

Leaching of brannerite in the ferric sulphate system — Part 1: Kinetics and reaction mechanisms

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Abstract

The uranium titanate mineral brannerite, UTi_2O_6 is the most common of the uranium minerals which is considered refractory. Ore containing brannerite mineralisation has been mined and processed in several locations around the world. Under typical uranium ore processing conditions, brannerite is often lost to tailings. In order to design an effective process for the leaching of high-brannerite uranium ores, it is first necessary to understand the mechanism of the chemical processes through which brannerite dissolves in the absence of interferences from the host rock. In the present study, a specimen of brannerite obtained as a single crystal was leached in sulphuric acid (10–200 g/L) and ferric sulphate (2.8 g/L Fe^{3+}) solution at 25–96 °C for 5 h. The rate of titanium dissolution was monitored along with uranium. Comparisons between the rates at which these two elements dissolved and the morphological changes that were observed to take place during the dissolution process indicated two different sets of leaching reaction mechanisms. At low temperatures, uranium dissolved at a much higher rate than titanium initially, leaving titanium rich areas on the brannerite particles similar to observations reported in earlier investigations which suggest incongruent dissolution. The calculated activation energies for uranium and titanium dissolution were 36 and 48 kJ/mol respectively. At higher temperatures, uranium and titanium dissolved at similar rates in constant proportions suggesting congruent dissolution. The calculated activation energy for this reaction was 23 kJ/mol. The transition between incongruent and congruent dissolution took place at lower temperatures when the acid concentration was higher. Titanium appeared to undergo hydrolysis after dissolution, forming anatase. This side reaction was most favourable at lower acid concentrations and high temperatures.

Keywords: Brannerite; Leaching; Dissolution; Kinetics; Reaction mechanism; Sulfuric acid; Uranium; Titanium; Ferric

1. Introduction

Brannerite, ideally UTi_2O_6 has been identified in many uranium and rare earth element deposits around the world. Under typical uranium processing conditions, brannerite dissolves slowly if at all. The results of many laboratory studies and industrial reports on brannerite leaching under varied conditions were compared in a literature review by Gilligan and Nikoloski (2015).

Brannerite is reported to dissolve in ferric sulphate and sulphuric acid releasing uranium into the solution as uranyl sulphate complexes. Titanium dioxide subsequently forms as a secondary solid phase (Gogoleva, 2012; Ifill et al., 1996; Smits, 1984). To improve the uranium extraction from

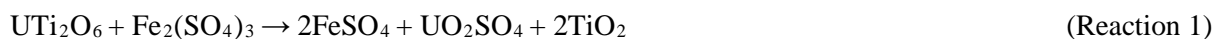
brannerite, it is necessary to better understand the mechanism of the dissolution reaction for both uranium and titanium. Few studies on the leaching of natural brannerite material have reported the rate of titanium dissolution under conditions similar to those used in uranium ore processing operations. Comparisons of the rate of uranium and titanium dissolution along with detailed characterisation of the leached residues and composition of any secondary solid phases formed can provide important information on the nature of the dissolution reaction mechanism under different conditions.

There have been a number of qualitative studies on the dissolution of brannerite grains in uranium ores from various locations, such as the work of Ovinis et al. (2008), Ifill et al. (1996) and Smits (1984). Ifill et al. (1996) examined the appearance of brannerite (~ 30% U, ~ 20% Ti), uraniferous titania (~ 4% U, 40–50% Ti) and aggregates of these two phases in ore from the Elliot Lake district of Ontario Canada during leaching. As leaching progressed the surfaces became pitted, with the rate of pit formation controlling the overall leaching rate. Uranium rich areas dissolved faster than titanium rich areas.

In similar experiments, Smits (1984) observed polished sections of uranium ore from the Witwatersrand area of South Africa at regular intervals during leaching. Brannerite did not undergo leaching at ambient temperature in 10 g/L H₂SO₄ and 3 g/L Fe³⁺. After one hour at 60 °C under the same conditions however, the surface had become etched with a pale brown scaly film of amorphous titanium oxide.

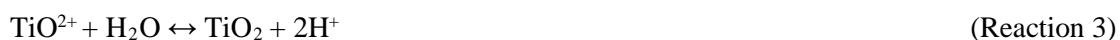
Gogoleva (2012) leached a refractory uranium ore containing brannerite over a broad range of conditions, investigating the effect of varying the temperature, sulphuric acid concentration, ferric concentration, particle size and agitation rate. The Arrhenius plot for uranium produced from this data had a typical shape for a leaching reaction (Gupta, 2003). At lower temperatures between 15 and 35 °C, the overall rate was controlled by the rate of the uranium oxidation reaction and had an activation energy of 50.5 kJ/mol. From 35 to 90 °C, the rate of leaching was controlled by the rate of diffusion of ferric ions through a titanium oxide product layer, and had an activation energy of 30.3 kJ/mol.

Gogoleva concluded that brannerite dissolves in acidic ferric sulphate solutions via the following two reactions (Gogoleva, 2012). Ferric ions oxidise uranium to the more soluble hexavalent form, while sulphuric acid attacks the titanium oxide product.



Uranium forms stable aqueous species over a much broader range of conditions than titanium (Fig. 1).

While acid is not directly involved in the oxidative dissolution of uranium (Reaction 1), increasing the acid concentration will drive the equilibrium in Reaction 2 to the right, increasing the amount of titanium stable in solution. However, Reaction 2 is a reversible process and titanium dioxide may precipitate out of solution (Reaction 3). Several polymorphs of titanium dioxide are known including anatase, rutile and brookite. The polymorph of titanium dioxide formed through the hydrolysis of Ti(IV) species depends on the anions present. Chloride ions favour the formation of rutile while sulphate ions favour the formation of anatase (Li and Afanasiev, 2011).



Gogoleva (2012) concluded that the formation of this titanium dioxide product hindered the dissolution of uranium from brannerite, and that the effect of the sulphuric acid is to dissolve this product layer. Increasing the concentration of acid should inhibit the hydrolysis of titanyl ions, reducing the formation of this titanium dioxide layer. At higher temperatures, the hydrolysis of TiO^{2+} to TiO_2 becomes more favourable and precipitation of titanium dioxide becomes more likely. The equilibrium constant for Reaction 3 was calculated over a range of temperatures from 0 °C to 150 °C for anatase and rutile. Considering the reverse reaction, these results indicate that the solubility of titanium dioxide reaches a minimum and the hydrolysis of titanyl ions is most favourable around 115–130 °C. Gogoleva (2012) observed the formation of a secondary amorphous rutile-like titanium dioxide phase when leaching brannerite containing ore between 35 and 90 °C, but not at 15 or 25 °C. The ore leached by Gogoleva contained rutile along with brannerite, which may have interfered with this reaction.

If the rate determining step at higher temperatures is actually diffusion through a titanium oxide product layer formed through a process similar to Reactions 3 and 4 then the temperature at which this effect is observed should vary with the acid concentration. Increasing the acid concentration should keep titanium in solution to a higher temperature, increasing the minimum temperature at which titanium hydrolysis and precipitation occur. This should result in the shape of the Arrhenius plot changing, with the transition from the high activation energy step to the low activation energy step taking place at higher temperatures. Results show that elevated acid concentration had the opposite effect on the shape of the Arrhenius plots and leads us to suggest a different reaction mechanism.

2. Materials and methods

2.1. Feed sample

In the first published description of brannerite, Hess and Wells (1920) describe brannerite crystals from Custer County, Idaho, USA as brownish yellow on the outside with an opaque black interior. The outer weathered layer was of a similar or lesser thickness to a sheet of paper, while the inside was filled with minute cracks, containing quartz. The mineral had a dark greenish brown streak (Hess and Wells, 1920). The material used in the experiments in the present study was a sample of a 100 g single crystal (Fig. 2), crushed to a d_{80} of 128 μm by a local commercial mineral laboratory. This specimen was used in two earlier studies, the work of Costine et al. (2013) as well as that of Nikoloski and Chong (2012). Costine et al's study covered the effects of varied sulphuric acid concentration, varied ferric concentration, varied particle size and varied temperature on the rate of uranium leaching from brannerite over 24 h. The earlier work of Nikoloski and Chong (2012) studied the effects of varied $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio, varied temperature, varied acid concentration and varied total iron concentration on the rate of uranium and titanium leaching over 30 min.

The sample originates from the Dieresis deposit, near Cordoba, Spain and was coated in a white-pale yellow/brown alteration layer similar to the description given by Hess and Wells (1920). X-ray diffraction analyses by Costine et al. (2013) have shown that the alteration layer consisted of anatase. The pale yellow/brown material appeared to extend inwards below the surface. The interior of the crystal appeared dark green, and slightly transparent, casting a green tinged shadow on a grey backdrop.

X-ray diffraction analyses on the sub-sample leached in this study show anatase. No crystalline uranium phases were identified. This was attributed to the metamict nature of the sample. SEM–EDX analyses showed that the mineral specimen consisted of two major phases: brannerite and anatase. This anatase contained minor amounts of uranium and appeared to be highly refractory compared to brannerite. The full details of the XRD and SEM–EDX analyses are reported in part 2 of this paper (Gilligan et al., under review).

2.2. Leaching tests

Each leaching test was run for 5 h in a 1 L thermostatic leaching vessel stirred at 600 ± 30 rpm. The temperature in different tests ranged from 25 to 96 °C. The temperature was taken to be the measured temperature of the reactor, rather than the set points, for more accurate calculations. The lixiviant was prepared using deionised water, analytical reagent (AR) grade sulphuric acid (98.3% H₂SO₄) and laboratory reagent (LR) grade hydrated ferric sulphate. The value of x in the Fe₂(SO₄)₃·xH₂O reagent was 6.82, determined using a gravimetric method (Sohn and Park, 1998), whereby a sample of the reagent was heated to 300 °C overnight in an oven to remove the water of crystallisation. However this was not hot enough to decompose the sulphate.

The concentration of Fe(III) in all tests was kept constant at 2.79 g/L (50 ± 1 mmol/L) while the sulphuric acid concentration in different tests was one of 25, 50 or 100 g/L as 98% H₂SO₄. The tests conducted at 52 and 96 °C were also done with acid concentrations of 10 and 200 g/L to determine the effect of acid concentration over a wider range. Around 500 mg of brannerite was added to 500 mL of lixiviant once the temperature had reached the set point. Samples of leach solution were assayed for U and Ti, and leach curves plotted. Residues were collected on grade GF/C glass microfiber filters by vacuum filtration and dried overnight under vacuum.

All samples were analysed at a certified commercial mineral processing laboratory NAGROM Pty Ltd by inductively coupled plasma mass spectrometry (ICP-MS) for uranium and by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for titanium. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) measurements were conducted at Murdoch University to characterise the solid residue samples.

3. Results and discussion

3.1. Feed properties

Assay of the brannerite feed sample showed that while it was mostly uranium–titanium oxide, five other elements (Th, Pb, Ca, Fe and Si) exceeded 1% of the mass (Table 1). Cerium, a common substituent in brannerite was not detected in the chemical analysis, nor did it appear to be present in any of the EDX analyses.

Some specific features of brannerite are worth noting. Stoichiometric brannerite, UTi₂O₆, contains 55.4% uranium and 22.3% titanium by mass. A comparison of brannerite specimens from several locations (Gilligan et al., under review) shows that the uranium concentration (by mass) ranges from 26–48% (~ 35% on average) while titanium varies from 19–23%. Most natural brannerite samples including the specimen used in this study contain less than the stoichiometric amount of uranium and an amount of titanium close to the stoichiometric amount. Hence, natural brannerite is typically deficient in uranium relative to titanium. SEM and EDX analyses of this sample show that it is mostly uranium–titanium oxide with a second minor phase consisting of titanium oxide containing minor amounts of uranium.

The composition of brannerite has been reported to affect the extent of dissolution under similar conditions, with the replacement of uranium by cerium and other elements resulting in decreased uranium extraction (Charalambous et al., 2010). Charalambous (2013) leached two specimens of brannerite under a similar range of conditions to those used in this study, and reported lower uranium extractions than those found in this study. Both specimens used by Charalambous were much higher in thorium and light rare earths compared to the specimen used in this study. This may explain the differences in extraction rate. Comparisons of different brannerite from other locations are needed to determine the effect of composition on leaching kinetics in greater detail. The variations in

composition and their possible effects on leaching are discussed further in a separate paper (Gilligan et al., under review).

3.2. Leaching kinetics

3.2.1. Effect of temperature

Comparing rates and extent of leaching at different temperatures under the same chemical conditions, it was clear that temperature had a major effect on both the initial rate of uranium and titanium extraction and on the final extraction of these elements from brannerite (Figs. 3 and 4). The final uranium extraction increased from 29% at 25 °C to 99% at 96 °C (Fig. 3), while the final titanium extraction increased from 25% to 89% (Fig. 4).

At higher temperatures, uranium extractions of up to 99% were readily achieved. At 96 °C, up to 89% of the uranium dissolved in 30 min and almost all of the uranium was extracted within the first hour. However only 30–40% of the uranium had dissolved after five hours at 25 °C. The percentage of uranium extracted was always higher than that of titanium. At higher temperatures and lower acid concentrations, the titanium concentration appeared to decrease after an hour of leaching. This is due to the occurrence of a side reaction, in which titanyl complexes hydrolyse to titanium dioxide at higher temperatures. Acid inhibits this process, which is why it was only observed at lower acid concentrations.

3.2.2. Activation energy

Two separate linear regions were observed on the Arrhenius plots for uranium and titanium (Fig. 5). This is not uncommon for leaching reactions and indicates that there are at least two steps in the process. Similar observation was made by Gogoleva (2012) during the leaching of brannerite ore in 0.01 mol/L Fe^{3+} and 0.50 mol/L H_2SO_4 . Under these conditions, the activation energy for the uranium leaching reaction was reported as 50.5 kJ/mol from 15 to 35 °C, and 30.3 kJ/mol from 35 to 90 °C.

Our results showed that the temperature at which the rate determining step appears to change varies with the acid concentration. The transition from high to low activation energy was observed to occur at a lower temperature when the acid concentration was higher (Fig. 5). At lower temperatures, the activation energy for uranium dissolution was 36 kJ/mol, significantly lower than for titanium dissolution which was around 48 kJ/mol. At higher temperatures, the activation energies for the dissolution of both metals were similar but reduced to 23 kJ/mol (Table 2). The observation that at higher temperatures, the rates of uranium and titanium dissolution were relatively close whereas their difference at lower temperatures also suggests that different reaction mechanisms may be taking place at different temperatures.

Costine et al. (2013) leached a similar sample of brannerite in 40 g/L H_2SO_4 , at 40, 60 and 80 °C for different ferric ion concentration but did not report the activation energy. Using Costine's data to do this calculation gives an activation energy for the uranium dissolution of 32.9–39.4 kJ/mol, varying with the iron concentration. The average value of 37 kJ/mol was consistent with the current study (Table 3). On the other hand, the activation energy estimated by Gogoleva (2012) for the dissolution of uranium from brannerite ore was higher.

Gogoleva estimated the activation energy for brannerite dissolution from rate constants extracted from the shrinking sphere and shrinking core kinetic models, whereas the rate constants in this study were determined from the extent of dissolution at the 15 minute time point. These kinetic models were not used in this study because the shrinking sphere or core models were not consistent with the SEM images of the leached residues. None of the leached brannerite particles appeared to be coated with titanium oxide.

3.2.3. Effect of acid concentration

Increasing the acid concentration increased the rate of uranium dissolution (Fig. 6) and had a slightly greater effect in increasing the rate of dissolution of titanium (Fig. 7). However, above 25 g/L H_2SO_4 the effect was much less pronounced than the effect of temperature. For example, at 52 °C, a temperature increase of only 10 °C had a similar effect on the final uranium and titanium extractions to quadrupling the acid concentration.

Another effect of acid concentration was that at lower acid concentrations (10–25 g/L) and at 96 °C, the titanium concentration in the solution was observed to markedly decrease after the initial stage of dissolution. Titanium was observed to precipitate as anatase in these leaching experiments. The decrease of titanium concentration after the first hour of leaching at 96 °C in 10, 25 and 50 g/L sulphuric acid is summarised in Table 4. This effect can likely be attributed to the hydrolysis of TiO^{2+} and precipitation of TiO_2 being more thermodynamically favourable at higher temperature.

Another interesting observation is that there appeared to be an upper limit to how much titanium would dissolve from the feed. Comparing the dissolution data in Figs. 6 and 7 for the leaching at 96 °C, the resulting leaching curves in 100 g/L and 200 g/L acid appear nearly identical with 89% of the titanium and 97% of the uranium dissolved after 5 h. EDX analyses showed that the residues from these two leaching experiments were mostly Ti/Ti–Fe oxides, while some of these particles also contained small amounts of uranium. EDX analyses of the unleached material show that it is mostly composed of brannerite and titanium oxide. This titanium oxide also contains minor amounts of uranium. Comparisons of the residue with the unleached material suggest that this titanium oxide phase is refractory under these leaching conditions (Gilligan et al., under review).

The initial rate of uranium and titanium dissolution had a greater dependence on the acid concentration at 63 °C and below. The slopes of the lines in Fig. 8 indicate that above this temperature, variations in acid concentration had less of an effect on the initial rate of reaction. The order of the reaction with respect to acid was lower at high temperatures than at low temperatures. This was also apparent from the Arrhenius plots (Fig. 5), with the lines being closer together at higher temperatures. The order of uranium dissolution with respect to H_2SO_4 was on average 0.43 in the temperature range from 25 °C to 63 °C and 0.23 between 79 °C and 96 °C. Titanium dissolution had a relatively greater dependence on the acid concentration, with the order being 0.56 from 25 °C to 63 °C and 0.26 between 79 °C and 96 °C.

3.2.4. Correlations between uranium and titanium leaching rates

The greatest divergence between the initial uranium and titanium dissolution rates was observed at the lower temperatures. On the other hand, at the higher temperatures, where the low activation energy step controlled the rate of the dissolution process, the rates of uranium and titanium dissolution were close and of a consistent ratio. As discussed earlier, this suggests that two separate leaching reaction mechanisms apply to the brannerite leaching process.

The difference between the initial rates of uranium and titanium extraction at higher temperatures can be explained by the presence of a second low-uranium titanium oxide phase identified by SEM–EDX analyses. This phase contained a greater fraction of titanium than uranium. The consistent ratio of dissolution rates at higher temperature suggests congruent dissolution of the main brannerite phase. Around 2.55–2.60 mol of titanium dissolved with every mole of uranium in the first 15 min of leaching at higher temperatures (Fig. 10). The bulk chemical analysis shows that the brannerite specimen contains 2.79 mol of titanium for every mole of uranium. At lower temperatures, the larger difference between uranium and titanium dissolution points to incongruent dissolution in the initial stage of the leaching process. (See Fig. 9.).

In most leaching experiments, the molar extraction ratio of titanium to uranium approached 2.58 (Fig. 11). The only exceptions were the leaching experiments in which titanium oxide precipitation occurred. These experiments include the 79 °C, 25 g/L H₂SO₄ experiment and the 96 °C experiments in 10, 25 and 50 g/L H₂SO₄. Even when the leaching reaction starts as an incongruent dissolution process, the ratio of titanium to uranium in the solution eventually approaches the value associated with congruent dissolution. This indicates the initial formation of a secondary titanium oxide phase which is subsequently attacked by acid.

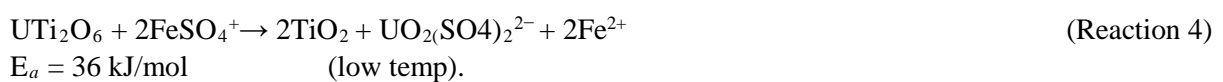
The final uranium extraction was always slightly higher than the final titanium extraction, but not by much (Fig. 12). Large differences between the final uranium and titanium extractions were only seen when the titanium concentration dropped during the leaching. These points all occur within the oval at the top of Fig. 12. All other points in Fig. 12 appear close to the line corresponding to 2.6 mol of titanium dissolving per mole of uranium.

3.3. Reaction mechanism

In all following reactions, aqueous metal species are assumed to be present as the most stable ion or complex as indicated by calculations performed with HSC chemistry v7.1.1 (Royne, 2011). Uranyl ions form complexes with sulphate ions of the general formula UO₂(SO₄)_n²⁻²ⁿ with log β_n values of 3.15 ± 0.02, 4.15 ± 0.06 and 3.02 ± 0.38 for n = 1, 2 and 3 (NEA, 2003). These stability constants show that the strongest complex is the disulphate complex, hence UO₂(SO₄)₂²⁻ is likely to be the dominant species. Likewise, iron (III) forms strong complexes with sulphate ions (NEA, 2013).

The dissolution of brannerite in acidic ferric sulphate media appears to take place via two separate reactions depending on the temperature and acid concentration. Increasing the acid concentration decreases the temperature at which the transition occurs between the low and high temperature reactions. The present research shows that at low temperatures, uranium initially dissolves at a much faster rate than titanium. The extent of titanium dissolution eventually approaches that of uranium however, suggesting a two step process. Electrochemical experiments by Nicol et al. (1975) on the leaching of uraninite in acidic media have shown that ferric ions oxidise uranium (IV) very slowly in the absence of sulphate, suggesting that the ferric sulphate complex FeSO₄⁺ rather than Fe³⁺ is the actual oxidant. Similarly, sulphate increased the rate of anodic dissolution of uranium dioxide.

It is proposed that in the first step, uranium is oxidised and dissolved, leaving a titanium rich layer.

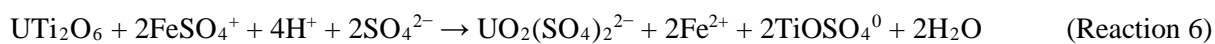


In the second step, this titanium oxide material is attacked by acid:



This second step has a higher activation energy than the first step, and a greater dependence on the sulphuric acid concentration. The uranium dissolution step has an order of 0.43 with respect to H₂SO₄, while the titanium dissolution step has an order of 0.56. The role of acid is clear in the titanium dissolution step given the reaction between hydrogen ions and titanium oxide. The apparent effect of sulphuric acid concentration on the uranium dissolution rate is more likely due to variations in sulphate concentration influencing the rate of uranyl sulphate complex formation than through the increased acid concentration attacking a titanium oxide layer.

At higher temperatures, uranium and titanium dissolve in a consistent ratio, suggesting that the titanium oxide material formed in Reaction 4 is consumed as fast as it is formed. The apparent reaction during congruent dissolution at higher temperatures is:

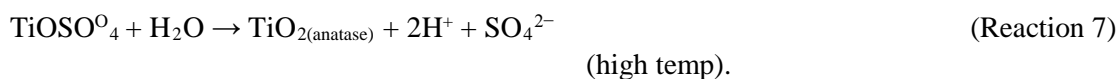


$$E_a = 23 \text{ kJ/mol} \quad (\text{high temp}).$$

The molar ratios of titanium to uranium in the solution during this reaction suggest that the congruent dissolution of a $\text{U}_{\sim 0.85}\text{Ti}_{\sim 2.15}\text{O}_6$ (other elements unknown) phase, leaving behind a small amount of a minor native TiO_2 phase containing traces of uranium as described earlier.

At higher temperatures ($> 79 \text{ }^\circ\text{C}$) and lower acid concentrations ($< 50 \text{ g/L H}_2\text{SO}_4$), the concentration of titanium appeared to drop after 1 h of leaching. The decrease in titanium concentration was associated with the appearance of a red–brown precipitate in the residue. EDX analyses show that iron and sulphur are often incorporated into these precipitates, likely from the ferric sulphate lixiviant. This material formed through Reaction 7 did not contain uranium and appears distinct from the unleached titanium oxide present in the original brannerite specimen. These SEM images are presented in a separate paper (Gilligan et al., under review).

The likely explanation for these observations is that after initially dissolving rapidly, the titanium concentration exceeded saturation and precipitated via the following reaction. Thermodynamic calculations performed with HSC Chemistry v7.1.1 (Royne, 2011) show that this reaction is most favourable around $115\text{--}130 \text{ }^\circ\text{C}$.



4. Conclusions

A specimen of brannerite was leached at different temperatures ($25\text{--}96 \text{ }^\circ\text{C}$) and acid concentrations ($10\text{--}200 \text{ g/L H}_2\text{SO}_4$) to determine the effects of these parameters on the rates of uranium and titanium dissolution. Three Arrhenius plots for uranium and titanium dissolution were produced for the full range of temperatures in $25, 50$ and $100 \text{ g/L H}_2\text{SO}_4$. As with the Arrhenius plot produced by Gogoleva (2012), the Arrhenius plots produced in this study had two separate linear regions.

The average activation energy for uranium dissolution at lower temperatures was calculated to be 36 kJ/mol , while the average activation energy for titanium dissolution was calculated to be 48 kJ/mol . The brannerite appeared to be dissolving incongruently in the early stages of the reaction. At higher temperatures, the average activation energy for the dissolution of both metals was 23 kJ/mol . The Ti/U mole ratio remained constant and the brannerite appeared to be dissolving congruently.

The temperature at which the transition between the high activation energy incongruent dissolution reaction and the low activation energy congruent dissolution reaction occurred varied with the acid concentration. Increasing the acid concentration shifted this transition to a lower temperature. Based on these experimental results, new reactions for uranium and titanium leaching at low temperatures and at high temperatures have been proposed.

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Fig. 1. Expected speciation of uranium (left) and titanium (right) under acidic conditions at 50 °C in 1.00 M sulphate. U and Ti concentrations correspond to approximately 1000 mg/L brannerite (at 36% U by mass). Pourbaix diagrams produced in HSC Chemistry 7.1.1 (Roynes, 2011) with thermodynamic data for synthetic brannerite obtained from Williamson et al. (2001).

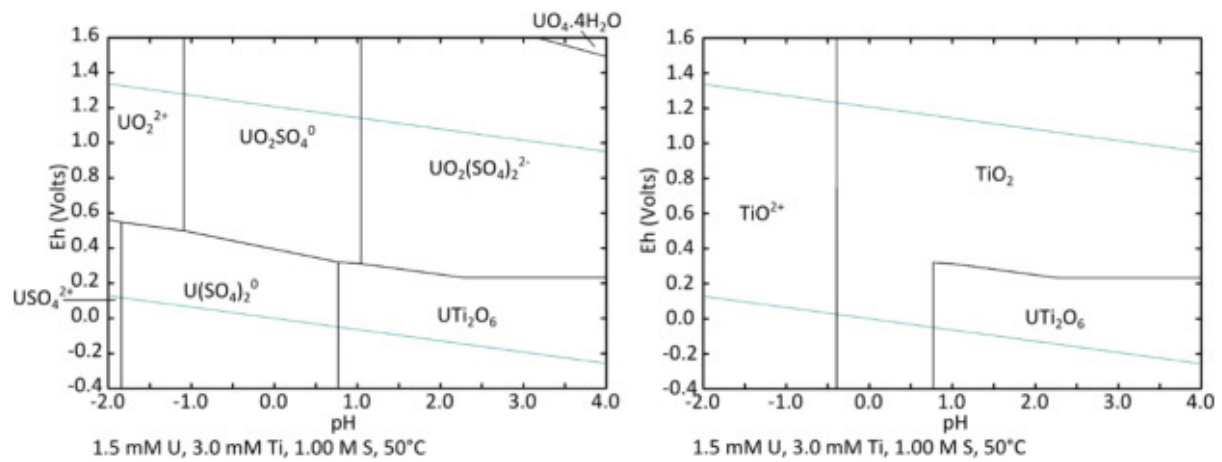


Fig. 2. The brannerite specimen; left: outer surface; right: the inside of the crystal.

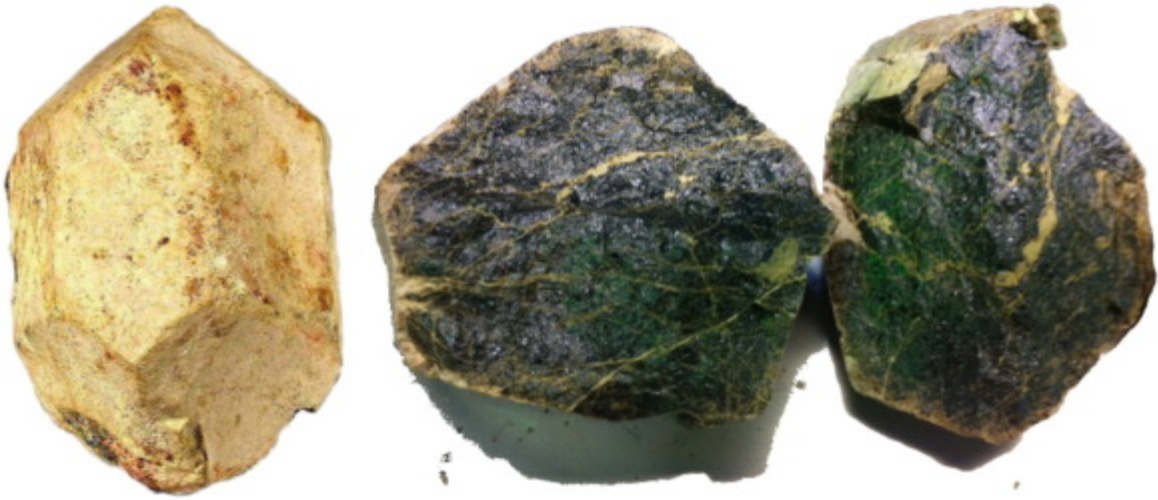


Fig. 3. Uranium leaching curves in 2.79 g/L Fe^{3+} and 25–100 g/L sulphuric acid at varied temperature.

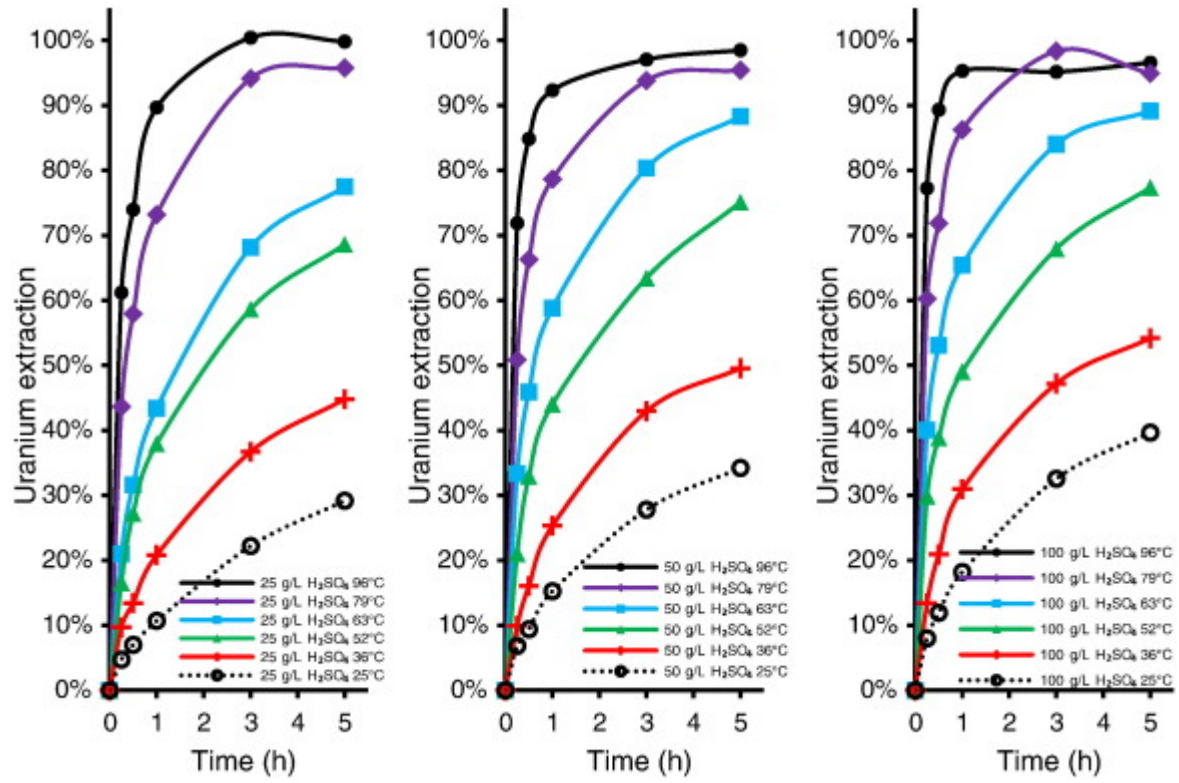


Fig. 4. Titanium leaching curves in 2.79 g/L Fe^{3+} and 25–100 g/L sulphuric acid at varied temperature.

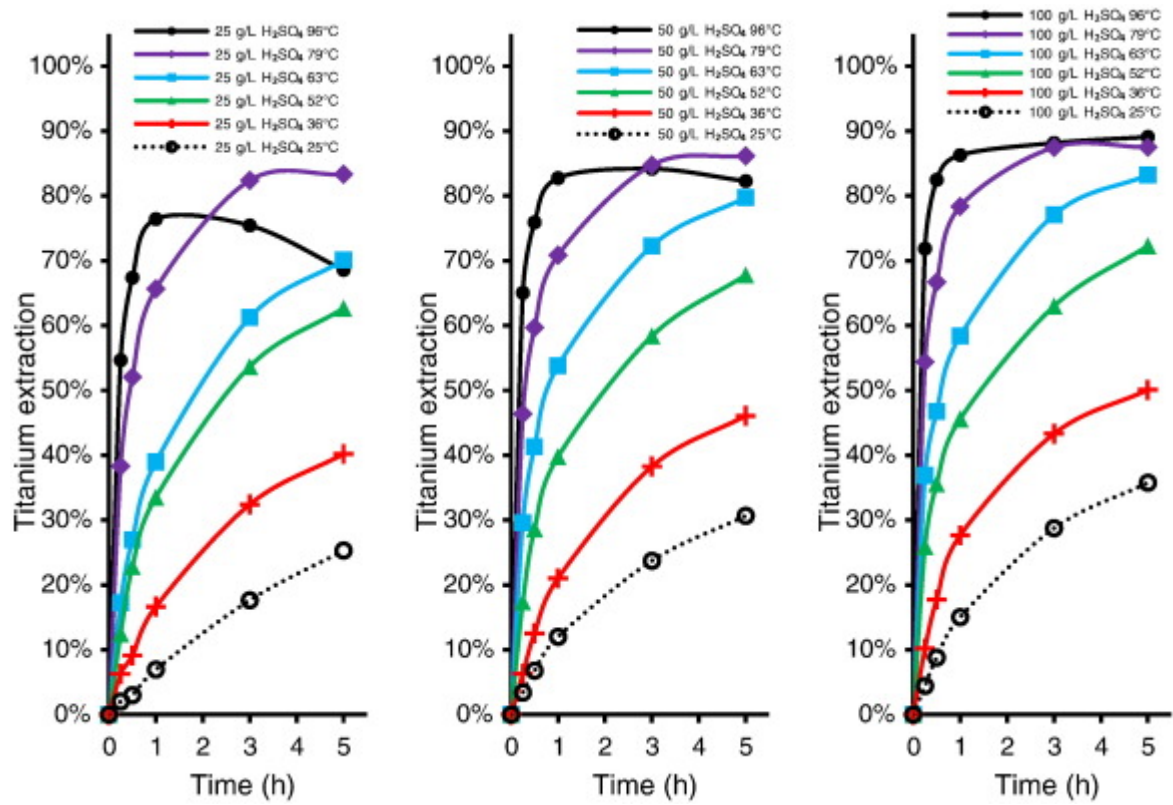


Fig. 5. Arrhenius plots for uranium (left) and titanium (right) dissolution at different acid concentrations.

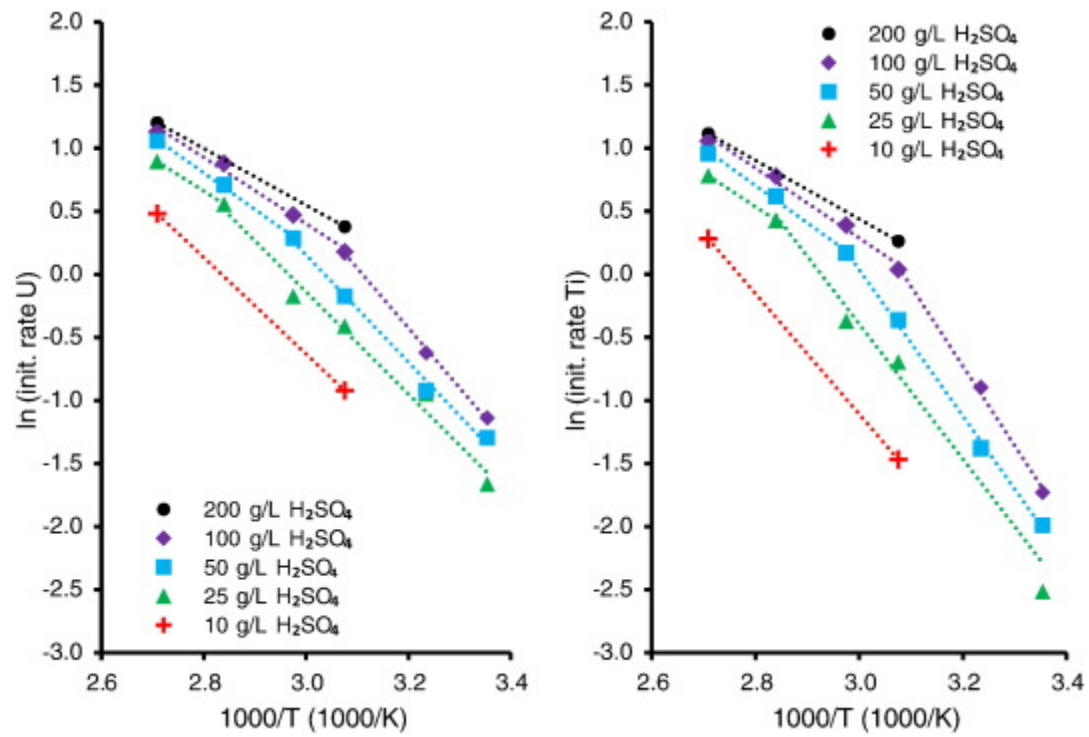


Fig. 6. Uranium leaching curves at varied acid concentration and constant temperature.

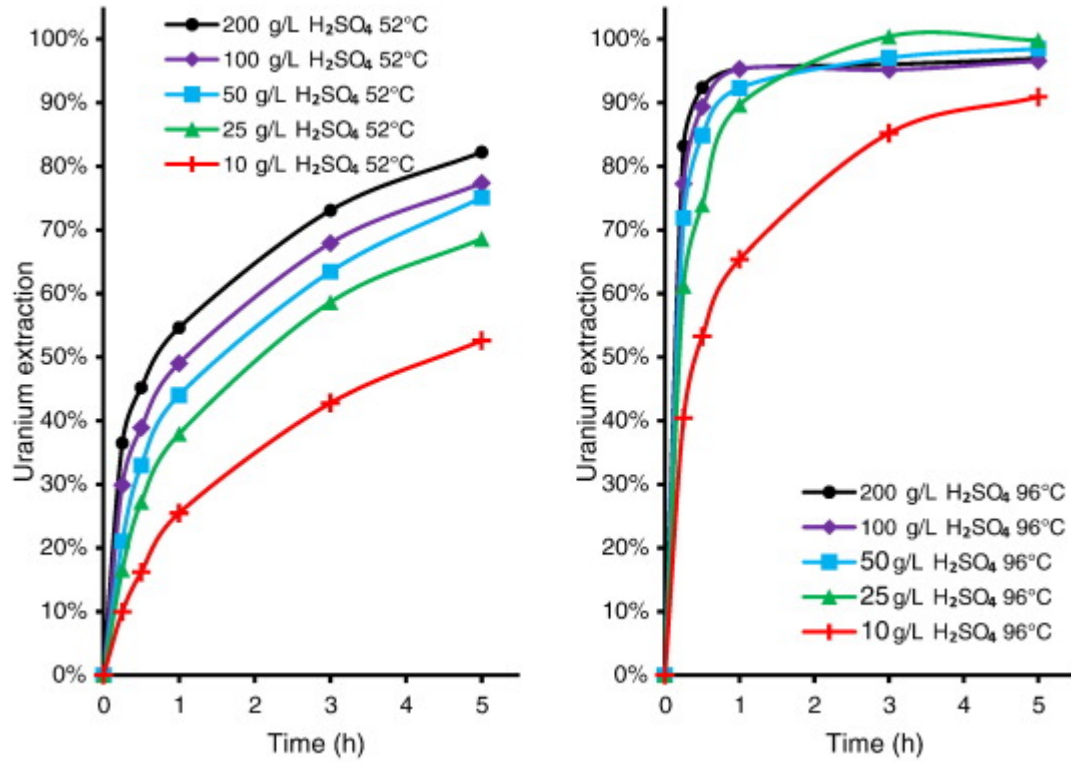


Fig. 7. Titanium leaching curves at varied acid concentration for two different temperatures.

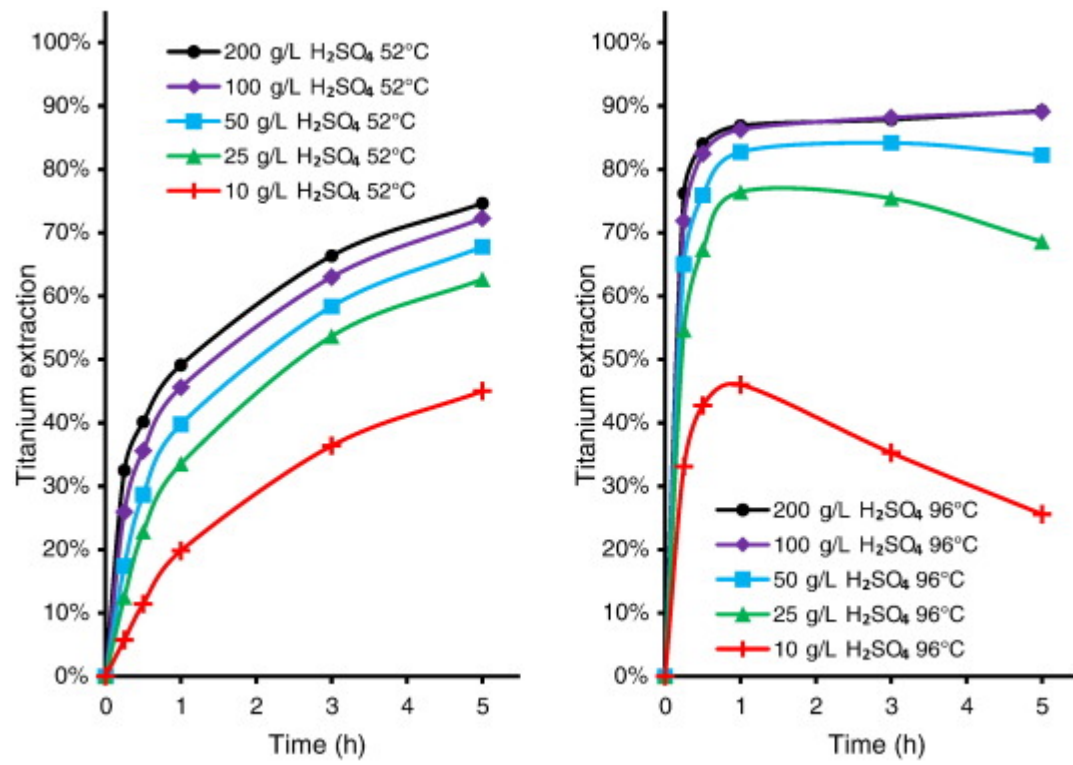


Fig. 8. The effect of acid concentration on the initial rate of uranium (left) and titanium (right) extraction.

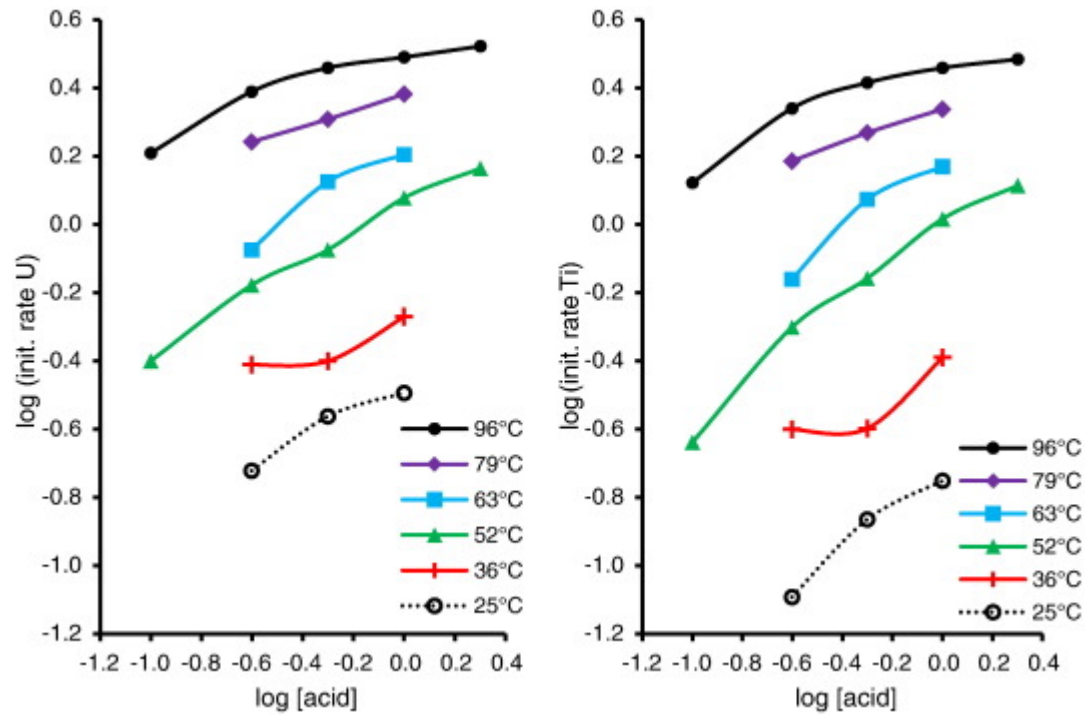


Fig. 9. Arrhenius plots for uranium and titanium in 50 and 100 g/L H₂SO₄.

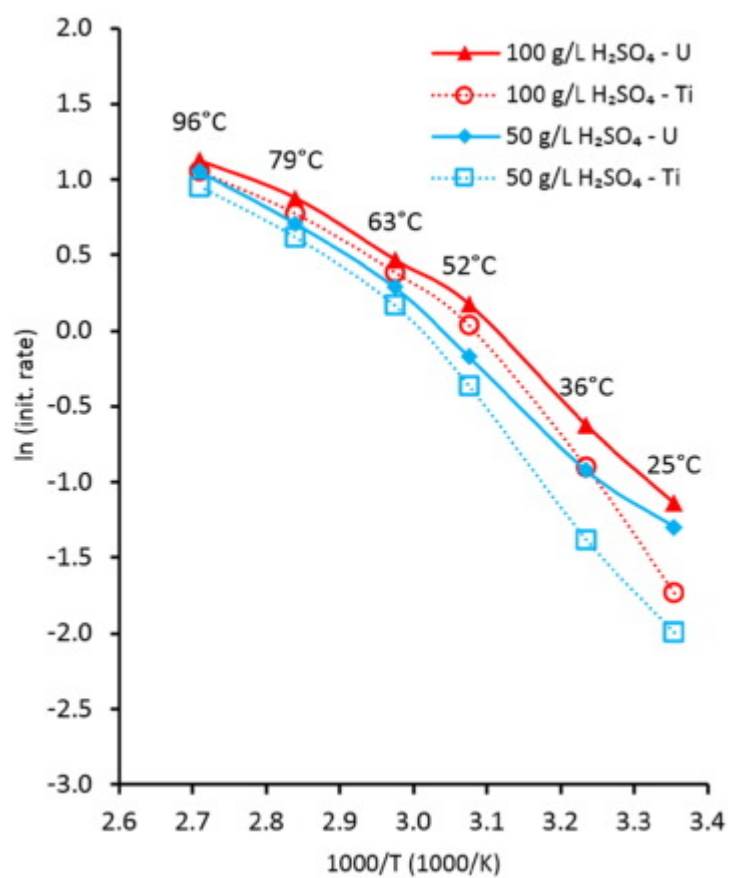


Fig. 10. Initial Ti:U molar ratio at varied temperature.

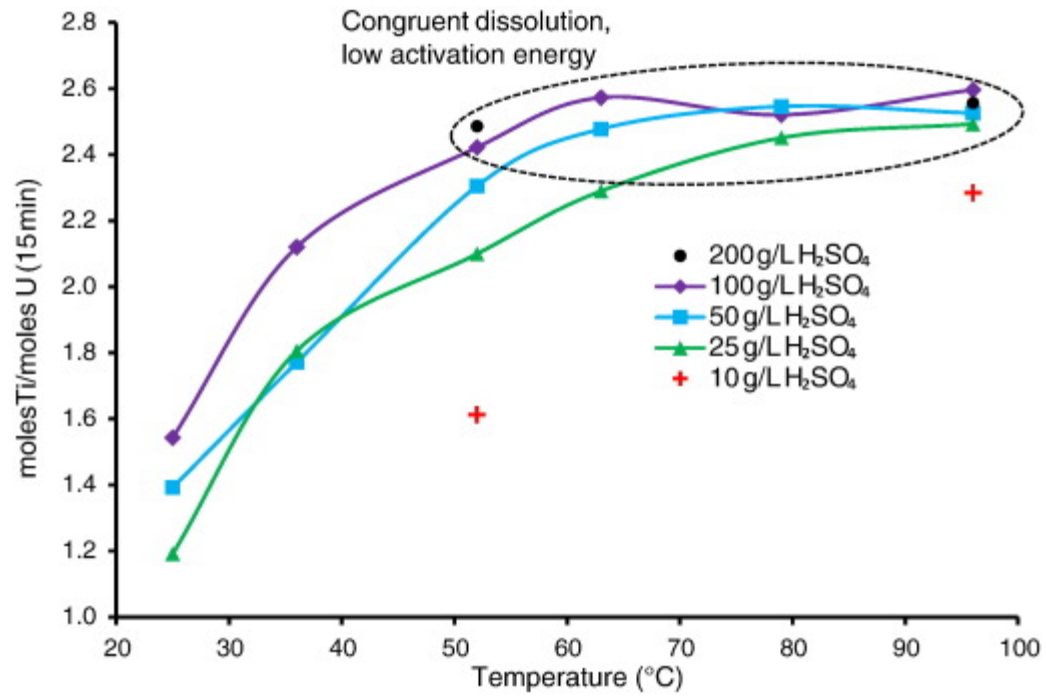


Fig. 11. Ti:U molar ratios over time at varied temperatures.

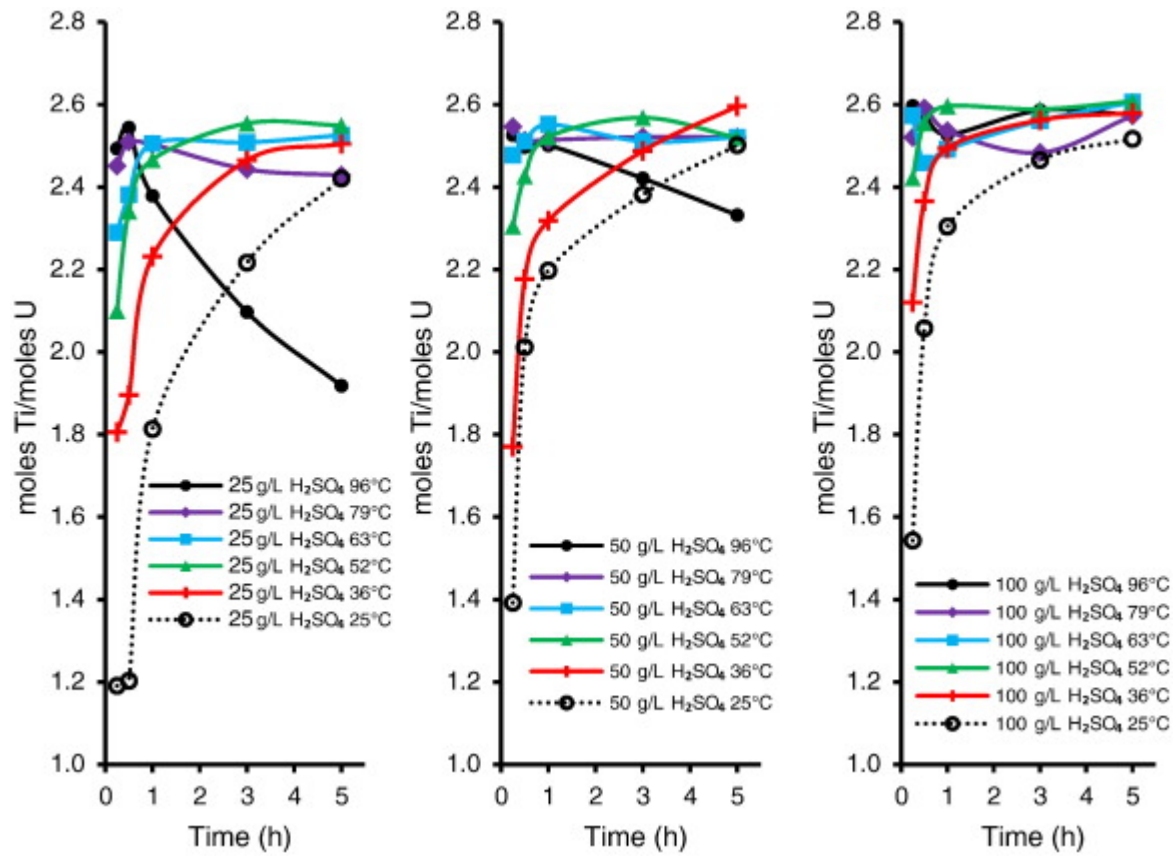


Fig. 12. Final uranium and titanium extractions. Circled area: Experiments in which titanium dioxide precipitation was observed.

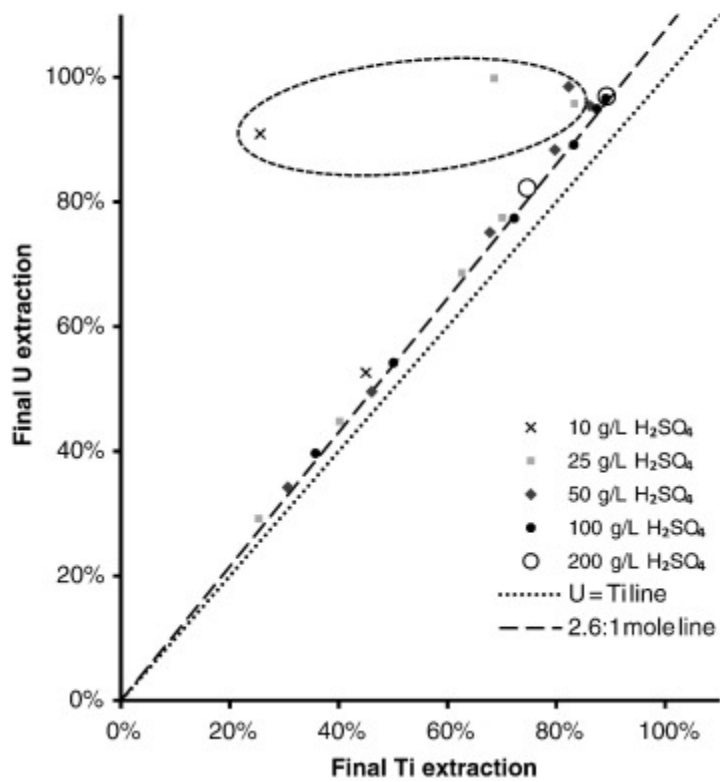


Table 1. Bulk chemical analysis of the brannerite specimen.

Element	(%)	Element	(%)	Element	(%)
U	35.8	Al	0.453	Na	0.087
Ti	20.1	P	0.296	Ba	0.086
Th	2.89	Y	0.271	Dy	0.072
Pb	2.51	Mn	0.139	Gd	0.064
Ca	1.88	Yb	0.104	Zr	0.062
Fe	1.67	K	0.095		
Si	1.31	Mg	0.089		

Table 2. Activation energy for uranium and titanium dissolution at high and low temperatures.

Acid concentration (g/L)	Activation energy (kJ/mol)			
	Uranium extraction		Titanium extraction	
	Low T	High T	Low T	High T
25	33.7	21.5	44.5	22.6
50	35.3	24	48.2	24.6
100	39.4	21.9	52.5	23.1
Average	36.1	22.5	48.4	23.4

Table 3. Activation energies calculated from initial extraction rates. Values apply to uranium unless otherwise specified.

	Low T range	Low T average	High T range		High T average	
Costine et al. (2013)	32.9	39.4	36.7	NA		NA
This study — U	33.7	39.4	36.1	21.5	24	22.5
Gogoleva (2012)	NA		50.5	NA		30.3
This study — Ti	44.5	52.5	48.4	22.6	24.6	23.4

Table 4. Titanium dissolved after 1 h and 5 h at 96 °C.

Acid concentration (g/L)	Ti dissolved (%)	
	1 h	5 h
10	46	25.6
25	76.4	68.6
50	82.7	82.3
100	86.3	89.1
200	86.9	89.3