The kinetics of leaching galena concentrates with ferric methanesulfonate solution

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ABSTRACT

A new hydrometallurgical leaching process, which dissolves lead concentrates with acidic ferric methanesulfonate solution, was proposed and investigated. The leaching kinetics of galena-containing concentrate from Red Dog Mine (Teck) was studied with respect to variables such as stirring speed, temperature, concentrations of free acid and ferric ions as well as particle size. It was found that stirring speed and acid concentration had no influence on the leaching rate, while increasing temperature moderately increased the rate. The leaching data best fitted the product-layer diffusion control mechanism based on the shrinking core model with an apparent activation energy value 36.15 kJ/mol. The apparent reaction constant for the mean value of particle size and the reaction order for initial ferric concentration were very close to the theoretical values of 2 and 1, respectively.
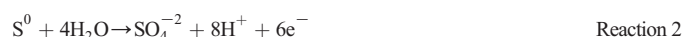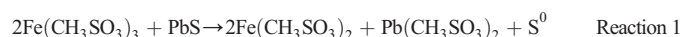
1. Introduction

The pyrometallurgical smelting process is the primary route to treat galena concentrates. However, it generates both SO_2 and volatile lead compounds, which may lead to serious environmental problems if not carefully controlled. The conventional smelting process is not well suited to treat complex sulfides or low-grade sulfide ores. Hydrometallurgical routes of leaching lead concentrates can avoid the above problems. The acidic medium has been commonly studied for leaching lead, since low pH is more favorable for lead dissolution (Kobayashi et al., 1990; Peters, 1976). A number of solvents have been tested as lixiviants for lead leaching including sulfate (Lee, 2009), nitrate (Lee, 2009), chloride (Awakura et al., 1980; Olanipekun, 2000), fluosilicate (Chen and Dreisinger, 1994; Taylor, 1992, 2003) and fluoborate (Pyatt and Maccagni, 2010) medium. However, most of the solutions possess a very low solubility of lead, and some are highly corrosive. Fluosilicate and fluoborate are prone to hydrolysis to release fluoride, resulting in lead fluoride reprecipitation and lead recovery decrease.

Methanesulfonic acid (MSA) medium shows a moderately high solubility for lead and some other heavy metals. The inherent advantages of MSA, such as high conductivity, stability against hydrolysis, low toxicity and weak corrosiveness, make it a very promising alternative for lead production and very safe for workers to handle (Gernon et al., 1999). As a result it has largely replaced fluoboric acid, the previous industrial standard for electroplating tin/lead solder over the past 20 years (Gernon et al., 1999). MSA also has the potential application for other metal production, such as an emerging electrolyte choice for electroplating pure tin (Low and Walsh, 2008) and for copper deposition (Hasan, 2010). MSA is also reported as a leaching agent to remove lead from brass (O'Brien, 1997) and to dissolve lead for lead methanesulfonate production (Onuoha, 2002). However, the kinetics study of galena dissolution in ferric methanesulfonate solution has not yet been studied.

In this study, the leaching kinetics of galena by ferric methanesulfonate is undertaken. Ferric ion, compared to hydrogen peroxide and oxygen, is more economic in use. The chemistry of galena leaching with ferric methanesulfonate is as follows. Elemental sulfur may be further oxidized to sulfate (SO_4^{-2}) which precipitates lead (Pb^{+2}) to form lead sulfate ($PbSO_4$) product.

$$2Fe(CH_3SO_3)_3 + PbS \rightarrow 2Fe(CH_3SO_3)_2 + Pb(CH_3SO_3)_2 + S^0 \qquad \text{Reaction 1}$$

$$S^0 + 4H_2O \rightarrow SO_4^{-2} + 8H^+ + 6e^- \qquad \text{Reaction 2}$$

Ferric methanesulfonate may be regenerated by the anodic reaction in the electrowinning of lead in a divided cell.

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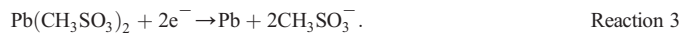E-mail address: zhenghui.wu@alumni.ubc.ca (Z. Wu).

Nomenclature

τ	time required for complete leaching
ρ	molar density
d_0	the original particle size
k	the solid–solid transfer coefficient
D_A	the effective diffusivity of lixiviant
C_A^b	the bulk concentrate of lixiviant
k_l	rate constant in product-layer diffusion control kinetics process

Fig. 1. Experimental apparatus for leaching tests. (1—glass reactor; 2—syringe; 3—nitrogen aeration tubing; 4—stirring motor; 5—thermometer; 6—condensor; 7—nitrogen flow meter; 8—water tank; 9—hollow balls).

Table 1
Reitveld X-ray diffraction results for as received galena concentrate.

Mineral	Ideal formula	wt.%
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	0.9
Galena	PbS	59.8
Anglesite	$PbSO_4$	7.2
Sphalerite	(Zn,Fe)S	21.2
Pyrite	FeS_2	6.8
Marcasite	FeS_2	1.3
Quartz	SiO_2	2.8
Total	–	100

Table 2
Chemical composition of galena concentrate ($-75 + 45$ μm).

Element	Pb	Zn	Fe	Cu	$C_{inorganic}$	S_{total}	SO_4
wt.%	54.27	15.29	5.07	0.0092	0.14	20.36	40.29

Cathode:

$$Pb(CH_3SO_3)_2 + 2e^- \rightarrow Pb + 2CH_3SO_3^-.$$ Reaction 3

Anode:

$$2Fe^{+2} \rightarrow 2Fe^{+3} + 2e^-.$$ Reaction 4

Cell reaction:

$$Pb(CH_3SO_3)_2 + 2Fe(CH_3SO_3)_2 \rightarrow Pb + 2Fe(CH_3SO_3)_3.$$ Reaction 5
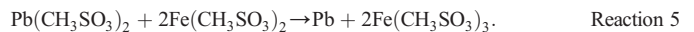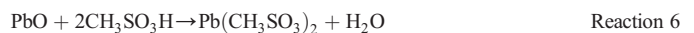
2. Material and methods

The galena concentrate used in this study was from Red Dog Mines (Teck Resources Ltd., Canada). All experiments were carried out with ground and sized concentrate. Sized materials were prepared by wet screening into various fractions and drying at room temperature to minimize mineral oxidation. The mineralogy and the chemical composition of the studied concentrate were shown in Table 1 and Table 2, respectively.

All chemicals used in the preparation of lixiviants were of analytical grade. The methanesulfonic acid provided by BASF (Germany) was of 100% purity. The preparation of ferric methanesulfonate stock solution consisted of two steps: the first step is the addition of lead oxide to a methanesulfonic acid solution to form the lead methanesulfonate salt; and the second one is the addition of ferric sulfate to interconvert the soluble salt to ferric methanesulfonate and precipitate insoluble lead sulfate. This was shown in the following chemical reactions:

$$PbO + 2CH_3SO_3H \rightarrow Pb(CH_3SO_3)_2 + H_2O$$ Reaction 6

$$3Pb(CH_3SO_3)_2 + Fe_2(SO_4)_3 \rightarrow 2Fe(CH_3SO_3)_3 + 3PbSO_4\downarrow.$$ Reaction 7

After filtration to remove the $PbSO_4$ precipitate, the pink supernatant solution was used in the leaching experiments as the stock solution, containing 0.5 M Fe^{+3}, 0.5 M free acid and 1 g/L Pb^{+2}. The presence of a small amount of soluble lead ensured that sulfate (from added ferric sulfate) was fully removed from the stock solution.

The leaching tests were conducted in a covered 1 L glass reactor with three baffles. Openings were incorporated in the cover for insertion of a stirring rod, a thermometer, a condenser, nitrogen sparger (to prevent oxygen ingress) and two sampling ports (one port for adding sieved galena samples and one port for withdrawing solution samples). Nitrogen gas kept sparging over the process and the flow rate in this study was 1 L/min (Fuerstenau et al., 1987). The surface of the temperature control tank was covered by plastic balls to prevent heat and water vapor loss (Fig. 1).
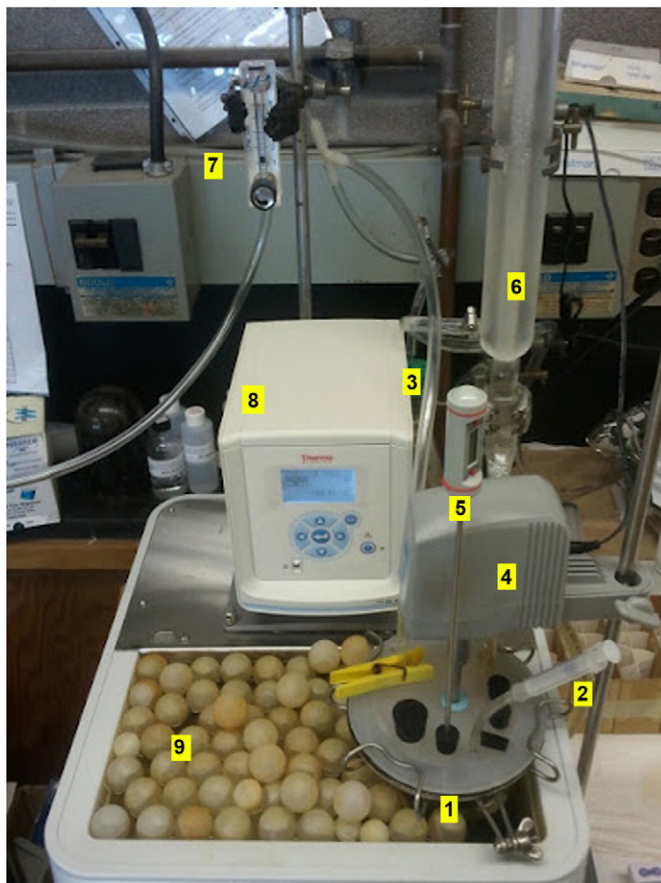
Table 3
Base operating conditions.

Sample weight (gram)	2
Sample particle size (μm)	$-75 + 45$
Stirring speed (rpm)	400
Lead concentration (g/L)	0.5
Temperature (°C)	65
Lixiviant volume (mL)	500
Free MSA concentration (M)	0.5
Ferric concentration (M)	0.25