The leaching of uranium from betafite

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ABSTRACT

Betafite is a uranium–titanium–tantalum–niobium complex oxide mineral generally described as $(Ca,U)_2$ $(Ti,Nb,Ta)_2$ O_6 (OH). Significantly lower uranium extractions have been observed when betafite containing ores has been treated via conventional process flow sheets. Therefore it is necessary to understand the leaching behaviour of this mineral in order to open the potential for it to become an economic source of uranium in the future.

The leaching kinetics and reaction mechanism of uranium from a natural, metamict betafite sample have been investigated using varied temperature under oxidative acidic conditions. The practically complete extraction of uranium was observed by leaching the natural betafite in a solution containing 214.5 g/L H_2SO_4 and 2.0 g/L Fe^{3+} at 89 °C for a period of 48 h. Alternative leaching conditions using 57.1 g/L H_2SO_4 and 36.7 g/L Fe^{3+} at the same temperature also resulted in practically complete extraction of uranium but improved the selectivity for uranium over titanium, tantalum and niobium. Kinetic modelling has indicated that the rate of the leaching process is controlled by the rate of diffusion of products or reactants involved in the dissolution reaction to the reacting surface through a solid product layer containing niobium.

A portion of the betafite mineral sample used in the leaching testwork was recrystallised by heating in air at 1100 °C. The crystalline form of betafite was then leached under conditions similar to those applied to the metamict mineral to determine how crystal structure may affect the extraction of uranium. Less than 12% uranium was extracted from the recrystallised betafite under the conditions that gave practically complete extraction of uranium from the natural betafite sample which gives strong evidence that heat treatment prior to leaching should be avoided. The thermal recrystallisation of betafite in the present study appears to have resulted in tantalum enrichment on the surface of the betafite particles, which may be related to the lower extraction of uranium observed.

1. Introduction

Over the past sixty years, uranium has become an important source of energy with global demand exceeding supply since the early 1990s (World Nuclear Association, 2012). Once the supply of uranium from easy to process ore deposits is exhausted, the mining industry will be required to turn to more challenging deposits, including those that contain uranium locked within refractory minerals such as betafite.
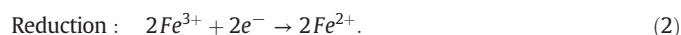
Significantly lower uranium extractions observed when betafite containing ores are treated via conventional process flow sheets are attributed to the uranium being locked in the betafite (Grunig, 1981; Abraham, 2009; Taylor, 2011). Betafite has extensive crystal lattice substitutions containing complex associations of uranium with titanium, tantalum and niobium, which make it difficult to predict its exact leaching behaviour. This possibly is one of the reasons why there are very few studies that have focused on the extraction of uranium

from this mineral. Indeed, rather than study its leaching from a hydrometallurgical point of view, previous studies have assessed the dissolution of uranium from betafite in a geological setting in order to determine its potential suitability as a stable host mineral that could be doped with high levels of nuclear waste or weapons grade plutonium and safely immobilised in a long term geological repository (Lumpkin and Ewing, 1996, Ewing et al., 2004, Geisler et al., 2005). To the author's knowledge, only one other study has been completed that has focused on the leaching of uranium from a pure betafite mineral with the intention of extracting it as a commodity (McMaster et al., 2012). The study by McMaster et al. (2012) used acidic, oxidative conditions and achieved a maximum extraction of 43% uranium. In most multiple oxide minerals, uranium is present as the relatively insoluble tetravalent ion and requires oxidative leaching conditions to convert it into the more soluble hexavalent uranyl ion (UO_2^{2+}). Ferric ions are a widely used reagent in uranium leaching systems to provide the oxidative conditions required for the desired dissolution reaction and can be added or generated in-situ by the parallel dissolution of an existing iron containing mineral source present within the ore. Assuming that uranium is present in the host mineral as a tetravalent ion, the oxidative
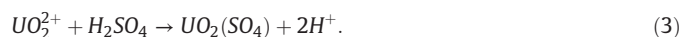
dissolution process is expected to occur according to Reaction 1, coupled with the reduction of Fe^{3+} shown by Reaction 2:

$$\text{Oxidation}: \quad UO_2 \rightarrow UO_2^{2+} + 2e^- \tag{1}$$

$$\text{Reduction}: \quad 2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}. \tag{2}$$

The hexavalent uranyl ion can then form stable uranyl sulphate complexes in the acidic aqueous solution (Langmuir, 1997) as shown by Reaction 3:

$$UO_2^{2+} + H_2SO_4 \rightarrow UO_2(SO_4) + 2H^+. \tag{3}$$

The E_h-pH diagram in Fig. 1 shows the stability regions of the predominant uranium species in sulphate solution under nominal leaching conditions. HSC Chemistry software (version 7.1) was used to study the thermodynamics of the system (Roine, 2011).

Excess ferric ions were used to maintain a relatively constant E_h with only minor regeneration of Fe^{3+} by the oxidation of Fe^{2+} in air via Reaction 4:

$$2FeSO_4 + H_2SO_4 + \frac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O. \tag{4}$$
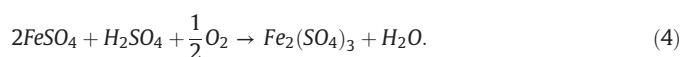
Uranium rich betafite is generally found in a metamict state. The term 'metamict' is used to describe the destruction of the crystal structure caused by internal radiation resulting in an amorphous formation. Previous studies by Lumpkin and Ewing (1988) have shown that the metamict transformation from crystalline to amorphous state progressed as a function of geological age. In many cases, the metamict state enabled an increased dissolution of uranium and thorium in geological settings (Lumpkin and Ewing, 1996; Geisler et al., 2005; Pöml et al., 2007). To better understand the leaching behaviour of this mineral under oxidative acidic sulphate conditions, the leaching kinetics and reaction mechanism of uranium from a natural, metamict betafite as well as from betafite recrystallised by heating were investigated.

2. Materials and methods

This study investigated the rate and extent of uranium dissolution from metamict and recrystallised betafite as a function of time, initial sulphuric acid concentration, initial ferric concentration and temperature. Details of the testwork are outlined in this section.
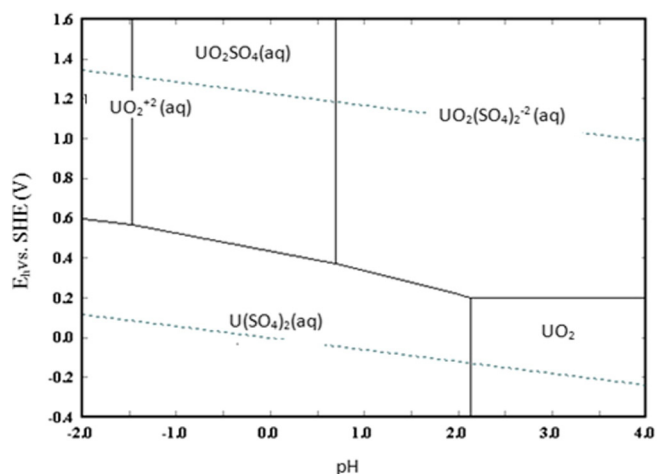

Fig. 1. E_h-pH diagram for uranium in sulphate solution. Conditions: 25 °C, [U] = 4.0×10^{-3} M, [S] = 1.0 M.

2.1. Sample preparation

The betafite crystal used in this study originated from the Silver Crater Mine, Basin Property, in Ontario, Canada. The Basin Property hosts a coarsely crystalline, cream coloured calcite body with large crystals of betafite, black mica, hornblende, apatite and zircon (Satterly and Hewitt, 1955). The $270 \times 220 \times 160$ mm 18.537 g sample had two well-developed crystal phases, showing intergrown cubic faces with a small amount of residual apatite on one side. The sample was prepared by crushing the whole rock with a pestle and mortar to provide a feed material with a P_{80} of 75 μm for the leaching tests. Approximately 6.8 g of the sample was roasted in air for 18 h at 1100 °C to reform the betafite crystal structure and generate an alternative crystalline feed material for comparative leaching experiments. The natural (metamict) and roasted (recrystallised) materials were weighed into 0.3 g portions and packaged in vials prior to the commencement of the leaching testwork. The remainder of the sample was used for further physical and chemical characterisation and analyses.

2.2. Reagents

The two main chemical reagents used in the study were analytical grade sulphuric acid (H_2SO_4) (98%) and hydrated ferric sulphate [$Fe_2(SO_4)_3 \cdot 5.235H_2SO_4$]. The hydration of the ferric sulphate was determined by heating 6.026 g $Fe_2(SO_4)_3 \cdot xH_2O$ in a ceramic crucible at 300 °C for 18 h. The difference in mass between the hydrated and anhydrous solids was used to calculate the hydration coefficient ($x = 5.235$) and determine the mass of $Fe_2(SO_4)_3 \cdot 5.235H_2O$ required to make up the leach solutions to the designated ferric concentrations.

The solutions were mixed with a magnetic stirrer for 18 h and then analysed to verify the initial free acid concentration and the actual iron concentration in solution. The free acid concentrations were determined by titration using potassium oxalate with a Titrando 842 automatic titration system to accurately report the four different acid concentrations of 53.3, 57.1, 106.0 and 214.5 g/L H_2SO_4. The initial iron concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and the densities were measured with a digital Anton Paar DMA 35 density metre.

2.3. Dissolution studies

A total of 36 leaching tests were conducted using the facilities at the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australian Minerals Research Centre in Waterford, Western Australia.

Leaching tests were conducted with 53.3, 57.1, 106.0 and 214.5 g/L H_2SO_4. Exactly 0.2 L of the lixiviant containing 2.0, 11.1, 19.5 or 36.7 g/L Fe^{3+} was added to clean, labelled 0.25 L high density polyethylene (HDPE) bottles and placed in a Thornton Engineering thermostatic bottle roller to provide an "end-over-end" agitation at 23 revolutions per minute (rpm). Temperatures of 25, 60 and 89 °C were chosen, where 25 °C provided a baseline for the study, 89 °C was the maximum temperature the bottle roller could maintain, and 60 °C was selected as an intermediate temperature.

The bath water was preheated to the required temperature for each experiment and the solutions were agitated for as long as required to equilibrate and reach the set leaching temperature prior to adding the betafite. The initial E_h and pH of the leach solutions were measured with a Thermo Scientific Orion ORP electrode with a combined platinum redox sensing electrode and Ag/AgCl reference electrode in a 3 M KCl solution (Epoxy Sure-Flow Combination Redox/ORP Electrode Cat. No. 9678 BNWP).

The 0.3 g solid betafite feed samples were added to each of the preheated leach solutions. The exact time of addition was recorded as t = 0. The bottles were removed from the bottle roller periodically at t = 0.25, 0.5, 1, 3, 6, 8, 24 and 48 h to monitor the weight, temperature,