Factors influencing the release rate of uranium, thorium, yttrium and rare earth elements from a low grade ore

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ABSTRACT

This paper presents data from laboratory leaching of a mineralogically complex low grade ore containing uranium (U), thorium (Th), yttrium (Y), rare earth elements (REEs) and accessory pyrite. The study examines the influence of varying the leaching protocol on the rate of release of U, Th, Y and REEs. Leaching protocols were designed to simulate a range of heap/in situ stope leaching scenarios. Protocol variants included flushing frequency, leachate recycle, nutrient (9 K salts) addition and ferric sulphate addition to cells. Maximum extractions over 52 weeks were: 58% U, 50% Th, 36% Y and 45% of the REEs; observed in cells flushed fortnightly with a ferric sulphate lixiviant (0.5 g/l, pH 3.5). Flushing with tap water once monthly resulted in second highest observed extractions (57% U, 6% Th, 27% Y, 37% REEs) with the exception of Th, where the lower release was due to insufficiently low pH for Th mobilisation. Pourbaix plots indicate that redox potentials within the leaching system were buffered by coffinite dissolution. The high redox potentials, acidic pH and elevated sulphate concentrations required for metals dissolution were found to be a consequence of (a) direct addition of ferric sulphate as a lixiviant or (b) in situ generation of acidity and ferric sulphate via microbially-mediated oxidation of accessory pyrite. Generation and maintenance of acidic sulphate-rich interstitial water appear to control the dissolution of Th, Y and REEs in addition to U. The presented data highlight that significant U, Th, Y and REEs can be mobilised from rock materials by the addition of a ferric sulphate lixiviant, furthermore periodic flushing with water alone is sufficient to achieve similar release of U, Y and REEs where accessory pyrite is available in the reacting system. These findings have significant implications for recovery of valuable elements from low grade and marginal ores or materials previously considered as wastes.

1. Introduction

The efficiency of leaching of elements such as uranium and Rare Earths (REEs) is a major factor in determining the economic viability of mining low grade ores. In cases where uranium concentration is too low to be economical to extract alone the recovery of REEs as a leaching by-product can boost profitability. Such ores may contain a variety of complex REE bearing mineral phases as well as uraninite and pitchblende and while the leaching kinetics of uraninite have been widely studied, the interrelationship between complex mineralogy, mineral liberation and leaching behaviour in low grade mixed ore deposits is not yet well defined and often site specific.

The processes which operators seek to maximise during mineral extraction operations by contrast need to be minimised with respect to natural weathering of waste rock piles which can lead to the release of uranium and other heavy metals into the environment with implications for eco-toxicity. Understanding the processes occurring within rock piles is therefore essential not only in terms of maximising the profitability of mining operations, but also in reducing their environmental impact over the long term.

1.1. Uranium chemistry

Uranium is most commonly found in the +4 oxidation state as UO₂⁻ (uraninite and pitchblende being different crystalline phases with the same chemical composition). Hexavalent uranium is readily solubilised in acidic solution forming a uranyl cation (Eq. (1)) with tetravalent uranium requiring oxidation, often by Fe(III) liberated from accessory pyrite or added during leaching (Eq. (2)).

\[
\text{UO}_3^+ + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O}
\]  

(1)

\[
\text{UO}_2 + 2\text{Fe}^{3+} \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+}
\]  

(2)

In sulphate systems a soluble complex is formed under mildly acidic conditions (Eq. (3)) with hydrolysis favoured above pH 5–6 resulting in the formation of an insoluble hydroxyoxide precipitate (Eq. (4)).

\[
\text{UO}_2^{2+} + 2\text{OH}^- \rightarrow \text{UO}_2^{2+} \cdot 2\text{H}_2\text{O}
\]  

(3)

\[
\text{UO}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} \cdot \text{H}_2\text{O}
\]  

(4)
\[ \text{UO}_2^{2+} + n\text{SO}_4^{2-} \rightarrow \text{UO}_2\left(\text{SO}_4\right)_n^{2n-2} \]  \hspace{1cm} (3)

\[ \text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightarrow \text{UO}_2\left(\text{OH}\right)_2 \cdot \text{H}_2\text{O} + 2\text{H}^+ \]  \hspace{1cm} (4)

1.2. Heap/stope leaching

Despite the increasingly widespread use by the mining industry of heap leaching for the recovery of uranium and other elements the method is still limited by low recoveries and long extraction times (Ghorbani et al., 2011). Similarly attempts to carry out heap leaching underground, so called in situ (or in-place) stope leaching (e.g. Campbell et al., 1987) incurs the same set of constraints. The processes controlling the rate of leaching range from the molecular scale such as diffusion of reacting species towards and away from the mineral surface to the transport of water, air and heat throughout the entire heap. It is widely recognised that in many heap/stope leach operations microbial catalysis of redox processes is an important factor in the liberating metals from their ores (McCreary et al., 1986; Dwivedy and Mathur, 1995; Muhoz et al., 1995; Ghorbani et al., 2011). Bacteria such as Acidithiobacillus ferrooxidans which oxidise Fe(II) provide an important source of Fe(III) for reaction with and solubilisation of U(IV) (Eq. (2)). In order to encourage the growth and activity of these bacteria nutrients may be added to lixiviants. Other options include the addition of acidic solutions or dosing with Fe(III) salts to encourage the chemical oxidation and dissolution of the metals present.

1.3. This study

The aims of this study were to determine the effects of varying the leaching protocol on the release of uranium, thorium, yttrium and REEs from a low grade uranium ore. This included the addition of nutrients and Fe(III) salts, variation in the length of the leaching cycle and recycling of the leachate to simulate the effects of variations in solute concentrations throughout a rock pile and recycling of lixiviants.

2. Materials and methodology

2.1. Materials

A uranium-bearing quartz pebble conglomerate ore was used in this evaluation. The material was sourced from the Denison mine, Elliot Lake district of Ontario, Canada, where conventional uranium mineral processing has historically been combined with heap leaching and in situ stope leaching (Fisher, 1966; MacGregor, 1966; Campbell et al., 1987). The paleoplacer conglomerate is composed of quartz pebbles cemented by a matrix comprising fine-grained quartz,feldspar, and sericite with variable (5–25%) amounts of pyrite (Derry, 1960) and a wide variety of other heavy minerals. Uranium, thorium, yttrium and rare earth element-bearing minerals occur as both primary (detrital) phases and secondary alteration phases (see Table 1) within the cement matrix, with grain sizes ranging from 1 to 600 μm. Detailed descriptions of the mineralogy/textural descriptions of the quartz pebble conglomerate from this area and the geological setting can be found in Derry, 1960; Robertson and Steenland, 1960; Burton and Fraileck, 2003.

2.2. Materials preparation and physicochemical characterisation

Approximately 50 kg of raw material was crushed through jaw and gyratory crushers and homogenised so that a final grain size of 100% passing 10 mm was achieved. Indicative experiments in the field has shown that blasting of similar material resulted in 28% material passing 12.7 mm (Campbell et al., 1987) and as has been found in acid rock drainage prediction work (e.g. Price, 1997) most of the reactive surface area is concentrated in these smaller size fractions. A portion of the bulk homogenised material was then milled to <20 μm for determination of the head grade of U, Th, and the Rare Earth Elements (REEs) Ce, Y, La, Pr, Nd, Yb, Dy and Sm. Uranium assays were carried out by digesting 0.1 g samples of the finely milled material with 2 ml HF and 6 ml aqua regia (50 ml HCl and 50 ml HNO₃) in a microwave oven-digester. The resultant solutions were diluted to 50 ml and analysed by ICP-OES. Further chemical assays for thorium and REEs were carried out by an external laboratory. All assays were carried out in triplicate. Samples of the bulk material, and size fractions isolated by wet sieving (milled to ≈50 μm in a ring mill), were analysed by X-ray Diffraction (XRD) using a Philips PW1710 diffractometer in order to establish the dominant crystalline mineral phases.

2.3. Leaching experiments

The experimental setup was designed to mimic in situ stope leaching. In this process the leaching is conducted via flooding an underground heap of blasted rock (e.g. Campbell et al., 1987) with water for 24 h (this step is referred to here as a ‘flood leach’). The heap material is then drained to unsaturated conditions with the rock remaining in contact with the residual interstitial water until the next flood leach (this step is referred to here as the ‘rest period’). Water is then introduced to begin the next flood leach and this represents the completion of one cycle.

It was noted early on in the research that the process of cyclic flood leaching and rest periods is readily mimicked in so called humidity cell testing procedures which are routinely used for the assessment of ARD potential in mine wastes. It was therefore decided to adopt an experimental setup based on humidity cells to imitate the process of stope leaching.

The cells were constructed from Perspex cylinders of 100 mm in diameter. The crushed ore was riffled into representative 1 kg portions and loaded into the cells, the packed length of the columns was approximately 0.11 m. The material sat on a filter mesh which was supported by a perforated Perspex plate. Lixiviant was introduced rapidly from the bottom of the cell from the reservoir above under gravity, this was done for three reasons: (i) To prevent problems of ‘air-locks’ forming within the material and ensure effective contact between lixiviant and rock – this is a common problem in humidity cell procedures (Sapsford et al., 2009) and can lead to incomplete contact of the sample with water during the flood leach. (ii) Flood leaching in this fashion circumvents problems encountered with incomplete or unequal contact of all of the rock material with lixiviant caused by unpredictable flow paths during trickle leaching. (iii) In situ stope leaching commonly involves containment of material through stope walling of rubbized ore material and flooding of the ore rather than trickle irrigation as would occur in a standard heap leach. This reflects limitations in being able to construct suitable pipe and irrigation work underground in a confined stope (Campbell et al., 1987). Consequently a similar method was selected in this study that mimicked this approach used in the field. In total 14 of these cells were constructed and used for the experiments. The following steps were followed:

1. Dry crushed ore loaded into the cell.
2. Ore flood leached with 750 ml of lixiviant.
3. Ore left in contact with lixiviant for 24 h.
4. Reactor drained under gravity.
5. Ore left to react during rest period.
6. Steps 2–5 repeated for total of 12 months but using 500 ml of lixiviant.
2.3.1. Variations in leaching protocol

Table 2 gives the protocol variations explored during the experiments. In total seven different protocols were investigated with each test carried out in duplicate. Variations were made with respect to both the length of the rest period (1 week, 2 week, 4 week) and the lixiviant used to carry out the leaching. In addition to tap water the effect of nutrient addition (‘9 K salts’), oxidant addition Fe2(SO4)3 at pH 3.5 and sulphate by ion chromatography. Samples were filtered using a syringe and 0.45 l m cellulous nitrate filter tip. Samples collected for ICP-OES analysis were acidified with 100 L of 10% HNO3.

Two samples were collected for analysis of metals by ICP-OES and sulphate by ion chromatography. Samples were filtered using a syringe and 0.45 µm cellulous nitrate filter tip. Samples collected for ICP-OES analysis were acidified with 100 µL of 10% HNO3.

2.5. Test work completion procedure

After the final flush the cells were disconnected and weighed individually with their contents. The cells were then dried at 40 °C for 3 days and re-weighed. The duplicate samples were recombined, representative samples were riffled and milled to <20 µm and 0.1 g portions were taken for microwave digestion and analysis as described in Section 2.1. The results of these assays for the column residues were then used in reconstituted head grade calculations for each of the columns according to Eq. (5) (see Table 3).

Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Head grade ore (mg/kg)</th>
<th>Reconstituted head (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>391 (25.7)</td>
<td>359 (18.6)</td>
</tr>
<tr>
<td>Th</td>
<td>41.5 (12.6)</td>
<td>53.3 (25.6)</td>
</tr>
<tr>
<td>Ce</td>
<td>143 (14.6)</td>
<td>145 (18.6)</td>
</tr>
<tr>
<td>Y</td>
<td>323 (1.90)</td>
<td>343 (4.2)</td>
</tr>
<tr>
<td>La</td>
<td>102 (8.13)</td>
<td>103 (14.0)</td>
</tr>
<tr>
<td>Pr</td>
<td>19.0 (1.72)</td>
<td>19.1 (2.4)</td>
</tr>
<tr>
<td>Nd</td>
<td>65.1 (5.88)</td>
<td>69.9 (14.6)</td>
</tr>
<tr>
<td>Yb</td>
<td>4.96 (0.36)</td>
<td>4.72 (0.26)</td>
</tr>
<tr>
<td>Dy</td>
<td>16.1 (0.65)</td>
<td>21.1 (12.9)</td>
</tr>
<tr>
<td>Sm</td>
<td>13.6 (0.85)</td>
<td>14.7 (3.1)</td>
</tr>
</tbody>
</table>

Reconstituted head grade = concentration in column residue + total leached over 52 weeks

3. Results

3.1. Material characterisation

The elemental composition of the head grade ore with respect to U, Th and REEs are shown in Table 2. Analysis by XRD demonstrated that the material was primarily composed of quartz with minor (2–5%) pyrite. The principal minerals carrying uranium, thorium and REEs can be split into primary phases and secondary alteration phases as shown in Table 1.

3.2. Leachate chemistry

Mean and final values recorded for pH for each of the leaching protocols are shown in Table 4. It can be seen that the lowest pH values and highest Eh values (most oxidising conditions) were observed for the ferric sulphate addition and the leachate recycle protocols. It should also be noted that pH and Eh showed a negative correlation with the length of the flushing cycle, i.e. more frequent flushing resulted in higher pH and less oxidising conditions. Addition of the nutrient appeared to buffer the pH of the system at around pH 6.

3.3. Element extraction

The results for the total extraction of U, Th and REE over the entire 52 week test are summarised in Table 5. The data shown in the table were calculated based on a reconstituted head grade value (Table 3) for each of the cells in order to minimise the errors that
might be incurred using the average head grade composition. The addition of ferric sulphate resulted in the largest recoveries for the majority of the elements under investigation, with the double flush and weekly flushes giving the lowest recoveries. Nearly 58% of the U content of the ore was leached and 50% of the Th content. For the REEs Dy showed the greatest percentage leached at 76% (equivalent to 40 mg/kg) and Cerium the lowest at 16.3% (equivalent to 28.8 mg/kg).

Cumulative extraction of U and Th over time are shown in Fig. 1. It can be seen that for both U and Th the addition of ferric sulphate resulted in the most efficient leaching. By contrast recycling of the leachate resulted in the lowest overall U extraction, but the second highest overall Th extraction. Also of great interest (especially to the practical application of heap leaching/stope leaching) is the observation that the second highest U, Y and REE extractions were from the cells leached on a monthly basis. Where pH remained above 4, regardless of the leaching protocols, thorium extraction was negligible.

Cumulative data for the leaching of Y and REEs are compared in Fig. 2. Similar patterns of extraction are seen for all of the elements with ferric sulphate addition and/or monthly flushing giving the highest overall percentage extraction in all instances. In the cases of La, Pr and Ce the recycled leachate gave the highest leaching rate between weeks 12 and 38, after which point results show decreasing concentrations of the elements suggesting precipitation. As with U and Th the double flush and weekly flush protocols showed the worst leaching performance for all elements.

### Table 4

<table>
<thead>
<tr>
<th>Protocol</th>
<th>Leachate pH</th>
<th>Leachate Eh (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Final</td>
</tr>
<tr>
<td>Control</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>561</td>
<td>561</td>
</tr>
<tr>
<td>Double flush</td>
<td>6.6</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>579</td>
</tr>
<tr>
<td>Nutrient</td>
<td>5.6</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>507</td>
<td>493</td>
</tr>
<tr>
<td>Ferric</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>821</td>
<td>807</td>
</tr>
<tr>
<td>Recycle</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>748</td>
<td>766</td>
</tr>
<tr>
<td>Weekly</td>
<td>6.4</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>526</td>
<td>580</td>
</tr>
<tr>
<td>Monthly</td>
<td>4.0</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>704</td>
</tr>
</tbody>
</table>

Table 4: pH and Eh values for each of the leaching protocols investigated.

Table 5: Total elemental extraction after 52 weeks (based on reconstituted head).

<table>
<thead>
<tr>
<th>Leaching protocol</th>
<th>Uranium % mg/kg</th>
<th>Thorium % mg/kg</th>
<th>Yttrium % mg/kg</th>
<th>Total REE % mg/kg</th>
<th>Cerium % mg/kg</th>
<th>Praseodymium % mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>41.9 163</td>
<td>0.10 0.02</td>
<td>18.8 6.41</td>
<td>26.3 223</td>
<td>9.70 15.6</td>
<td>10.6 2.02</td>
</tr>
<tr>
<td>Double flush</td>
<td>16.0 65.1</td>
<td>0.00 0.01</td>
<td>7.40 2.30</td>
<td>9.40 77.0</td>
<td>2.30 3.06</td>
<td>1.50 0.26</td>
</tr>
<tr>
<td>Nutrient</td>
<td>17.1 52.1</td>
<td>0.00 0.00</td>
<td>9.40 3.43</td>
<td>9.90 79.0</td>
<td>4.00 5.99</td>
<td>4.30 0.80</td>
</tr>
<tr>
<td>Ferric</td>
<td>18.5 43.4</td>
<td>38.9 19.4</td>
<td>18.2 5.60</td>
<td>17.4 104</td>
<td>10.6 13.3</td>
<td>12.3 1.80</td>
</tr>
<tr>
<td>Recycle</td>
<td>20.4 80.1</td>
<td>0.00 0.01</td>
<td>8.10 2.60</td>
<td>12.4 93.0</td>
<td>3.00 3.56</td>
<td>2.60 0.41</td>
</tr>
<tr>
<td>Weekly</td>
<td>56.6 226</td>
<td>5.50 2.69</td>
<td>27.0 11.3</td>
<td>36.7 313</td>
<td>17.4 26.8</td>
<td>22.4 3.65</td>
</tr>
<tr>
<td>Monthly</td>
<td>13.4 13.34</td>
<td>21.2 17.5</td>
<td>10.3 0.49</td>
<td>10.4 1.67</td>
<td>20.3 3.33</td>
<td>20.3 3.33</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>3.60 3.27</td>
<td>2.90 1.77</td>
<td>2.80 0.13</td>
<td>3.00 0.46</td>
<td>4.00 0.52</td>
<td>4.00 0.52</td>
</tr>
<tr>
<td>Neodymium</td>
<td>7.70 7.74</td>
<td>9.60 6.78</td>
<td>3.70 0.17</td>
<td>5.50 0.86</td>
<td>10.3 1.56</td>
<td>10.3 1.56</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>22.6 23.1</td>
<td>34.5 34.1</td>
<td>20.7 1.16</td>
<td>76.1 39.6</td>
<td>41.3 8.85</td>
<td>41.3 8.85</td>
</tr>
<tr>
<td>Samarium</td>
<td>13.9 10.7</td>
<td>11.2 6.32</td>
<td>10.3 0.51</td>
<td>12.1 1.66</td>
<td>13.1 1.57</td>
<td>13.1 1.57</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>4.60 3.64</td>
<td>2.50 1.39</td>
<td>4.30 0.20</td>
<td>5.60 0.55</td>
<td>3.00 0.37</td>
<td>3.00 0.37</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>24.6 21.9</td>
<td>18.7 12.78</td>
<td>18.5 1.01</td>
<td>20.2 3.36</td>
<td>21.8 3.17</td>
<td>21.8 3.17</td>
</tr>
</tbody>
</table>

3.4. Uranium leaching rate

Rates of U leaching in mg/kg/day, averaged over an entire cycle (U leaching rate = quantity leached/cycle length) for each of the leaching protocols are shown in Fig. 3. It can be seen that ferric sulphate addition produced the highest leaching rate by at least a factor of 3 over the first flushing cycle compared to any of the other protocols, reducing from a maximum of 1.7 mg/kg/day to a 0.18 mg/kg/day after 52 weeks. Leaching rate using the monthly protocol increased significantly over the first three cycles (12 weeks). By contrast U leaching rate was effectively zero after 12 weeks where recycled leachate was used.

Fig. 1. Comparison of U and Th cumulative leaching for each of the protocols investigated.
4. Discussion

4.1. General controls on leaching

The dominant factors controlling leaching rate vary between the different elements investigated in this study. This is evidenced by the extent to which changing leaching protocol affects the quantities of each element extracted. In terms of their behaviours, U and Th may be considered separately, with Y and REEs exhibiting broadly similar characteristics.

4.1.1. Uranium

As discussed in Section 1.1 the rate of U leaching will depend on the proportion of the element available as the soluble U(VI) compared to the insoluble U(IV). The U extraction efficiency of the leaches was as follows: Ferric sulphate > Monthly flush >
Control > Weekly flush > Recycled flush > nutrient flush > double flush. For successful U leaching one of the critical factors will therefore be a sufficiently high Eh to cause U(IV) oxidation on the timescale of the leaching protocol, hence the benefit of ferric sulphate addition – this sulphate-rich low pH lixiviant also serving to increase the solubilisation of U(VI) through formation of the UO₂(SO₄)²⁻/CO₂⁻ complex (see Fig. 4).

Of interest (particularly to commercial heap/stope leaching) is that with the exception of the nutrient/ferric addition, the other protocols were adding only tap water to the system, yet it can be seen especially in the case of the monthly flush that extraction of U, Y and REEs was almost as high as with the ferric sulphate addition. The authors suspect that microbial oxidation of the accessory pyrite in the system created favourable Eh/pH conditions and sulphate concentrations for extraction of U, Th, Y and REEs. The suggested mechanism is the establishment of acidophilic Fe(II) oxidising microbes in the system which rapidly recycle system Fe(II) to Fe(III) thus maintaining the high redox potential required to oxidise pyrite (releasing further Fe(II) for the microbes to process and sulphuric acid) (cf. Sapsford et al., 2009). The maintenance of high Eh (Fe(III)/Fe(II) dominated) serves to oxidise U(IV) and the low pH/high sulphate concentrations serve to solubilise U(VI), Th, Y and REEs. The lengthening of the ‘rest’ period between flushes allows the posited microbial action to take best effect, this might be due to kinetic or mass transfer constraints such that leaching efficiency is increased as contact time with the high Eh/low pH interstitial water with the U, Th, Y, REE bearing phases increases. Another possible explanation is that more frequent flushing of the material flushes planktonic Fe(II) oxidising microorganisms from the system and hinders the establishment of a sessile microbial population. It is important to note that the addition of the ferric sulphate lixiviant will also promote the establishment of sessile microbial populations as shown by Sand et al. (2001). The low extraction efficiencies observed with the addition of a nutrient-rich lixiviant are due to the pH buffering effect of the solution.

It is also important to highlight that although the microbes are probably responsible for increases in redox potential, Fig. 4 clearly shows that the Eh is buffered by contact with coffinite bearing phases, and suggests that where coffinite had formed in the ores then this U(IV) appears easier to oxidise than the more refractory brannerite phase.

4.1.2. Thorium

The major controlling factor in the release of Th in these leaching tests is likely to be pH, with sulphate concentration having an important secondary role. Under the conditions in the leaching cells Th will be present as Th(IV), which, in the absence of dissolved sulphate forms the highly insoluble ThO₂ in aqueous systems above approximately pH 1.5 (Pourbaix, 1966). The addition of sulphate increases Th solubility by expanding stability region of the Th⁴⁺ ion through the formation of soluble Th(SO₄)₂ and ThSO₄²⁻. The pH range over which Th is soluble increases as a function of sulphate concentration, though it remains insoluble at circumneutral and alkaline pH values (Kim and Osseo-Asare, 2012).

4.1.3. Yttrium and rare earth elements

As with Th, the oxidation state of Y and the REEs is unlikely to change during leaching and so Eh is not a factor of primary concern. In the case of these elements the major controlling factors are sulphate concentration and pH. REEs can form solid sulphate phases at high sulphate concentrations, indeed precipitation of REEs sulphate has been shown to be an effective step in their recovery from Monzanite digestate (Abreu and Morais, 2010). The effect of pH on the solubility of the sulphate complexes varies
between the different REEs and therefore will be of varying importance in determining leaching rate (Kim and Osseo-Asare, 2012).

4.2. Effect of lixiviant composition

Of the three different lixiviants used (ferric sulphate dosed, nutrient dosed and recycled leachate), the ferric sulphate dosed lixiviant showed the best overall leaching properties with respect to both U and Th as well as Y and REEs. This lixiviant combined low pH with strong oxidising conditions and moderate sulphate concentration providing all of the conditions necessary to increase the solubility of the elements under investigation. Conversely the nutrient dosed lixiviant showed reduced leaching rates compared to the control experiment across all elements. In terms of the leachate chemistry the nutrient dosed lixiviant resulted in higher pH and lower Eh, most likely as a result of buffering by the 9 K salts. The low leaching rates can be accounted for by these relatively high pH values which would have favoured the formation of insoluble metal oxides and hydroxides.

The recycled lixiviant showed the greatest variation in its effect on leaching rate of the different elements. This can be explained in terms of the mechanisms by which the different elements are released into the leachate and the solubility of their sulphate complexes. In the case of U, higher concentrations within the ore relative to the other elements are likely to have resulted in saturation relatively early on in the experimental period. For Th however, increasing sulphate concentration and decreasing pH (see Fig. 5) over time led to increasing solubility.

For Y and the REE's the decreasing pH is likely to have resulted in increased solubility during the first half of the test work. Subsequent decreases in REEs concentration within the recycled leachate can be explained by the precipitation of solid M₂(SO₄)₃ phases as the concentration of sulphate increased (Kim and Osseo-Asare, 2012). An important alternative mechanism for reducing REE concentrations could be co-precipitation and/or adsorption onto Fe(III) oxyhydroxide precipitates generated in situ.

4.3. Effect of varying cycle length

With the exception of Nd, the 4 week cycle resulted in the greatest extraction rates compared to the 2 week or 1 week cycles, and was in many cases comparable to the extraction rates achieved with ferric sulphate addition to the lixiviant. Where no additional solutes are present in the lixiviant, leaching rates are largely dependent on the development of low pH, oxidising conditions within the pore water which arise as a result of accessory pyrite oxidation. Less frequent flushing allows for greater concentrations of dissolved Fe(III) to build up within the pore water, with an associated reduction in pH. Dissolved Fe(III) concentrations were up to three orders of magnitude higher in the monthly flush leachate compared to the weekly flush leachate with average pH values of 4.0 and 6.4 respectively.

5. Conclusions

It has been shown that for a mineralogically-complex Elliot Lake ore up to 57% of uranium, 50% thorium, 36% yttrium and between 16% and 76% of REEs can be extracted by periodic flow leaching of the material. Mobilisation of U, Th, Y and REEs was due to the development of acidic conditions favouring the direct solubilisation of U(VI) and the Fe(III)-mediated oxidation of insoluble U(IV) to soluble U(VI), with the dominant control of U mobilisation being the dissolution of coffinite. Whilst the most effective leaching protocol used an acidic (pH < 3) and strongly oxidising (iron (III) sulphate) lixiviant (which resulted in maximum U, Th, Y and REE extraction) it was found that similar recovery of U, Y and REEs could be achieved simply by flushing the material once monthly with tap water. It was also found that the frequency of flushing has a significant effect on leaching efficiency. Less frequent flushing (monthly) resulted in an increase in the extraction efficiency of 2–4 times for the REEs and three times for U compared to more frequent (weekly) flushing. Longer periods between flushing allow for more pyrite oxidation, generating acidic Fe(III) rich conditions in situ. A nutrient-bearing lixiviant was found to buffer the leachate at a pH of around 6–8. This resulted in low leaching efficiencies as U(VI) is insoluble within the circumneutral pH range. Recycling of the leachates (a common strategy in water constrained mining environments) resulted in an overall reduction in U and REE extraction, probably as a result of the solution reaching saturation with respect to U(VI) over time. Overall this study demonstrates the importance of optimising the leaching protocol for in situ stope leaching and heap leaching for the economic viability of recovery of U, Th, Y and REEs from Elliot lake ore and similar ores. The study demonstrates that in the absence of reagent addition, optimising the leaching environment to promote microbial oxidation of accessory pyrite can lead to comparable recoveries of U, Y and REEs and in effect make the ore ‘self-leaching’.

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References


