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Impact of gypsum supersaturated solution on surface properties of silica and sphalerite minerals

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ABSTRACT

In some sulphide mineral flotation operations, the process water contains high concentrations of calcium and sulphate ions that exceed the solubility limit of gypsum. It has been speculated that the gypsum supersaturated process water would lead to precipitation of gypsum which could coat on mineral surfaces by either nucleation or coagulation, resulting in reduced flotation recovery and selectivity. In this study, a laboratory prepared gypsum supersaturated solution is used to represent the gypsum supersaturated process water, the effect of gypsum supersaturated solution on the surface properties of silica and sphalerite minerals was investigated using zeta potential distribution measurements, scanning electron microscope (SEM), X-ray photon spectroscopy (XPS), Auger electron spectroscopy (AES), and quartz crystal microbalance with dissipation (QCM-D). Our results show that silica and sphalerite minerals carry identical surface charge (−10 mV of zeta potential) in the gypsum supersaturated solution at pH 10 although they are charged differently in simple electrolyte solution at the same pH. Needle shape gypsum precipitates are found in both silica and sphalerite minerals systems conditioned with gypsum supersaturated solution. The gypsum precipitates do not grow on the minerals surfaces but form in the bulk gypsum supersaturated solution. The heterocoagulation between the examined minerals and gypsum particles is insignificant in the gypsum supersaturated solution. It is the high calcium concentration in the gypsum supersaturated solution that has significant effect on the surface properties of silica and sphalerite minerals. The zeta potentials of silica and sphalerite in a 800 ppm calcium solution (similar to the calcium concentration in the gypsum supersaturated solution) are similar to those measured in the gypsum supersaturated solutions. Both silica and sphalerite minerals surfaces are indiscriminately coated with calcium. The surface coating of calcium results in the identical surfaces between silica and sphalerite minerals, and ultimately causes problems for the flotation separation of silica and sphalerite.

1. Introduction

Water quality is a critical parameter in mineral flotation (Bicak et al., 2012; Levay et al., 2001; Muzenda, 2010; Schumann et al., 2003). Many current mineral flotation plants recycle the tailings water in the process to reduce the demand of fresh water and minimize the discharge of tailings water (Brown, 2003). However, the recycle of the tailings water can have adverse effects on the process water quality and ultimately impact the flotation performance of minerals (Johnson, 2003; Levay et al., 2001; Liu et al., 1993).

In sulphide mineral flotation plants especially those practicing water recycling, the process water usually contains high concentrations of calcium and sulphate ions. In some operations, the calcium concentration in the process water can exceed 1000 ppm (Woodcock and Jones, 1970), and sulphate concentration can be as high as 2500 ppm (Grano et al., 1995). At Pb–Zn Operation, for example, the process water could contain high total dissolved solids (up to 4000 ppm) which are supersaturated with respect to the solubility of calcium sulphate. The concentration of calcium and sulphate ions in the process water of Pb–Zn Operation could be as high as 800 ppm and 2800 ppm, respectively.

The high concentrations of calcium and sulphate ions in the process water can cause problems in the sulphide mineral flotation practice. Problems in galena flotation recovery were noted when lime was used to adjust the pH to depress pyrite (Rao, 2004). The flotation of chalcopyrite was also reported to be depressed in an alkaline pH when lime was used as a pH modifier or when calcium ions were introduced in the pulp (Liu and Zhang, 2000). An extensive investigation into the problem of galena flotation recovery at the Hilton concentrator (Mount Isa Mines, Australia) suggested that the flotation rate of galena was retarded due to surface coating of precipitated gypsum (Grano et al., 1997b). Cullinan (Cullinan, 1999) found that the flotation of fine galena pure mineral was

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depressed when using water of high dissolved salt content, which was gypsum supersaturated. The adverse effect on the fine galena floatability was enhanced by the decrease of particle size and an increase pulp condition temperature.

The adverse effect of high concentrations of calcium and sulphate ions on the flotation of sulphide minerals can be attributed to one or two mechanisms. One possible mechanism is the depression action of calcium ions. In sphalerite flotation, the presence of calcium ions might reduce the exchange rate of activation ions resulting in a deceased recovery (Moignard et al., 1977). However, Lascelles et al. (2003) showed that the presence of calcium (500 ppm) and/or magnesium (120 ppm) ions had no impact on the uptake of copper and xanthate on sphalerite. The presence of calcium ions can enhance the heterocoagulation between target minerals and gangue minerals (DiFeo et al., 2001; Xu et al., 2000). It has been reported that calcium ions decrease the negative surface charge on the mineral surfaces, reducing electrostatic repulsion and the dispersion of mineral particles (Rao, 2004). Another possible mechanism is the gypsum slime coating on mineral surfaces by either nucleation or heterocoagulation, retarding the flotation of the desired minerals. It has been implied that the flotation rate of galena was retarded due to the presence of an overlayer of precipitated gypsum (Grano et al., 1995, 1997a). The precipitates were speculated to deposit on mineral surface by heterocoagulation. However, other investigations on silica and/or sphalerite in gypsum saturated or supersaturated systems showed no trace of gypsum precipitates on mineral surfaces (Beauchamp et al., 2006; Rashchi et al., 1998; Sui et al., 1998). It should be noted that gypsum is considerable soluble (Gardner and Glueckauf, 1970) with a solubility in water of 2400 ppm at 25 °C. The formation of gypsum precipitates depends on various factors including fluid hydrodynamics, solution chemistry, supersaturation level, surface chemistry and topography of solids as well as temperature (Hoang et al., 2007, 2006; Klepetsanis et al., 1999; Le Gouellec and Elimelech, 2002; Lin et al., 2011). Therefore, the sample preparation procedure for the surface analysis is extremely important. In many of the previous studies, the sample rinsing with water was applied after being conditioned in the calcium sulphate solutions. It is possible that the rinsing with water might have washed away the gypsum precipitates resulting in misleading results of surface analysis.

In this study, we focus on the impact of process water of high calcium and sulphate ion concentrations on the surface properties of minerals. The aim of this study is to develop a fundamental understanding of the adverse effect of gypsum supersaturated process water on the flotation performance of sphalerite. An in-house prepared gypsum supersaturated solution is used to represent the gypsum supersaturated process water. Pure silica and single sphalerite minerals are used to represent the gangue mineral and valuable mineral of a zinc sulphide ore. The surface properties of silica and sphalerite minerals in the gypsum supersaturated solution are investigated using zeta potential distribution measurement, quartz crystal microbalance with dissipation (QCM-D), and surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and auger electron spectroscopy (AES). The results of this study answer the questions of whether gypsum precipitates form on mineral surfaces or in the bulk gypsum supersaturated solution, and whether the minerals heterocoagulate with gypsum particles in the gypsum supersaturated solution. The effects of gypsum supersaturated solution on the surface properties and flotation behaviors of silica and sphalerite minerals are discussed.

2. Experimental

2.1. Materials and reagents

The sphalerite mineral was obtained from Ward's Natural Science Establishment. It contained 66.36% Zn, 32.27% S, and trace amounts of Fe (0.25%), Al (0.26%) and Si (0.06%). The sphalerite sample was crushed to −4.75 mm and any impurities present were hand sorted. The sample was then dry ground to −45 μm. The Min-u-sil 5 silica (98.3% SiO_2, 97% −5 μm) from U.S. Silica was used as supplied. The quartz crystal sensors with coating of either SiO_2 or ZnS were purchased from Q-Sense. Silica wafers were purchased from the NanoFab (University of Alberta).

The following reagents were of A.C.S. reagent grade: sodium hydroxide (NaOH) and hydrochloric acid (HCl) from Fisher Scientific were used for pH adjustment; potassium chloride (KCl) and potassium sulphate (K_2SO_4) from Fisher Scientific for preparation of supporting electrolyte solution; calcium chloride ($CaCl_2$), Fisher Scientific, for preparing calcium solution; calcium sulphate ($CaSO_4$), Fisher Scientific, for gypsum saturated solution. Commercial grade calcium sulphate hemi-hydrate ($CaSO_4 \cdot 1/2H_2O$) from US Gypsum Corporation was used as supplied.

2.2. Preparation of gypsum saturated and supersaturated solution

In this research, laboratory gypsum saturated and supersaturated solutions were prepared using deionized water (Milli-Q water) from a Millipore Elix 5 purification system, and pH was adjusted using HCl and NaOH. A new solution was prepared for each day of testing.

The gypsum saturated solution was prepared by dissolving 4 g of calcium sulphate in 1 L of Milli-Q water that was adjusted to pH 10. The mixture was stirred with a magnetic stirrer at room temperature for one hour, and was then filtered with a 1.6 μm filter to remove undissolved solids. The solids were collected and dried for the determination of the total dissolved solids concentration. The total dissolved solids concentration of the prepared solution determined by this method is around 2500 ppm. Atomic absorption analysis indicated that the solutions contained about 600 ppm calcium, which translates to 2580 ppm gypsum (solubility of gypsum in water is 2400 ppm at 25 °C) (Gardner and Glueckauf, 1970).

A similar procedure was used to prepare the gypsum supersaturated solution with calcium sulfate hemi-hydrate ($CaSO_41/2H_2O$). In this case, 10 g of calcium sulfate hemi-hydrate was dissolved in 1 L of Milli-Q water. The pH value of the solution was maintained at 10. The mixture was stirred at room temperature for 30 min, and was then filtered with a 1.6 μm filter to remove undissolved solids. Atomic absorption analysis results indicate that the calcium concentration in the gypsum supersaturated solution is 845 ppm, which translates to 3612 ppm gypsum as compared to the solubility of gypsum in water to be 2400 ppm at 25 °C (Gardner and Glueckauf, 1970). The calcium concentration in this laboratory gypsum supersaturated solution is similar to that in the processing water of Pb–Zn Operation (840 ppm).

2.3. Zeta potential distribution measurement

2.3.1. Suspension preparation

Suspensions of silica and sphalerite were analyzed in supporting electrolyte solution (10^{-2} M KCl or 25×10^{-3} M K_2SO_4), with and without calcium solution (800 ppm Ca), and in gypsum supersaturated solutions. A stock silica suspension was prepared by adding 1 g of Min-u-sil 5 (−5 μm) to 50 mL Milli-Q water. For preparation of sphalerite stock suspension, fine sphalerite (−45 μm) was further ground to −5 μm and then transferred to a beaker with 50 mL Milli-Q water. A fresh sphalerite stock suspension was prepared for each testing. The gypsum stock solution was prepared by adding 1 g of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, −2 μm) in 50 mL gypsum saturated solution.