Minerals Engineering 98 (2016) 169–176

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Rare earth metal ion solubility in sulphate-phosphate solutions of pH range −0.5 to 5.0 relevant to processing fluorapatite rich concentrates: Effect of calcium, aluminium, iron and sodium ions and temperature up to 80 °C

G. Senanayake [a,*], S. Jayasekera [a,b], A.M.T.S. Bandara [a], E. Koenigsberger [a], L. Koenigsberger [a], J. Kyle [a,b]

[a] Chemical & Metallurgical Engineering & Chemistry, School of Engineering and Information Technology, Murdoch University, 90, South Street, Murdoch, WA 6150, Australia
[b] Formerly Consultants to Arafura Resources Limited, Australia

ARTICLE INFO

Article history:
Received 10 June 2016
Revised 28 July 2016
Accepted 29 July 2016

Keywords:
Rare earth
Solubility
Sulphate
Phosphate
Cations
Anions
pH
Temperature

ABSTRACT

The extraction of rare earth oxides from fluorapatite rich phosphate concentrates often involves a weak acid leach of fluorapatite and a sulphuric acid bake of the leach residue followed by water leach and precipitation to obtain an intermediate product. The main aim of this study was to determine and rationalize the solubility of rare earth metal ions in synthetic solutions representing various process liquors at the temperatures 40, 60 and 80 °C. The liquors contained different acid and metal ion concentrations with respect to sulphuric acid, phosphoric acid and sulphate salts of sodium, magnesium, aluminium, potassium, calcium and iron(III). A solid of mixed rare earth carbonates was used as the source of rare earth metal ions. The solubility tests and characterisation of solids using XRD were conducted at Murdoch University laboratories as part of the process development for the Arafura Resources Nolans rare earth project. The composition of initial carbonate solids and the solids and solutions formed after saturation were analysed for rare earth and other elements at TSW Analytical Laboratories in Perth using ICP-MS and ICP-OES. The precipitated solid in sodium-rich acidic sulphate solutions is the double salt $NaRE(SO_4)_2$ based on the solid assays. However, in acidic solutions free of sodium or of low concentrations of sodium the precipitated solid appears to be $RE_2(SO_4)_3$.

1. Introduction

The rare earth (RE) phosphate minerals such as monazite ($(Ce,La,Th,Nd,Y)PO_4$), florencite ($(La,Ce)Al_3(PO_4)_2(OH)_6$), xenotime ($YPO_4$), cheralite ($(Ca,Ce)(Th,Ce)(PO_4)_2$) and britholite ($(Na,Ce,Ca)_5(OH)[(P,Si)O_4]_3$) are often associated with fluorapatite (Gupta and Krishnamurthy, 2005). The treatment of fluorapatite for RE extraction commonly requires a pre-leach stage with a mineral acid as shown in Eqs. (1)–(4). Calcium, sodium, magnesium, aluminium, potassium, iron, manganese and a range of other metals such as uranium and thorium may enter the solution depending upon the oxide/phosphate mineralogy (Bandara and Senanayake, 2015; Stone et al., 2016). Further processing may involve partial neutralisation to precipitate any rare earth metal ions which may have solubilised during pre-leach, acid bake of the residue/precipitate with sulphuric acid, water leach followed by purification and precipitation (Beer et al., 2008). Previous studies describe the RE extraction process routes (Zhang and Edwards, 2012; Abreu and Morais, 2010; Wang et al., 2010; Preston et al., 1996; Kuzmin et al., 2012; Kul et al., 2008) and highlight the importance of thermodynamic data of rare earth metal ion species in order to predict their behaviour in hydrometallurgical unit operations including leaching, separation, concentration, precipitation and recovery (Kim and Osseo-Asare, 2012). Some of the existing data on equilibrium constants are listed in Tables 1–3. The nature of the anions, cations, pH and temperature can affect the leaching and precipitation of rare earth metal ions. The deportment of the rare earth elements (REEs) depends on either the solubility products of rare earth metal ion species, or their propensity to adsorb on other solid species. The sulphuric acid digestion of phosphate minerals producing hemihydrate (x = 0.5) or dihydrate, gypsum (x = 2) (Eq. (2)) allows the enrichment of REEs in the phosphor-gypsum with only 20–30% REEs in the phosphoric acid leach liquor (Wang et al., 2010).

$$Ca_5(PO_4)_3F + 10HCl = 5CaCl_2 + 3H_3PO_4 + HF \tag{1}$$

---

* Corresponding author.
E-mail address: G.Senanayake@murdoch.edu.au (G. Senanayake).

http://dx.doi.org/10.1016/j.mineng.2016.07.022

Table 1
Solubility products of some RE double sulphate salts.

RE sulphate	T °C	pK_{SP} (M = Na)	pK_{SP} (M = K)
$MPr(SO_4)_2{\cdot}H_2O$	20	7.1	5.5
$MNd(SO_4)_2{\cdot}H_2O$	20	7.1	5.8
$MGd(SO_4)_2{\cdot}H_2O$	20	5.5	
$MLa(SO_4)_2{\cdot}H_2O$	20	6.8	5.8
	25	5.7	
$MCe(SO_4)_2{\cdot}H_2O$	20	8.4	6.0
	25		4.9

Literature data from Lokshin et al. (2007).

Table 2
Calcium phosphate complexes and associated formation constants.

Reaction	Log K (25 °C)
$Ca^{2+} + PO_4^{3-} + H^+ = CaHPO_4^0$ (aq)	15.1
$Ca^{2+} + HPO_4^{2-} = CaHPO_4^0$ (aq)	2.80
$Ca^{2+} + SO_4^{2-} = CaSO_4^0$ (aq)	2.11
$Ca^{2+} + PO_4^{3-} + 2H^+ = Ca(H_2PO_4)^+$ (aq)	20.9
$Ca^{2+} + HPO_4^{2-} + H^+ = Ca(H_2PO_4)^+$ (aq)	8.30

Sillen and Martell (1964).

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 5xH_2O = 3H_3PO_4 + 5CaSO_4 \cdot xH_2O + HF \tag{2}$$

$$Ca_5(PO_4)_3F + 10HNO_3 = 5Ca(NO_3)_2 + 3H_3PO_4 + HF \tag{3}$$

$$Ca_5(PO_4)_3F + 7H_3PO_4 = 5Ca(H_2PO_4)_2 + HF \tag{4}$$

Wang et al. (2010) summarized some of the important findings by previous researchers: (i) a higher leaching efficiency of REEs can be achieved by introducing aluminium and/or iron and/or silica minerals into the slurry indicating the effect of ionic interactions on solubility, (ii) the rare earth metal ion solubility can also be increased by increasing the phosphoric acid concentration to achieve a leaching efficiency increasing in the ascending order of the atomic number of REE and solubility products of RE phosphates, (iii) the increase in concentration of phosphoric acid (as P_2O_5) from 5% to 25% increases RE leaching efficiency from 32% to 72%, (iv) depending on the composition and nature of the phosphate ore the RE leaching passes through a maximum at H_2SO_4/CaO = 1.1/1.0, as the excess H_2SO_4 affects the solubility and super-saturation of gypsum, (v) the RE leaching efficiency decreases from 61.4% at 70 °C to 25.1% at 75 °C as a result of the decrease in RE phosphate solubility with the increase in temperature. These results indicate the importance of a systematic study on the RE solubility in sulphate-phosphate solutions in the absence or presence of various cations and anions relevant to the processing of rare earth oxide/phosphate ores.

This work was specifically aimed at determining the maximum solubility of REEs in predominantly sulphate media and to consider the effect of the concentrations of sulphuric and phosphoric acids, pH, temperature and the presence of other cations on the saturated solubility of REEs. The study also investigated the nature of RE solids precipitated from acidic solutions under varying conditions of pH and temperature. More specifically the test work program had six main objectives: (i) to investigate the effect of anion by comparing the solubility of REEs in solutions of 1 mol/L perchloric and sulphuric acid, (ii) to examine the effect of varying sulphuric acid concentration on solubility of REEs, (iii) to compare the solubility of REEs in the presence or absence of sodium ions, (iv) to examine the effect of pH adjusted using perchloric acid, (v) to examine the use of different RE-carbonate solid samples, and (vi) to examine the effect of temperature on solubility of REEs.

2. Experimental

Different rare earth carbonate solid samples were provided by Arafura Resources Limited. They were prepared in a pilot plant from Arafura Resources high grade ore utilizing the flowsheet described by Beer et al. (2008). They were characterised by X-ray Diffraction (XRD) and Inductively Coupled Plasma Spectroscopy (ICPS). The solutions of different compositions denoted by A, B and C were prepared by dissolving sulphate salts of analytical grade reagents in deionized water in the presence or absence of H_2SO_4 and H_3PO_4. The pH was adjusted to between pH 2.5 and 3.0 (solution B) with $HClO_4$. This solution was filtered to remove the undissolved/precipitated $CaSO_4{\cdot}2H_2O$ and the filtrate was used for the solubility measurements. The RE carbonate sample (2–3 g) was added to 70 mL of solutions in a glass vessel with a water jacket, thermometer and a reflux condenser. Nitrogen gas was bubbled through the synthetic liquors (A, B and C) before and after adding the carbonate solid and the slurry was magnetically stirred overnight to achieve saturation. The final saturated solutions, which were prepared in order to mimic possible Nolans project

Table 3
Formation constants (β) for rare earth metal ions and solubility products (K_{SP}) for phosphates.

Metal	Equilibrium constants					
	Log β $[RE(SO_4)]^+$	Log β $[RE(SO_4)_2]^-$	Log β $[RE(HPO_4)]^+$	Log β $[RE(HPO_4)_2]^-$	Log β $[RE(H_2PO_4)]^{2+}$	$-$Log K_{sp} (pK_{sp}) [RE.PO_4 (solids)]
Y	(4.26)[a]	(4.78)[a]				24.7 (25.7)[b]
La	3.62	4.93	4.10		2.50	26.2 (26.4)[b]
Ce	3.62		4.32		2.43	
Pr	3.62		4.45		2.37	26.1 (26.7)[b]
Nd	3.64 (4.00)[c]	(5.44)[c]	4.54 (4.69)[c]	(7.68)[c]	2.31	25.9 (26.2)[b]
Pm	(4.56)[a]					
Sm	3.65				2.23	26.0
Eu	3.66				2.21	25.7
Gd	3.66				2.22	25.4
Tb	3.64				2.19	25.1
Dy	3.61				2.20	25.2
Ho	3.59				2.21	25.6
Er	3.59				2.24	25.8
Tm	3.59				2.27	26.1
Yb	3.59				2.32	26.2
Lu	3.59				2.38	25.4

Johnson et al. (1995), Ziya et al. (2005), values in parentheses:

[a] HSC 6.1 database.

[b] Liu and Byrne (1997).

[c] Kim and Osseo-Asare (2012).