The process chemistry and mineralogy of brannerite leaching

by R. Gilligan*, and A.N. Nikoloski*

Synopsis

Brannerite (UTi_2O_6) is the most important uranium mineral after uraninite and coffinite, and the most common refractory uranium mineral. As the more easily leachable uranium ores are becoming exhausted, it is necessary to process the complex and refractory ores in order to meet the growing demand for uranium as an energy source. This typically requires either more intense leaching conditions or a better-designed process based on sound understanding of feed mineralogy and reaction chemistry. The present study was carried out to provide information that will enable the development of a more effective processing strategy for the extraction of uranium from ores containing brannerite. The leaching behaviour of brannerite in sulphate media under moderate temperature conditions was investigated and compared with its relative leachability in alternative acid and alkaline systems. The feed and the leached residues were characterized by XRD and SEM-EDX techniques. Brannerite dissolutions of up to 95% after 5 hours of leaching in ferric sulphate media, up to 89% in ferric chloride media under similar conditions, and up to 82% in 24 hours in sodium carbonate media were obtained. Since alkaline leaching was considered promising for acid-consuming ores, leaching was repeated with a high-carbonate brannerite-bearing ore, with comparable extractions. Mineralogical characterization showed that altered and amorphous regions are a regular feature of brannerite, and that pitting is typically observed on the surface of the leached grains. The leaching results, coupled with mineralogical data, showed that the uranium and titanium in brannerite generally dissolve congruently, with faster dissolution of the altered and amorphous regions in the brannerite grains than of the crystalline regions. We conclude that the extent of brannerite alteration is a key factor in process selection, along with the grade, liberation size, and gangue mineralogy.

Keywords
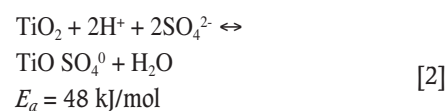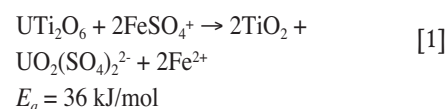uranium, brannerite, leaching, acidic, alkaline, kinetics.

Introduction

Brannerite (UTi_2O_6) is present as a major uranium mineral phase in many uranium and rare earth element (REE) deposits around the world. It is the most important uranium mineral after uraninite and coffinite (Finch and Murakami, 1999). Brannerite is a refractory uranium mineral and dissolves slowly compared to other uranium minerals under typical processing conditions (Gilligan and Nikoloski, 2015a; Lottering *et al.*, 2008).

Brannerite is typically metamict, rendered amorphous by self-irradiation. A study of brannerite specimens from different locations and of varying ages showed that this process takes less than 10 million years (Lumpkin,

Leung, and Ferenczy, 2012), much less than the age of most uranium ores. Altered and metamict brannerite is more reactive than crystalline brannerite. Recrystallizing brannerite by heating it in a furnace greatly reduces the rate of uranium extraction during leaching (Charalambous *et al.*, 2014).

Brannerite dissolves under oxidizing conditions in the conventional acidic ferric sulphate system, releasing uranium into solution as uranyl sulphate complexes such as $UO_2(SO_4)_2^{2-}$ (Equation [1]) and forming secondary titanium oxide through the reversible hydrolysis of titanyl ions and complexes (Equation [2]) (Gilligan and Nikoloski, 2015b; Gogoleva, 2012; Smits, 1984). This process is driven by the presence of ferric ions in solution which oxidize uranium to the hexavalent state, sulphate ions which complex uranium, and acid which attacks the titanium oxide.
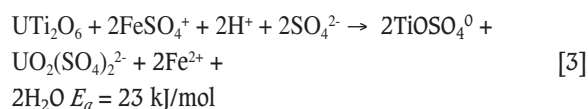
$$UTi_2O_6 + 2FeSO_4^+ \rightarrow 2TiO_2 + UO_2(SO_4)_2^{2-} + 2Fe^{2+} \qquad [1]$$
$$E_a = 36 \text{ kJ/mol}$$

$$TiO_2 + 2H^+ + 2SO_4^{2-} \leftrightarrow TiOSO_4^0 + H_2O \qquad [2]$$
$$E_a = 48 \text{ kJ/mol}$$

The activation energy (E_a) values were derived from initial extraction rates measured by Gilligan and Nikoloski (2015b). At higher temperatures and under more strongly acidic conditions, the uranium and titanium in brannerite dissolve congruently through Equation [3] (Gilligan and Nikoloski, 2015b).

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$$UTi_2O_6 + 2FeSO_4^+ + 2H^+ + 2SO_4^{2-} \rightarrow 2TiOSO_4^0 +$$
$$UO_2(SO_4)_2^{2-} + 2Fe^{2+} + \quad [3]$$
$$2H_2O \; E_a = 23 \text{ kJ/mol}$$

The resulting Fe^{2+} ions are re-oxidized to Fe^{3+} with an oxidant, which is usually pyrolusite (MnO_2), sodium chlorate ($NaClO_3$), or oxygen gas, depending on availability and process economics.

The majority of the work on brannerite leaching published to date has studied only the conventional ferric sulphate system. There is little information available on alternatives such as ferric chloride or sodium carbonate media. In this study, these alternatives were investigated as well as the ferric sulphate system.

The effects of deleterious ions such as phosphate on uranium extraction processes are well documented, though little if any information exists on the effects of these ions specific to brannerite. It is important to understand these interactions, as brannerite is often associated with apatite. Therefore selected acid leaching experiments were repeated with the addition of fluorapatite and fluorite.

Materials and methods

Bulk chemical analyses of the feed brannerite were performed by a local commercial mineral laboratory. The feed and residue solids were characterized by X-ray diffraction (XRD) and scanning electron microscopy using energy dispersive X-ray analysis (SEM-EDX) techniques following the procedures described in Gilligan, Deditius, and Nikoloski (2016).

We performed all ferric sulphate leaching experiments using the procedure described by Gilligan and Nikoloski (2015b). Similar procedures were used for the leach tests with alternative lixiviants, with some minor changes, such as the substitution of $FeCl_3/HCl$ for $Fe_2(SO_4)_3/H_2SO_4$ in the chloride leaching experiments, or the addition of 10 g/L CaF_2 or $Ca_5(PO_4)_3F$ in the gangue interaction tests.

Alkaline leaching tests were run for 24 hours. The total carbonate concentration was kept constant at 1.00 mol/L, usually as 0.66 mol/L $NaHCO_3$ and 0.34 mol/L Na_2CO_3.

Characterization of the brannerite sample

We used a specimen of brannerite from the Dieresis deposit, in the Sierra Albarrana area of Spain. Bulk chemical analysis showed that the brannerite was within the typical range of compositions for brannerite (Gilligan, Deditius, and Nikoloski, 2016).

EDX analyses and element maps showed brannerite as the dominant phase, with lesser amounts of titanium oxide. Titanium oxide often formed linear zones through the brannerite surrounded on either side by silicon-enriched zones (Figure 1), consistent with published descriptions of altered brannerite (Lumpkin, Leung, and Ferenczy, 2012).

Despite the large amounts of brannerite identified by EDX, no crystalline brannerite was detected in the XRD analyses. These results indicate that the brannerite phase is metamict, as is typical for brannerite. Two broad peaks were present on the X-ray diffraction pattern, similar to brannerite from other localities (Charalambous et al., 2012; Lumpkin et al., 2012). The first broad peak ran from 20 to 35° 2θ, the second from 40 to 65° 2θ (Figure 6).

Some anatase (TiO_2) was detected in XRD analyses, as was crystalline thorutite ((Th,U,Ca)Ti_2O_6) (Figure 6). Fine-grained anatase is a common alteration product of brannerite from several localities (Charalambous et al., 2012; Lumpkin, Leung, and Ferenczy, 2012; Smits, 1984). The specific alteration products vary between deposits, and are affected by the geochemistry of the area (Gilligan, Deditius, and Nikoloski, 2016; Lumpkin, Leung, and Ferenczy, 2012). Calculations using the Scherrer formula (Equation [4]) indicate that the anatase crystallites are 10–20 nm in size.

$$t = \frac{0.9\,\lambda}{B \cos\theta_B} \quad [4]$$

where t is the crystallite size, λ is the X-ray wavelength, B is the peak width in radians at half the maximum height, and θ_B is the diffraction angle, also in radians.

Leaching results

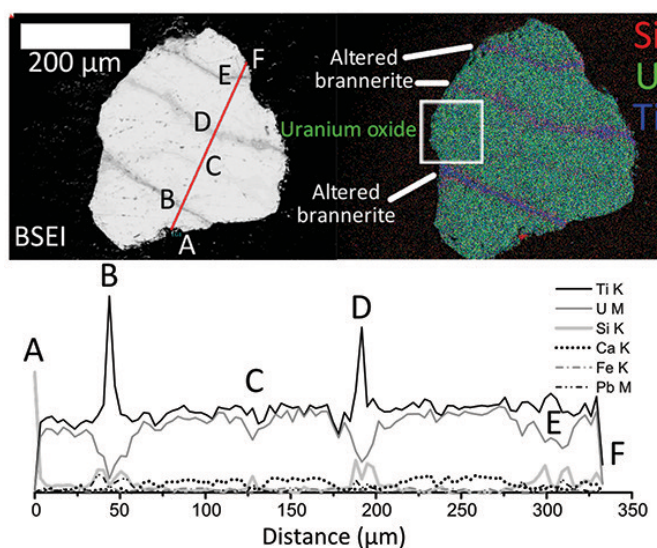The extent of uranium extraction in the leaching experiments

Figure 1—Backscattered electron image (top left), element map (top right), and EDX line analysis (bottom) of an unleached brannerite particle. The position of the line analysis is shown on the BSE image. Letters on the line analysis correspond to points on the BSE image

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always exceeded titanium extraction. This is due partly to the presence of insoluble anatase, which is much more resistant to leaching than brannerite. Secondary titanium oxide formed in many experiments. This side-reaction was typically observed at higher temperatures and/or lower acid concentrations. Titanium leaching curves have been omitted from this paper for brevity.

Leaching in different media

Sulphate media were more effective than chloride media at the same temperature and acid concentration, with the exception of 2.00 M acid at 52°C (Figures 2 to 4). Leaching studies on synthetic brannerite suggest that the dissolution of brannerite is promoted by the formation of uranium (VI) complexes at the surface (Thomas and Zhang, 2003). Sulphate and carbonate ions form stable complexes with uranyl ions, while chloride ions do not.

Alkaline carbonate leaching is slow compared to acid leaching, with much longer leaching times required. Alkaline carbonate leaching is typically reported as difficult or unfeasible for refractory uranium ores containing brannerite, yet our results show that it is possible. Calculations indicate that the reaction between carbonates and brannerite is thermodynamically favourable, while experiments (Figure 2) show that it is kinetically slow. Alkaline carbonate media do not attack gangue, leading to reduced reagent consumption

and fewer problematic species such as phosphate entering solution. Brannerite has been identified as associated with alkaline gangue in uranium deposits in Queensland, Australia (Wilde *et al.*, 2013) and in the Central Ukrainian Uranium Province (Cuney *et al.* 2012). Many of these deposits also contain apatite, which dissolves rapidly in acidic solutions and suppresses uranium dissolution (Figure 5). For this reason, alkaline carbonate leaching may be the only viable option for processing alkaline refractory uranium ores.

Effect of acid concentration

Variations in acid concentration had only a slight effect on the rate of leaching in sulphate media, but a much larger effect on the rate of leaching in chloride media (Figure 3). The most likely explanation for this lies in the nature of the aqueous uranium species formed. Uranyl chloride complexes are weak compared to uranyl sulphate complexes. Acid has a more active role in attacking brannerite in chloride leaching. Based on the extractions after 15 minutes, the rate of uranium dissolution is approximately first-order with respect to acid in chloride media. In sulphate media, the order of reaction with respect to acid concentration is approximately 0.5. Higher concentrations of acid are required for effective uranium extraction in chloride media compared with sulphate media.
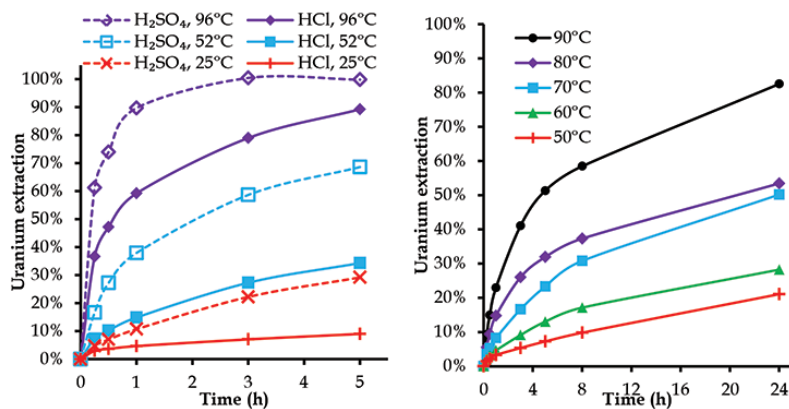

Figure 2—Uranium leaching curves for different temperatures. Left: acid media, 0.25 mol/L H_2SO_4/HCl with 0.05 mol/L Fe^{3+}. Right: alkaline media, 0.66 mol/L $NaHCO_3$, 0.34 mol/L Na_2CO_3 with 0.025 mol/L $K_3Fe(CN)_6$
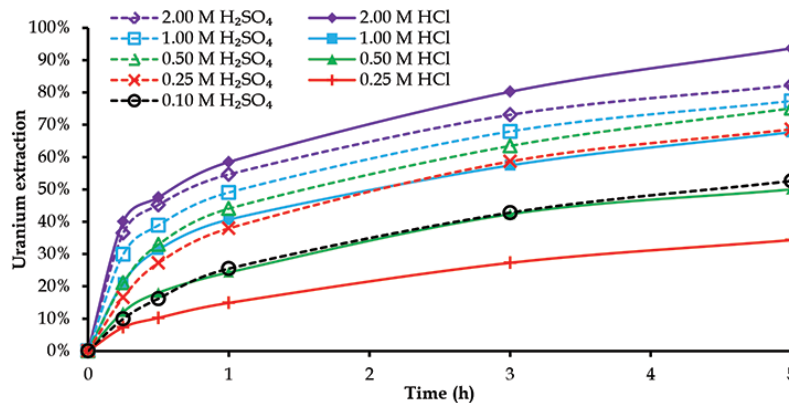

Figure 3—Uranium extraction curves at varied acid concentration at 52°C. Dashed lines: sulphate media; solid lines: chloride media

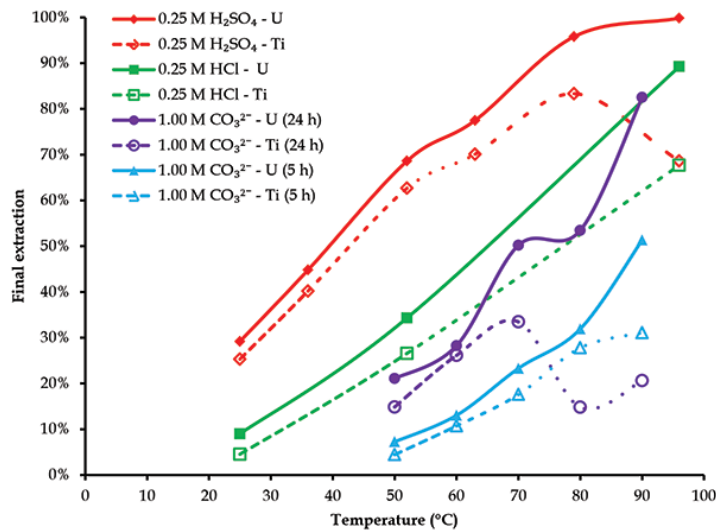# The process chemistry and mineralogy of brannerite leaching

Figure 4—Final extractions of uranium (solid lines) and titanium (dashed lines) *vs* temperature in different leaching systems. 5-hour leaching points from the alkaline tests are shown to simplify comparison between acidic and alkaline media
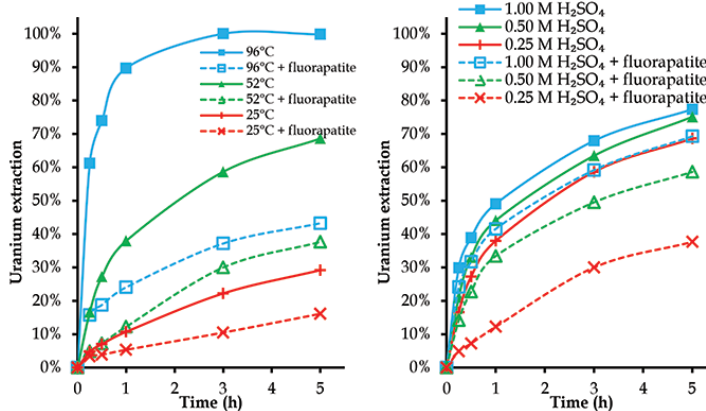

Figure 5—Uranium leaching curves in ferric sulphate media with and without phosphate. Left: varied temperature, 0.25 mol/L H_2SO_4. Right: varied acid concentration, 52°C

Chloride leaching offers no clear advantages over sulphate leaching. However, some preliminary results (based on data to be published in future) suggest that chloride leaching may be a promising alternative for high-phosphate uranium ores.

Effect of temperature

The rate of uranium leaching is strongly dependent on temperature, as has been commonly reported. In sulphate media, a 10°C increase in temperature has a similar effect on the rate of uranium extraction as a four-fold increase in acid concentration. Leaching at higher temperatures enables effective extraction at lower acid concentrations. The optimum temperature and acid concentration will vary with the nature of the gangue. Higher temperatures will also increase the rate at which acid-soluble gangue dissolves, increasing the amount of acid that must be added to control the pH (Ring, 1979).

Temperature has an even stronger effect on the rate of leaching in alkaline carbonate media. Increasing the leaching temperature from 50 to 90°C increased the uranium

extraction over 24 hours in alkaline carbonate media from 21 to 83% (Figure 4). High temperatures, ideally over 100°C, appear to be required for alkaline leaching of refractory uranium ores to be effective.

Effect of gangue minerals

Phosphates are known to inhibit uranium leaching by binding to ferric ions, reducing the rate at which ferric ions oxidize uranium (IV) (Nicol, Needes, and Finkelstein, 1975). When leaching brannerite in ferric sulphate media, phosphate released by dissolving apatite suppresses uranium and titanium dissolution. In our experiments, this effect was decreased at higher acid concentrations (Figure 5). Higher sulphate concentrations favour the formation of ferric sulphate complexes over ferric phosphate complexes. Ferric sulphate complexes are more effective oxidants for uranium (IV) than ferric phosphate complexes (Nicol, Needes, and Finkelstein, 1975).

EDX analysis of brannerite particles leached in sulphate media along with apatite shows that many particles were coated with titanium oxide. This coating was enriched in

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phosphorus. Phosphate appears to initiate the formation of the titanium oxide coating. The exact mechanism for this is not clear, though the speciation of titanium is known to influence the solid products formed through the hydrolysis of titanium (IV) ions. For example, the presence of sulphate ions favours the formation of anatase over rutile during hydrolysis and precipitation of titanium dioxide (Dambournet, Belharouak, and Amine, 2010). This coating was not observed on brannerite leached in the absence of phosphates. Typically, secondary titanium oxide only formed in sulphate media at less than 0.50 mol/L H_2SO and above 75°C.

Phosphates did not adversely affect uranium extraction in chloride media – instead, phosphates actually improved extraction. Chloride leaching may be an effective alternative for high-phosphate uranium ores, based on data to be published in future

Characterization of residues

Structural characterization (XRD)

The broad peaks, associated with metamict brannerite, in the X-ray diffraction pattern for the original brannerite are absent in the patterns for the residues from leaching with all lixiviants (Figure 6). These changes were most apparent for the leaches at higher temperature.

Metamict brannerite is known to be much more soluble than crystalline brannerite (Charalambous *et al.*, 2014). This explains the disappearance of the broad peaks on the XRD patterns of the leached residues. Brannerite feed samples that have undergone more alteration are less refractory.

Crystalline thorutite and microcrystalline anatase were also present in the leach residues. Anatase and thorutite are resistant to leaching over the range of conditions studied. Some of the anatase in the residues was from the original material, while other anatase formed during leaching. The difference between these phases is described in detail in Gilligan, Deditius, and Nikoloski (2016). In brief, anatase in the unleached material contained uranium, while anatase formed during leaching typically contained iron.

Microscopy and EDX analysis

After leaching at 25°C, much of the surface of the brannerite particles remained intact, with some pitted areas. When the leaching temperature was increased to 52°C, these pits covered the entire surface. Under the most intense acid-leaching conditions (0.50–2.00 mol/L H_2SO_4, 96°C), brannerite was entirely absent from the leached residues. Based on the observation of a large number of particles leached over the full range of conditions, the depth of the leach pits was around 10–20 μm after 5 hours of leaching. Some examples are shown in Figure 7.

The linear inclusions of titanium oxide in the feed particles (shown in Figure 1) are resistant to leaching, as is evident from the way they protrude from the surfaces of leached brannerite particles (Figure 7). The silicon-enriched altered brannerite surrounding these titanium oxide inclusions is more readily leached than the associated brannerite, as is evident from the depth of corrosion around the titanium oxide inclusions.

The reaction front at the base of the leach pits was cracked. EDX line analysis shows that the ratio of uranium to titanium is constant across the reaction front (Gilligan, Deditius, and Nikoloski, 2016). Although titanium dioxide is often reported to form a coating on the surface of leached brannerite particles (Gogoleva, 2012; Smits, 1984), there was no evidence for this happening in sulphate media.

In acidic media, a titanium oxide coating formed only in the presence of phosphates. The titanium oxide layer was enriched in phosphorus. This coincided with unusually low titanium to uranium extraction ratios. Phosphates released through the dissolution of gangue minerals such as apatite stabilize secondary titanium oxide on the surface of the brannerite, further inhibiting leaching (Gilligan and Nikoloski, 2016).

Brannerite leached in alkaline media at higher temperatures (80–90°C) was coated with titanium oxide. According to the leaching kinetics results, the titanium concentration began to decrease after 5–8 hours of leaching. Secondary titanium oxide formed faster at higher leaching temperatures. Line EDX analysis showed a sharp transition between the brannerite core and the secondary titanium oxide. The pitted and cracked brannerite underneath the titanium oxide coating resembled brannerite leached in acidic media around 60°C.
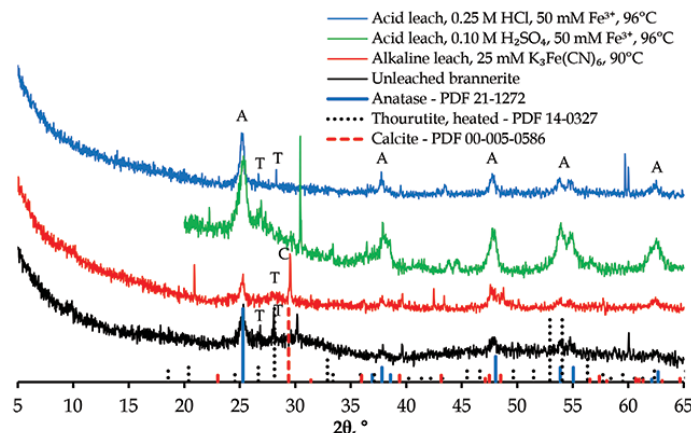

Figure 6—XRD patterns of selected leach residues compared with the unleached material. A: anatase, T: thorutite, C: calcite

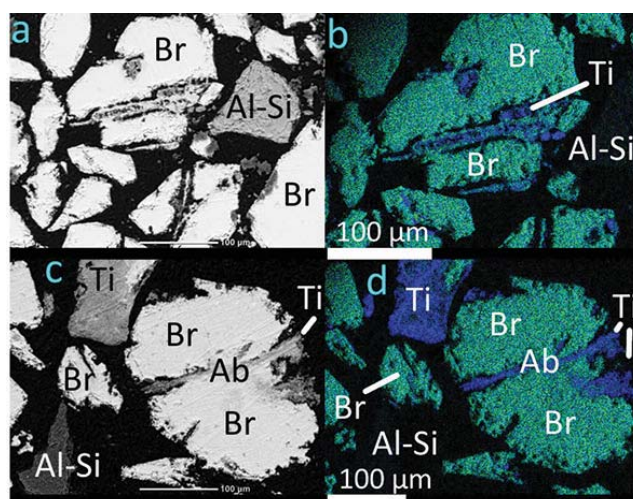# The process chemistry and mineralogy of brannerite leaching

Figure 7—BSEI images (a, c) and element maps (b, d) of leached brannerite particles. Uranium is shown in green, titanium in blue. a and b: 0.50 mol/L H₂SO₄, 25°C; c and d: 0.10 mol/L H₂SO₄, 52°C. Phases: Ab: altered brannerite, Al–Si: aluminium silicate gangue, Br: brannerite, Ti: titanium oxide

Conclusions

Leaching experiments in several different lixiviants showed that the rate of uranium leaching from brannerite is strongly dependent on temperature, less so on acid concentration. Acidic ferric sulphate is an effective lixiviant for brannerite, though ferric chloride may be a better option when the ore contains soluble phosphates. While alkaline leaching is often assumed to be ineffective for the leaching of refractory uranium ores, our results show that it is possible and effective with sufficient time and/or temperature.

Altered zones of the brannerite were more heavily corroded compared to less-altered zones of the brannerite. These findings suggest that more heavily altered brannerite is less refractory than unaltered brannerite. The extent of alteration and the texture of brannerite grains vary between deposits. In light of these findings, it is proposed that the texture of the uranium minerals is an important consideration, along with grade, liberation size, and gangue mineralogy, in predicting the leaching behaviour of refractory uranium ores.

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