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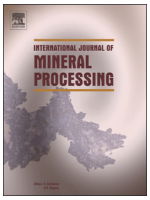

Uranium leaching from synthetic betafite: $[(Ca,U)_2(Ti,Nb,Ta)_2O_7]$

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 betafite, was investigated in acid sulfate media. Uranium leaching curves obtained over a range of time, temperature, $[H_2SO_4]$, $[Fe_{TOT}]$ 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 betafite 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 betafite 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.

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 gangue mineralogy. Generally, the uranium minerals preferentially targeted for processing/extraction are the primary uranium minerals uraninite (UO_2), pitchblende (U_3O_8) and coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$). This is due to their abundance in many uranium ore deposits at comparatively 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, betafite, $A_2B_2O_{7-x}(OH)_x$ 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 betafites 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 betafite due to radiation damage from α-decay of uranium (Lumpkin and Ewing, 1988). This leads to many natural betafites being amorphous, although some Ca-rich betafites have been reported as non-metamict and/or partially metamict (Cámara et al., 2004). Chemical alteration due to weathering of metamict betafite 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 betafite structure is achieved via hydration from water in the environment (Lumpkin et al., 1985). Lumpkin and Ewing (1996) also described a secondary alteration whereby betafite decomposes into pyrochlore $[(Ca,Na)_2Nb_2O_7]$ and microlite $[(Ca,Na)_2Ta_2O_7]$ after *A* site cationic migration of Ca and Na. The remaining unstable mineral reacts further to form uranpyrochlore $[(U,Ca)_2Nb_2O_7]$, liandratite (UNb_2O_{10}) and rutile (TiO_2). More recently, McMaster et al. (2015) showed that after primary alteration, naturally

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[*] Corresponding author at: Centre for Advanced Materials and Industrial Chemistry, School of Applied Sciences, RMIT University GPO Box 2476 Melbourne 3001 New Zealand.
E-mail address: s.mcmaster@massey.ac.nz (S.A. McMaster).

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altered amorphous betafite contains liandratite and rutile which react forming $UTiNb_2O_{10}$ (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, $[H_2SO_4]$, $[Fe_{TOT}]$ 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_2SO_4, 3 g/L $[Fe_{TOT}]$, 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 betafites. 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_2SO_4, 3 g/L Fe^{3+} at 89 °C for 48 h. They also noted that <12% uranium was extracted from the same betafite when recrystallised in air at 1100 °C (Nettleton et al., 2015).

In the current study, a high-purity, crystalline betafite was synthesised for the fundamental leaching experiments. The use of a non-metamict sample should provide information for the *minimum* extraction of uranium from betafite whereas for natural samples, the combination of a metamict state in association with the presence of uranium-rich decomposition products, leads to variable, but usually enhanced, uranium solubilities.

2. Materials and methodology

2.1. Synthesis

Betafite 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: $(U_{0.32}Ca_{0.42})(Nb_{0.41}Ti_{1.78}Ta_{0.10})O_7$. 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_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 Endeavor high throughput X-ray diffractometer using CuK_α radiation, an incident beam monochromator and a scintillation detector. A 1° divergence slit was used to analyse the 2θ 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 ($Ca_2Nb_2O_7$) 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