1996; Power and Ritchie, 1981; Power et al., 1982; Zembura, 1968), by comparing the relative polarization degrees of the anodic and cathodic reactions using mixed potential theory.

Moreover, although it is generally accepted that ferric ion is an effective oxidant for chalcopyrite leaching and increased $FeSO_4$ concentration substantially decreases the leaching rate (and the mixed potential) (Hirato et al., 1987), Hiroyoshi et al. (1997, 2000, 2001) have observed that some chalcopyrite samples were more effectively leached in ferrous sulfate solution than in ferric sulfate solution. This raises some concerns about the role of ferrous during ferric leaching of chalcopyrite. Speciation analysis of the acidic iron sulfate system can help explain this discrepancy.

In addition, during the oxidation of chalcopyrite, there are a number of solution species that can interact by forming complexes that may exert influence on the overall process. Dutrizac et al. (1969) and Hirato et al. (1987) have shown that chalcopyrite's leaching rate is strongly affected by ferric ion concentration only at concentrations less than 0.01 or 0.1 M; at higher concentrations the effect is negligible. Hirato et al. attributed this to the variation of Fe^{3+} and/or $FeHSO_4^{2+}$ concentrations, according to the species distribution analysis for acidic ferric sulfate solution. A similar trend was observed by Crundwell (1987), who found that the dissolution rate of sphalerite in acidic ferric sulfate solutions was proportional to the sum of the concentrations of the Fe^{3+} and $FeHSO_4^{2+}$ species. Although $FeSO_4^+$ was the dominant species present under the leaching conditions, it was inactive as an inner-sphere complex. Clearly, the leaching kinetics at higher ferric concentration may be related to the distribution of iron species in solution.

Therefore, based on the above analyses, solution speciation is required to better understand and determine the factors affecting the leaching process, so as to establish the optimum conditions and improve the leaching rates for copper recovery. However, although several studies have examined the speciation of the quaternary acidic iron sulfate system (Casas et al., 2005a; Cifuentes et al., 2006; Dry and Bryson, 1988; Filippou et al., 1995; Sapieszko et al., 1977; Stipp, 1990), to our knowledge, most of these are limited to lower concentrations and temperatures. There are very few published data pertaining to a systematic study on the speciation of the H_2SO_4–$Fe_2(SO_4)_3$–$FeSO_4$–H_2O system, especially at higher concentrations and temperatures where most of the chalcopyrite hydrometallurgical processes operate. Moreover, ferric is a very common oxidant for many other metal sulfide leaching systems, thus its distribution in sulfate solutions is also of general importance.

The present work was initiated to explore the possibility of establishing an aqueous speciation diagram of the quaternary acidic iron sulfate system, thereby obtaining more detailed information about the electrolytes involved and further providing the data that can enable one to study the kinetics of the cathodic reduction reactions on chalcopyrite in industrially relevant leaching systems, at different temperatures from 25 °C to 150 °C. Herein thermodynamic data are collected and critically reviewed for the calculation of activity coefficients and equilibrium constants. The speciation for the quaternary acidic iron sulfate system is investigated as a function of the initial amounts of iron, acidity, nominal Fe^{3+}/Fe^{2+} ratio and temperature. The model results are further compared with our own experimental data and results published by other authors. A particular focus is placed on the temperature dependence of the free ferric and ferrous concentrations and their real ratios to systematically study the reversible potential of the Fe^{3+}/Fe^{2+} couple. According to these results, an equation, obtained from our speciation model, and based only on the variables of temperature and nominal Fe^{3+}/Fe^{2+} ratio is developed to calculate the redox potential of the Fe^{3+}/Fe^{2+} couple. This information will be used in further investigations of the electrochemical reduction kinetics of the Fe^{3+}/Fe^{2+} couple on chalcopyrite as well as to shed light on the mechanism of chalcopyrite leaching.

2. Model development

When iron sulfates are present in sulfuric acid solution they are distributed as soluble species such as simple cations, neutral or charged complexes, as well as precipitates such as Fe_2O_3, which form at high temperatures. Because of the lack of thermodynamic data and analytical techniques for in-situ measurement of ions and ionic complexes at high temperature, chemical modeling is a very useful tool to predict and understand the behavior of complex aqueous processing systems, provided that reliable models exist with acceptable predictive power based on the limited available experimental data (Casas et al., 2005b).

However, modeling the speciation in the H_2SO_4–$Fe_2(SO_4)_3$–$FeSO_4$–H_2O system at the temperature and concentration of interest requires reliable values of the thermodynamic properties for all species existing in the system. These properties include the standard Gibbs free energy of species to calculate the equilibrium constants, and the activity coefficients of species as a function of solution composition and temperature to describe the non-ideal thermodynamic behavior.

2.1. Activity coefficient model-B-dot equation

The activity coefficients for ions can be estimated by using different models such as the Debye–Hückel equation and its extensions, the B-dot, Pitzer, electrolyte NRTL, Bromley–Zaemaitis and the mixed solvent electrolyte (MSE) models. These models have been employed in hydrometallurgical applications, and reviewed by several authors (Casas et al., 2005b; Liu and Papangelakis, 2005a,b).