

THE EXTRACTION OF URANIUM FROM BRANNERITE

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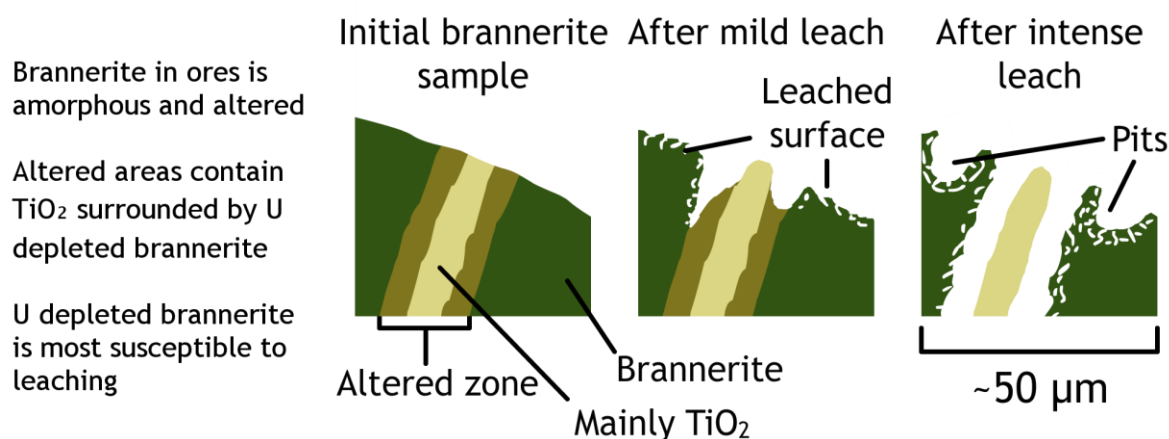
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ABSTRACT

Brannerite, UTi_2O_6 is the most important uranium mineral after uraninite, UO_2 and coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$. It is also the most common refractory uranium mineral. Ores containing brannerite typically require intense conditions (>50 g/L H_2SO_4 , $>75^\circ C$) compared to other uranium ores for effective uranium extraction to occur. To develop an effective process for the extraction of uranium from brannerite containing ores and improve the extraction from the ores currently being processed, it is necessary to understand the chemistry of the brannerite leaching process.

As this study has shown, brannerite is typically an altered and amorphous mineral, with an extent of alteration depending on the age of the sample and the geological history of the deposit. A sample of brannerite from Cordoba, Spain, was leached over a range of conditions in acidic ferric sulphate media. The sample was filled with cracks and altered zones containing anatase (TiO_2). Process parameters studied included temperature ($25-96^\circ C$), acidity ($10-200$ g/L H_2SO_4) and the effect of adding selected gangue minerals (apatite, fluorite and ilmenite). The feed and the leached residues were characterised in detail by XRD and SEM-EDX techniques.

The results of this study showed that brannerite dissolution has a stronger dependence on temperature and lesser dependence on free acid concentration. Comparisons between the residues and the feed showed that the altered and amorphous areas of the brannerite sample are more readily leached than crystalline areas. The crystalline areas of the brannerite dissolved congruently, with titanium subsequently precipitating as anatase physically separated from the original brannerite grains.



Keywords: Uranium, Titanium, Brannerite, Leaching, Kinetics, Mineralogy

INTRODUCTION

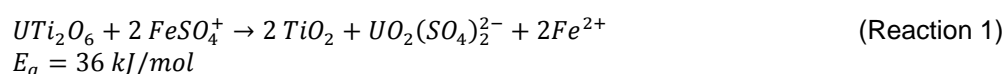
Brannerite, UTi_2O_6 is the most important uranium mineral after uraninite, UO_2 and coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$ (Finch and Murakami, 1999). It is also the most common refractory uranium mineral. It has been identified in many uranium and rare-earth element deposits around the world, including several in Australia.

Brannerite is typically metamict, rendered amorphous by self-irradiation. The degree of metamictisation varies with age (Lumpkin et al., 2012) and has been found to influence leachability (Charalambous et al., 2014).

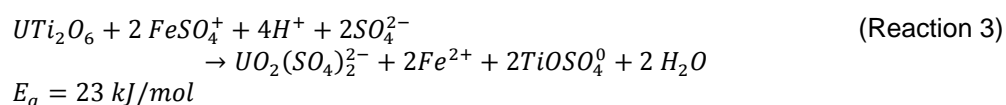
Ores containing brannerite require relatively intense conditions for processing. The results of numerous laboratory and industrial studies were summarised in a literature review by Gilligan and Nikoloski (2015a). Lottering et al. (2008) leached three South African uranium ores at 60°C for 24 hours with reagent dosages of 16.3 kg/t H_2SO_4 and 4.0 kg/t MnO_2 . Under these conditions nearly all of the uraninite and coffinite were dissolved while most of the brannerite remained intact.

The leaching of high-brannerite ores has required high temperatures (~75 °C), high free acid concentrations (60–75 g/L) and long leaching times (36–48 h) to achieve satisfactory uranium extraction (LaRocque and Pakkala, 1979; Hester, 1979; Ifill et al., 1996). Stanrock Uranium Mines, in the Elliot Lake district, have successfully leached brannerite and thucholite (U/Th oxides associated with organic matter) in 50 g/L H_2SO_4 for 60 h at 65–70 °C (Merritt, 1971). A few of these mines in the Elliot Lake area have also successfully extracted uranium through bioleaching (Mac Gregor, 1969; Wadden and Gallant, 1985).

Brannerite dissolves under oxidising conditions in the conventional acidic ferric sulphate system, releasing uranium into solution as uranyl sulphate complexes such as $UO_2(SO_4)_2^{2-}$ [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.



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).



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. The choice of oxidant has little to no effect on the rate of uranium extraction as long as the E_h is maintained constant (Ring et al., 1984).

MATERIALS AND METHODS

Brannerite was leached for five hours in an aqueous leach solution containing ferric sulphate and sulphuric acid over a range of temperatures (25–96°C) and acid concentrations (10–200 g/L H_2SO_4). The ferric sulphate concentration was kept constant at 2.8 g/L Fe^{3+} .

Both uranium and titanium extraction kinetics were studied, though the latter have been omitted from this paper for brevity. For the full explanation of titanium dissolution kinetics, see Gilligan and Nikoloski (2015b).

The brannerite and all leached residues were characterised by XRD, SEM and SEM-EDX methods. For details of the analyses, see Gilligan et al. (2016).

SAMPLE CHARACTERISATION

The brannerite used in this study originated in the Dieresis deposit near Cordoba in the Sierra Albarrana region of Spain. It is within typical range of brannerite compositions (Gilligan et al, 2016). The sample was obtained as a single crystal. The brannerite itself was translucent and dark green in colour. The crystal was coated with a thin layer of pale yellow/brown anatase and interlaced with cracks containing the same material, which is indicative of natural alteration.

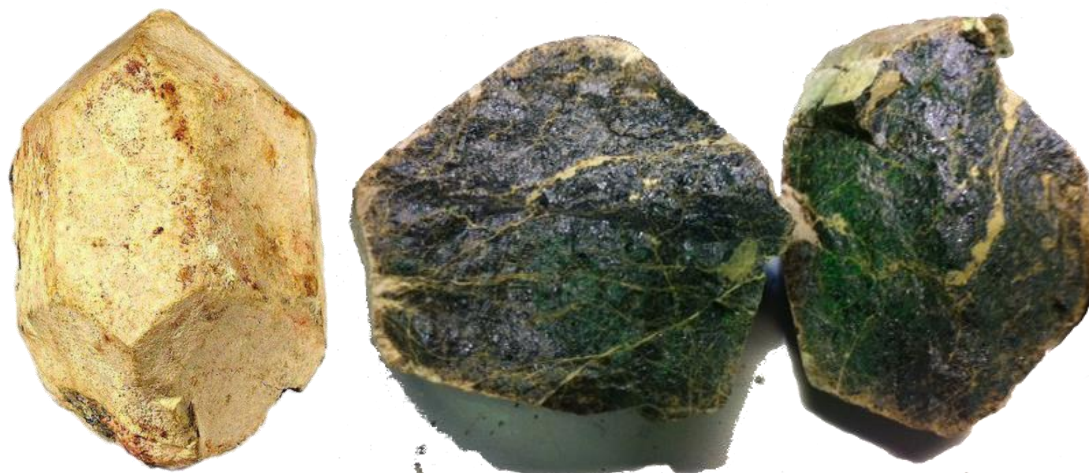


Figure 1: The brannerite specimen; left: outer surface; right: the inside of the crystal

The cracks in the brannerite were clearly visible in backscattered electron SEM images and element maps. These zones were enriched in titanium and depleted of uranium and calcium. The edges of these altered zones were enriched in silicon and lead (Figure 2).

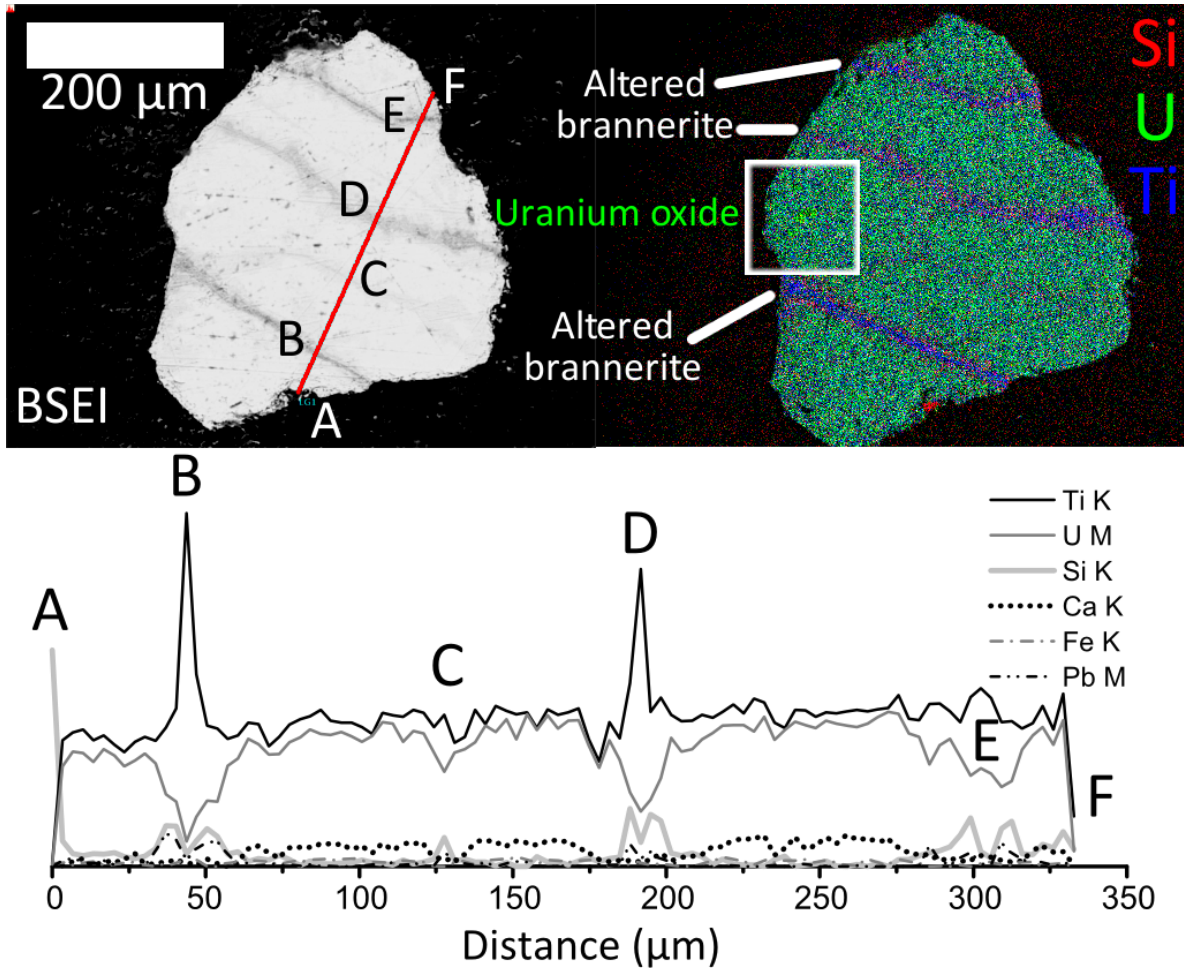


Figure 2: Backscattered electron image (top left), element map (top right) and EDX line analysis (bottom) of an unleached brannerite particle. The position of the line analysis is shown on the BSE image. Letters on the line analysis correspond to points on the BSE image.

X-ray diffraction analyses showed that the brannerite was metamict. Broad humps were identified on the XRD pattern of the feed material from 20-35° and from 40-65°, characteristic of metamict material. Microcrystalline anatase was present as a minor phase, along with small amounts of crystalline thorutite, $(\text{Th,U,Ca})\text{Ti}_2\text{O}_6$. Calculations indicate that the size of the anatase crystallites was around 10-20 nm. The structure and crystal chemistry of the brannerite specimen are described in detail in a separate paper focusing on the mineralogical aspects of the study (Gilligan et al., 2016).

LEACHING KINETICS

Effect of acid concentration

Variations in solution acid concentration had a small effect on the rate of uranium extraction. Increasing the acid concentration beyond 25-50 g/L H₂SO₄ did not significantly improve the rate of uranium extraction. Higher acid dosages were shown to result in increased gangue dissolution, which in turn leads to higher acid consumption (Gilligan and Nikoloski, 2015a).

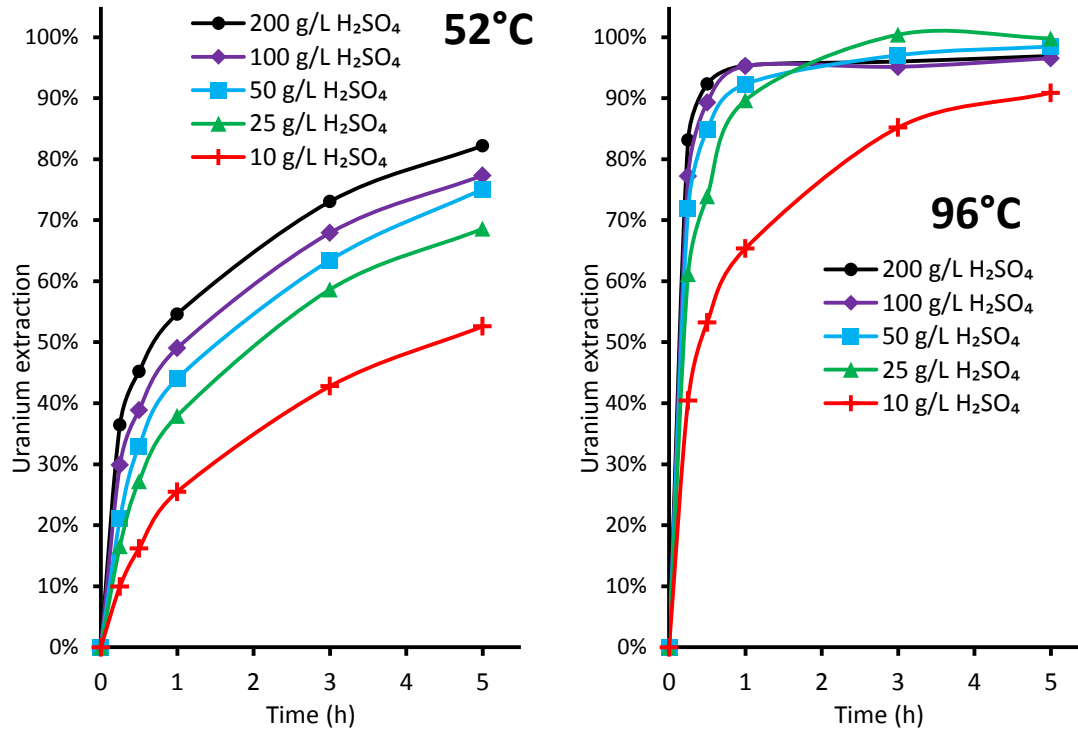


Figure 3: Uranium extraction at varied acid concentrations. Left: 52°C; right: 96°C.

Higher acid concentrations are known to suppress the dissolution of uranium. For uraninite, this concentration is >35 g/L H₂SO₄ (Merritt, 1971). There is some evidence for a limiting acid concentration when leaching brannerite. Gogoleva (2012) found that this was around 100 g/L H₂SO₄. The optimum acid dosage for brannerite leaching is higher than that for uraninite, but not excessively high.

The optimum acid dose is affected by the gangue mineralogy. When the ore contains phosphates, the optimum acid dosage will be higher. These observations will be reported in a forthcoming paper by Gilligan and Nikoloski (under review) and are briefly described under here the heading *Effects of gangue additives*.

Effect of temperature

Temperature was shown to have a strong effect on the rate of uranium leaching as commonly reported. Raising the leaching temperature by 10°C had a similar effect to raising the sulphuric acid concentration by a factor of 4.

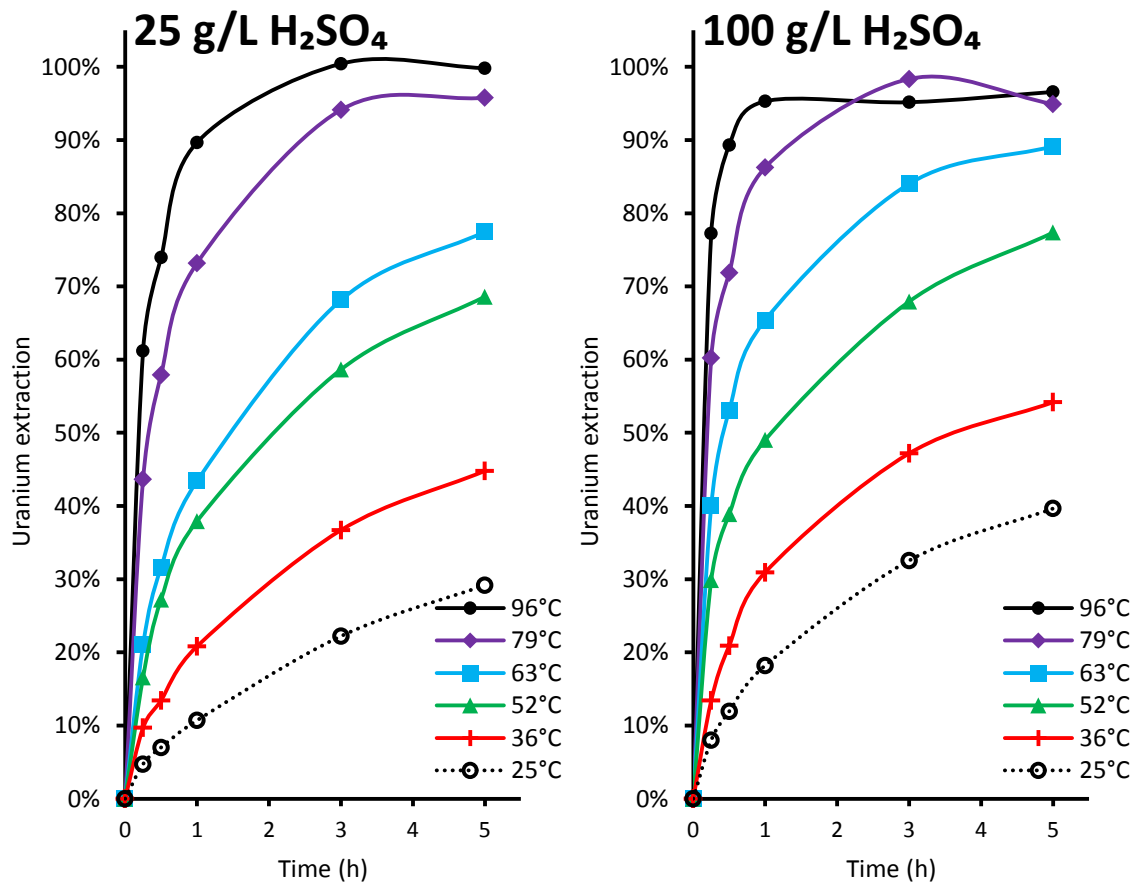


Figure 4: The effect of temperature on uranium extraction; left: 25 g/L H₂SO₄; right: 100 g/L H₂SO₄.

At higher temperatures and lower acid concentrations, titanium was observed to re-precipitate after initially dissolving. The solubility of titanium dioxide reaches a minimum around 115-130°C based on calculations with HSC Chemistry 7.1.1 (Roine, 2011).

For more details on the effect of temperature on the rate and extent of uranium leaching from brannerite, see Gilligan and Nikoloski (2015b).

Effects of gangue additives

Due to the geological processes involved in the formation of brannerite, apatite is often present with brannerite containing ores as a gangue mineral. It is therefore important to understand the indirect interaction between these two minerals during the leaching process. To this end some of the brannerite leaching tests reported above were repeated with the addition of fluorapatite. Tests were also carried out with other gangue minerals. Detailed results of this work will be published in a separate paper but a brief summary is provided here.

The results have shown that the addition of phosphate as apatite suppressed the dissolution of both uranium and titanium. When brannerite is leached in isolation, variations in temperature have a much greater effect on the rate of leaching than variations in acid concentration (Figure 5).

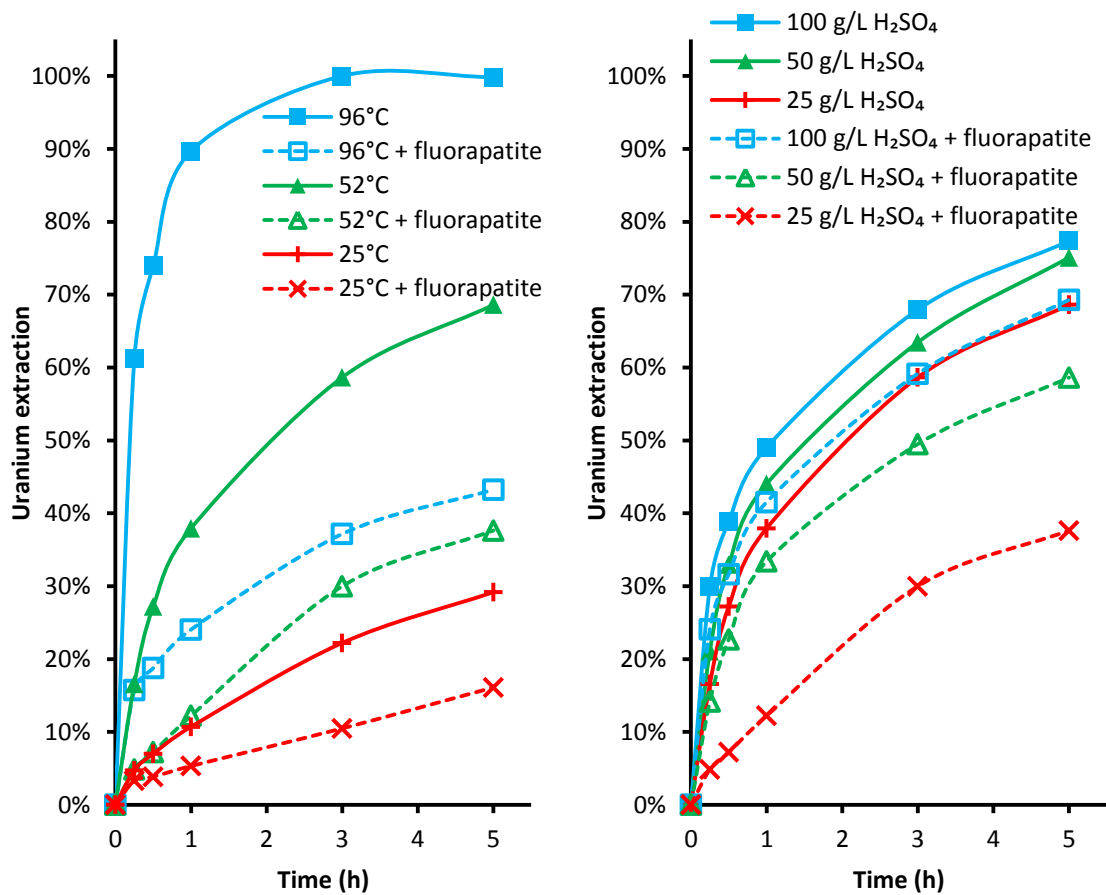


Figure 5: Effect of fluorapatite on the extraction of uranium from brannerite. Left: varied temperature, 25 g/L H₂SO₄; Right: varied acid concentration, 52°C

On the other hand, the addition of fluorite (also called flourspar) (CaF₂) was shown to significantly increase the rate of brannerite dissolution, likely due to the formation of hydrofluoric acid in the leach solution after the dissolution of this additive.

RESIDUE CHARACTERISATION

Microscopy and EDX analysis

Examination of a large number of brannerite particles leached over the full range of conditions showed that the leached material was covered in pits 10-20 μm deep. The fraction of the surface covered by these pits increased with the leaching temperature. Brannerite leached at 52°C and above was completely covered in pits. The reaction front at the base of the leach pits was cracked. EDX line analyses of several pits showed that the ratio of uranium to titanium was constant across the base of the leached pits (Gilligan et al., 2016).

Images of cross sections show that altered zones of the brannerite are more susceptible to corrosion, while the associated anatase is much less susceptible to corrosion. Two examples are shown in Figure 6.

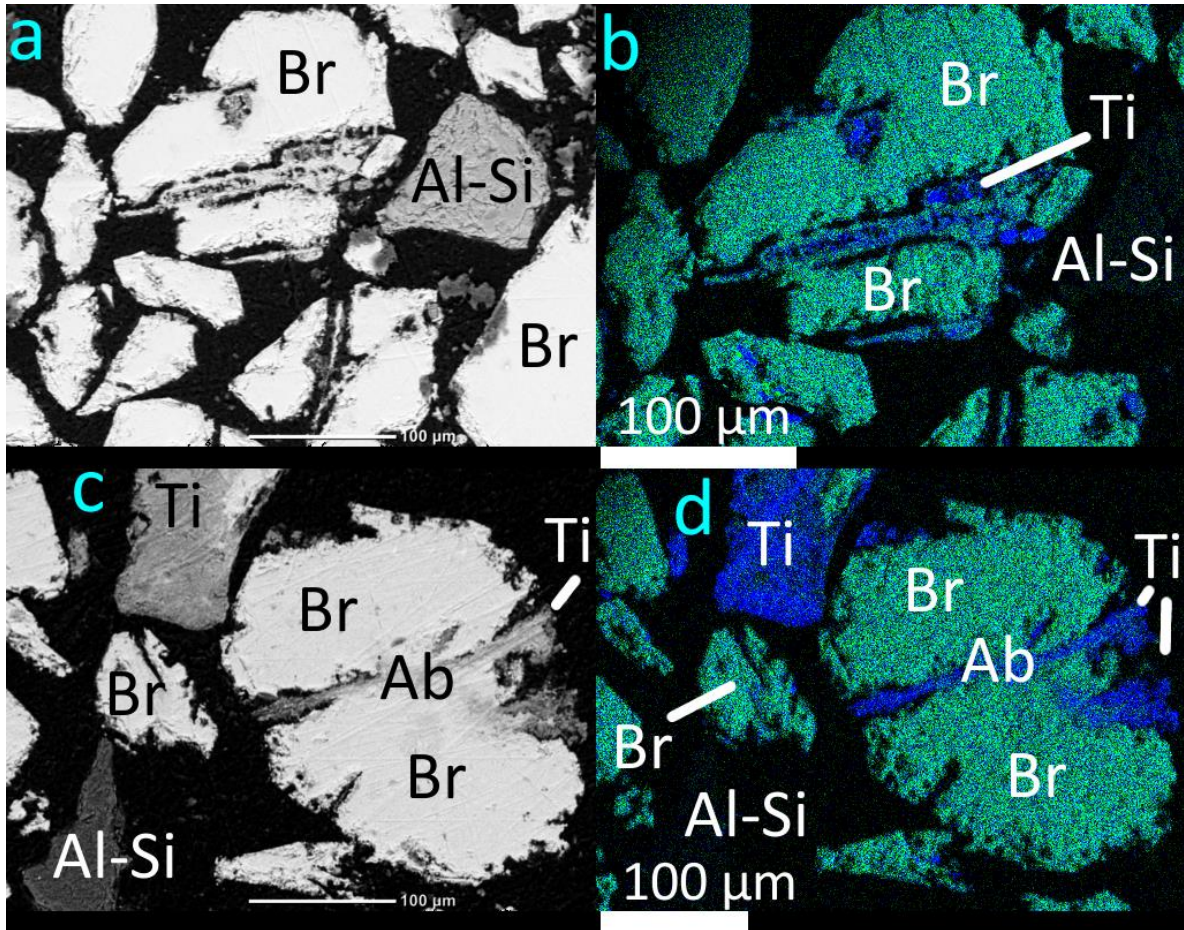


Figure 6: BSEI images (a, c) and element maps (b, d) of leached brannerite particles. Uranium is shown in green, titanium in blue. a/b: 0.50 mol/L H₂SO₄, 25°C; c/d: 0.10 mol/L H₂SO₄, 52°C. Phases: Ab: altered brannerite, Al-Si: aluminium silicate gangue, Br: brannerite, Ti: titanium oxide

One of the important findings of the mineralogical characterisation study (Gilligan et al., 2016) was a dependence of the leaching effectiveness on the texture of the brannerite grains. The results have shown that brannerite that has been altered naturally is more susceptible to leaching, with the extent of alteration having a strong influence on the leaching process. This introduces a new process performance parameter which will vary with age and geological history of a deposit.

It's often reported that a titanium oxide layer forms at the surface of brannerite during leaching. This was not observed in any of the experiments, with the exception of the leaches investigating the apatite interaction (Figure 7). In some of these tests, titanium dioxide formed as a secondary product, separate from the brannerite. This side reaction occurred at higher temperatures and lower acid concentrations, when the titanium concentration in solution exceeded saturation.

This secondary titanium oxide phase was distinct from the titanium oxide in the original material. EDX analyses showed that it contained iron; while XRD analyses showed that it was anatase. The peaks were shifted slightly, indicating that the associated iron had been incorporated into the crystal structure. Unlike the anatase in the original material, this phase did not contain uranium (Gilligan et al., 2016).

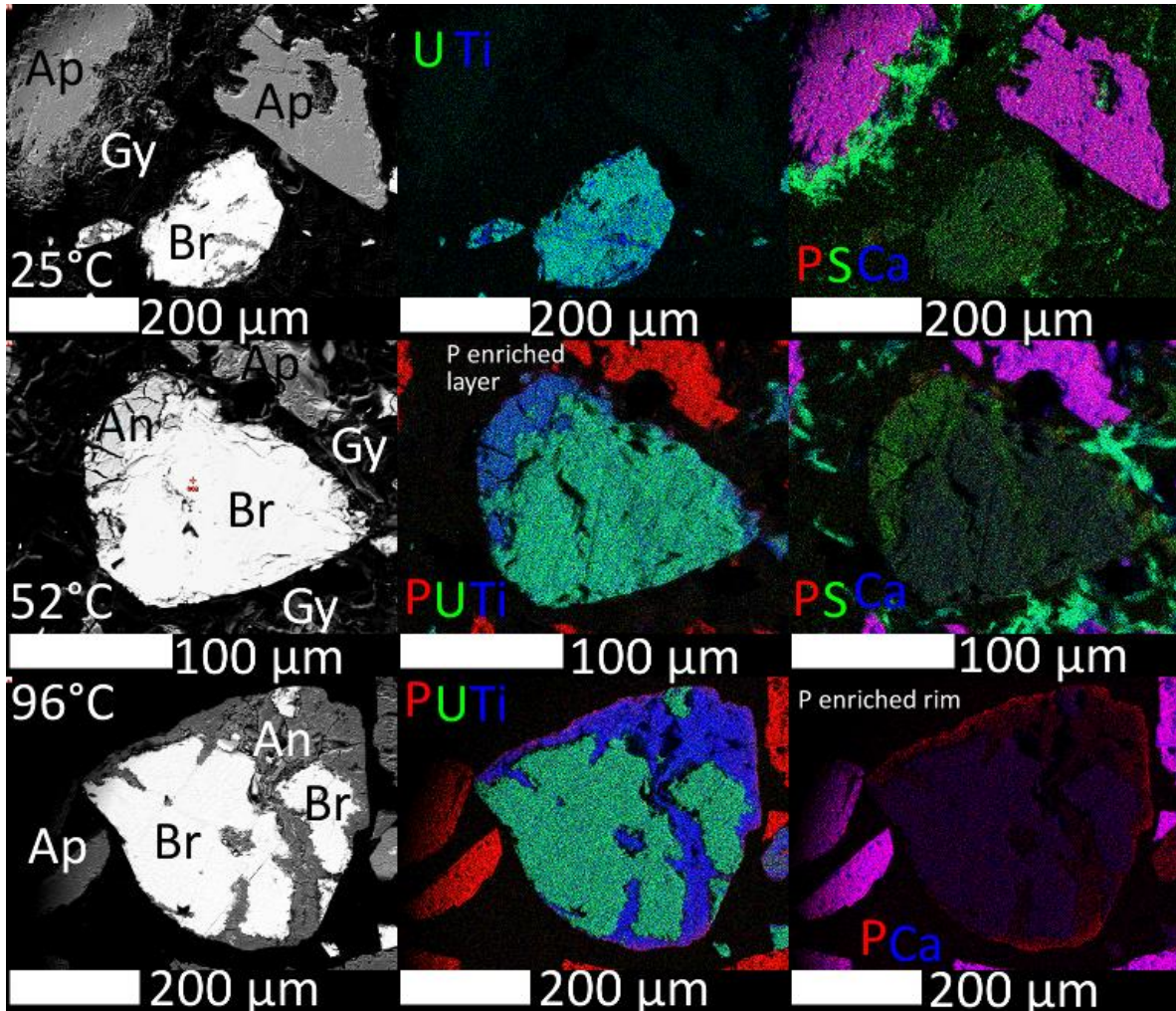


Figure 7: Backscattered electron images and elemental x-ray maps of corroded brannerite particles leached in 25 g/L H_2SO_4 and 2.8 g/L Fe^{3+} at varied temperature in the presence of fluorapatite. An: anatase, Ap: fluorapatite, Br: brannerite, Gy: gypsum.

The influence of apatite and phosphates on the leaching of brannerite is complex. Phosphate was observed to interfere with the reactions between ferric ions and uranium, which is a well-documented effect. Phosphate also appeared to stabilise and promote the formation of a titanium oxide coating on leached brannerite, as is apparent from the association of titanium and phosphorus in Figure 7. This effect was reduced at higher acid concentrations.

X-ray diffraction analyses

The broad humps from 20–35° and 40–65° were absent in the x-ray diffraction scans of the leached residues, suggesting that the majority of the amorphous material dissolved during leaching. Anatase was identified in all of the residues, with the anatase peaks being more prominent in the high temperature leach residues. Crystalline thorutite was identified in all of the residues by XRD, indicating that it was extremely resistant to leaching.

CONCLUSIONS

A specimen of brannerite was leached at different temperatures (25–96 °C) and acid concentrations (10–200 g/L H_2SO_4) to determine the effects of these parameters on the rates of uranium and titanium dissolution. Variations in temperature had a much larger effect on the rate of brannerite dissolution than variations in acid concentration.

Fluorapatite, a gangue mineral often associated with brannerite in uranium deposits was found to interfere with the leaching of brannerite in sulphuric acid media. If fluorapatite is present in a refractory uranium ore, higher concentrations of acid will be required, to counteract the effects of phosphate on uranium and titanium leaching. Increasing the leaching temperature is not as effective for increasing uranium extraction when dealing with high-phosphate refractory uranium ores. When phosphates are present in refractory uranium ore, the preferred acid concentration is higher (>50

g/L H₂SO₄) and the preferred leaching temperature is likely to be lower (~60°C) compared to when low-phosphate refractory uranium ores are treated.

Examination of the brannerite specimen showed that it was altered and heterogeneous, consisting of more than two phases. Comparisons of the XRD analyses of the original material with those of the residues showed that the amorphous brannerite phase was much more susceptible to leaching than the anatase phase or the possible crystalline thorutite phase. While titanium dioxide has been reported to form at the surface of brannerite particles during leaching, no such layer was identified in the leaching experiments conducted as part of this study.

The extent of natural alteration appeared to affect the susceptibility of brannerite to leaching. There is a relationship between the texture of the brannerite grains and the leach recoveries, with heavily altered grains being more readily leached. The extent of alteration and texture of brannerite grains varies between deposits and has been found to affect the degree of leaching. It is shown that the texture of the brannerite minerals in an ore is an important process performance indicator along with the grade, liberation size and gangue mineralogy.

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