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Alkaline leaching of brannerite. Part 1: Kinetics, reaction mechanisms and mineralogical transformations

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ABSTRACT

Refractory uranium ores containing uranium as multiple oxides typically require leaching at elevated temperatures (>75 °C) and acid concentrations (>50 g/L H_2SO_4) in order to effectively extract the uranium. Some uranium ores contain large amounts of acid-soluble gangue, such as carbonates or soluble silicates and when the carbonate content exceeds approximately 8%, the acid consumption by gangue may render acid leaching uneconomical. In these situations, leaching in alkaline-carbonate is a potential option. The advantages of this approach include improved selectivity for uranium over other elements, reduced gangue dissolution and the ability to recycle the lixiviant. One disadvantage is slower rates of leaching and hence the need for finer grinding. However, when a uranium ore contains significant amounts of acid-soluble gangue with refractory uranium mineralisation (a double refractory ore), the process options are more limited. Refractory uranium minerals, such as brannerite, are often reported as slow to dissolve in alkaline carbonate media. If a double refractory uranium ore is to be processed effectively, it is necessary to understand the behaviour of minerals like brannerite in the alkaline leaching system. In the present study, a sample of brannerite was leached in a sodium carbonate solution (1 mol/L total carbonate) for 24 h at temperatures from 50 to 90 °C. The effect of potassium ferricyanide (25 mmol/L) added as an oxidant was also examined. All residues were characterised by XRD and SEM-EDX techniques, and both uranium and titanium dissolution rates were monitored. Uranium extraction reached 83% after 24 h of leaching. The leaching rate showed a high dependence on temperature with an activation energy of 45 kJ/mol. The residue was pitted, similar to what has been observed previously after leaching in acidic media. At 80 °C and 90 °C, the titanium re-precipitated within the pits, potentially slowing the dissolution process.

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1. Introduction

Many uranium deposits including some in northern Queensland (Wilde et al., 2013) and in central Ukraine (Cuney et al., 2012) contain refractory uranium mineralisation associated with alkaline gangue. There is very little information available in the literature on the alkaline leaching of such ores. Alkaline lixiviants are not typically used in the leaching of refractory uranium minerals, such as brannerite (Gilligan and Nikoloski, 2015a), as they tend to produce only slow dissolution. It may sometimes be necessary to consider leaching an ore under alkaline conditions however, when the ore contains high amounts of acid consuming gangue minerals such as calcite or dolomite, or gangue minerals such as apatite which can also dissolve in acid, releasing species which inhibit uranium extraction (Gilligan and Nikoloski, 2016). If an ore is too high in acid soluble minerals such as carbonates, acid leaching becomes uneconomical. The exact cut-off point will vary from ore to ore, though it is typically around 8% (IAEA, 1993; Yan and Connelly, 2008). If a double refractory uranium ore is to be processed effectively under alkaline conditions, it is necessary to understand the behaviour of minerals like brannerite in the alkaline leaching system.

Current evidence suggests that brannerite will dissolve slowly in alkaline media under oxidising conditions according to the following reaction:

$$UTi_2O_6 + \frac{1}{2}O_2 + H_2O + 3CO_3^{2-} \rightarrow 2TiO_2 + UO_2(CO_3)_3^{4-} + 2OH^- \quad \text{(Eq. 1)}$$

Higher temperature and/or oxygen pressure will increase the rate of this reaction. Alkaline leaching is often performed in autoclaves (IAEA, 1993). Potassium ferricyanide, $K_3Fe(CN)_6$ and potassium permanganate, $KMnO_4$ may also be used as oxidants (Fig. 1) and are among the most effective of the many oxidants tested for alkaline leaching (Magno and DeSesa, 1957).

All potentials were calculated in HSC Chemistry v7.1.1 (Roine, 2011) assuming a temperature of 70 °C and a pH of 10.0. Calculated potentials

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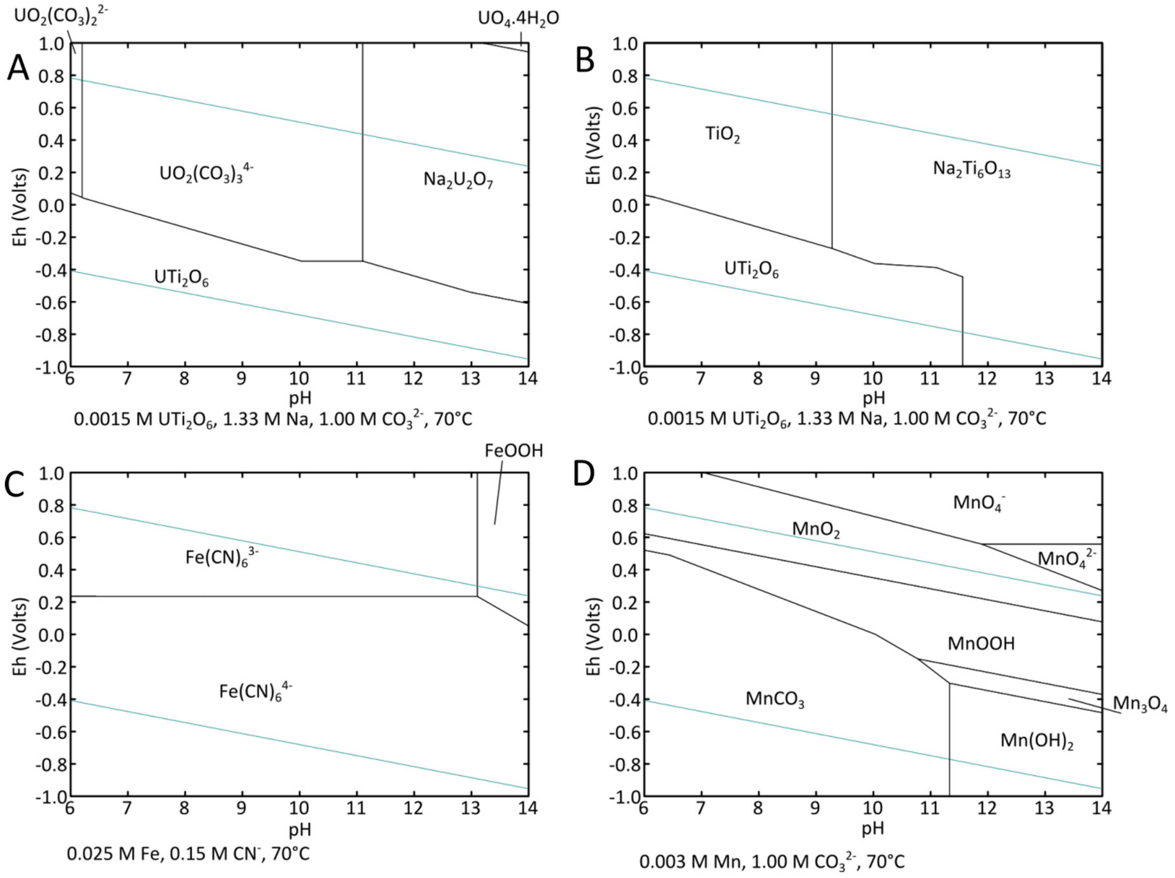

Fig. 1. Pourbaix diagrams showing the speciation of uranium (A) and titanium (B) with stability fields for ferricyanide (C) and permanganate (D) under alkaline leaching conditions.

show that permanganate is a stronger oxidant than potassium ferricyanide (Reaction 2 and Reaction 3).

$$\mathrm{Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-}}\ \ E_{70^\circ C} = 236\ \mathrm{mV} \qquad \text{(Eq. 2)}$$

$$\mathrm{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-}\ \ E_{70^\circ C, pH\ 10.0} = 908\ \mathrm{mV} \qquad \text{(Eq. 3)}$$

However, permanganate is potentially less effective for leaching as the product is insoluble. Magno and DeSesa (1957) observed a manganese dioxide coating forming on uraninite during leaching with permanganate in carbonate media. Ferricyanide was said to be much more effective for uranium oxidation (Magno and DeSesa, 1957) due its ability to be regenerated with oxygen similar to the role of iron in sulphuric acid leaching. This process has been successfully trialled in a uranium leaching plant in New Mexico. Further tests showed that ferricyanide could be generated in the grinding mill (Reaction 4) through the addition of commercially available calcium cyanide for a lower cost than adding $Na_3Fe(CN)_6$ into the leaching circuit (McLean and Padilla, 1960).

$$\mathrm{Fe_{grinding\ ball} + 6CN^- + \frac{1}{2}O_2 + H_2O \rightarrow Fe(CN)_6^{4-} + 2OH^-} \qquad \text{(Eq. 4)}$$

High concentrations of hydroxide formed as a by-product of oxidation can cause sodium diuranate to precipitate out (Reaction 5). The

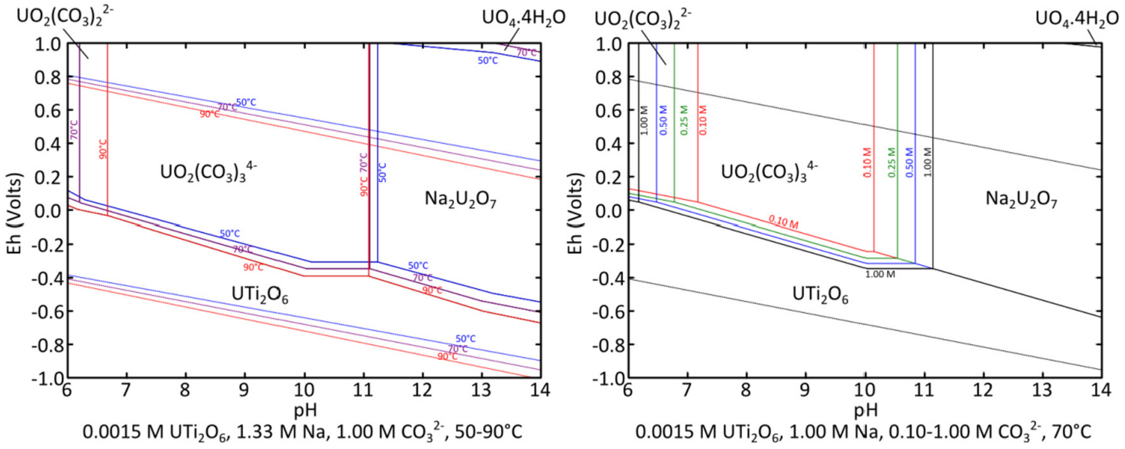

Fig. 2. Stable U phases in sodium carbonate solution at different temperature (left) and carbonate concentration (right).

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