EFFECT OF MINERALOGY AND OXIDANT TYPE ON AQUEOUS DISPERSION OXIDATION-REDUCTION POTENTIAL AT LOW PH

Catherine Y.K. Fung, Jason N. Connor*, Jonas Addai-Mensah

Ian Wark Research Institute, University of South Australia
Mawson Lakes SA 5095
*Email address: jason.connor@unisa.edu.au

ABSTRACT

Oxidation-reduction potential (ORP) studies are important for quantifying the impact of process water quality and oxidative conditions on complex ores' leaching behaviour. For mineralogically and chemically complex plant pulps, ORP monitoring is often utilised during value mineral extraction but its interpretation is difficult. The objective of this work was to determine whether ORP can be practically related to the individual constituent minerals of complex ores during leaching at low pH and high temperature. To understand the relationship between mineralogy and ORP during isothermal batch leaching, two common model mineral dispersions, hematite (Fe_2O_3) and mica group chlorite clay ($[Mg_{3.56}Fe(II)_{0.39}Al_{1.33}Fe(III)_{0.71}][Al_{1.30}Si_{2.70}]O_{10}(OH)_8$) and their mixture (maintained at pH 1 and 70 °C over 3 h) were investigated. The effect of oxidant type (sodium chlorate *vs.* hydrogen peroxide) on ORP was also evaluated. The ORP was found to be controlled by the Fe(II/III) couple. The ORP remained practically constant after the first half hour in the absence of an oxidant for all mineral dispersions. Thereafter, it varied according to the mineralogy with hematite giving the highest ORP values and chlorite the lowest. The presence of oxidant caused the initial ORP to increase for all leach pulps. When chlorate was present, the ORP of the hematite increased steadily corresponding to increased Fe(III)/Fe(II) ratio while that for chlorite decreased steadily due to a decreasing Fe(III)/Fe(II) ratio. The ORP for the mixed mineral system appears to be a non-linear combination of the two. Sodium chlorate was also found to be a more effective oxidant compared with hydrogen peroxide in these experiments as it increased the ORP by a larger degree.

INTRODUCTION

Oxidation-reduction potential

Oxidation-reduction potential (ORP) measurement provides a convenient method for monitoring electrochemical reactions within aqueous environments. Despite the simplicity of ORP measurement, interpretation of the ORP data is generally difficult because it is influenced by many different factors such as solution chemistry, temperature, pH, and the electrode material. There are a number of systems both natural and synthetic where a combination of minerals were leached and found to affect the ORP (Bibi et al., 2008, Vilcaez et al., 2009). Indeed, ORP is often used to monitor these processes as exemplified by several investigations of leaching complex ore mixtures (Nirdosh, 1985, Vilcaez et al., 2009, Avvaru et al., 2008, Sommer et al., 1973). Notwithstanding the many reported studies, the contribution of the individual minerals to ORP during complex mineral leaching operations has not been well studied, particularly under industrially relevant conditions of low pH and high temperature. In many ORP measurements, where a Pt electrode is employed, the species that often determines the measured potential is Fe (Ring, 1980, Sommer et al., 1973). The availability of Fe in solution is dependent upon the water quality, solubility and mineralogy of the ore undergoing leaching. The question is, how does the different Fe-bearing minerals' leach behaviour contribute to the measured ORP? As an initial step towards addressing this issue, the ORPs of simple common mineral systems of hematite, chlorite and their mixture were investigated.

In ideal electrochemical systems where the redox couples are reversible, the ORP can be predicted using the Nernst equation (Hibbert, 1993, Grundl, 1995):

$$E_h = E^0 + \frac{RT}{nF}\ln\left(\frac{[Oxidised\ State]}{[Reduced\ State]}\right), \qquad (1)$$

where E_h is the half cell potential, E^o is the standard electrode potential of the redox reaction, R is the gas constant, T is the temperature of the reaction, n is the number of electrons transferred during the reaction, F is the Faraday constant (9.65×10^4 C/mol of electrons), and [*Oxidised State*] and [*Reduced State*] are the activities (often approximated using concentrations) of the oxidised and reduced species respectively.

The ORP is therefore determined by the redox couple ratio rather than the absolute concentrations of the individual species. Furthermore, there are several limitations associated with the Nernst equation. It is only applicable when the system is at equilibrium with redox couples that are reversible at the electrode (Grundl, 1995). Also, the Pt|Ag/AgCl electrode, which is widely used in commercial measurement, appears to be only sensitive to certain redox couples such as Fe(II/III) and Mn(II/IV) (Grundl, 1995). If this is the case then there should be some correlation between the leach ability of the Fe from the constituent minerals and the measured ORP.

Model minerals: hematite and chlorite

Complex ore bodies by their very nature contain many types of minerals. Two common mineral groups often found within an ore are the iron oxides and clays. These minerals provide an ideal starting point for studying the relationship between ORP and mineralogy since iron oxide is chemically simple and clays are relatively more chemically complex.

Hematite (iron oxide) is one of the most abundant oxide minerals on earth. There have been a number of studies of hematite in organic and inorganic acid media (Taxiarchou et al., 1997, Majima et al., 1985). Very often, the focus has been on the performance of the acids as well as the effect of chelating agents (*e.g.* EDTA) on their effectiveness during leaching, rather than the nature of the ORP in these systems. During acid leaching pure hematite releases Fe (III) ions which are expected to increase the measured ORP. Because of this and because of its practical importance, single mineral hematite provides a model system for investigating ORP during acid leaching.

Chlorite is a common mica group clay mineral with a structure made up of alternating tetrahedral-octahedral-tetrahedral (T-O-T) aluminosilicate and brucite-like layers (Ralph and Chau, 2002). It has been reported that the octahedral brucite layer, where most of the Fe(II/III) ions substitution in the lattice occurs, dissolved more easily than the tetrahedral Al-O-Si layer (Brandt et al., 2003). Chlorite was chosen as a model single mineral for this study because of its chemical complexity and the fact that it leaches both Fe(II) and Fe(III) ions. Dissolution of chlorites in both organic and inorganic acid have been extensively studied (Ross, 1969, Kodama and Schnitzer, 1972, Brandt et al., 2003, Hamer et al., 2003, Lowson et al., 2005, Okada et al., 2005). In inorganic acid, the dissolution rate was found to increase with increasing Fe content and decreasing Mg content (Ross, 1969). Upon leaching at high H_2SO_4 concentrations (5 N and 7 N) and high temperature (70 to 90 °C), the dissolution sequence was reported to be Mg > Fe > Al (Okada et al., 2005). Sulphuric acid was employed throughout the current study since the aforementioned investigations found it to be more effective than other acids for leaching hematite and chlorite.

MATERIALS AND METHODS

Mineral samples

Composition of the hematite sample (as determined by quantitative XRD) and chlorite sample (as determined by XRF) are given in Tab. 1 and Tab. 2 respectively.

Tab. 1: Quantitative XRD analysis for hematite.

Phase	Formula	Weight %
Hematite	Fe_2O_3	58
Goethite	$FeO(OH)$	7
Kaolinite	$Al_2Si_2O_5\,(OH)_4$	7
Quartz	SiO_2	7
Amorphous Material		22
Total		100

Tab. 2: XRF analysis for chlorite.

Materials	Formula	Weight %
Silica	SiO_2	28.3
Aluminum oxide	Al_2O_3	20
Magnesium oxide	MgO	20.9
Iron oxide	Fe_2O_3	18.7
Potassium, Titanium, Manganese, Sodium, Calcium	K, Ti, Mn, Na, Ca	Trace

The chlorite sample used in this work may be described by the following formula according to electron microscope analysis:

$$[(Mg_{3.56}Fe(II)_{0.39}Al_{1.33}Fe(III)_{0.71})][Al_{1.30}Si_{2.70}]O_{10}(OH)_8$$

The particles were sized using laser diffraction (Malvern Mastersizer X, Malvern UK), giving d_{10}, d_{50}, d_{80} of 2, 12, 24 μm respectively for hematite and 5, 32, 70 μm for chlorite.

Reagents

The pre-leach slurry was prepared with high purity Milli-Q water. AR grades of 98 wt.% sulphuric acid (BDH Australia), 30 wt.% hydrogen peroxide (Chem Supply) and (99 wt.% pure) sodium chlorate (Unilab) and were used during leaching experiments.

Leaching Experiments

The leaching experiments were carried out in a 400 cm^3 beaker with approximately 300 g of suspension at 57 wt.% solids. All experiments were conducted isothermally at 70 °C with a hotplate and at a constant agitation rate of 500 rpm using an overhead stirrer. The pulp pH was maintained at 1.1 ± 0.1 by an auto-titrator (842 Titrando, Metrohm-Tiamo) to prevent it dropping below a pH of 1. Samples were removed periodically at various times during leaching and then centrifuged (Centrifuge 5416, Eppendorf) at 11000 rpm for 6 min. The liquor samples were diluted by a factor of 10 with pH 1 solution prepared from sulphuric acid and stored at 4 °C prior to analysis. The solids samples were dried in the oven at 60 °C overnight.

The ORP was measured using a combined Pt|Ag/AgCl electrode connected to a high impedance ORP meter (WP-80D, TPS). The reliability of the ORP electrode at elevated temperature was verified by performing a series of tests using Fe(II/III) sulphate solutions at pH 1 and 70 °C. The electrode was routinely reconditioned by immersion into saturated KCl solution after each experiment.

Chemical Analysis

Fe(II) concentrations were determined by potentiometric titration (Tim 854, Radiometer) with cerium(IV) sulphate as the titrant (AR grade, Chem Supply). Total iron, Fe(II/III), analysis was carried out with a flame atomic absorption spectrometer (FAAS) (AA-6300, Shimadzu) that was calibrated using ammonium ferrous sulphate (AR grade, BDH Australia).

RESULTS AND DISCUSSION

Three mineral systems were investigated: 100% hematite, 100% chlorite, and a 5 wt.% chlorite and 95 wt.% hematite mixture. Chander's (2003) and others (Garrels and Christ, 1965, Grundl, 1995) have reported that only reversible redox couples may cause changes in the ORP reading. In the investigated mineral systems and for this particular electrode arrangement, it was assumed that the dominant redox couple would be Fe(II) and Fe(III).

Leaching with no oxidant

Fig. 1 shows the variation of ORP during the leaching of the three different mineral systems. Leaching of hematite without oxidant resulted in an ORP increase of 26 mV over the duration of the experiment. Chlorite on the other hand, exhibited opposite behaviour with the ORP decreasing by about 60 mV in the first 30 min before stabilising. The progressive decrease in ORP indicates the Fe(III)/Fe(II) ratio is also decreasing with time and this is confirmed in Fig. 2.

For the mixed system, comprising 5 wt.% of chlorite and 95 wt.% of hematite, the ORP measurements were between those of the two single minerals systems. Although the trend most closely resembles that of hematite the measured values do not appear to be proportionate to the relative masses of the two minerals. This will be discussed in more detail later. Of the three mineral systems the hematite sample had the highest ORP. This is expected since hematite leaches predominantly Fe(III). Hence, the Fe(III)/Fe(II) ratio would be high.

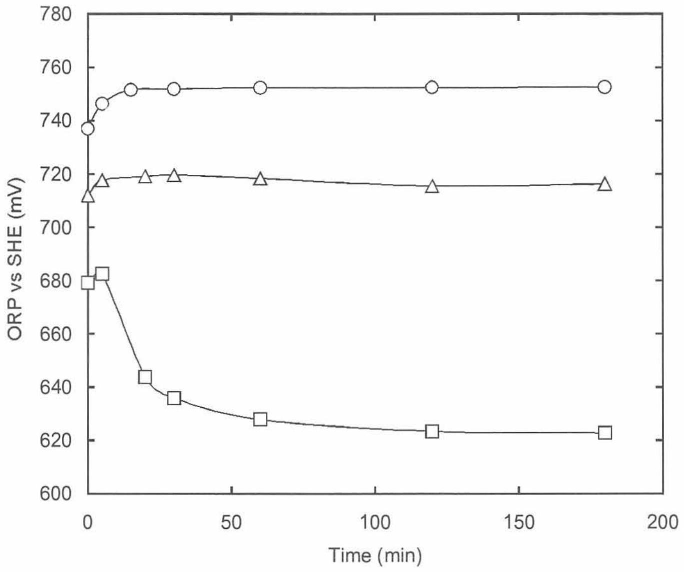

Fig. 1: ORP measurement during the leaching of hematite (circles), chlorite (squares) and 5 wt.% chlorite + 95 wt.% hematite (triangles).

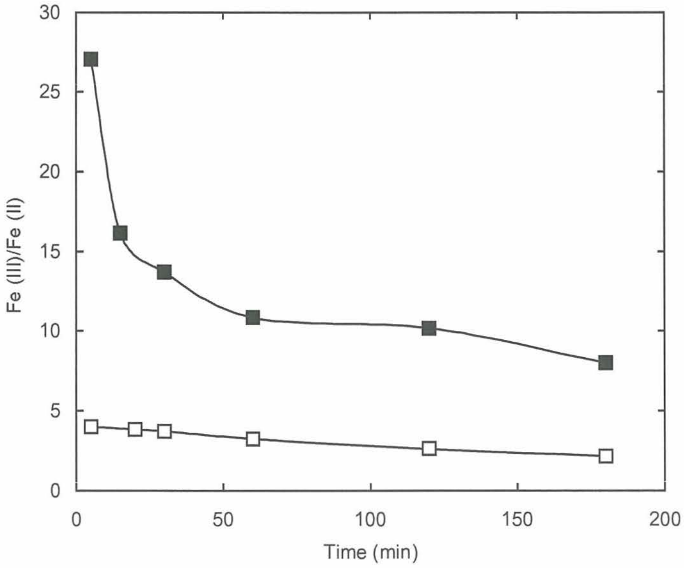

Fig. 2: Fe(III)/Fe(II) as a function of leaching time for chlorite with no oxidant (open squares) and with chlorate (solid squares).

Leaching with oxidant

Chlorate

The effect of chlorate on the ORP as a function of time is illustrated in Fig. 3. For all three systems, the addition of oxidant resulted in an ORP that was higher than without it. This would be expected since the Fe(II) concentration would decrease as it was oxidised by the chlorate to Fe(III) causing the Fe(III)/Fe(II) ratio to increase.

For hematite, the ORP rose by 150 mV in the first 30 min and continued to increase gradually for the remaining period. Although pure hematite does not leach out Fe(II) ions, the sample used in this work contained 22 wt.% amorphous material as well as some kaolinite and quartz, some of which may contain Fe(II). In addition, Fe(III) tends to reduce to Fe(II) particularly in acid media (Alian et al., 1981), which would also increase the Fe(II) concentration. Therefore, the increased ORP during hematite leaching in these experiments is probably due to the oxidation of extraneous Fe(II) to Fe(III) enhancing the Fe(III) concentration in the solution.

The ORP for the chlorite sample increased by about 65 mV in the first 5 min after which it gradually decreased. It is likely that in the first 5 min, rapid oxidation of Fe(II) took place consuming most of the oxidant. However, once the oxidant depleted, the Fe(II) concentration gradually increased, causing the Fe(III)/Fe(II) ratio, and hence the ORP, to gradually decrease (Fig. 2). It was also noted that, although the oxidant appears to have depleted as the experiment progressed, there was enough Fe(III) present in solution from the initial oxidation reaction to maintain a high ORP relative to that for the chlorite leaching without oxidant addition. For the mixed system with chlorate, the ORP trend was similar to that without chlorate. The ORP values were between those of the two single mineral systems with the overall behaviour similar to that for hematite. However, the ORP increased more slowly in comparison with the hematite system. This is probably due to Fe(II) oxidation from the small portion of chlorite present, promoting the decrease of the Fe(III)/Fe(II) ratio.

Hydrogen peroxide

The effect of hydrogen peroxide was investigated for the hematite and mixed systems. It was expected that these two systems display quite similar behaviour since 95% of the mixed system was hematite. As noted previously, the weight % of the mineral components in the mixture does not appear to directly control how the ORP is established. Fig. 3 shows that, in the case of hematite, the ORP was stable for the first 15 min after which it increased sharply by about 110 mV in the following 45 min. Thereafter the ORP decreased gradually. This can possibly be explained in the manner of several researchers (Dunford, 2002, Gonzalez-Davila et al., 2005, Paczesniak and Sobjowiak, 2003) who reported the reaction of hydrogen peroxide with Fe would first lead to oxidation of Fe(II) to Fe(III) but eventually, the HO_2 free radical would react with Fe(III) ions and regenerate Fe(II). Since the leach liquor of hematite was predominantly Fe(III), once Fe(III) started to reduce to Fe(II), the reaction between Fe(II) and hydrogen peroxide could take place. This may have lead to a rapid increase in Fe(III) concentrations followed by the regeneration of Fe(II), resulting in a decreasing ORP after the first 60 min.

The mixed system, on the other hand, behaved differently compared with the hematite at the initial stage. Again, the presence of Fe(II) would have allowed its oxidation to occur faster than for hematite with peroxide leaching. Also, unlike for the hematite case, although the ORP started to decrease after the first 5 min, it increased again after 30 min due to increased Fe(II) dissolution (and hence increased Fe(II) oxidation). Although data on chlorite's response to oxidation by peroxide are not available, the initial ORP variation for the mixed system is very similar to that observed for the case of chlorite oxidised by chlorate, with some depletion of oxidant occurring after the first 5 min. It seems that the mixed system is exhibiting a non-linear combination of the oxidisation features of both minerals.

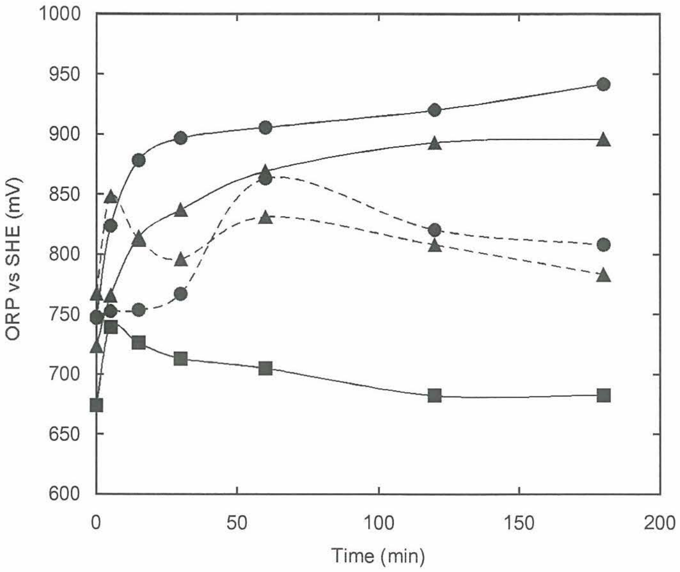

Fig. 3: ORP measurement during the leaching of hematite with chlorate (circles), with hydrogen peroxide (circles with dashed line) ; chlorite with chlorate (squares); 5 wt.% chlorite + 95 wt.% hematite with chlorate (triangles), with hydrogen peroxide (triangles with dashed line).

ORP and the mixed mineral system

The results show that, regardless of whether oxidant is present or not, the resultant ORP for the mixed system did not vary in proportion to the masses of the individual mineral constituents. Rather, it appears to be more consistent with the relative ease at which Fe is leached from each of the minerals. Although hematite is the main component by mass in the mixed system and there is a tendency for the ORP to reflect the Fe(III) leached from this phase, the variation in the ORP is disproportionate, *i.e.* a 5 % change in mass does not result in a 5 % change in the ORP for the mixed system. For instance, after 180 min, the ORP is essentially stable for the hematite (equivalent to 0% chlorite) and chlorite (equivalent to 100 % chlorite). This sets the bounds of the ORP between 620 and 730 mV *vs*. SHE. If the behaviour was linear with mass of chlorite, 5% of chlorite would change the ORP by approximate 5 mV, however, a 30 mV (~30 %) change is observed (upper graph of Fig. 4). A similar trend was observed when oxidant (chlorate) was added, with a 15 % drop in ORP observed (lower graph of Fig. 4). Hence, the amount of Fe that leached from the chlorite was significant enough to influence the ORP noticeably.

A mass balance of the total Fe leaching from each mineral provides a useful clue regarding the above observation. Depending on whether oxidant was added or not, between 20 and 40 % of the Fe in chlorite was leached. In contrast < 0.5 % of the total Fe of the hematite sample was leached under similar conditions, which is in agreement with the observations of others(Lu and Muir, 1988). Fig. 5 shows the total Fe measured in solution for all systems studied. It is clear that the total Fe liberated from the chlorite is substantially greater than that from the hematite by a factor of 10 (and even higher with oxidant added). Hence, a small amount of chlorite in the mixed system would be expected to contribute a significant amount of Fe to the leach solution. Using data presented in Fig. 5, it is possible to do a simple mass balance to predict the contribution from the chlorite and hematite to the total amount of Fe in the mixed system. Although chlorite only made up 5% of the mass, from this estimate, it contributed almost half of the total Fe in the mixed system. The Fe(II) and Fe(III) concentrations follow their relative abundance according to the stoichiometry of the mineral.

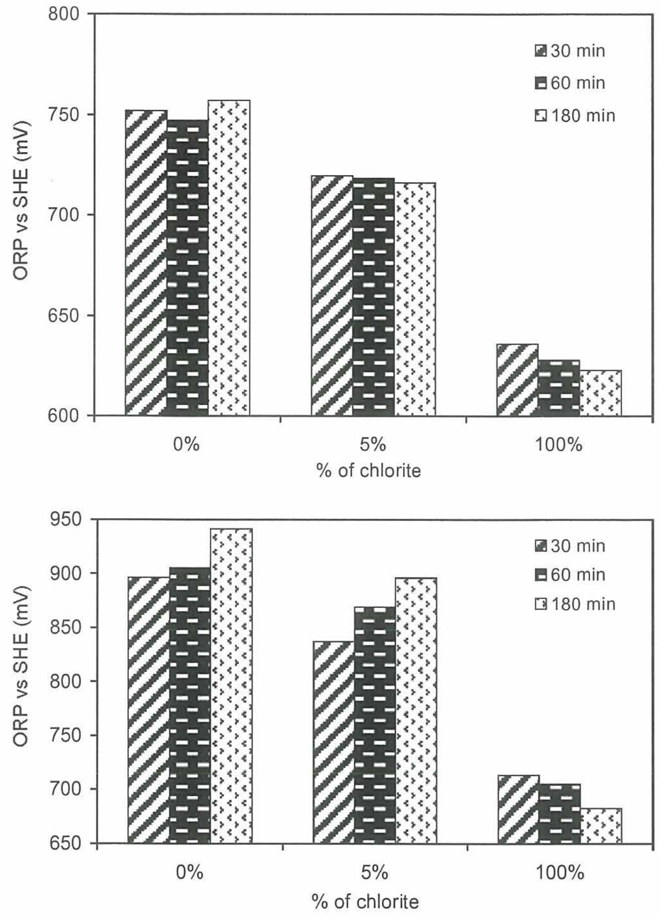

Fig. 4: Variation of ORP as a function of the percentage of chlorite in the hematite-chlorite mixed system at different times during leaching. Upper graph: no oxidant; lower graph: with chlorate addition.

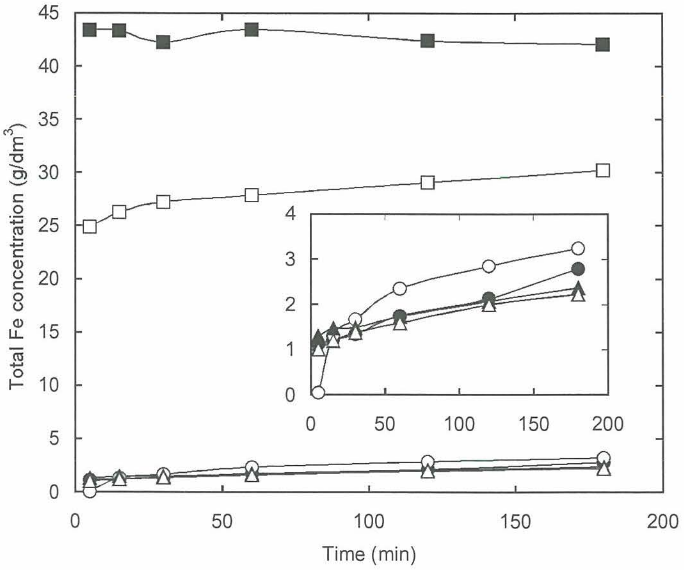

Fig. 5: Total Fe(II/III) concentration as a function of leaching time for hematite with no oxidant (open circles) and with chlorate (solid circles); chlorite with no oxidant (open squares) and with chlorate (solid squares); 5 wt.% chlorite + 95 wt.% hematite with no oxidant (open triangles) and with chlorate (solid triangles). The inset shows an enlarged version of the low concentration data.

This simple analysis suggests that knowledge of the stoichiometry and solubility of the Fe species from the component single minerals could be used to predict the relative amounts of Fe(II) and Fe(III) that are likely to be present during the leach. The total Fe(II) and Fe(III) concentrations for the combined minerals can then be calculated and incorporated into the Nernst equation (equation 1) to calculate, to a first approximation, the ORP of a mixed minerals system. Alternatively, if the ORP and total Fe are known for a dominant mineral (e.g. hematite) by mass it may be possible to follow leaching of minor minerals within the mixed mineral system, particularly if they contain a significant amount of Fe.

CONCLUSIONS

Although the results are for a limited number of minerals, there appears to be good correlation between the ratio of Fe species in solution and the ORP during leaching at low pH and elevated temperature. Other species present in solution do not seem to affect the ORP noticeably when using a Pt electrode unless they oxidise or reduce the Fe. This observation alone would simplify the interpretation of the ORP significantly and needs to be investigated further. In the systems studied the ORP is highest when hematite is leached with and without oxidant and this is consistent with what would be expected. For chlorite pulp, however, the ORP exhibits opposite behaviour. Oxidant addition increased the Fe(III)/Fe(II) ratio and hence the ORP. When oxidant is added, understanding the chemistry of the oxidation process for each mineral also becomes important. When the minerals were mixed the solution Fe ratio was governed by the ease at which Fe leached from the constituent minerals. Even though the mixed system only contained 5 wt.% of chlorite, it contributed approximately half of the total Fe throughout the leach process and this clearly influenced the measured ORP. This indicates that the behaviour of complex mineral systems may be substantially predicted if information about the solubilities of multivalent cations, with differing oxidation states, and stoichiometry of the component minerals are also available.

REFERENCES

Alian, A., El-Assy, B., Issa, M., Raheim, F. A. & Roushdy, H. (1981) A radioactive tracer and radiation study of the stability of ferric and ferrous ions and ascorbic acid. *Journal of Radioanalytical Chemistry,* 67**,** 83-93.

Avvaru, B., Roy, S. B., Ladola, Y., Chowdhury, S., Hareendran, K. N. & Pandit, A. B. (2008) Sono-chemical leaching of uranium. *Chemical Engineering and Processing,* 47**,** 2107-2113.

Bibi, M. H., Ahmed, F. & Ishiga, H. (2008) Geochemical study of arsenic concentrations in groundwater of the Meghna River Delta, Bangladesh. *Journal of Geochemical Exploration,* 97**,** 43-58.

Brandt, F., Bosbach, D., Krawczyk-Barsch, E., Arnold, T. & Bernhard, G. (2003) Chlorite dissolution in the acid pH-range: A combined microscopic and macroscopic approach. *Geochimica et Cosmochimica Acta.,* 67**,** 1451-1461.

Chander, S. (2003) A brief review of pulp potentials in sulfide flotation. *Internation Journals of Mineral Processing,* 72**,** 141-150.

Dunford, H. B. (2002) Oxidations of iron(II)/(III) by hydrogen peroxide: from aquo to enzyme. *Coordination Chemistry Reviews,* 233-234**,** 311-318.

Garrels, R. M. & Christ, C. L. (1965) *Solutions, Minerals and Equilibria,* New York and Tokyo, Harper & Row, John Weatherfill, Inc.

Gonzalez-Davila, M., Santana-Casiano, J. & Millero, F. (2005) Oxidation of iorn (II) nanomolar with H_2O_2 in seawater. *Geochimica et Cosmochimica Acta.,* 69, 83-93.

Grundl, T. (1995) Determination of redox status in sediments. IN HERBERT, E. A. (Ed.) *Metal contaminated aquatic sediments.* Chelsea, Mich, Ann Arbor Press.

Hamer, M., Graham, R. C., Amrhein, C. & Bozhilov, K. N. (2003) Dissolution of ripidolite (Mg, Fe-Chlorite) in organic and inorganic acid solutions. *Soil Science Society of America Journal,* 67, 654-661.

Hibbert, D. B. (1993) Electrodes and electrochemical cells. *Introduction to electrochemistry.* Lodon, The Mamcmillan Press LTD.

Kodama, H. & Schnitzer, M. (1972) Dissolution of chlorite minerals by fulvic acid. *Canadian Journal Of Soil Science,* 53, 240-243.

Lowson, R. T., Comarmond, M. C. J., Rajaratnam, G. & Brown, P. L. (2005) The kinetics of the dissolution of chlorite as a function of pH and at 25 °C. *Geochimica et Cosmochimica Acta.,* 69, 1687-1699.

Lu, Z. Y. & Muir, D. M. (1988) Dissolution of metal ferrites and iron oxides by HCl under oxidising and reducing conditions. *Hydrometallurgy,* 21, 9-21.

Majima, H., Awakura, Y. & Mishima, T. (1985) The leaching of hematite in acid solutions. *Metallurgical Transactions B,* 16B, 23-30.

Nirdosh, I. (1985) Ferric nitrate leachings of uranium and radium from uranium ores. *Hydrometallurgy,* 15, 63-76.

Okada, K., Arimitsu, N., Kameshima, Y., Nakajima, A. & Mackenzie, K. J. D. (2005) Preparation of porous silica from chlorite by selective acid leaching. *Applied Clay Science,* 30, 116-124.

Paczesniak, T. & Sobjowiak, A. (2003) The influence of solvent on the reaction between iron (II), (III) and hydrogen peroxide. *Journal of Molecular Catalysis A Chemical,* 194, 1-11.

Ralph, J. & Chau, I. (2002) Chlorite group. North Carolina, USA.

Ring, R. J. (1980) Ferric sulphate leaching of some Australian uranium ores. *Hydrometallurgy,* 6, 89-101.

Ross, J. G. (1969) Acid dissolution of chlorites: Release of magnesium, iron and aluminum and mode of acid attack. *Clays and Clay Minerals,* 17, 347-354.

Sommer, G., Ormrod, G. T. W. & Chaix, R. P. (1973) Recent developments in the instrumentation and automation of uranium-processing plants. *Journal of the South African Institute of Minning and Metallurgy,* 73, 413-420.

Taxiarchou, M., Panias, D., Douni, I., Paspaliaris, I. & Kontopoulos, A. (1997) Dissolution of hematite in acidic oxalate solutions. *Hydrometallurgy,* 44, 287-299.

Vilcaez, J., Yamada, R. & Inoue, C. (2009) Effect of pH reduction and ferric ion addition on the leaching of chalcopyrite at thermophilic temperatures. *Hydrometallurgy,* 96.

BRIEF BIOGRAPHY OF PRESENTER

Catherine Fung is studying a Bachelor of Engineering (Chemical) and a Bachelor of Mathematical Science (Applied Mathematics) at the University of Adelaide. In between her studies, she has spent the last year working at the Ian Wark Research Institute, University of South Australia, investigating the use of oxidation-reduction potentials for understanding mineral leaching circuits.