



Thermodynamics of metal ion complex formation in the $\text{Zn}_2\text{SiO}_4\text{-NH}_3\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ system (II): Analysis of Si(IV) components and experimental verification

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ABSTRACT

The thermodynamics of Si(IV) complex equilibrium and effect of $[\text{NH}_3]/[\text{NH}_3]_{\text{T}}$ molar ratio on the components in the $\text{Zn}_2\text{SiO}_4\text{-NH}_3\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ system were studied. Mass conservation, simultaneous chemical equilibrium, and electronic charge neutrality principles were employed. By varying the concentration of the total ammonia (0–7 mol/L), the pH values were calculated and the Si(IV) complexes in the system identified. The obtained results were then employed to plot the thermodynamic diagrams. Experimental verification based on thermodynamic analysis was carried out simultaneously. The results revealed that the $[\text{NH}_3]/[\text{NH}_3]_{\text{T}}$ molar ratio and the concentration of SiO_2 in the leaching agent could be employed to predict the leaching behavior of Zn_2SiO_4 in the $\text{NH}_3\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ system; The best leaching effect was observed at an $[\text{NH}_3]/[\text{NH}_3]_{\text{T}}$ molar ratio of 0.5; this is consistent with the results obtained from thermodynamic analysis.

1. Introduction

The zinc in refractory zinc oxide ores exists in different states (Peng, 2003). Moreover, zinc silicate is difficult to mine and smelt, thereby directly affects the recovery of valuable elements. Acid leaching of zinc silicate minerals has been extensively reported in literature. Recent studies have revealed that the sludge obtained from the leaching process is difficult to filter and the leaching efficiency of zinc is low in the acid leaching process of high-silica zinc oxide ores. Matthew and Elsner (1977) dispersed a silicate-coated zinc oxide ore via continuous zinc silicate leaching (Electrolytic Zinc Company of Australasia Ltd., EZ) and removed silica from solution by a precipitation–polymerization process. Bodas (1996) studied the process of sulfuric acid leaching of a zinc oxide ore from Thailand. They also invented a new flocculant, Magnafloc 156, which displays a high efficiency for silicon removal. Thus, only 0.5 g of this flocculant is necessary to remove silicon from solution in the leaching process of 1 kg of a zinc oxide ore under experimental conditions. Li (2005) and Xu et al. (2010) leached a high-silicon zinc oxide ore via an improved EZ method to afford a zinc leaching efficiency > 96%. In their study, they added a two-step acid leaching process that reduced acid consumption by half. Espiari et al. (2006) studied the kinetics of acid leaching process of tailings from Iran, which were mainly composed of smithsonite. They also reported the removal of silicon from solution by using lime as a neutralizer. Qin et al. (2008)

investigated the factors (including the acidity, method of adding acid, solid/liquid ratio, ore size, and temperature) that affect the leaching rate of zinc in high silicon and low-grade zinc oxide ores. Although zinc leaching efficiency could be increased to 99.02% under optimum conditions, a significant amount of alkaline gangue remained in the ore and acid consumption was very large. Moreover, they suggested that the flotation process should be added before the leaching process to remove impurities and reduce the acid consumption. Li et al. (2009, 2010) and Xu et al. (2010) studied the high-pressure selective leaching of a silicon zinc ore. Their study revealed that the leaching efficiency of zinc was 97%, that of iron < 0.77%, and that of silicon, which was precipitated in quartz and remained in the residues, < 4%. In addition, the leaching slurry displayed good filtration performance. Zhang et al. (2016) studied zinc recovery from a low-grade zinc oxide ore of high-silicon content by sulfuric acid curing and water leaching. They discovered that zinc recovery could reach 99.22% and that the use of silicic gel could be effectively avoided. He et al. (2010, 2011) reported the kinetics of the high-pressure acid leaching process of a high silicon zinc oxide ore. The diffusion rate of the leaching agent and resultant in the solid film is the main step to control the leaching reaction. Moreover, both the leaching rate of zinc and the filtration rate of pulp can be improved by increasing the temperature and sulfuric acid concentration.

To date, many scholars have studied the leaching behavior of zinc

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silicon ores in ammoniacal solutions. Ding et al. (2010) and Yin et al. (2010) leached hemimorphite in an ammonia–ammonium chloride solution. Studies have revealed that hemimorphite can dissolve in an ammonia–ammonium chloride solution and that the dissolution rate increases with increasing specific surface area, temperature, and total ammonia concentration. In our previous studies (Liu et al., 2012a; Liu et al., 2012b), we investigated the leaching behavior of hemimorphite and willemite in $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4$ solution and discovered that the zinc and silica present in hemimorphite simultaneously dissolved in solution with subsequent precipitation of amorphous silica. The leaching efficiency of zinc in hemimorphite reached 95%, whereas most of the silicon remained in the residue. We also reported that the limiting factors of willemite leaching in this system are the low solubility of silica in the solution and the slow precipitation rate of the silica gel.

The silicon in zinc silicate minerals can be dissolved by acid, alkaline, and ammonia leaching. Additionally, silicon leaching has a significant effect on the further leaching of zinc silicate minerals. The leaching thermodynamics of Zn(II) in $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ has been reported in literature. However, to the best of our knowledge, the thermodynamic analysis of the effect of silicon dissolution on the leaching of silica and other high-silica zinc oxide ores has not been reported to date. Thus, it is necessary to analyze the dissolution behavior of silicon in the leaching process.

2. Discussion and analysis of the calculation results

A silicon relative thermodynamic model based on the thermodynamic data and calculation method reported in our previous paper Liu et al. (2018) is proposed herein.

2.1. Dissolution of amorphous silica in the $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system

The SiO_2 species in the solution are complex and are affected by dissolution, polymerization, and precipitation, as well as the interactions with other elements, substances, and interfaces. Although there are several papers reporting on the SiO_2 species, no consensus has been reached and research is still in progress. In this work, the dissolving equilibrium concentration of amorphous silica in the $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system was calculated based on the reactions and their equilibrium constants, (Table 1). The log C plot of amorphous silica [$\text{SiO}_2(\text{amorph})$] in the $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system was then plotted using these data.

Fig. 1 illustrates the solubility equilibrium diagram of amorphous silica in the $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system at an $[\text{NH}_3]/[\text{NH}_3]_T$ molar ratio of 0.5. It reveals that the total silicon concentration ($[\text{Si}]_T$) increases with increasing total ammonia concentration. In addition, the H_4SiO_4 concentration remained unchanged, while that of the other ions increased. The dominant components of the system were $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$, H_3SiO_4^- , and $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$.

The curves of the solubility of amorphous silica against pH in aqueous solution were then plotted using the data in Table 1 (Fig. 2). Fig. 2 reveals that $[\text{Si}]_T$ increased with increasing pH. Stumm et al. (1967) studied the amorphous silica species in aqueous solution and discovered that the total silicon concentration increased with increasing pH.

Fig. 3 presents the effect of the total ammonia concentration on

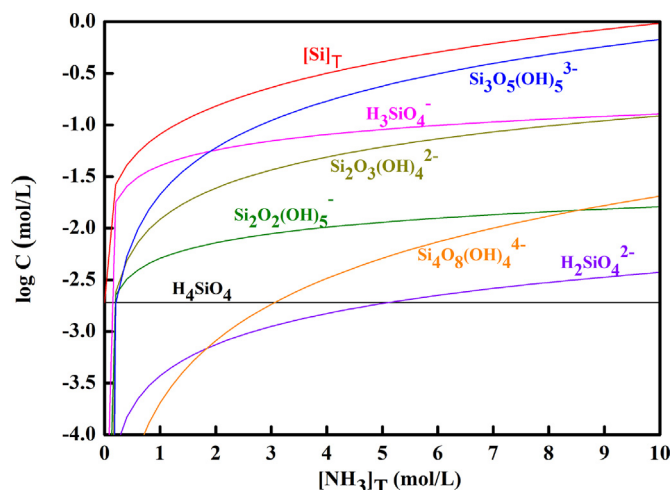


Fig. 1. Equilibrium diagram of amorphous silica dissolved in the $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system ($[\text{NH}_3]/[\text{NH}_3]_T = 0.5$).

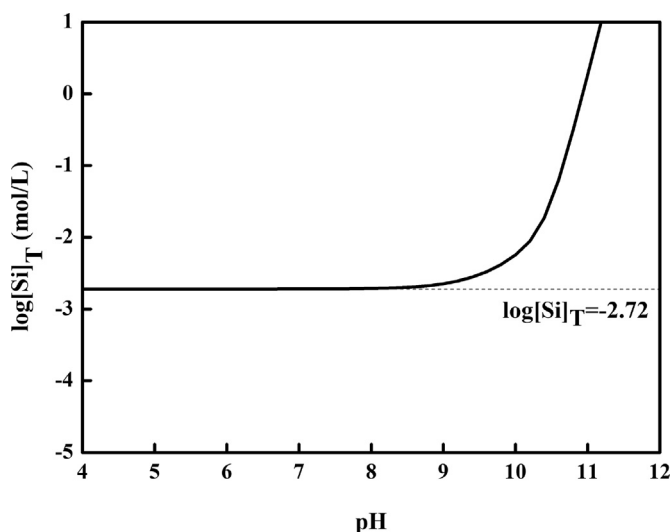


Fig. 2. Relationship between pH and solubility of amorphous silica in solution.

$[\text{Si}]_T$ in the $\text{Zn}_2\text{SiO}_4\text{--NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system. At different total ammonia concentrations, the pH ranges at which $\text{H}_4\text{SiO}_{4(\text{aq})}$ was saturated in solution are different from those in which amorphous silica precipitated was observed. Thus, combining the solubility of amorphous silica in an aqueous solution yields the pH range of amorphous silica precipitated in the $\text{Zn}_2\text{SiO}_4\text{--NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ system at different ammonia concentrations (Table 2). When the pH value was out of this range, no amorphous silica was observed in the system and the only solid phase detected was Zn_2SiO_4 . Moreover, with a higher total ammonia concentration, the pH range of amorphous silica precipitation became wider, thereby affecting the dissolution of Zn_2SiO_4 in the system and increasing the solubility.

Table 1

Equilibrium constant of the reaction of Si(IV) formation in the system ($T = 298.15\text{ K}$, 1 atm).

Species	Equation	lgK	Reference
$\text{SiO}_2(\text{amorph})$	$\text{SiO}_2(\text{amorph}) + \text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	-2.72	Rimstidt and Barnes (1980)
H_3SiO_4^-	$\text{H}_4\text{SiO}_4 = \text{H}_3\text{SiO}_4^- + \text{H}^+$	-9.6	Smith et al. (2004)
$\text{H}_2\text{SiO}_4^{2-}$	$\text{H}_4\text{SiO}_4 = \text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+$	-21.4	Smith et al. (2004)
$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$	$2\text{H}^+ + 2\text{H}_2\text{SiO}_4^- = \text{Si}_2\text{O}_3(\text{OH})_4^{2-} + \text{H}_2\text{O}$	27.27484	Smith et al. (2004)
$\text{Si}_2\text{O}_2(\text{OH})_5^{2-}$	$3\text{H}^+ + 2\text{H}_2\text{SiO}_4^- = \text{Si}_2\text{O}_2(\text{OH})_5^{2-} + 2\text{H}_2\text{O}$	38.06162	Smith et al. (2004)
$\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$	$3\text{H}^+ + 3\text{H}_2\text{SiO}_4^- = \text{Si}_3\text{O}_5(\text{OH})_5^{3-} + 2\text{H}_2\text{O}$	42.10968	Smith et al. (2004)
$\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$	$4\text{H}^+ + 4\text{H}_2\text{SiO}_4^- = \text{Si}_4\text{O}_8(\text{OH})_4^{4-} + 4\text{H}_2\text{O}$	54.68614	Smith et al. (2004)

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