Effect of mineralogy and temperature on atmospheric acid leaching and rheological behaviour of model oxide and clay mineral dispersions

Jennifer MacCarthy, Ataollah Nosrati, William Skinner, Jonas Addai-Mensah *

Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia

ABSTRACT

The atmospheric acid leaching mechanism and kinetics and rheological behaviour of model iron oxide (hematite and goethite) and clay (kaolinite and smectite) mineral dispersions were investigated. Isothermal, batch leaching tests were conducted at pH 1 for 4 h at 25 and 70 °C. Both clays displayed incongruent leaching where lattice substituted species (e.g., Na, Ca, Mg, K) leached faster than Al—Si—O framework species (Al and Si) initially. For the iron oxides, Fe released from goethite was considerably greater than hematite. Temperature elevation to 70 °C led to dramatically enhanced leaching rates for the iron oxides but had subtle effect on that of clay minerals. Furthermore, the clays consumed more acid than the iron oxides, reflecting former's greater acid neutralization capacity. During leaching, all dispersions displayed non-Newtonian, shear thinning, rheological behaviour. Generally, lower pulp shear yield stresses (<5 Pa) and viscosities (<10 mPa s) were displayed by the iron oxides compared with clays (5-20 Pa and 15–65 mPa s). Whilst the yield stresses and viscosities of the hematite and kaolinite dispersions were time-independent, those of goethite and smectite increased and attenuated with increasing leaching time, respectively. The leaching mechanism of kaolinite and smectite followed a porous layer, volume diffusion-controlled shrinking core model with activation energies (E_a) of 13.8 and 21.6 kJ/mol, respectively. Hematite and goethite leaching mechanism, on the other hand, was both chemical and diffusion-reaction controlled, following an empirical, shrinking particle power law kinetics of order 1.5 with E_a of 28.7 and 24.6 kJ/mol, respectively.

© 2015 Published by Elsevier B.V.

1. Introduction

Complex, low-grade lateritic ores containing valuable metals (e.g., nickel, copper, uranium) also contain large quantities of high acid consuming clays (e.g., kaolinite and smectite) and oxides (e.g., goethite and hematite) as gangue mineral phases [1,2]. The value metals are often finely disseminated in all phases of laterite ores meaning physical separation to upgrade the ore prior to hydrometallurgical operations such as atmospheric acid leaching (AL) is not generally technologically and economically viable [3]. The presence of acid reactive, alumina-silicate clay and oxide gangue mineral phases in complex ores sometimes leads to challenges during their AL process such as high acid consumption and processing difficulties (e.g., mixing, pumping) [4–6].

These processing challenges are mainly linked to gangue mineral-mediated pulp chemistry changes and particle interactions during leaching. Variation in mineralogy and chemistry of model minerals and complex nickel laterite ores has been shown to play a pivotal role in determining their acid leaching behaviour [3,7–10]. For example, several studies have reported that during H_2SO_4 leaching, Ni release is faster in ores dominated by reactive clays (e.g., smectite and saprolite)

compared with those rich in refractory oxides such as goethite [11–16]. From laboratory column leaching experiments carried out over 100 d on saprolitic and goethitic nickel laterite ores, it was revealed that greater Ni extraction was achieved from the former (~90%) than the latter (~63%) [16]. Similarly, work carried out by Quast et al. [17] showed that for siliceous goethitic nickel laterite ores whose composition lies between that of the goethitic and saprolitic ores, Ni extraction of ~81% may be achieved within the same time frame. This reflects the complex nature of nickel laterites and hence, the need to understand the behaviour of different minerals. The difference in the leaching behaviour of saprolitic and goethitic laterites is attributed to their dominant Ni host-gangue minerals. Saprolitic ores in general are associated with more acid reactive minerals (e.g., smectite, serpentine) whilst the goethitic ores are dominated by more refractory iron oxides (e.g., goethite, hematite) [17–19].

In their study on the impact of feed mineralogy on the leaching of different iron oxides in 0.5 M HCl at 25 °C, Sidhu et al. [10] showed that leaching rate decreased in the order of lepidocrocite > magnetite > akaganiete > maghemite > hematite > goethite. In other iron oxide leaching studies [20,21], on the other hand, the rate followed the order of ferrihydrite > goethite > hematite. Large differences have also been reported between the rheological behaviour of smectite, kaolinite, hematite and goethite dispersions [22]. Several factors such as particle

* Corresponding author. Tel.: +61 8 8302 3673; fax: +61 8 8302 3683.
E-mail address: Jonas.Addai-Mensah@unisa.edu.au (J. Addai-Mensah).

size and shape, pulp density or solid loading, stirring speed and time have been shown to affect slurry rheology [22]. A better understanding of the leaching mechanisms and kinetics, pulp chemistry and rheological behaviour of single oxide and clay mineral dispersions which constitute predominant mineral phases of typical lateritic ores is necessary to device effective strategies to improve their AL behaviour and enhance value metal extraction rates.

1.1. Mechanisms and kinetics of acid leaching processes

Elucidating the exact mechanism for a chemical reaction to take place relies on several factors such as stoichiometry, reaction order, rate constant, activation energy and data correlation [23]. In heterogeneous reactions (e.g., solid–liquid), the overall mechanism often depends on three main process steps: transport of reactants to the reaction site, chemical reaction at the reaction site and the rate of transport of products away from the reaction site.

Depending on the controlling leaching mechanism during solid-acid leaching reactions, several kinetic models have been developed [24,25]. The shrinking core model is widely used in understanding the mechanism of leaching different minerals [25–27]. This model assumes that the solid particle retains its bulk size whilst its unreacted core shrinks progressively with reaction time leading to the formation of a peripheral porous layer [24,25,27]. The overall acid leaching reaction involves proton diffusion through the liquid film and the reacted porous layer, chemical reaction at the surface of the unreacted core and volume diffusion of reaction products through the porous layer and into the liquid film back into the bulk solution. The leaching rate is controlled by the slowest of these processes. Eqs. (1)–(3) summarize the shrinking core models.

$$x = kt, \tag{1}$$

$$1 - 3(1-x)^{2/3} + 2(1-x) = kt, \tag{2}$$

$$1 - (1-x)^{1/3} = kt \tag{3}$$

where x is the fraction of metals (e.g., Ni, Co), k (min^{-1}) is the rate constant and t (min) is time. Eq. (1) assumes that the controlling step is volume diffusion, Eq. (2) assumes that it is controlled by porous layer diffusion and Eq. (3) assumes that the controlling step is the chemical reaction on the surface of the unreacted core.

Alternatively, generic semi-empirical rate laws may also be developed for describing the kinetics of leaching reactions. These models take into account the level of undersaturation, time, surface area and reaction order in determining the reaction rate. Eq. (4) below shows the leaching process for solid particles:

$$\frac{dC}{dt} = -Ak(C_e - C)^n = (AC_e^n)k\left(1 - C/C_e\right)^n \tag{4}$$

where C (mol/m^3) is the concentration measured at any given leaching time, C_e (mol/m^3) is the measured equilibrium solubility, t (s) is the time, k (1/m^2 s for n = 1 and 1/m$^{0.5}$ mol$^{0.5}$ s for n = 1.5) is the reaction rate constant, A (m^2) is the total surface area and n is the exponent of the undersaturation driving force or the overall reaction order. Typically, the overall chemical reaction order (n) for volume diffusion or mass transfer controlled dissolution process is 1 whilst for chemical reaction controlled processes, n can be 1 or greater. For specific cases such as n = 1 and 1.5, the integrals of Eq. (4) are given in Eqs. (5) and (6), respectively:

$$\ln(C_e - C) = -Akt + \ln(C_e), \tag{5}$$

$$\frac{2}{(C_e - C)^{1/2}} = Akt + \frac{2}{(C_e)^{1/2}}. \tag{6}$$

Based on the rate constants obtained, the activation energy (E_a) for the reaction can be determined by using the Arrhenius law (Eq. (7)):

$$k = k_0 e^{-E_a/RT} \tag{7}$$

where E_a (kJ/mol) is the activation energy, R (8.314 J/Kmol) is the ideal gas constant, k_0 (min^{-1}) is the pre-exponential factor and T (K) is thermodynamic or absolute temperature. For volume diffusion controlled processes, the E_a is generally low (<20 kJ/mol) whilst for chemical reaction controlled processes it is high (>40 kJ/mol) [28–30]. Quantifying the dissolution kinetics of hematite, goethite, smectite and kaolinite which are predominant mineral phases of complex, low-grade nickel laterite ores will foster our understanding and help elucidate the prevailing mechanisms during AL of such lateritic ores.

As the main aim and focus of this study, H$_2$SO$_4$ acid-based leaching mechanisms and kinetics and rheological behaviour of 15–57 wt.% solid dispersions of hematite, goethite, kaolinite and smectite were investigated. Specifically, the influence of leaching time (up to 4 h) and temperature (25 and 70 °C) at pH 1 were studied to establish links between pulp mineralogy/chemistry, temperature, shear rheology and the leaching mechanisms and kinetics. Furthermore, kinetic analysis was carried out to understand and establish the exact mechanism/s underpinning leaching.

2. Experimental methods

2.1. Materials

Four, polydispersed (1–150 μm), model clay (kaolinite and smectite: Na-montmorillonite) and oxide (hematite and goethite) (Unimin and Aldrich, Australia) mineral samples were used in this study. Fig. 1 and Tables 1–3 summarize their properties. From the size analysis data in Fig. 1, smectite particles were notably finer than those of kaolinite. In the case of the oxide minerals, the hematite particles were relatively finer than the goethite particles. XRF analysis showed significant differences in the concentration of species from both oxides and clays (Table 1). Whereas all the samples were relatively pure, they contained noticeable amounts of impurity elements to different extents. From mineralogical analysis, whilst the hematite, kaolinite and smectite samples were highly crystalline, there was ~2.4% amorphous content in the goethite sample (Table 2). For the possible presence of trace amounts of amorphous phase in hematite, kaolinite and smectite at very low concentrations (e.g., <0.5 wt.%), this could not be established by the XRD analysis. BET specific surface area analysis revealed that the two clay minerals had markedly higher values than the oxide minerals (Table 3). The observed differences in feed properties (PSD, mineralogy/chemistry and BET specific surface area) will have a marked
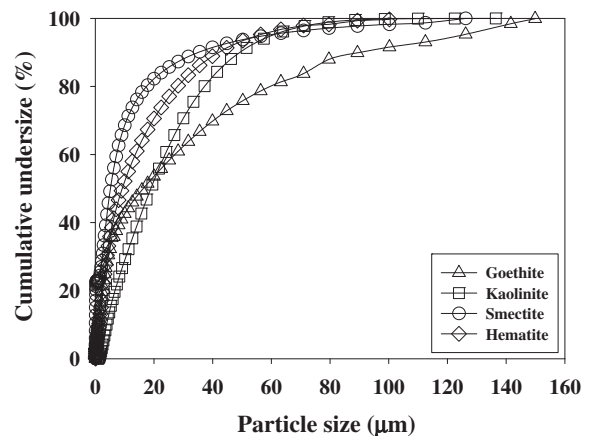

Fig. 1. Particle size distributions of single mineral feeds used in the study.