Uranium leaching from synthetic beta

Scott A. McMaster a,b,* , Rahul Ram b , Nebeal Faris b , Mark I. Pownceby c , James Tardio b , Suresh K. Bhargava b

a Chemistry - Institute of Fundamental Sciences, Massey University, Private Bag, 11 222 Palmerston North 4442, New Zealand
b Centre for Advanced Materials and Industrial Chemistry, School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne, Vic 3001, Australia
c CSIRO Mineral Resources, Private Bag 10, Clayton South, Victoria 3169, Australia

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ABSTRACT

The leaching of uranium from of a synthetic form of the naturally occurring pyrochlore group mineral betaafite, was investigated in acid sulfate media. Uranium leaching curves obtained over a range of time, temperature, [H2SO4], [Fe2O3] and redox potential conditions were similar with each having three discrete segments representing significantly different rates of uranium leaching. The first segment occurred in the initial min and involved extremely rapid leaching. This segment made up for the majority of the overall uranium leaching obtained over the test period (~2.10% U). The high rate of leaching in this segment was demonstrated to be attributed to liberation of surface oxidized uranium from the betaafite structure. The second segment between 1 and 120 min was characterised by slow uranium leach rates which could be partially influenced by altering the experimental conditions. Uranium leaching within this period was most likely due to oxidation of uranium by ferric iron which was progressively slowed by the competing diffusion reaction. The uranium leach rate in the third segment was negligible. This negligible leach rate was demonstrated to occur when approximately 2.10% U had leached from the sample and was shown to be due to passivation of the sample surface. Investigations into leaching betaafite using various iron salts showed the uranium leaching more than doubling when iron fluoride was substituted for iron sulfate. The additional solubility was attributed to leaching of Nb, Ti and Ta due to the in-situ formation of HF, where the HF either slowed the formation of a passivating layer or the HF was able to slowly dissolve the passivating layer.

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1. Introduction

There can often be vast differences in chemistry and mineralogy between uranium ores sourced from different deposits. These may include: differences in the types and amounts of uranium minerals, the composition of the uranium minerals present and the associated gange mineralogy. Generally, the uranium minerals preferentially targeted for processing/extraction are the primary uranium minerals uraninite (UO2), pitchblende (U3O8) and coffinite (U(SiO4)1–x(OH)x). This is due to their abundance in many uranium ore deposits and high concentrations and the ease of extraction of uranium (Pownceby and Johnson, 2014; Bhargava et al., 2015). As depletion of high grade deposits occurs, there is an increased focus on the processing of refractory uranium ore minerals (Charalambous et al., 2013). One such refractory mineral receiving increased attention is the uranium pyrochlore group mineral, betaafite, A2B2O7–y(OH)y where A = Na, K, Ca, Sr, Sn, Ba, Pb, Bi, REE, U and B = Ti, Nb, Ta, Zr, Al (Hogarth, 1961, 1977; Lumpkin and Ewing, 1996).

Multiple studies conducted on naturally occurring betaafites have demonstrated considerable stoichiometric variation. The most notable variation within these samples was the B site cation (Nb, Ti or Ta) concentration (Hogarth, 1961). As well, metamictisation occurs in betaafite due to radiation damage from α-decay of uranium (Lumpkin and Ewing, 1988). This leads to many natural betaafites being amorphous, although some Ca-rich betaafites have been reported as non-metamict and/or partially metamict (Cámara et al., 2004). Chemical alteration due to weathering of metamict betaafite has also been shown to occur in most natural samples (Eyal et al., 1986; Frost and Reddy, 2010; Hogarth, 1961; Lumpkin and Ewing, 1996). Primary alteration consists of the loss of A site cations Na, Ca, and U via cationic mobilisation. Up to 20–30% of the initial uranium can be lost in the primary alteration step (Lumpkin and Ewing, 1996). After the primary alteration stage, charge stabilisation of the betaafite structure is achieved via hydration from water in the environment (Lumpkin et al., 1985). Lumpkin and Ewing (1996) also described a secondary alteration whereby betaafite decomposes into pyrochlore [(Ca,Na)2Nb2O7] and microlite [(Ca,Na)2Ta2O7] after A site cationic migration of Ca and Na. The remaining unstable mineral reacts further to form uranpyrochlore [(U,Ca)2Nb2O7], liandratite (UNb2O10) and rutile (TiO2). More recently, McMaster et al. (2015) showed that after primary alteration, naturally

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altered amorphous betafite contains liandratite and rutile which react forming U{sub}Ti{sub}N{sub}b{sub}O{sub}7(McMaster et al., 2015).

Despite high concentrations of uranium and associated alteration and metamictisation, betafite is considered a refractory uranium ore mineral and difficult to process (Abraham, 2009; Geisler et al., 2005; McMaster et al., 2013). The aim of the current work is to conduct a systematic study of the parameters that affect uranium leaching from betafite in acid sulfate media. The approach is to initially prepare a synthetic betafite sample and then to determine the uranium leaching over a range of time, temperature, [H{sub}2{sub}SO{sub}4], [Fe{sub}3{sub}+] and redox potential conditions. The leaching matrix chosen for the current work was selected based on leaching parameters commonly varied in commercial uranium leaching circuits.

1.1. Previous work

Little previous work has been conducted on the leaching of betafite with acid ferric sulfate solution. van Rensburg (2014) conducted small scale leaching studies conducted on betafite-containing ore from Rössing, Namibia. Betafite accounts for ~5% of the total uranium found in the Rössing deposit (Berning et al., 1976; van Rensburg, 2014), the remainder being present predominantly as uraninite and minor amounts of coffinite and uranophane. Under acidic, oxidative conditions similar to those used in the Rössing leach circuit, ~80% of the uranium was leached. The remaining unleached uranium was present in betafite, coffinite and poorly liberated uranophane. McMaster et al. (2012) also studied the leaching of natural betafite under Rössing uranium leach circuit conditions. They showed only ~5% of the uranium was leached from betafite (McMaster et al., 2012).

In a further study, McMaster et al. (2014a, 2014b) investigated the leaching of two natural betafite samples over a range of processing conditions. Significant differences in leaching were observed between samples (~58% U for sample A and 5% U for sample B). The conditions under which maximum uranium was leached from both samples was; 100 g/L H{sub}2{sub}SO{sub}4, 3 g/L [Fe{sub}3{sub}+], ORP (510 mV vs. Ag/AgCl), 35 °C, 6 h. The degree of chemical alteration/weathering was shown to significantly influence the rate of leaching with the highly altered sample more readily leached. The leach rate was shown to decrease however when the altered and metamict samples were annealed to restore crystallinity (McMaster et al., 2014b). McMaster et al. (2015) confirmed the increase in leach rate caused by chemical weathering in metamict natural betafite. In the most recent betafite leaching study, Nettleton et al. (2015) observed complete extraction of uranium from leaching of natural betafite under extreme conditions in a solution containing 214.5 g/L H{sub}2{sub}SO{sub}4, 3 g/L Fe{sub}3{sub}+ at 89 °C for 48 h. They also noted that ~12% uranium was extracted from the same betafite when re-crystallised in air at 1100 °C (Nettleton et al., 2015).

In the current study, a high-purity, crystalline betafite was characterised by XRD prior to leaching to ensure the sample was of high purity and there was no other uranium containing minerals present in the sample which would result in inaccurate uranium leaching data. The XRD pattern is shown in Fig. 1. Rutile and a minor amount of pyrochlore (Ca{sub}2{sub}Nb{sub}2{sub}O{sub}7) were the only impurity phases identified. The leaching of synthetic betafite was investigated over a range of conditions with parameters selected to reflect those encountered in commercial processing of uranium ores.

2. Materials and methodology

2.1. Synthesis

Betalite was synthesised using the method given in (McMaster et al., 2014a). Briefly, synthetic betafite was prepared via solid state reaction between uranyl nitrate, calcium carbonate, titanium dioxide, niobium (V) oxide and tantalum (V) oxide to achieve the following stoichiometry: (U{sub}0.32Ca{sub}0.42)(Nb{sub}0.41Ti{sub}1.78Ta{sub}0.10)O{sub}7. The aforementioned metal salts and oxides were dry ground for 20 min and then added to a platinum lined alumina boat which was placed in a tube furnace for 48 h at 1150 °C in a dry N{sub}2 atmosphere.

Approximately 8 g of synthetic betafite was prepared in multiple synthesis batches. Each batch was characterised via XRD, Raman spectroscopy and ICP-MS to insure consistent mineralogical and elemental composition between the multiple batches. These batches were then pooled together resulting in approximately 8 g of material which was then thoroughly mixed and dry sieved through a 63 μm sieve prior to the leaching experiments being conducted. This insured any differences in leaching due to batch variation could be negated.

2.2. Powder X-ray diffraction (XRD)

Dry powdered samples (pre- and post-leach) were evenly scattered onto a flat glass XRD plate within a circular poly methyl methacrylate holder and then covered by Kapton film prior to analysis. X-ray powder diffraction patterns were collected using a Bruker D4 Endevor high throughput X-ray diffractometer using CuK{alpha} radiation, an incident beam monochromator and a scintillation detector. A 1° divergence slit was used to analyse the 20 range 5–90° with a step size of 0.02° 2θ and counting times of 2 s/step. The instrument was calibrated using quartz and corundum standards prior to use.

2.3. Leaching studies

For the leaching tests 250 mL of the desired sulfuric acid concentration was added to a 250 mL three-neck flask. The solution was then agitated using an overhead mechanical stirrer and heated to the required temperature using a heating mantle. Once at temperature, ferric and ferrous sulfate was added to create the required oxygen redox potential (ORP). The solution was then allowed to equilibrate for 10 min before 0.05 g of ~63 μm synthetic betafite was added. The time upon addition of sample was determined to be 0 min and solution samples were collected at pre-determined intervals throughout the experiments.

Specific reaction condition used and in the leaching test matrix was given in Table 1.

Analysis of the leach solutions was conducted using an Agilent HP 7700 series ICP-MS. The instrument was calibrated using commercial uranium, niobium, titanium and tantalum standards. An internal standard containing Sc, Ge, Rh, In, Tb, Lu, Bi, was added to all calibration and test samples. The error in measurement on the instrument was calculated to be ± 2.5%.

3. Results and discussion

3.1. Overview of leaching tests

The synthetic betafite was characterised by XRD prior to leaching to ensure the sample was of high purity and there was no other uranium containing minerals present in the sample which would result in inaccurate uranium leaching data. The XRD pattern is shown as Fig. 1. Rutile and a minor amount of pyrochlore (Ca{sub}2{sub}Nb{sub}2{sub}O{sub}7) were the only impurity phases identified. The leaching of synthetic betafite was investigated over a range of conditions with parameters selected to reflect those encountered in commercial processing of uranium ores.

3.2. Leaching of synthetic betafite using Rössing uranium leach circuit conditions

An initial leaching experiment was conducted at conditions similar to those used at the Rössing uranium mine (Test 1, Table 1). Results showed ~0.5% of the total uranium present leached in the initial 1 min of leaching (Fig. 2). The rate of leaching then slowed within the next ~45 min after which time a total of ~1.4% U had been leached. The leach rate after ~45 min continued to decline and after a total leach time of 6 h, 2.04 ± 0.03% of the U had been leached.
3.3. Effect of temperature, \([\text{H}_2\text{SO}_4]\), \([\text{FeTOT}]\) and redox potential

The leaching of synthetic beta fite was investigated under conditions (temperature, \([\text{H}_2\text{SO}_4]\), \([\text{FeTOT}]\) and ORP), comparable to the range of conditions used in commercial leaching of uranium-bearing ores (Tests 1–20, Table 1). The effects of varying each of these parameters are discussed individually below:

3.3.1. Temperature

The influence of temperature on uranium leaching was investigated at 35, 50, 65, 80 and 95 °C (Table 1, Tests 2–6). All other parameters were kept constant excluding ORP due to the interrelationship between redox potential and temperature. Results are presented in Fig. 3.

The extent of uranium leaching after 6 h increased marginally with an increase in leach temperature from 1.97% U (Test 2 at 35 °C) to 2.16% U (Test 6 at 95 °C). The major effect of temperature on the leaching was however only observed in the first 15–20 min, where the leach rate was highest in all tests; beyond this time, the rate of uranium leaching decreased by a similar extent in all tests. The reaction kinetics for synthetic beta fite leaching most closely fitted a first order rate between the 15–75 min (Table 2, Fig. 4). The range between 15 and 75 min was chosen for calculating the kinetics as the rate was significantly different either side of this interval. The change in leaching mechanism is discussed in a later section.

3.3.2. Sulfuric acid concentration

Studies were conducted to investigate the influence of sulfuric acid concentration at 35 °C on the leaching of uranium by varying the acid concentration while other parameters remained constant (Tests 1, 7–11, Table 1). Results shown in Fig. 5 indicate that the total amount of uranium leached in 6 h varied between 1.90 and 2.10% U suggesting that for the range of sulfuric acid concentrations used, there was no significant effect on the overall amount of uranium leached.

The leaching curves had similar profiles to those observed in the influence of temperature tests – a region of fast leaching (0–30 min), particularly in the first min, followed by a region of moderately fast leaching (30–120 min), and a final region beyond 120 min where the leach rate was significantly reduced. The rapid leach rate in the first min was most likely due to the higher acid concentrations causing faster leaching of oxidized uranium on the surface of the synthetic beta fite. The leach rate between 30 and 120 min however was not significantly impacted by acid concentration.

### Table 1

| Test No | \([\text{H}_2\text{SO}_4]\) (M) | \([\text{FeTOT}]\) (mM) | Fe\(^{3+}\):Fe\(^{2+}\) | ORP (mV vs. \(\text{Ag|AgCl}\)) | Temperature (°C) | Other |
|--------|------------------|-----------------|----------------|------------------|----------------|--------|
| 1      | 0.051            | 53.6            | 9:1            | 520              | 35             |        |
| 2      | 0.51             | 53.6            | 9:1            | 520              | 35             |        |
| 3      | 0.51             | 53.6            | 9:1            | 560              | 50             |        |
| 4      | 0.51             | 53.6            | 9:1            | 590              | 65             |        |
| 5      | 0.51             | 53.6            | 9:1            | 620              | 80             |        |
| 6      | 0.51             | 53.6            | 9:1            | 640              | 95             |        |
| 7      | 0               | 53.6            | 9:1            | 530              | 35             |        |
| 8      | 0.015            | 53.6            | 9:1            | 520              | 35             |        |
| 9      | 0.102            | 53.6            | 9:1            | 520              | 35             |        |
| 10     | 0.153            | 53.6            | 9:1            | 520              | 35             |        |
| 11     | 0.51             | 53.6            | 9:1            | 520              | 35             |        |
| 12     | 0.51             | N/A             | N/A            | N/A              | 50             |        |
| 13     | 0.51             | 26.8            | 9:1            | 520              | 50             |        |
| 14     | 0.51             | 107.1           | 9:1            | 520              | 50             |        |
| 15     | 0.51             | 160.7           | 9:1            | 520              | 50             |        |
| 16     | 0.51             | 214.3           | 9:1            | 520              | 50             |        |
| 17     | 0.51             | 53.6            | 0:1            | 330              | 50             |        |
| 18     | 0.51             | 53.6            | 2:3            | 430              | 50             |        |
| 19     | 0.51             | 53.6            | 12:13          | 465              | 50             |        |
| 20     | 0.51             | 53.6            | 1:0            | 620              | 50             |        |
| 21     | 1.02             | 53.6            | 1:0            | 730              | 95             | FeF\(_3\) |
| 22     | 1.02             | 53.6            | 1:0            | 630              | 95             | FeCl\(_3\) |
| 23     | 1.02             | 53.6            | 1:0            | 600              | 95             | FeBr\(_3\) |
| 24     | 1.02             | 53.6            | 1:0            | 840              | 95             | FePO\(_4\) |
| 25     | 1.02             | 53.6            | 1:0            | 900              | 95             | Fe(NO\(_3\))\(_3\) |
| 26     | 1.02             | 53.6            | 1:0            | 840              | 95             | Fe\(_2\)(SO\(_4\))\(_3\) |
| 27     | 1.02             | N/A             | N/A            | 0.5 M            | 50             |        |
| 28     | 1.02             | 0               | N/A            | 0.5 M            | 50             |        |
| 29     | 1.02             | 0               | N/A            | 0.5 M            | 50             |        |
| 30     | 1.02             | 53.6            | 1:0            | 620              | 50             |        |
| 31     | 1.02             | 53.6            | 1:0            | 630              | 50             | 0.5 M FeF\(_3\) |
| 32     | 1.02             | 53.6            | 1:0            | 650              | 50             | FeCl\(_3\) |
| 33     | 1.02             | 53.6            | 1:0            | 620              | 50             | FeBr\(_3\) |
| 34     | 1.02             | 53.6            | 1:0            | 710              | 50             | FePO\(_4\) |
| 35     | 1.02             | 53.6            | 1:0            | 760              | 50             | HCL |
| 36     | 1.02             | 53.6            | 1:0            | 710              | 50             | CH\(_3\)COOH |
| 37     | 1.02             | 53.6            | 1:0            | 830              | 50             | HNO\(_3\) |
| 38     | 1.02             | 53.6            | 1:0            | 730              | 50             | HBr |
| 39     | 1.02             | 53.6            | 1:0            | 560              | 50             | H\(_3\)PO\(_4\) |

* Indicates equivalent normalised proton concentration used for each acid.

Fig. 1. X-ray diffraction pattern of the synthetic beta fite used in the leaching experiments.
3.3.3. Total iron ([Fe\textsubscript{TOT}])

The effect of varying total iron concentration, [Fe\textsubscript{TOT}], on uranium leaching is shown in Fig. 6. All experiments were conducted at a constant temperature, acid concentration and ORP (Table 1).

The experiment at 0 mM [Fe\textsubscript{TOT}] (Test 12) showed all uranium leaching occurred within the initial 1 min. of the experiment representing the solubility of surface oxidized uranium. The uranium concentration then remained constant with no further leaching. For tests using iron concentrations ranging from 26.8 to 214.3 mM, the data showed that the overall amount of uranium leached was greater than that measured without any iron present however, in general, varying [Fe\textsubscript{TOT}] had no significant effect on uranium leaching. The only observable difference was that [Fe\textsubscript{TOT}] had a slight influence on the rate of leaching in the first ~120 min, where the rate of leaching was slowest in tests using high [Fe\textsubscript{TOT}]. After 120 min however, all tests with iron produced the same level of uranium solubility reaching a maximum of ~2.10% U. Beyond 120 min total leach time the leach rate was not influenced by [Fe\textsubscript{TOT}] remaining constant at 2.10% U.

3.3.4. Redox potential

Five experiments were conducted to investigate the influence of redox potential on U leaching. A range of Fe\textsuperscript{3+}:Fe\textsuperscript{2+} ratios were used ranging from 0:1 (330 mV vs. Ag|AgCl) to 1:0 (610 mV) while the [Fe\textsubscript{TOT}] was kept constant (Tests 3, 17–20, Table 1).

As the ratio of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} is increased, the extent of U leaching increased over the duration of the experiment (Fig. 7). Results of the 420 and 475 mV experiments (Tests 18 & 19) showed a lesser amount of U leaching in the initial min of leaching relative to the others. Ram et al. (2013) describe lower leaching of UO\textsubscript{2} at redox potentials of 470 mV due to excess sulfate present leading to the formation of less reactive iron sulfate complexes. Although no oxidation step was noted to occur over this period with beta\textsubscript{f}ite, these more stable sulfate complexes could be the possible cause of the slow U leaching over the initial min at low redox potentials. At the end of the 6 h leach period both Tests 18 & 19 had an increasing amount of U leaching which indicated that the extent of leaching had not yet reached a maximum. The two tests conducted at the highest redox potentials (Tests 3 & 20) both showed that ~2.10% U leaching was attained in both cases although this value was reached in ~15 min at the higher ORP (610 mV) compared to ~90 min at 520 mV. Test 17 conducted at 330 mV (~100% Fe\textsuperscript{2+}) showed no significant increase beyond the initial 1 min following removal of oxidized surface uranium. Although auto-oxidation of Fe\textsuperscript{2+} will occur, the time required to reach equilibrium at the acid concentrations and temperature used is significantly longer than the duration of the experiment and hence Fe\textsuperscript{3+} oxidation of uranium is negligible (Pollard et al., 1961).
Given in Table 2.

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Rate (k)</th>
<th>Intercept</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 2 (35 °C)</td>
<td>$4.55 \times 10^{-5}$</td>
<td>$-0.358$</td>
<td>0.96</td>
</tr>
<tr>
<td>Test 3 (50 °C)</td>
<td>$4.75 \times 10^{-5}$</td>
<td>$-0.283$</td>
<td>0.97</td>
</tr>
<tr>
<td>Test 4 (65 °C)</td>
<td>$5.00 \times 10^{-5}$</td>
<td>$-0.217$</td>
<td>0.92</td>
</tr>
<tr>
<td>Test 5 (80 °C)</td>
<td>$5.14 \times 10^{-5}$</td>
<td>$-0.148$</td>
<td>0.90</td>
</tr>
<tr>
<td>Test 6 (95 °C)</td>
<td>$5.30 \times 10^{-5}$</td>
<td>$-0.145$</td>
<td>0.94</td>
</tr>
</tbody>
</table>

3.4. Effect of Fe counter ion, fluoride ion and lixiviant

3.4.1. Fe counter ion

The influence of different Fe counter ions ($SO_4^{2-}$, $NO_3^-$, $PO_4^{3-}$, $Br^-$, $Cl^-$ and $F^-$) on betaite leaching was investigated under the following conditions: 53.6 mM [FeTOT], 9:1 Fe$^{3+}$:Fe$^{2+}$ (560 mV ORP) $T = 95$ °C (Tests 21–26, Table 1). The different counter ions were selected because they are commonly found within gangue minerals typically associated with betaite-containing ores (Abraham, 2009; Berning et al., 1976; van Rensburg, 2014). Results are shown in Fig. 8.

In general, similar extents of uranium leaching were obtained using the different Fe counter ions reaching a maximum leaching of ~2% U after about 45 min. This observation was true except in the case of fluoride where FeF$_3$ significantly increased the uranium leaching to ~4.5% U. A weak trend of higher leaching was observed over the initial min for iron halides than for the oxyanions, sulfate, nitrate and phosphate, but the differences were minor. The redox potential was lower with iron halides than the oxyanions indicating the higher initial rate of leaching was not due to a higher oxidation potential in the solution and was most likely due to monodentate halides forming more reactive complexes in solution compared to the bidentate or polydentate oxyanions (Laxen, 1971; Levanon et al., 1969).

While the effect of iron halides had a positive effect on U leaching from betaite over the initial 30 min, it is known that the rate of leaching for the anions studied can be influenced by several factors. These include: the reactivity of the species formed at the Fe$^{3+}$:Fe$^{2+}$ ratios and [FeTOT] studied; the redox potential effect of the anion ligand; the stabilised complexes formed with the uranyl ion, and; the solubility of the Fe salts and their stability constants (Cardarelli, 2000; Laxen, 1971; Levanon et al., 1969; Nicol et al., 1975; Ram et al., 2013). For this reason deducing the influence of the Fe counter ion is difficult in this limited data set. All leaching experiments conducted except for F$^-$ showed the leach rate remained constant after approximately 45 min. This was most probably due to causes explained previously for the effects of acid strength, [FeTOT], temperature and ORP.

Test 24 showing the effect of iron phosphate on U leaching initially showed a lower leach rate over the initial 120 min before reaching a similar extent to all others. We also noted a significant amount of FePO$_4$ precipitate in the leach solution. In an electrochemical study on the influence of PO$_4^{3-}$ on leaching of UO$_2$, Nicol et al. (1975) reported complexes such as FeH$_2$PO$_4$ and FeHPO$_4$$_2$ were more reactive than Fe$^{3+}$, FeOH$_2^+$ and Fe$_2$OH$_2^+$ complexes. Assuming the presence of such compounds, the underlying insolubility of FePO$_4$ appeared to have negated any influence of these complexes on uranium leaching. Moreover, the slow rate of leaching over the initial 120 min was assumed due to the betaite grains acting as seeds for the precipitation of FePO$_4$ and hence passivating the surface temporarily and resulting in limited active sites available for leaching.

The effect of nitrate on uranium leaching was shown to have no substantial impact (Test 25). Ram et al. (2013) examined the effect of NO$_3^-$ on the leaching of uraninite and showed that increasing the concentration of NO$_3^-$ increased the rate of UO$_2$ leaching. This was attributed to the increase in redox potential due to oxidation of Fe$^{2+}$ from NO$_3^-$ to NO$_2^-$. Moreover the excess NO$_3^-$ could form uranyl nitrate complexes with the solubilised UO$_2^{2+}$ (Ram et al., 2013). Although this had a positive influence on leaching of uraninite, the influence of the aforementioned factors were shown to have negligible effect on betaite leaching.

3.4.2. Fluoride ion

Three fluoride salts were used to investigate the influence of fluoride on betaite leaching. The salts used were NaF, KF and NH$_4$F which were added at amounts sufficient to form 0.5 M F$^-$ in each experiment. Experiments were conducted with either 53.6 mM Fe (as the sulfate salt – Tests 30–32, Table 1) or with no Fe added (Tests 27–29, Table 1). Results of these experiments are presented in Figs. 9 and 10.

Both sets of experiments with the addition of fluoride show a greater extent of uranium leaching in the presence of fluoride compared to F$^-$ free systems. Addition of fluoride to the iron-containing leach solutions showed 2.6, 3.25 and 3.25% U was leached in experiments using NaF, KF and NH$_4$F, respectively. Furthermore, when fluoride was added with no iron present, the amount of uranium leached was greater and the leach rate was still positive even after 360 min of leaching (Fig. 10).

Increased uranium leaching in the presence of fluoride ions is primarily due to dissociation of the fluoride salt into F$^-$ ions leading to the formation of hydrofluoric acid (Eq. (1)). Over time however, the HF will react with Fe$^{3+}$ forming more stable and less reactive complexes.

![Fig. 4](image-url) Plots of Ln (U leached) vs. time (s) between 15 and 75 min (900 and 4500 s) for the leach tests conducted at different temperatures. The calculated reaction rates and R² values are given in Table 2.
(e.g. Eq. (2)) leading to a gradual decrease in the leach rate (Dodgen and Rollefson, 1949).

\[
2\text{NaF} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{Na}_2\text{SO}_4 \tag{1}
\]

\[
3\text{HF} + \text{Fe}^{3+} \rightarrow \text{FeF}_3 + 3\text{H}^+ \tag{2}
\]

Ferric fluoride (FeF₃) will preferentially form when ferric sulfate is added to a dilute hydrofluoric acid solution (Teufer, 1964). However, octahedral Fe³⁺ complexes with fluoride in the presence of H₂O ligands will stabilise the ferric iron and hence direct Fe²⁺/U⁴⁺ oxidation is less likely to occur. Levanon et al. (1969) reports species [Fe(H₂O)₂F₃] and [Fe(H₂O)F₄⁻] complexes are likely to be present at the 1.02 M sulfuric acid concentration and ~9.3:1 F/Fe ratio used in this experimental series. This mechanism explains the lower extent of leaching when a comparison between ferric iron and no iron is made (Figs. 9 and 10). When no iron is present in the system the formation of the ferric fluoride complexes does not occur.

Niobium, titanium and tantalum are known to be easily leached in HF (Gupta and Suri, 1993) and therefore it is presumed that the increase in leaching compared to sulfuric acid/iron sulfate leaching is due to increased Nb, Ti and Ta solubilising in the HF solution. This mechanism allows more uranium to be exposed to the solution thereby allowing more U leaching overall. It is important to note however, that even though the group 4 and 5 metals are dissolving, the rate of their leaching also slows throughout the experiment. No correlation between Nb, Ti or Ta and leached U concentration could be determined suggesting that the higher rate of uranium leaching was not due to congruent leaching of B site metals in the betafite structure. We speculate that the leaching mechanism is therefore similar to those previously discussed, where the uranium leaching is more heavily influenced by the solid/liquid interface reactions through a series of ligands allowing effective electron transfers to solubilise the uranium.

As indicated above, the type of fluoride salt used also had an effect on the leach rate of uranium. In the presence of iron, over the initial 30 min NaF showed a higher U solubility rate than KF and NH₄F possibly due to a more rapid dissociation to form HF than for the other fluoride salts. Thereafter the solubility of uranium remained constant while in the case of KF and NH₄F salts, uranium leaching continued. The highest rate of U leaching occurred when 0.5 M ammonium fluoride was added. The redox potential for NH₄F is ~650 mV whereas for NaF and KF it was 620 and 630 mV respectively. It was therefore assumed that the cause of the higher rate of leaching for addition of NH₄F was a due to a redox potential effect.

Similar trends were observed when fluoride salts were added in the presence of iron. The biggest difference however was that in all cases the rate of uranium leaching reached a plateau after approximately 100 min (NaF) and 250 min (KF). This is most likely due to the
The influence of lixiviant was studied to investigate the effect of the conjugate base on uranium leaching (Tests 33–39, Table 1). In this experimental series the proton equivalent of 0.51 N (1.02 M) H₂SO₄ was used for the respective acids.

The results in Fig. 11 show the majority of the mineral acids produced leaching curves similar to those observed previously. There was an initial rapid rate of leaching within the first min caused by surface oxidized uranium followed by a period up to 45–50 min where the rate of uranium leaching increased until eventually reaching a plateau. The amount of uranium leaching approximated the trend in the acid dissociation constants (pKₐ) with a lower pKₐ resulting in greater leaching. Sulfuric acid however caused a higher rate of leaching than the other acids even though it had the 3rd highest pKₐ under the conditions of this study. This was due to the increased concentration of the sulfate oxo-anion which reacts with iron and forms the more reactive iron sulfate complexes, FeSO₄⁺ and Fe(SO₄)₂⁻, both of which increase the rate of uranium leaching.

Phosphoric acid produced the lowest rate and amount of uranium leaching from betaafite. The acid reacts with Fe³⁺ to form insoluble FePO₄ (Haynes, 2014) which decreases the redox potential and prohibits the Fe²⁺/U⁴⁺ oxidation reaction:

\[
2H₃PO₄(aq) + Fe₂(SO₄)₃(aq) \rightarrow 2FePO₄(s) + 3H₂SO₄(aq)
\]  (3)

The slow rate of leaching over the initial period is due to betaafite particles seeding the precipitation of the sparingly soluble FePO₄ (confirmed via XRD). This inhibits the redox process from occurring and hence initially the only uranium leached is the surface oxidized uranium. Huang et al. (2004) showed the precipitation of FePO₄ occurred quicker when a seeding compound was added to the phosphate containing effluent (Huang et al., 2004). It was assumed a similar mechanism occurred in this leaching experiment where betaafite acted as the seed; although confirming that FePO₄ had coated the surface was difficult due to the vast excess of FePO₄ precipitate with respect to betaafite in the leach solution. Over the duration of the experiment however,
the FePO₄ does partially dissolve and re-precipitate allowing newly exposed areas of betafite to undergo leaching. A maximum leaching limit of ~1.30% U was reached after approximately 120 min. This value was significantly lower than in the other experiments.

The amount of uranium leaching was also observed to be greatly diminished when oxalic acid was used for leaching. Again, the majority of the leaching occurred in the initial min of the experiment. Oxalic acid is known to be a reducing agent and forms insoluble Fe²⁺ and Fe³⁺ salts such as FeC₂O₄ and Fe₂(C₂O₄)₃ (Haynes, 2014). Moreover, soluble ferrioxalate ion [Fe(C₂O₄)₃]⁻ will form when Fe³⁺ reacts with oxalic acid (Jeong and Yoon, 2005). Initially however, no precipitate was observed indicating that the iron was likely present as the soluble [Fe(C₂O₄)₃]⁻ and [Fe(C₂O₄)₂]²⁻ complexes or [Fe₂(SO₄)₃] which are used in the redox process to solubilise the uranium. The results show a very similar leach curve to that conducted with 53.6 mM ferrous iron (Fig. 7, Test 17) where no Fe³⁺ was present and hence the U/Fe³⁺ oxidation appears not to take place. This suggests that the reduction of Fe³⁺ by C₂O₄²⁻ has occurred and hence no oxidation of U follows which results in the small amount of uranium leached.

3.5. Discussion of leaching

In experiments to determine the solubility of betafite under varying conditions, similar uranium leach curves were observed for the majority of the tests. The leach curves were typically comprised of three relatively distinct segments, which are described below and shown in Fig. 12.

1. 0–1 min: A period of initial rapid leaching which accounts for the majority of the leaching of uranium (80% of the total leaching). In each experiment ~1.80% of the uranium in the sample was leached out in the initial min (segment 1). This instantaneous leaching is proposed to be due to the liberation of oxidized surface uranium U(VI) from the sample.

2. 1–120 min: A very slow leach rate interval that continues to slow until ~120 min. Of all the segments, this was the one where changes in leach rate were most closely influenced by variations in experimental conditions. The second leaching segment was likely due to the more traditional ferric oxidation/sulfate liberation reactions and discussed more extensively in previous sections.

![Fig. 9. Effect of fluoride ion with 3 g/L [FeTOT] as (Fe₂(SO₄)₃) present on the leaching of betafite. All other parameters were kept constant as per Table 1.](image1)

![Fig. 10. Effect of fluoride ion with no Fe present on the leaching of betafite. All other parameters were kept constant as per Table 1.](image2)
3. 120–360 min: The third segment showed very little leaching in most cases. By this stage it is likely that the surface of the beta-fite has become passivated by leaching of the exposed uranium sites leaving behind a uranium-depleted layer that is impermeable to the leach solution.

Slight variations in the presence/absence and length of each of these segments are noted depending on variations in the experimental set-up.

There are two possible explanations for the overall low yield of uranium leaching from synthetic beta-fite. The first explanation is that as the oxidized uranium is removed from the mineral structure the insoluble metals Nb, Ti and Ta remain causing the new uranium sites to become less exposed to the solution. The other explanation is leaching and re-precipitation of the sparingly soluble metals Nb, Ti and Ta could be forming an insoluble layer coating the beta-fite and hence creating a passivation layer. This therefore limits the leaching by creating a diffusion controlled mechanism between 1 and 120 min. Beyond 120 min the leach rate approaches zero due to two possible factors. These factors include:

- The overall change in the speciation of uranium as leaching occurs.
- Passivation due to re-precipitation of semi-soluble group 4 and 5 metals or structural rearrangement of mineral once some uranium has been liberated.

In work conducted by Nettleton et al. (2015) characterisation of annealed natural beta-fite showed an increased amount of tantalum was observed on the surface layer of the annealed material. This was suggested to have caused the reduced rate of leaching in the recrystallised samples (Nettleton et al., 2015). This is supportive of the previously discussed hypothesis where an insoluble layer could be forming on the surface of the synthetic beta-fite upon leaching which inhibits any further leaching of the sample. If this is proved correct, further studies should examine the potential for preferentially attacking the passivating layer and removing the semi-soluble metals.
4. Summary

High purity betafite was synthesised and used for leaching studies. The parameters investigated were; temperature, \([\text{H}_2\text{SO}_4\)], \([\text{FeT}O_4]\), redox potential, iron salt, fluoride salt and lixiviant. The results showed the leaching of uranium occurring in three distinct segments. The first segment had a high rate of leaching and occurred in the initial min. This leaching was due to liberation of surface oxidized uranium. The second leaching segment between 1 and 120 min was shown to be due to the typical redox reaction between ferric iron and uranium. This segment was most affected by changes in leaching parameters such as acid concentration, total iron concentration and redox potential. As the experiments progressed the leach rate decreased due to the redox and diffusion reaction competing. By the start of the third segment at approximately 120 min the leach rate had slowed to a negligible rate and remained slow for the remainder of the experiment. The extent of U leaching in the majority of the experiments was demonstrated to be <2.00% U demonstrating the highly refractory nature of the mineral.

References


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