Minerals Engineering 55 (2014) 172–180

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Impact of gypsum supersaturated process water on the interactions between silica and zinc sulphide minerals

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A R T I C L E I N F O

Article history:
Received 21 May 2013
Accepted 27 September 2013
Available online 5 November 2013

Keywords:
Hetero-aggregation
Quartz crystal microbalance with dissipation (QCM-D)
Silica and sphalerite (ZnS)
Gypsum supersaturated solution
Atomic force microscopy (AFM)
DLVO theory

A B S T R A C T

Flotation recovery and selectivity problems have been reported in the flotation of fine sulphide minerals in gypsum supersaturated process water. In this study, the effect of gypsum supersaturated solution on the interactions between silica and sphalerite (ZnS) minerals was examined by observing deposition behaviour of silica nanoparticles on sphalerite surface using a quartz crystal microbalance with dissipation (QCM-D). Significant deposition of silica nanoparticles on ZnS coated sensor surface was observed in the gypsum supersaturated solution, indicating consequential slime coating of silica fines on sphalerite mineral surface. Substantial deposition of silica nanoparticles on SiO_2 coated surface was also observed suggesting strong homo-aggregation of silica fines in the gypsum supersaturated solution. The interaction behaviour between silica–sphalerite and silica–silica is mainly attributed to the high calcium concentration of the gypsum supersaturated solution. Similar deposition behaviour of silica nanoparticles onto ZnS or SiO_2 coated sensor surface was observed in 800 ppm calcium solution, which is similar to the calcium concentration of the gypsum supersaturated solution. Colloidal force measurement between a silica particle and a fractured sphalerite surface or a silica wafer surface by an atomic force microscopy (AFM) revealed attractive van der Waals force between the mineral particles in both gypsum supersaturated solution and 800 ppm calcium solution. The high calcium concentration of the gypsum supersaturated solution induced the hetero-aggregation between silica and sphalerite, accounting for the observed decrease in flotation selectivity.

1. Introduction

In flotation system, a variety of uncontrolled species exist in the pulp, arising from the water source, involved minerals and/or deliberate additives. The role of these species on the interactions between minerals in zinc sulphide flotation has received considerable attention. Measurements of zeta potential distribution, settling rate, and particle size distribution, and direct colloidal force measurements in combination with model predictions have been carried out to study the homo- and hetero-aggregation of zinc sulphide and silicate minerals (Atkins and Pashley, 1993; Beauchamp et al., 2006; DiFeo et al., 2001; El-Ammouri et al., 2002; Lange et al., 1997; Liu and Xu, 2007; Mirnezami et al., 2003; Muster et al., 1996; Ren et al., 2012a,b,c; Sui et al., 1998; Toikka et al., 1996, 1998; Xu et al., 2000). The effect of pulp pH, ionic strength, calcium ion, and other additives including activator, depressant and collector on the interactions between silicate and zinc sulphide minerals has been investigated extensively. Calcium has been proven to have a significant effect on the interactions between zinc sulphide and silicate minerals (DiFeo et al., 2001; Xu et al., 2000). The calcium concentration used in these previous studies was no more than 0.5 mM (20 ppm). In real zinc sulphide flotation plants, especially those using recycle water; however, the calcium ion concentration in the process water could be as high as 20 mM (800 ppm) (Grano et al., 1997b; Nesset et al., 1998). Meanwhile, saturation or supersaturation of gypsum in water has been a concern in sulphide mineral flotation. Flotation recovery and/or selectivity problems have been reported when processing some of the sulphides in gypsum saturated or supersaturated medium (Cullinan, 1999; Grano et al., 1995, 1997a,b). In this study, we focus on the impact of gypsum supersaturated process water on flotation separation of zinc sulphide and silicate minerals. The purpose of this study is to examine the effect of supersaturation of water with gypsum on the interactions between zinc sulphide and silica minerals.

Quartz crystal microbalance with dissipation (QCM-D) has been widely used to monitor the adsorption kinetics of polymers (Irwin et al., 2005; Olanya et al., 2008; Sakai et al., 2006), DNA (Nguyen and Elimelech, 2007; Xu et al., 2011), and proteins (Fraser et al., 2012; Kaufman et al., 2007) on various substrates. QCM-D has also been proven to be a powerful tool to investigate the interactions

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0892-6875/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mineng.2013.09.017

between particles and clean or functionalized surfaces in aqueous solutions (Fatisson et al., 2009, 2010; Jiang et al., 2010; Nypelö et al., 2012; Quevedo et al., 2013; Xu et al., 2010; Yi and Chen, 2011). In this study, QCM-D was used to evaluate the interactions of silica nanoparticles and ZnS or SiO_2 coated quartz crystal surface in 800 ppm calcium solution and gypsum supersaturated solution. To better understand the interactions between silica and zinc sulphide minerals in the presence of calcium or in gypsum supersaturated solution, the colloidal forces between a silica particle and a fractured sphalerite mineral surface or a silica wafer surface were measured. AFM results and calculations based on the classical DLVO theory were employed to verify the QCM-D observations. The results were discussed in the context of selective flotation of sphalerite from silica.

2. Experimental

2.1. Materials and reagents

Sphalerite mineral samples obtained from Ward's Natural Science were used in this study. XRF analysis showed that the sphalerite sample 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, followed by dry grinding to −45 μm and then stored in freezer until being used. Ultra-pure sphalerite crystal samples were used for AFM force measurement. Silica particles of two size fractions (15 nm and 30 μm, 98% pure) were purchased from US Silica. Silica spheres from Polysciences Inc., (Warrington, PA, USA) were used as probe in AFM colloidal force measurement. Silica wafer with (001) orientation was purchased from NanoFab, University of Alberta. The quartz crystal sensors with ZnS or SiO_2 coatings were purchased from Q-Sense. Ultrahigh purity chemicals, including potassium chloride, sodium hydroxide, hydrochloric acid, calcium chloride, copper sulphate pentahydrate, and sodium sulphate, were purchased from Fisher Scientific and used in this study as received. Sodium isopropyl xanthate (SIPX: $(CH_3)_2$-CH_2-O-CS_2Na) from Prospec Chemicals, Canada was used as a collector. The commercial SIPX was purified by dissolving in warm acetone (40 °C), recrystallization and washing with acetone for three cycles. The purified SIPX was stored frozen. The water (Milli-Q water) used in this study was prepared using an Elix-5 with a Millipore-UV plus unit (Millipore, Canada).

2.2. Solutions and suspension preparation

The 800 ppm calcium solution was prepared by dissolving the calcium chloride in Milli-Q water. Gypsum supersaturated solution was prepared by mixing equal volume of 40 mM (1600 ppm) calcium chloride and 50 mM (4800 ppm) sodium sulphate solutions, leading to a supersaturated solution of 800 ppm calcium and 2400 ppm sulphate. Silica nanoparticle suspensions were prepared by adding 0.1 g of 15 nm silica nanoparticles to 100 mL desired solutions. The suspensions were placed in ultrasonic water bath for 10 min prior to the experiments.

2.3. Quartz crystal microbalance with dissipation (QCM-D)

The QCM-D measurements were performed with a Q-Sense E4 unit (Q-Sense AB, Sweden), which simultaneously monitors the changes in frequency (Δf) and energy dissipation (ΔD) of a quartz crystal sensor. In general, the changes in resonance frequency (Δf) of the quartz crystal are related to the changes in mass (Δm) attached to the crystal surface. An increase in mass, Δm, induces a proportional decrease in resonance frequency, Δf. For homogenous, rigid and thin deposited layers, the change in mass (Δm) on the quartz surface is related to the changes in frequency (Δf) of the crystal through the Sauerbrey relationship (Sauerbrey, 1959).

$$\Delta m = -\frac{C \cdot \Delta f}{n} \qquad (1)$$

where C is the mass sensitivity constant equal to 17.7 ng cm^{-2} Hz^{-1} when f = 5 MHz, and n is the overtone (n = 3, 5, 7, or 9) of the resonance frequency of the applied voltage across the electrodes. The dissipation factor, on the other hand, is proportional to the power dissipation in the oscillatory system, which provides information on rigidity of the attached materials. The dissipation is defined as:

$$D = \frac{E_{lost}}{2\pi E_{stored}} \qquad (2)$$

where E_{lost} is the energy lost during one oscillation cycle and E_{stored} is the total energy stored in the oscillator.

The Sauerbrey relation (Eq. (1)) (Sauerbrey, 1959) is only valid when the adsorbed mass causes low dissipation in frequency shifts between different overtones and/or the ratio of dissipation and frequency changes ($-\Delta D_n/\Delta f_n$) is small (Du and Johannsmann, 2004; Reviakine et al., 2011; Tellechea et al., 2009). Manufacturer of QCM-D (Q-Sense) suggests the threshold $-\Delta D_n/\Delta f_n$ value of 1×10^{-7} Hz^{-1}, while Reviakine et al. (2011) proposed a value of 4×10^{-7} Hz^{-1}. For high dissipation values or $-\Delta D_n/\Delta f_n$ ratios, the Sauerbrey equation (Eq. (1)) is believed to underestimate the adsorbed mass (Fatisson et al., 2010; Yi and Chen, 2011), and models taking into account of the viscoelastic properties of the adsorbed layer has been proposed (Du and Johannsmann, 2004; Johannsmann, 1999, 2008; Johannsmann et al., 1992, 2009; Kunze et al., 2006; Tellechea et al., 2009; Vittorias et al., 2010).

In this study, the impact of calcium and gypsum supersaturated solutions on the interactions between silica and sphalerite was investigated using QCM-D. A ZnS coated quartz sensor was used to represent the sphalerite mineral. The ZnS coated on the quartz sensor surface has similar crystalline structure as natural sphalerite mineral. Detail information about the ZnS sensor can be found elsewhere (Teng et al., 2012). The ZnS sensors were cleaned with diluted HCl (pH 2) solution to remove any oxidation species before mounted in the QCM-D modules. Effect of calcium on the interactions between silica and silica was also studied. In this case, a SiO_2 coated sensor was used. The SiO_2 sensors were cleaned by exposing to UV O-zone for 15 min followed by cleaning in 2% sodium dodecyl sulphate (SDS) solution in a sonication water bath for 30 min and then washed with Milli-Q water in a sonication water bath for additional 30 min. For a particular test, a clean quartz sensor with coatings of either ZnS or SiO_2 was carefully mounted in the flow module with the active surface facing the testing solutions or suspensions. The flow module was mounted on the chamber platform and a solution of interest was pumped into the flow module with an IPC-N peristaltic pump (Ismatec, Switzerland) at a flow rate of 150 μL/min. A particle-free calcium solution or gypsum supersaturated solution (baseline solution) was firstly introduced into the system to obtain a stable baseline. The silica suspension in ether 800 ppm calcium solution or gypsum supersaturated solution was then pumped into the flow module until reaching equilibrium. The baseline solution was then pumped into the system to remove loosely adsorbed or deposited layers. All QCM-D experiments were carried out at 22.00 ± 0.02 °C. The QCM-D chamber was placed upside down throughout the experiments. Frequency and dissipation shifts were continuously recorded during the entire experiment to avoid the deposition by gravity. The 3rd, 5th, and 7th overtone (n = 3, 5, 7) was used to interpret the results.