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Leaching behaviour of low and high Fe-substituted chlorite clay minerals at low pH

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ABSTRACT

The behaviour of low-Fe and high-Fe substituted chlorite mineral dispersions was investigated under industrially-relevant, atmospheric leaching conditions typical of low grade, uranium-bearing lateritic ore processing. The main focus was on the influential role played by the clay mineral chemistry. Preferential leaching of Al(III), Fe(II/III) and Mg(II) metal ions over tetrahedral Si species was indicated at pH 1 and 70 °C by supernatant speciation, the kinetics of which was faster at high-Fe than at low-Fe substitution. For the low-Fe chlorite, the incongruent leaching behaviour of Al(III), Fe(II/III) and Mg(II) species was substantially similar. In the case of the high-Fe chlorite however, despite its lower Mg(II) content, Al(III) and Fe(II/III) species leaching rates were relatively lower than that of Mg(II). Crystallo-chemical (XRD, XRF and EM) and spectroscopic (FTIR and XPS) analyses indicated that the incongruent leaching led to significant bulk particle and interfacial layer structures' modification, impacting dramatically upon pulp chemistry, mineralogy and particle interactions. Mineral chemistry-mediated formation of polycondensed, sub-crystalline aluminosilicate gel structures and secondary mineral phases prevailed in the course of leaching. A greater increase in high-Fe pulp particle interactions, in contrast with the low-Fe pulp, was observed during leaching, reflecting remarkably high, time-dependent shear yield stresses, reminiscent of highly viscous gels. The development of viscous gel structures whose strength is strongly dependent upon chlorite mineral chemistry has important implications for the efficacy of aqueous processing of clay-rich lateritic ores.

1. Introduction

Acid-consuming aluminosilicate clay gangue minerals such as chlorite and muscovite or sericite are commonly encountered in hydrometallurgical processing (e.g., pressure, atmospheric and heap leaching) circuits of complex, low grade laterite ores (Collier et al., 2000; Macnaughton et al., 2000; Ragozzini and Sparrow, 1987; Ragozzini et al., 1986; Secomb et al., 2000). Their presence as a major value metal's (e.g., uranium, nickel and cobalt) host mineral phases may result in high acid consumption and the formation of unwanted pulp gelation (Macnaughton et al., 2000; Nosrati, 2011; Nosrati et al., 2011b). Pulp gelation can have a striking impact on value metal leaching kinetics, recovery and yield, pulp viscosity and yield stress, transport power and solid–liquid separation in counter current decantation and thickening operations (Collier et al., 2000; Dreisinger, 2006; Macnaughton et al., 2000; Nosrati et al., 2011a, 2011b, 2012a, 2012b; Ragozzini and Sparrow, 1987; Ragozzini et al., 1986; Secomb et al., 2000; Wittington and Muir, 2000).

Although our understanding of clay mineral structure and reactivity in acidic media is well advanced, to date, there is still a dearth of knowledge and understanding of the interplay between ore mineralogy and chemistry during H_2SO_4 acid leaching of mica-group chlorite clays as typical, host lateritic gangue minerals (Collier et al., 2000; Macnaughton et al., 2000; Nosrati et al., 2011a, 2011b; Secomb et al., 2000). For instance, two mineralogically similar clay minerals which display noticeably different chemistries may also show dramatically different leaching and rheological behaviour that is difficult to predict (Nosrati et al., 2011b). Due to clay minerals' structural complexities and chemical variability, the several mechanisms involved in the acid leaching process are yet to be deconvoluted and well-defined (Adams, 1976; Adams and Kassim, 1983; Bain, 1977; Coffman and Fanning, 1975; Herbillon and Makumbi, 1975; Villieras et al., 1994). As a common lateritic host gangue, a better understanding of the leaching behaviour of chlorite minerals which have undergone different geochemical alterations or laterization is of significant interest. The new information gleaned from such leaching studies will lead to the design of more effective strategies for the mitigation of some of the clay mineral-mediated hydrometallurgical difficulties encountered in aqueous processing (atmospheric, pressure and heap leaching) of concentrated, low grade lateritic ore pulps.

Chlorites are generically layered phyllosilicate clay minerals of structures (e.g., $(Mg, Fe, Al)_6[AlSi_3O_{10}](OH)_8$) (Bailey, 1980). The crystal unit cell comprises of Al(III) octahedral (O) layer sandwiched by two Si(IV) tetrahedral (T) layers with an OH interlayer. Extensive substitution of the Si(IV) by Al(III) or Al(III) by Fe(III) or Fe(II) and Mg(II) occurs during laterization. Charge balancing cations (Mg(II), Fe(II) and Fe(III)) are located in the hydroxyl sheets of the TOT and inter-layer. Chlorite minerals' leaching behaviour has been extensively studied under acidic

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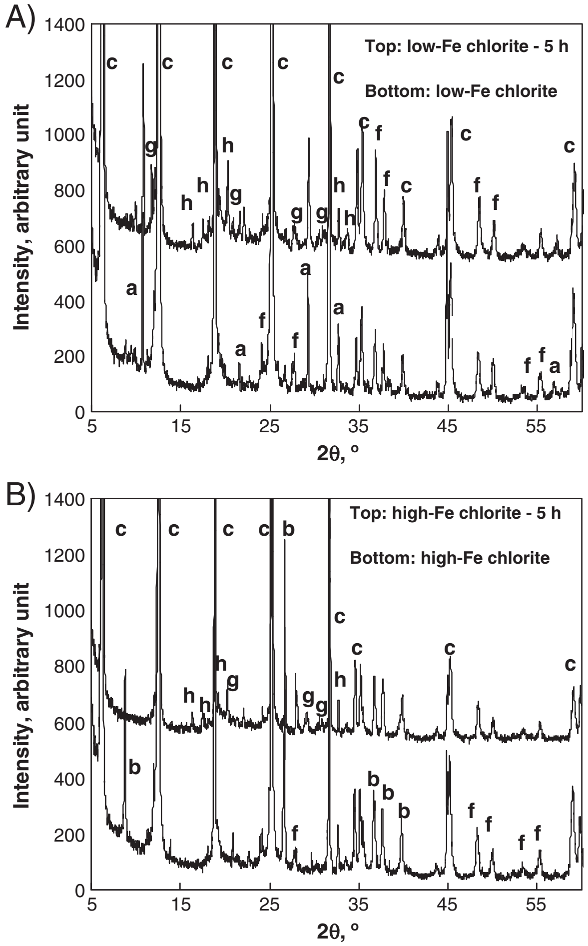

Fig. 1. XRD patterns for (A) low- and (B) high-Fe chlorites before and after 5 h leaching. The presence of other mineral phases is indicated as follows: a = anthophyllite, b = biotite, c = chlorite, f = albite, g = gypsum and h = hexahydrite.

weathering simulating conditions (Bain, 1977; Banfield and Murakami, 1998; Brandt et al., 2003; Herbillon and Makumbi, 1975; Herrmann, 1975; Lowson et al., 2005; Malmstrom et al., 1996). Primary chlorites may transform into interstratified vermiculite/smectite following incongruent leaching of certain structural cations (Banfield and Murakami, 1998).

A further consequence of incongruent leaching is supernatant supersaturation with metastable species and the potential precipitation of secondary mineral phases onto the altered chlorite particles (Hochella et al., 1999; Krawczyk-Barsch et al., 2001). Lowson et al. (2005, 2007) proposed that acidic leaching of chlorite may proceed through preferential proton attack of the lattice aluminium–oxygen bonds to release Al(III) species, leaving a hydrolysed silica framework structure. The hydrolysed structure subsequently dissolves through a rate defining step (Chou and Wollast, 1984; Nesbitt and Skinner, 2001; Oelkers, 2001a, 2001b). More recently, Kameda et al. (2009) reported that Mg-rich chlorite dissolution at pH 3 and 25 °C was non-stoichiometric, reflecting preferential leaching of Mg(II)/Al(III) species, leaving amorphous Si phase structures behind. Despite the useful information gleaned from the above studies, a lack of understanding of the potential impact of chlorite mineral-specific chemistry arising from Fe/Mg-substitutions on atmospheric leaching behaviour of lateritic ores at pH 1 and elevated temperatures (e.g., 70 °C) persists.

In this study, isothermal, batch leaching behaviour of two, well-characterised, mineralogically similar chlorites displaying marked chemical differences (mainly Fe/Mg substitutions and contents) was investigated at 70 °C and pH 1. These clay minerals may constitute a significant component of uranium lateritic ores in Australia, whilst the pH and temperature values are typical of those currently prevailing in some of the associated atmospheric acid leaching operations (Macnaughton et al., 2000; Nosrati, 2011; Secomb et al., 2000). The pristine and leach solid residues, pulps and solutions were fully characterised using standard techniques, including powder X-ray diffraction (XRD), X-ray fluorescent spectroscopy (XRF), electron microprobe (EM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), inductive coupled plasma-mass spectroscopy (ICP-MS) and the vane rheometer. The characterisation of leach solution and residue in combination with surface chemistry and rheological measurements provide a better understanding of the leaching behaviour and particle interactions of chlorite pulps.

2. Material and methods

2.1. Materials

Two types of chlorite minerals having substantially similar Si and Al contents, one with lowered **Fe** but higher Mg substitution (Geological Specimen Supplies Ltd, Australia) and the other with higher Fe but lower Mg substitution (Ward's Natural Science Est. LLC, US) were used in this study. Quantitative XRD analysis showed that the low-Fe chlorite contained 99% chlorite and traces of anthophyllite, and albite (Fig. 1). The high-Fe chlorite consisted of ~94.5% chlorite, 2.0% plagioclase, 3.5% biotite and a trace of ilmenite. The average compositions (Table 1) were determined by X-ray fluorescence spectroscopy (XRF). The electron microprobe analysis showed the molecular structures of the chlorites as follows:

Low-Fe chlorite:

$$[(\mathrm{Mg}_{3.48}\mathrm{Fe(II)}_{0.39}\mathrm{Al}_{1.33}\mathrm{Fe(III)}_{0.71}\mathrm{Ca}_{0.07}\mathrm{K}_{0.02})][\mathrm{Al}_{1.30}\mathrm{Si}_{2.70}]\mathrm{O}_{10}(\mathrm{OH})_8 \tag{1}$$

High-Fe chlorite:

$$[(\mathrm{Mg}_{2.55}\mathrm{Fe(II)}_{1.41}\mathrm{Al}_{1.30}\mathrm{Fe(III)}_{0.69}\mathrm{Ca}_{0.06}\mathrm{K}_{0.03})][\mathrm{Al}_{1.44}\mathrm{Si}_{2.56}]\mathrm{O}_{10}(\mathrm{OH})_8 \tag{2}$$

Subtle differences were observed in Si, Al, Fe, Ca, K and Mg concentrations between XRF and electron microprobe analyses, and these may be ascribed to the fact elemental composition data are gleaned from a much larger bulk sample volume for the former whilst that of the latter are largely based on smaller volumes. The as received samples were dry milled in a ring mill to produce similar sized (1–120 μm) feed samples with 80th percentile size (D_{80}) passing 75 μm. The BET surface areas of the milled products were 5.78 and 5.67 $m^2 g^{-1}$ for the low-Fe and high-Fe chlorite samples, respectively. Analytical grades sulphuric acid (98 wt.% purity, BDH Australia), KNO_3 (99.8 wt.% purity, BDH Australia), KBr (99.9 wt.% purity, BDH

Table 1
Chemical compositions of the chlorites by XRF.

Sample	Content (wt.%)										
	Al_2O_3	CaO	Fe_2O_3	K_2O	MnO	MgO	Na_2O	P_2O_5	SiO_2	TiO_2	LOI
Low-Fe chlorite	20.00	0.71	18.70	0.04	0.05	20.90	0.15	0.42	28.30	2.36	8.66
High-Fe chlorite	19.90	0.66	28.90	0.29	0.10	12.60	0.45	0.30	25.90	2.66	7.69