Brannerite, UTi$_2$O$_6$, is the most important uranium mineral after uraninite and coffinite, and the most common refractory uranium mineral. As the more-leachable ores become exhausted, it is necessary to process complex and refractory ores to meet the growing demand for uranium as an energy source. 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. A detailed study was carried out to understand the leaching behaviour of brannerite in sulphate media (10–200 g/L H$_2$SO$_4$) under moderate temperature conditions (25–96°C), and in alternative acid and alkaline systems. The feed and the leached residues were characterised by X-ray diffraction and scanning electron microscopy with energy-dispersive spectrometry techniques. The brannerite dissolved up to 95% after 5 h leaching in ferric sulphate media, up to 89% in ferric chloride media under similar conditions, and up to 82% in 24 h in sodium carbonate media. The alkaline leaching was repeated with a high-carbonate brannerite-bearing ore, which showed comparable extractions. Mineralogical characterisation 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. Brannerite was shown to generally dissolve congruently, with altered and amorphous regions in the brannerite grains dissolving faster than the crystalline regions, which implies that the extent of brannerite alteration is a key parameter in the process selection, along with the grade, liberation size and gangue mineralogy.

INTRODUCTION

Brannerite 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 mineral and will dissolve slowly compared with 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 examining brannerite specimens from different locations and of varying ages showed that this process takes less than 10 million years (Lumpkin et al., 2012), well below the age of most uranium ores. Altered and metamict brannerite is more reactive than crystalline brannerite. Recrystallising brannerite by heating it in a furnace greatly reduces the rate of uranium extraction during leaching (Charalambous et al., 2014).
Brannerite dissolves under oxidising conditions in the conventional acidic ferric sulphate system, releasing uranium into solution as uranyl sulphate complexes such as $\text{UO}_2(\text{SO}_4)_2^{2-}$ [1] and forming secondary titanium oxide through the reversible hydrolysis of titanyl ions and complexes [2] (Gilligan and Nikoloski, 2015b; Gogoleva, 2012; Smits, 1984). This process is driven by the presence of ferric ions in solution to oxidise uranium to the hexavalent state, sulphate ions to complex uranium and acid to attack the titanium oxide.

$$\text{UTi}_2\text{O}_6 + 2 \text{FeSO}_4^+ \rightarrow 2 \text{TiO}_2 + \text{UO}_2(\text{SO}_4)_2^{2-} + 2 \text{Fe}^{2+}$$

$E_a = 36 \text{ kJ/mol}$ [1]

$$\text{TiO}_2 + 2 \text{H}^+ + 2 \text{SO}_4^{2-} \leftrightarrow \text{TiOSO}_4^0 + \text{H}_2\text{O}$$

$E_a = 48 \text{ kJ/mol}$ [2]

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

$$\text{UTi}_2\text{O}_6 + 2 \text{FeSO}_4^+ + 2 \text{H}^+ + 2 \text{SO}_4^{2-} \rightarrow \text{UO}_2(\text{SO}_4)_2^{2-} + 2 \text{Fe}^{2+} + 2 \text{TiOSO}_4^0 + 2 \text{H}_2\text{O}$$

$E_a = 23 \text{ kJ/mol}$ [3]

The resulting Fe$^{2+}$ ions are re-oxidised 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.

Most work on brannerite leaching published to date has only studied 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 conventional 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, because brannerite is often associated with apatite. Selected acid leaching experiments were therefore repeated with the addition of fluorapatite and fluorite.

**MATERIALS AND METHODS**

Bulk chemical analyses of the feed brannerite were performed by a local commercial laboratory. The feed and residue solids were characterised by X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive spectrometric detection (SEM-EDX) using the procedures described in Gilligan et al. (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 lixivians with some minor changes, such as the substitution of FeCl$_3$/HCl for Fe$_2$(SO$_4$)$_3$/H$_2$SO$_4$ in the chloride leaching experiments, or the addition of 10 g/L CaF$_2$ or Ca$_5$(PO$_4$)$_3$F in the gangue interaction tests.

Alkaline leaching tests were run for 24 h. 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$_2$CO$_3$. 
CHARACTERISATION OF 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 expected compositions (Gilligan et al., 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 et al., 2012).

![Image](image.png)

**Figure 1.** Backscattered electron (BSE) 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.

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 humps were present on the XRD pattern, similar to brannerite from other localities (Charalambous et al., 2012; Lumpkin et al., 2012). Presented further in the text (Figure 6), the first broad hump ran from 20 to 35° 2θ, the second from 40 to 65° 2θ.

Some anatase (TiO₂) was detected in XRD analyses, as was crystalline thorutite ((Th₃U,Ca)Ti₂O₆) (Figure 6). Fine-grained anatase is a common alteration product of brannerite from several localities (Charalambous et al., 2012; Lumpkin et al., 2012; Smits, 1984). The specific alteration products vary between deposits, and are affected by the geochemistry of the area (Gilligan et al., 2016; Lumpkin et al., 2012). Calculations using the Scherrer formula [4] indicated that the anatase crystallites are 10–20 nm in size:

\[ t = \frac{0.9λ}{B \cos θ_B} \]  

where \( t \) is the crystallite size; \( λ \) is the x-ray wavelength; \( B \) is the peak width in radians at half the maximum height; \( θ_B \) is the diffraction angle, also in radians.
LEACHING EXPERIMENTS

The extent of uranium extraction in the leaching experiments always exceeded that of titanium. This is partially due to the presence of insoluble anatase, which is much more resistant to leaching than brannerite (Figure 6). 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 was more effective than chloride media at the same temperature and acid concentration, with the exception of the 2.00 M acid, 52°C leaching experiments (Figure 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 does 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 contain apatite as well, which is known to dissolve rapidly in acidic solutions and suppress 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 on Leaching

Variations in acid concentration had only a slight effect on the rate of leaching in sulphate media, but a much larger effect 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 with uranyl sulphate complexes. Acid has a more active role in attacking brannerite in chloride leaching. Based on
the extractions after 15 min, 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 3. Uranium extraction curves at varied acid concentration at 52°C. Dashed lines: sulphate media; solid lines: chloride media.](image)

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

**Effect of Temperature on Leaching**

The rate of uranium leaching is strongly dependent on temperature, as has been commonly reported in other studies. In sulphate media, a 10°C increase in temperature has a similar effect on the rate of uranium extraction to 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 h in alkaline carbonate media from 21 to 83% (Figure 4). High temperatures, ideally above 100°C, appear to be required for alkaline leaching of refractory ores to be effective.

**Effect of Gangue Additives on Leaching**

Phosphates are known to inhibit uranium leaching by binding to ferric ions, reducing the rate at which ferric ions oxidise uranium(IV) in the ore (Nicol et al., 1975). When leaching brannerite in ferric sulphate media, phosphate released by dissolving apatite suppresses uranium and titanium dissolution. In our experiments, this effect was reduced 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 et al., 1975).
Figure 4. Final extractions of uranium (solid lines) and titanium (dashed lines) as a function of temperature in different leaching systems. 5 h leaching points from the alkaline tests are shown to simplify the comparisons 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$_2$SO$_4$. Right: varied acid concentration, 52°C.
EDX analyses of brannerite particles leached in sulphate media along with apatite shows that many of them were coated in titanium oxide. This titanium oxide coating was enriched in phosphorus. Phosphate appears to initiate the formation of a titanium oxide coating on the leached brannerite. The exact mechanism for this is not clear, although 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 the hydrolysis and precipitation of titanium dioxide (Dambournet et al., 2010). This coating was not observed when leaching brannerite without phosphates. Typically, secondary titanium oxide only formed in sulphate media above 75°C and below 0.50 mol/L H₂SO₄.

Phosphates did not negatively affect uranium extraction in chloride media. Instead, phosphates actually improved uranium extraction in chloride media. Based on data to be published in future, chloride leaching may be an effective alternative when dealing with high-phosphate uranium ores.

CHARACTERISATION OF RESIDUES

Structural Characterisation
Comparing the XRD patterns of the leached residues with those of original brannerite shows the disappearance of the broad humps associated with metamict brannerite after leaching for all lixiviants (Figure 6). These changes were clearest when leaching took place 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 humps on the XRD patterns of the leached residues. Brannerite feed samples that have undergone more alteration are less refractory.

Figure 6. X-ray diffraction patterns of selected leach residues compared with the unleached material. A: anatase, T: thorurite, C: calcite.
Crystalline thorutite and microcrystalline anatase were also present in the leach residues. Anatase and thorutite were 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 et al. (2016). In brief, anatase in the unleached material contained uranium, while anatase formed during leaching typically contained iron.

**Microscopy and EDX Analyses**

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 H₂SO₄, 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 h leaching. Some examples are shown in Figure 7.

![Figure 7](image_url)

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

The linear inclusions of titanium oxide in the feed particles identified in Figure 1 were resistant to leaching, as was 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 was more readily leached than the associated brannerite, as was 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 analyses showed that the ratio of uranium to titanium was constant across the reaction front (Gilligan et al., 2016). While titanium dioxide is often reported to form a coating on the surface of leached brannerite particles (Gogoleva,
In acidic media, the formation of a titanium oxide coating only occurred 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, stabilise secondary titanium oxide on the surface of the brannerite, further inhibiting leaching (Gilligan and Nikoloski, under review).

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 h leaching. Secondary titanium oxide formed faster at higher leaching temperatures. Line EDX analyses 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.

CONCLUSIONS

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

Altered zones of the brannerite were more heavily corroded compared with less altered zones of the brannerite. These findings suggest that more heavily altered brannerite is less refractory compared with 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.

REFERENCES


Gilligan, R. and Nikoloski, A.N. (2015a). The extraction of uranium from brannerite—A literature


