



## The kinetics of zinc silicate leaching in sodium hydroxide

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### ARTICLE INFO

#### Article history:

Received 6 September 2009  
Received in revised form 16 December 2009  
Accepted 30 January 2010  
Available online 6 February 2010

#### Keywords:

Zinc silicate  
Sodium hydroxide  
Leaching kinetics  
Shrinking particle model  
Chemical control

### ABSTRACT

The alkaline leaching kinetics of a zinc silicate ore assaying 34.1% Zn, 11.1% Fe and 22.9% SiO<sub>2</sub> is studied in sodium hydroxide solutions. Speciation diagrams indicate zinc dissolution as [Zn(OH)<sub>4</sub>]<sup>2-</sup> and SEM analysis showed a progressive reduction in particle size during leaching which supports the shrinking particle model. The process is chemically controlled with an activation energy of 67.8 ± 9.0 kJ/mol and reaction order with respect to NaOH determined as 1.44 ± 0.46.

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### 1. Introduction

Zinc is mainly produced by the roasting–leaching–electrolysis route (RLE) which combines pyro- and hydrometallurgical operations. However, with the development of the acid leaching (AL)–solvent extraction (SX)–electrowinning (EW) process, non-sulphide zinc deposits now account for about 10% of world metallic zinc production. Unlike zinc sulphides treated by the RLE route, the processing of zinc silicates can follow different approaches. Solvent extraction is one alternative, while some companies have integrated zinc silicate and zinc sulphide leaching (Souza, 2007). Both routes use acid leaching to dissolve zinc from the ores/concentrates and special care is taken to avoid the formation of silica gel. This can be achieved by a stepwise addition of sulphuric acid, whereby the silicate is dissolved with a minimum silica gel formation (Souza et al., 2009).

The acid leaching of oxidized zinc ores and concentrates has some drawbacks. This is because zinc carbonates (smithsonite, ZnCO<sub>3</sub>; hydro-zincite, 2ZnCO<sub>3</sub>·3Zn(OH)<sub>2</sub>) and silicates are generally acid consumers. Also, they are usually associated with other acid consuming gangue minerals such as calcium carbonate. Therefore, for an efficient acid leaching of such materials, the content of the gangue minerals needs to be reduced which is usually attained by a concentration step. This sometimes results in large volumes of carbonate containing tailings with fairly reasonable zinc content for which a cost-effective leaching route is yet to be developed.

Zinc leaching from carbonate and oxide ores can be addressed applying alkaline solutions. Frenay (1985) studied the leaching of oxidized zinc ores in various solution media and pointed out the best results with caustic soda. The leaching in alkaline media (ammonia, caustic soda, and diethylene-triammine) showed that hemi-morphite could be leached with caustic soda at high temperature (85 °C). Ammonium carbonate enhanced the leaching of hemi-morphite but decreased that of smithsonite. Zhao and Stanforth (2000) studied the production of zinc powder by an alkaline treatment of smithsonite ores and observed that over 85% zinc could be leached at 90–95 °C, in 1.5 h with 5 mol/L NaOH. The alkaline leaching of a low grade smithsonite ore was also carried out in columns after pelletizing the ore with cement. The best results showed over 80% zinc dissolution for a 20 days leaching period (Feng et al., 2007).

The leaching kinetics of zinc ores and concentrates has been studied by many researchers (Bobeck and Su, 1985; Bodas, 1996; Feng et al., 2007; Ghosh et al., 2002), especially in sulphuric acid solutions (Abdel-Aal, 2000; Terry and Monhemius, 1983). The shrinking core model, SCM, (Levenspiel (1962)) was applied to describe the leaching data in most of those studies. Bodas (1996) studied the leaching kinetics of two different zinc ores and noticed that the leaching kinetics was diffusion-controlled with activation energies varying from 4 to 17 kJ/mol. Maximum zinc extractions reached 95% at 70 °C and 4.5 mol/L H<sub>2</sub>SO<sub>4</sub>, in 3 h. Terry and Monhemius (1983) have comprehensively studied the leaching kinetics of natural hemi-morphite, as well as natural and synthetic willemite. The authors observed that the acidic dissolution was diffusion-controlled for hemi-morphite and chemically-controlled for willemite leaching. Abdel-Aal (2000), studying the leaching kinetics of low grade zinc silicate, proposed that the process was

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**Table 1**  
Chemical analysis and surface area of zinc silicate concentrate screened fractions.

Parameter	Unit	Size fraction 105–75 $\mu\text{m}$	Size fraction 75–53 $\mu\text{m}$	Size fraction 53–45 $\mu\text{m}$	Size fraction 45–38 $\mu\text{m}$
Zn	(%)	39.7	35.6	35.2	34.1
Fe	(%)	9.8	11.7	10.3	11.1
SiO <sub>2</sub>	(%)	24.3	23.8	23.2	22.9
Surface area	m <sup>2</sup> /g	1.0	0.6	0.6	1.0
Total porous vol.	mm <sup>3</sup> /g	3.3	2.5	2.5	2.5
Pore ave. diameter	Nm	13.1	17.9	18.0	9.8

controlled by diffusion on an “ash” layer with an associated activation energy of 13.4 kJ/mol.

When the SCM model was unsuccessful in describing the leaching kinetics, the grain pore model, GPM, (Szekely et al., 1976) was applied (Souza et al., 2007; Souza et al., 2009). It has been shown that if the transport through the pores of the solid is the rate-determining step, the GPM model predicts an expression similar to the shrinking core model (SCM) with diffusion control (Georgiou and Papangelakis, 1998). This approach was applied by Souza et al. (2007) to the acid leaching of zinc silicates and an activation energy of  $59.5 \pm 2.9$  kJ/mol was obtained for the dissolution kinetics of a calcined zinc silicate. The same model was applied afterwards to the leaching of non-calcined zinc silicates containing either high (8–11%) or low (3%) iron content (Souza et al., 2009). The authors suggested that the iron content did not affect the leaching kinetics of the silicate concentrate as the activation energy was statistically similar for both materials ( $78.2 \pm 12.1$  kJ/mol and  $66.8 \pm 9.2$  kJ/mol, for the high- and low-iron silicate, respectively). As the leaching kinetics in alkaline medium is far less studied than in acid solutions, the purpose of the present work is to assess the leaching kinetics parameters of a zinc silicate ore in sodium hydroxide.

## 2. Materials and methods

The zinc silicate concentrate contains 34–39% Zn (Table 1). The XRD of the calcine (measured with a Shimadzu 600 diffractometer

equipped with an iron tube and graphite monochromator) showed the presence of willemite (Zn<sub>2</sub>SiO<sub>4</sub>) as the main zinc-containing phase as well as franklinite (ZnO·Fe<sub>2</sub>O<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) as minor constituents (Fig. 1). Mineralogical analysis also showed the presence of quartz and dolomite in the gangue (Souza et al., 2009) and the willemite content was estimated to be above 80%. Prior to the leaching experiments, the concentrate was dry ground and wet sieved to yield a particle size distribution between 150 and 38  $\mu\text{m}$ . Zinc, iron and silica content as well as surface area, total porous volume and pore average diameter of the different sieved fractions are also presented in Table 1.

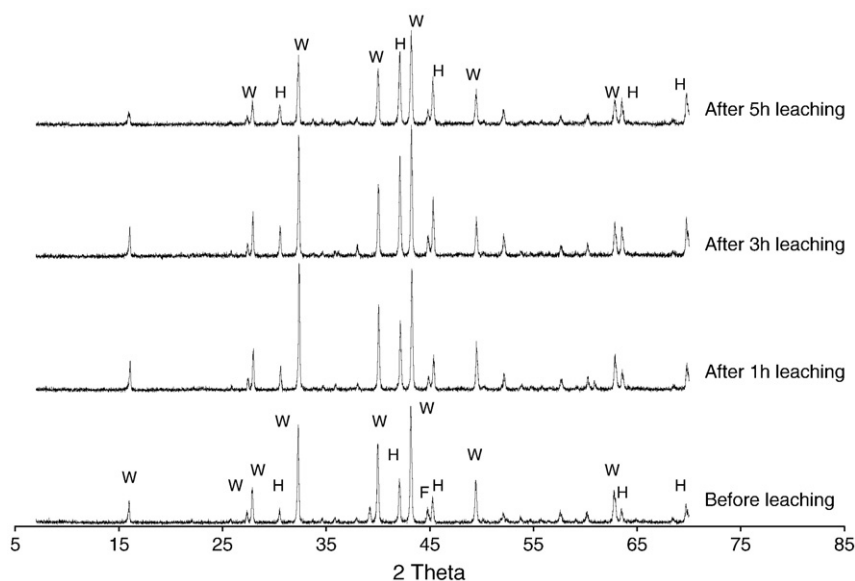
The chemical leaching experiments were carried out batch-wise in a closed water-jacket plastic reactor with 750 mL total volume. Agitation was provided by a magnetic stirrer (600 min<sup>-1</sup>) that enabled adequate dispersion of the mineral particles without evaporation loss of the solution. The solution volume was 500 mL and the solid concentration 1 g/L.

Leaching solutions were prepared using reagent grade chemicals (NaOH, Synth) and distilled water. Unless otherwise stated, the leaching experiments were carried out using 38–45  $\mu\text{m}$  particle size in 6 mol/L NaOH at 80 °C, and stirred at 600 min<sup>-1</sup>. At selected time intervals, a known amount (3 mL) of slurry was withdrawn and filtered.

The zinc extraction was determined by analyzing zinc concentration in solution (after dilution in HCl), by atomic absorption spectrometry (Perkin Elmer AAnalyst 100), and for every sample withdrawn from the reactor, the volume change was taken into account for the zinc extraction determinations. The effects of temperature (60–90 °C), sodium hydroxide concentration (4–10 mol/L) and particle size (38  $\mu\text{m}$ –105  $\mu\text{m}$ ) on the leaching kinetics were assessed.

Surface area and pore volume were determined by nitrogen adsorption. Nitrogen isotherms were performed with a Nova 1000 High Speed Gas Sorption Analyzer (Quantachrome). Sample degassing was carried out at 80 °C, for 24 h to avoid decomposition. Nitrogen adsorption was performed at –196 °C. Data were collected from a relative pressure ( $p/p_0$ ) of 0.05 to 0.98. A large sample (~4.0 g) was used and the Nova 1000 parameters (equilibration tolerance, time to remain in tolerance and maximum equilibration time) were set at 0.05, 360 and 720, respectively, to improve the accuracy of low surface area measurements with nitrogen adsorption.

The morphological features of the concentrate, leach residues and reaction products formed during alkaline leaching were studied by



**Fig. 1.** XRD pattern of the zinc silicate concentrate. H: hematite, W: willemite, F: franklinite.

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