



Review

A review of acid leaching of uraninite



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ABSTRACT

Uraninite is mined/processed more than any other uranium mineral for the production of uranium based compounds that are subsequently used to produce nuclear fuel. This review article provides a concise account of the available literature on one of the major processes involved in processing uraninite bearing ores, acid leaching. Improvements in the processes used to leach uraninite are required in order to ensure efficiency in the processing of lower grade uraninite bearing ores with minimal environmental impacts. This in turn requires improvements in our understanding of uraninite leaching. The main topics covered in this review include: uraninite structure, composition and low temperature geochemistry; the chemistry of uraninite leaching; key factors that influence uraninite leaching; and leach process technologies. The research that has been reviewed clearly establishes the influence of parameters such as temperature, acid concentration and particle size. The influence of other parameters however, such as solution Fe^{3+} to Fe^{2+} ratio (solution E_h), total Fe concentration, foreign ions present in the leach slurry and uraninite composition is yet to be established. Based on the literature available on the aforementioned factors the chemistry/processes involved in uraninite leaching are quite complex and require significant further studies. From the literature reviewed it is clear that variations in mineral chemistry in individual ore types across multiple deposits also make it essential that before any extraction process is considered, detailed ore characterisation studies of pre- and post-leach residues are of vital importance in order to fully understand the interrelationship between chemistry, mineralogy (ore and gangue), mineral liberation and potential leaching behaviour of uranium.

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1. Introduction

Uranium is widely distributed in the Earth's crust with estimates of its abundance varying between 2 and 4 ppm (Clark et al., 2006; Fleischer, 1955). Uranium in the crust is concentrated in over 200 mineral species that contain uranium as a necessary structural constituent in either the reduced U^{4+} or oxidised U^{6+} valence state. The main economic uranium minerals are the tetravalent species uraninite, pitchblende, coffinite and brannerite and to a lesser extent the more oxidised hexavalent species carnotite (Table 1). There are also approximately another sixty mineral species that contain minor amounts of uranium, or that contain uranium as an impurity (Burns and Finch, 1999; Finch and Murakami, 1999; Frondel et al., 1967; Krivovichev et al., 2006; Plant et al., 1999).

The most important uranium mineral is the simple oxide species uraninite (nominally UO_2), found in many deposits throughout the world (Frondel, 1958; Frondel et al., 1967; Laxen and Atmore, 1957; Macnaughton et al., 1999, 2000). Uraninite accounts for a significant proportion of the world's uranium supply (Burns et al., 1997; Clark et al., 2006; Morss et al., 2011; Peehs et al., 2007) and processing of uraninite has been the mainstay of uranium production as a result of its relative ease of extraction compared to other, more refractory uranium minerals (Merritt, 1971).

The focus of this article is to provide a concise review of available literature on the acid leaching of uraninite. The review focuses on the key parameters of the leach process under conditions typically used in commercial leaching operations. Other acid-based leach process technologies such as heap leaching, in-situ leaching and pressure leaching are only briefly considered. The chemistry behind acid leaching of uraninite applies in all these technologies and only specific factors that could potentially impact leaching are discussed.

2. Uraninite: occurrence, structure, composition and low temperature geochemistry

2.1. Occurrence (genesis)

Uranium resources are typically classified into fifteen main categories of uranium ore deposit types. Arranged, according to their approximate worldwide economic significance, they are as follows: (1) unconformity-related deposits; (2) sandstone deposits; (3) hematite breccia complex deposits; (4) quartz-pebble conglomerate deposits; (5) vein deposits; (6) intrusive deposits; (7) collapse breccia pipe deposits; (8) volcanic deposits; (9) metasomatic deposits; (10) surficial deposits; (11) phosphorite deposits; (12) metamorphic deposits; (13) lignite; (14) black shale deposits; and (15) other deposits (Bowell et al., 2011; Burns and Finch, 1999; Ceyhan, 2009; Cuney, 2009; Finch and Murakami, 1999; Frondel, 1958; Hazen et al., 2009; Seidel et al., 1993; I.A.E.A. et al., 2006; Kyser and Cuney, 2008; Morss et al., 2011; Peehs et al., 2005; Plant et al., 1999).

The chief sources of uraninite have historically been hydrothermal vein deposits, accounting for most of the world's historical uranium supply (Sharpe and Fayek, 2011). In such deposits, the uraninite usually occurs as fine-grained material commonly known as pitchblende (Ford, 1993). In more recent times, uraninite has been found to be associated with almost all deposit types (except the highly oxidised surficial deposit types) with most modern production coming from unconformity-related (Alexandre et al., 2009; Kyser and Cuney, 2008; Raffensperger and Garven, 1995), sandstone-hosted (Adams, 1991; Lovley and Phillips, 1992), quartz-pebble conglomerate (Robb and Meyer, 1995; Vennemann et al., 1992), vein (Kyser and Cuney, 2008) and breccia complex deposits (Reeve et al., 1990; Reynolds, 2000). Table 2 summarises a range of data including location, grade, deposit classification, and mineralogy from uraninite-containing deposits. Although dominated by uraninite, the data shows a variety of uranium-bearing minerals and gangue minerals associated with different deposit types. All have the potential to impact acid leaching of uraninite through increased consumption of reagent (gangue) or though reduced uranium extraction rates (other more refractory uranium minerals).

2.2. Structure and composition

Uraninite is commonly depicted using the chemical formula UO_2 . It is isometric (fluorite structure, space group $Fm\bar{3}m$, cell parameter $a = 5.4682 \text{ \AA}$, unit cell volume $V = 163.51 \text{ \AA}^3$) with the U^{4+} coordinated by eight O atoms in a face centred cubic arrangement with each O atom bonded to four U^{4+} cations at the corner of a regular tetrahedron (Fig. 1) (Belle, 1969; Fayek et al., 2000; Forster, 1999; Frondel, 1957; He et al., 2010; Kotzer and Kyser, 1993; Krivovichev and Plášil, 2013; Pouchot and Gauthier-Lafaye, 1998; Wilson et al., 1961). Uraninite that contains exclusively tetravalent U^{4+} is unknown in nature. Naturally occurring uraninite always has a portion of the uranium partially oxidised giving the general formula UO_{2+x} , with x typically in the range of 0.0 to 0.25–0.30 (Belle, 1969; Finch and Murakami, 1999; Janeczek and Ewing, 1991).

Table 1

Economically important uranium minerals.
Adapted after Pownceby and Johnson (2013).

Mineral type	Mineral name	Formula	Typical %U
<i>Tetravalent uranium minerals (U^{4+})</i>			
Oxides	Uraninite	$(U^{4+}_x - x, U^{6+}_x)O_{2+x}$ [ideally UO_2]	46–88
	Pitchblende	UO_2 amorphous	86–88
REE ± Ti ±	Brannerite	$(U, Ca, Y, Ce, La)(Ti, Fe)_2O_6$	26–44
Fe-oxides	Betafite	$(Ca, U)_2(Ti, Nb, Ta)_2O_6(OH)$	15–24
	Davidite	$(La, Ce)(Y, U, Fe)(Ti, Fe)_{20}(O, OH)_{38}$	1–6
	Orthobrannerite	$U_2Ti_4O_{12}(OH)_2$	~53
	Coffinite	$U(SiO_4)_1 - x(OH)_{4x}$	40–60
Silicates	Uranothorite	$(U, Th)SiO_4$	<10
<i>Hexavalent uranium minerals (U^{6+})</i>			
Phosphates	Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 10-12H_2O$	48–50
	Meta-autunite	$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 6-8H_2O$	~57
	Torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8-12H_2O$	47
Vanadates	Carnotite	$K_2(UO_2)_2(VO_4)_2 \cdot 1-3H_2O$	53–55
	Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$	~52
Silicates	Boltwoodite	$HK(UO_2)_2SiO_4 \cdot 1.5H_2O$	~55
	Sklodowskite	$(H_3O)_2 Mg(UO_2)_2(SiO_4)_2 \cdot 4(H_2O)$	49–54
	Uranophane	$Ca(UO_2)_2(SiO_3)(OH)_2 \cdot 5H_2O$	~41

Table 2

Data for selected mines which contain uraninite as the primary uranium source. Note the range of deposit types in which uraninite occurs. Data sourced from Ceyhan (2009), Finch and Murakami (1999), and I.A.E.A. et al. (2006). Note that not all mines are currently operating.

Mine	Location	Ore deposit type [†]	Uranium minerals	Grade %U	Major gangue minerals	Contained U (kT)	Reference
Olympic Dam	South Australia, Australia	IOCGU	Uraninite, brannerite, coffinite	0.05	Hematite, quartz, sericite, K-feldspar	1503	Macnaughton et al. (2000), Macnaughton et al. (1999)
Ranger	Northern Territory, Australia	UC	Uraninite, coffinite, brannerite	0.22	Quartz, chlorite dolomite, magnesite, calcite	49	Ring (1979)
McArthur River–Key Lake	Saskatchewan, Canada	UC	Pitchblende, coffinite, uraninite	0.66	Quartz, chlorite, kaolinite, sericite, calcite, epidote	8.5	Janeczek and Ewing (1992b)
McClellan Lake	Saskatchewan, Canada	UC	Pitchblende, uraninite, coffinite	2.4	Quartz, chlorite, sericite, calcite, dolomite	19	Janeczek and Ewing (1992b)
Central Mynkuduk	Chu-Sarsyu, Kazakhstan	S	Pitchblende, uraninite, coffinite, U-vanadates, U-phosphates	0.042	Quartz, feldspar, mica, pyrite, Fe- and S-rich organics	>100	Benes et al. (2001), Seidel et al. (1993), I.A.E.A. et al. (2006)
Rossing	Namibia	I	Uraninite, betafite, uranophane	0.03–0.05	Quartz, microcline, biotite, fluorite	140	Jansen van Rensburg (2014)
Akouta	Agadies, Niger	S	Pitchblende, uraninite, coffinite, U-vanadates, U-phosphates	0.46	Quartz, chlorite, pyrite, humate	25–50	Benes et al. (2001), Seidel et al. (1993), I.A.E.A. et al. (2006)
Krasnokamensk	Krasnokamensk, Russia	Vc	Pitchblende, uraninite, coffinite	0.38/0.04	Mo-sulfides, pyrite, fluorite, quartz, barite, jarosite, carbonates	60	Benes et al. (2001), Seidel et al. (1993), I.A.E.A. et al. (2006)
Crow Butte	Nebraska, USA	S	Pitchblende, uraninite, coffinite, U-vanadates, U-phosphates	0.42	Quartz, chlorite, pyrite, humate, ilmenite, magnetite	16	Grandstaff (1976), Zhao and Ewing (2000)
Elliot Lake	Ontario, Canada	Q–P	Uraninite, brannerite, coffinite, monazite	0.12	Rutile, anatase, pyrite, quartz	400	Janeczek and Ewing (1992b)
Witwatersrand	Witwatersrand Basin, South Africa	Q–P	Uraninite, brannerite, coffinite	0.03	Rutile, anatase, pyrite, quartz	500	Lottering et al. (2008)
Jachymov	Czech Republic	V	Uraninite, pitchblende, coffinite	0.24	Dolomite, quartz, albite, adularia, fluorite, barite	10	Benes et al. (2001)
Cigar Lake	Saskatchewan, Canada	UC	Uraninite, pitchblende, coffinite	0.88	Quartz, biotite, pyrite, calcite, illite, kaolinite, siderite, chlorite	135	Fayek et al. (1997), Grandstaff (1976)

[†] Key to ore deposit type abbreviations: IOCGU = Breccia complex; UC = unconformity-related; S = sandstone; Vc = volcanic; Q–P = quartz–pebble conglomerate; V = vein; I = intrusive.

Characterisation studies conducted on naturally occurring uraninite have shown that uraninite rarely exists without extensive incorporation of impurities (Borstel and Halbach, 1982; Cuney, 2009; Fayek et al., 1997; Forster, 1999; Janeczek and Ewing, 1992a; Pavicevic and El Goresy, 1987; Pownceby and Johnson, 2013; Ruskeeniemi et al., 1999;

Stefaniak et al., 2009; Sunder et al., 1987; Teterin et al., 1981; Zetterström, 1999). Impurities are incorporated as a result of cationic substitution during genesis, post-depositional alteration, and through decay of the uranium isotopes ^{238}U and ^{235}U into radiogenic lead and other radiogenic daughter products. The most important impurities in uraninite are Pb, Th, Ca Y and lanthanides (Deditius et al., 2007; Janeczek and Ewing, 1992a; Janeczek et al., 1996). Other elemental impurities in uraninite include Si, P, Al, Fe, Mg, Na and K (Alexandre and Kyser, 2005; Finch and Ewing, 1991, 1992; Finch and Murakami, 1999; Foord et al., 1997; Frondel, 1958; Berman, 1957; Pearcy et al., 1994; Ram et al., 2011b, 2013b). There is uncertainty regarding the nature of these latter impurities within the uraninite structure, either in interstitial sites or through substitution, as most of these elements are incompatible with the uraninite structure. Based on all known impurities, Janeczek and Ewing (1992a), proposed the following formula for naturally occurring uraninite:

$$\left(\text{U}_{1-x-y-z-v}^{4+} \text{U}_x^{6+} \text{REE}_y^{3+} \text{Mz}_z^{2+4-} \right) \text{O}_{2+x-(0.5y)-z-2v}$$

where x is the amount of excess oxygen equal to U^{6+} , y is the amount of trivalent cations (typically Y and REE), z is the amount of divalent cations (Pb and Ca), v is the number of uranium vacancies in the formula unit and $-$ indicates a vacancy.

The impurities (and their respective amounts) present in uraninite have been shown to have a significant influence on the stability of uraninite in natural systems (Alexandre and Kyser, 2005; Finch and Ewing, 1991, 1992). They have also been reported to influence uraninite leaching under conditions used in commercial leaching processes (Grandstaff, 1976; Casas et al., 1998; Macnaughton et al., 1999, 2000; Ram et al., 2013c, 2014; Ring, 1979).

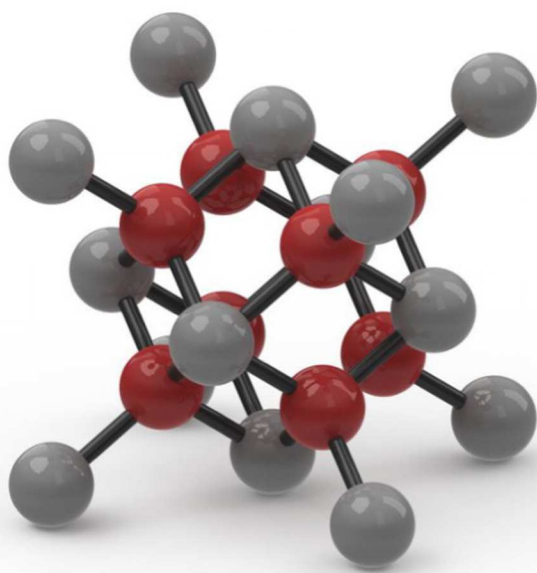


Fig. 1. Crystal structure of uraninite (UO_{2+x}) (O – red; U – grey). Copyright permission received from Ram (2013).

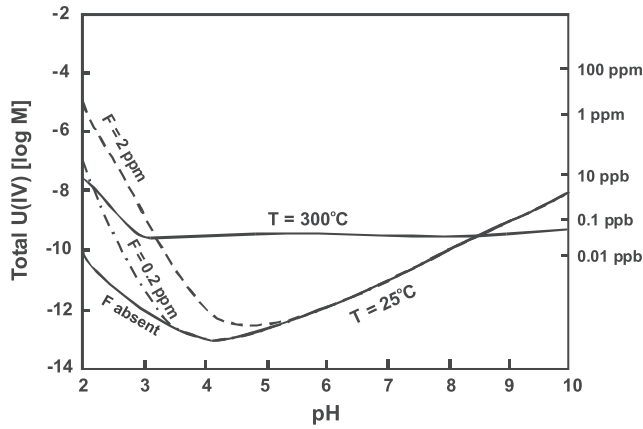


Fig. 2. Solubility of uraninite in water as a function of pH at 25 °C and 300 °C. Data also included showing the effect of fluorine on uraninite solubility at 25 °C. Copyright permission received from Langmuir (1978) and Shock et al. (1997). License No: 3485090573628; 3485090710744.

2.3. Uraninite low temperature geochemistry

An understanding of the low temperature aqueous and redox geochemistry of uraninite provides important background information as to the stability of uraninite under different environmental conditions (e.g. T, pH, and pO_2), all of which are relevant to understanding the behaviour of uraninite in commercial leaching processes.

The uranous ion (U^{4+}) has low basicity and forms an insoluble oxide in dilute acid and salts that hydrolyse readily. Uraninite is therefore only

sparingly soluble in water at neutral pH, low temperatures (Fig. 2) and reducing conditions (Langmuir, 1978; Parks and Pohl, 1988; Rai et al., 1990). Reported UO_2 solubilities vary between 10^{-7} (Bruno et al., 1991) and $\sim 10^{-15}$ M (Guillamont et al., 2003) in aqueous solution at $pH > 5$. The solubility depends on the degree of crystallinity of the uraninite, the oxidation state of uranium, the solution E_h and pH and the level of impurities.

Uraninite solubility increases markedly under oxidising conditions and in the presence of anions such as OH^- , Cl^- , CO_3^{2-} , F^- , SO_4^{2-} and PO_4^{3-} all of which form strong complexes with UO_2^{2+} (Guillamont et al., 2003; Langmuir, 1978). For example, uraninite is readily soluble in strongly acidic, oxidising water commonly associated with acid mine drainage because UO_2^{2+} sulfate complexes are stable below pH 4 (Fig. 3). At higher pH, uranyl hydroxide complexes dominate. Fig. 4 shows the stability field for UO_2 and uranyl sulfate complexes in the system U–S–H₂O at 25 °C as a function of redox potential (E_h) and pH. The plot illustrates the high stability of UO_2 at low E_h conditions where the tetravalent uranium cation is stable whilst high E_h conditions promote the stabilisation of hexavalent UO_2^{2+} and uranyl sulfate complexes. The relative stability of the UO_2^{2+} complexes with varying E_h and pH correlates strongly with conditions used to leach uraninite ores. For example, solutions with pH of about 1.5–1.8 and E_h of > 750 mV (vs. standard hydrogen electrode (SHE)) are typically used for uranium recovery from uraninite in commercial acid-leach processes.

3. Acid sulfate leaching of uraninite

Leaching using sulfuric acid solutions is the most widely used process for the extraction of uranium from uraninite ores because of the relatively low cost and wide availability of the acid. Acid sulfate

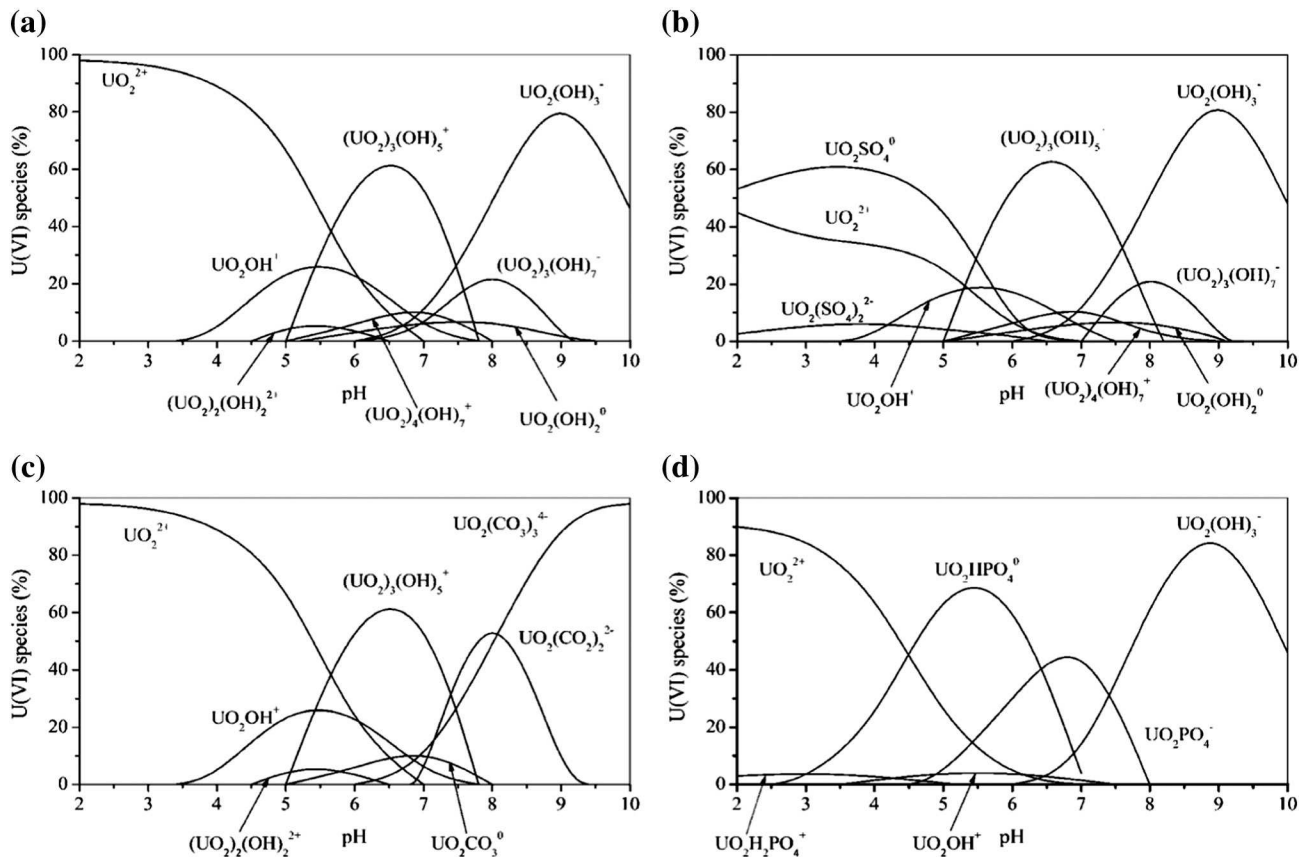


Fig. 3. (a) $U(VI)$ speciation in 0.01 M NaCl, $[U] = 5 \times 10^{-5}$ M; (b) $U(VI)$ speciation in 0.01 M NaCl + 0.005 M Na_2SO_4 , $[U] = 5 \times 10^{-5}$ M; (c) $U(VI)$ speciation in 0.01 M NaCl + 0.003 M $NaHCO_3$, $[U] = 5 \times 10^{-5}$ M; (d) $U(VI)$ speciation in 0.01 M NaCl + 0.003 M Na_2HPO_4 , $[U] = 5 \times 10^{-5}$ M. Copyright permission received from Bachmaf et al. (2008). License No: 3485100750915.

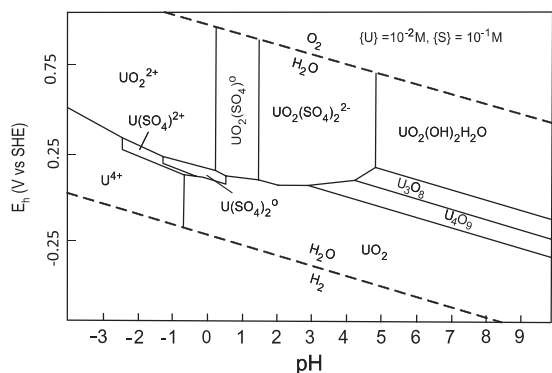
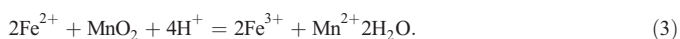


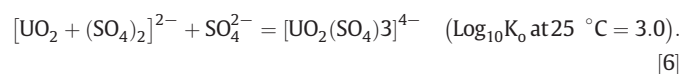
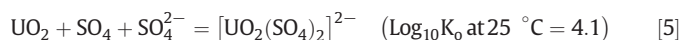
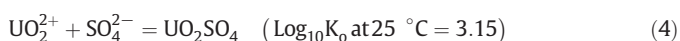
Fig. 4. E_h /pH diagram for the U–S–H₂O system at 25 °C. Copyright permission received from Lottering et al. (2008). License No: 3486391122173.

leach chemistry of uranium ores is discussed in detail by many authors including: Celeda and Lara (1965), Eary and Cathles (1983), Eary et al. (1986), Eligwe et al. (1982), Nesmeyanova and Chernushevich (1960), Galichon et al. (1977), Clegg and Foley (1958), Laxen (1971), 1973, Laxen and Atmore (1957), Lottering et al. (2008), Macnaughton et al. (1999), 2000, Merritt (1971), Nicol and Needes (1973), Nicol et al. (1975), Ram et al. (2013c), Ring (1979), Steward and Mones (1996), and Youlton and Kinnaird (2013).

The acid sulfate process involves treating ground ore slurry with sulfuric acid at elevated temperatures (typically 30–50 °C), with an oxidant to convert the U^{4+} to the hexavalent state. Other acids such as hydrochloric and nitric acids are more costly and pose more difficult environmental challenges than sulfuric acid (Edwards and Oliver, 2000). The uranium oxidation reaction requires the presence of Fe^{3+} , regardless of the reagent and oxidant used. Previous studies conducted on natural and/or synthetic UO_2 dissolution have shown that the ferric ion oxidises the insoluble UO_2 to its soluble uranyl (UO_2^{2+}) form, with the additional oxidant re-converting the ferrous ion back to ferric ion (Arden and Beaumont, 1950; Laxen, 1965, 1971). The oxidising agents most commonly used in uraninite leaching to convert ferrous ions to ferric ions are manganese dioxide (MnO_2 as pyrolusite) (Ho and Ring, 2007; Merritt, 1971); oxygen (Bovey and Stewart, 1979), hydrogen peroxide (DeVries, 1984; Lucas et al., 1983); Caro's acid (H_2SO_5) (Lucas et al., 1983; Venter and Boylett, 2009); sulfur dioxide/air (SO_2 /air) (Ford, 1993; Ho and Quan, 2007); and sodium chlorate (Merritt, 1971). An evaluation of various oxidants used in acid leaching of uranium can be found in Venter and Boylett (2009). Examples of these oxidation/reduction processes are thus summarised as follows:



The presence of Fe-containing gangue minerals present in the ore and grinding iron usually provides most, if not all, of the Fe required for the oxidation of UO_2 . The reintroduction of Fe^{3+} ions back into the solution forms a continuous cycle of redox reactions until most of the insoluble UO_2 is converted to the soluble UO_2^{2+} form. The subsequent reaction of UO_2^{2+} with sulfuric acid to form uranyl sulfate and complex uranyl sulfate anions includes:



The dissolved uranium may occur in any of the above forms, depending upon acid, sulfate and uranium concentrations, temperature and other complex variables in the system. In the presence of excess of sulfate ions, sulfate complexing reactions are kinetically favoured over uranium hydrolysis (Munoz et al., 1995b; Shying, 1973; Suzuki et al., 1990). Thus the presence of sulfate ions increases the driving force for the leaching reactions independent of the presence of protons (Mishra et al., 2013). As indicated previously, in an acidic environment the uranium dissolution process is confined to a specific E_h –pH window (Lottering et al., 2008). Potential for re-precipitation is an important consideration and failure to maintain oxidising conditions in the solution may result in formation of uranous salts which precipitate at pH values where the uranyl ion remains soluble.

A critical requirement of an acid leach process is that the associated gangue host mineralogy should have as low amount of acid-consuming minerals (e.g. carbonates and clays) as possible. This minimises the costs of acid consumption. Ore bodies containing less than 12–15% carbonates are typically acid leached (Merritt, 1971). The level of carbonate that makes an ore suitable for acid leaching is however strongly linked with the current economics of uranium minerals processing. Compared to an alkaline leach process, which is used for treating ores with large amounts of acid consuming gangue, the acid leach process has the advantage of relatively mild reagent concentrations, shorter leach times, relatively low temperatures and not requiring a finely ground feed. Uranium-bearing solutions produced via acid leaching are also well suited to subsequent processing by ion exchange and solvent extraction, the two processes most used to recover the uranium. Fig. 5 outlines a general acid leach flow sheet for processing uraninite ores.

The dissolution of UO_2 from uraninite ores using an acid sulfate leach process is influenced by a number of chemical process factors including: variations in leach time, initial uranium concentration, temperature, Fe^{3+}/Fe^{2+} , total Fe concentration ($[Fe]_{TOT}$), acid concentration, oxidation–reduction potential (E_h), and particle size. Additional factors likely to impact uranium extraction arise from the properties of the ore feed and include: the presence of foreign ions in the leach slurry due to dissolution of gangue minerals; the nature of the uraninite being leached (e.g. the uranium speciation, degree of alteration, crystallinity and levels and types of impurities and cationic substitutions occurring within the crystals); and the distribution of the UO_2 within the ore (liberation and association). Previous studies examining the influence of each of these factors on uranium extraction from uraninite are discussed in the following sections.

3.1. Uraninite redox chemistry

3.1.1. Effect of E_h

Uraninite leaching involves a redox process with oxidation of the uranium to U^{6+} leading to the release of soluble uranium species. Electrochemical studies on UO_2 and U_3O_8 electrodes have allowed a better understanding of the mechanism of the oxidation of UO_2 . Most of the detailed electrochemical studies have however been conducted with a view to understand corrosion of spent UO_2 fuel, which is beyond the scope of this review. Nonetheless, mechanistic information has been postulated on the assumed oxidation of primary uranium oxides in acidified ferric sulfate media in small scale laboratory studies (Table 3).

Detailed electrochemical experiments in acidic solution have shown that the anodic oxidation of UO_2 proceeds through two successive electrochemical reactions (in non-complexing media), with a U^{5+} intermediate at the UO_2 surface observable between the U^{6+} and U^{4+} oxidation

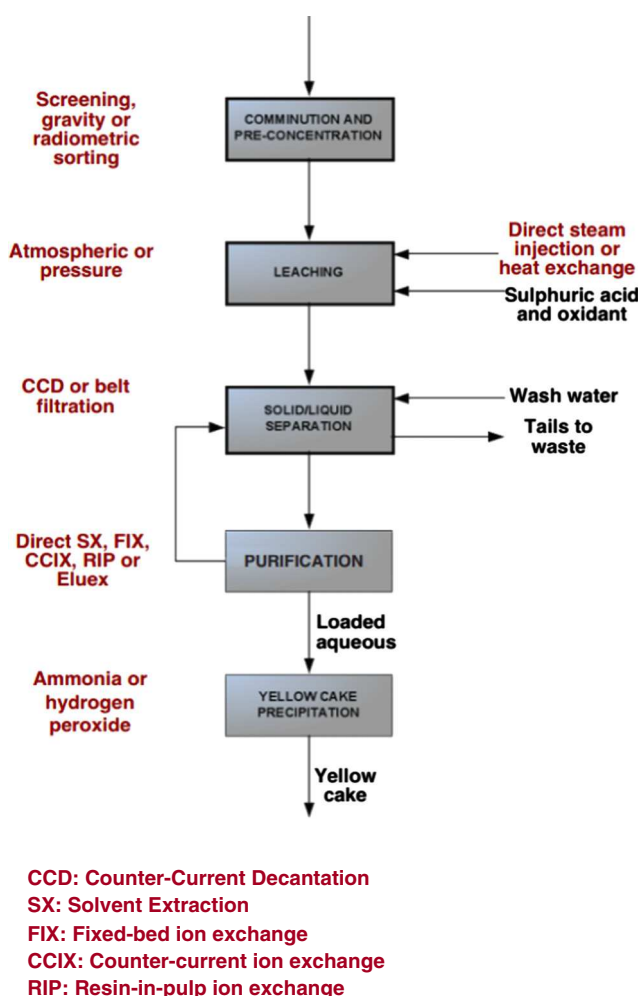


Fig. 5. A typical acid leach circuit operation. Copyright permission received from Lunt et al. (2007).

states which are the only two oxidation states stable in aqueous solution. Acidic media prevents formation of precipitates during oxidation, removing passivation concerns for pure UO_2 (Gaulard-Balandret et al., 2012). The threshold for the onset of anodic dissolution (640 mV vs. SHE) was shown not to change significantly between 20 °C and 60 °C. However the oxidation of the surface U^{4+} to the U^{5+} intermediate, and the rate of dissolution of the U^{6+} species are appreciably increased in rate at 60 °C, with higher anodic (dissolution) currents observed, as expected, when the temperature is raised (Broczkowski et al., 2007). Electrochemical studies on $\text{UO}_{2.0}$ films have shown that alkaline

solutions could lead to the presence of a $\text{UO}_{2.33}$ layer, which is not observed in acidic solutions, and this most likely contributes to the differences in dissolution rates between acidic and basic solutions (Miserque et al., 2001).

Studies on the effect of surface potential on the anodic dissolution of UO_2 have been conducted using a range of electrochemical methods (Nicol and Needes, 1973; Nicol et al., 1975; Shoesmith, 2000; Sunder et al., 1981). The general model proposed is considered valid either for exposure of the UO_2 to a solution of known E_h , or by electrochemical application of the potential. For a UO_2 potential of -1040 mV to -640 mV vs. SHE, oxidation of sub-monolayer quantities of UO_2 confined to the surface will occur, and from -640 to -340 mV irreversible oxidation of UO_2 to UO_{2+x} will take place, with increasing depth of oxidation at more positive potentials. UO_2 potentials above -340 mV vs. SHE are necessary for complete oxidation and dissolution. Rapid dissolution will always occur when the mineral attains a potential above 600 mV vs. SHE. Leaching studies are generally undertaken by controlling solution chemistry to control the E_h of the leaching solution. The potential of the UO_2 , whilst carefully controlled in electrochemical experiments, is not directly measured during a leaching study. Leach conditions are chosen to ensure that the corrosion potential of the UO_2 in the leaching solution is sufficient to ensure facile dissolution.

3.1.2. Effect of Fe^{3+} , Fe^{2+} , $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe_{TOT}

Ferric ion is the most common species used to oxidise the U^{4+} in UO_2 in commercial leaching processes (Laxen, 1971; Nicol et al., 1975). The influence of Fe^{3+} concentration on the dissolution of uraninite is heavily reliant on other factors such as the E_h of the solution (which is primarily determined by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio) and the temperature. The Fe^{3+} concentration in the leach liquor is controlled by adjusting the redox potential (E_h) by the addition of an oxidant. Due to the strong relationship between $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}]$, isolating the influence that $[\text{Fe}^{3+}]$ or $[\text{Fe}^{2+}]$ have on UO_2 dissolution from the influence of solution E_h is not possible without changing the composition of the solution. This in turn will also have an influence on uraninite dissolution (as seen in Fig. 6). From a uranium processing point of view, solution E_h is therefore the most commonly used parameter to control/monitor the uranium dissolution process (Filippov and Kanevskii, 1964; Lottering et al., 2008; Spitsyn et al., 1960, 1964).

For typical leaching conditions the relationship between the redox potential and the iron concentrations is given by the Nernst equation;

$$E_h(\text{mV}) = E_T^0 + 0.198T \log\left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}\right) \quad [7]$$

where E_h is the solution potential, $[\text{Fe}^{3+}]$ is the molar concentration and T is the temperature (K). E_T^0 is the standard reduction potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, which is 771 mV vs SHE at 25 °C under acidic conditions, with a temperature coefficient (dE^0/dT) of 1.18 mV/K (Bratsch, 1989). Complexation of the ferrous or ferric ions with anions in solution will cause E^0 variations, but the speciation is usually too complex to

Table 3

Summary of the kinetics of dissolution of uranium oxides in acidified ferric sulfate media. Data sourced from Dutrizac and MacDonald (1974).

Material	Medium	Fe^{3+} dependence on rate	Activation energy ($\text{KJ} \cdot \text{mol}^{-1}$)	Temperature (°C)	Rate controlling process	References
Syn UO_2	Ferric sulfate	Rate increased according to concentration of $(\text{Fe}^{3+})^{1/2}$	66.9	15–35	Surface adsorption controlled	Laxen (1973), Nicol et al. (1975)
Uraninite	Ferric sulfate	Directly dependent at low Fe^{3+} conc. independent of Fe^{3+} conc. >8 g/L	46–62.7	5–30	Surface adsorption controlled	Laxen (1965)
Syn U_3O_8	Ferric sulfate	Rate increased according to conc. of $(\text{Fe}^{3+})^{1/3}$	58.6, 20.9	25–50	Surface adsorption controlled	Sobkowski et al. (1966)
Syn U_3O_8	Ferric sulfate	Rate increased according to concentration of $(\text{Fe}^{3+})^{1/2}$	62.7–79.5	25–55	Surface reaction controlled by transformation of active centres	Celeda and Lara (1965)

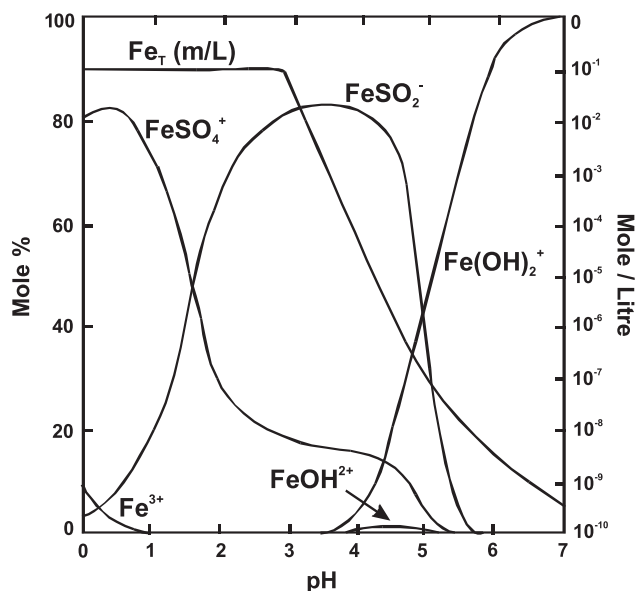


Fig. 6. Equilibrium iron species existing in a solution containing 0.1 M Fe^{3+} and 0.5 M total sulfate at 25 °C. Copyright permission received from Bhappu et al. (1969).

precisely define. In practical situations, pH variations and diverse solution chemistry due to gangue mineral dissolution will affect the measured E_h . However, Eq. (7) shows that at an E_h value of 771 mV vs. SHE, about 50% of the iron is in the ferric state, whilst only 2% remains as ferrous ion at 870 mV vs. SHE.

A satisfactory level of uranium extraction should be obtained for most ores containing uraninite by maintaining an oxidation potential greater than 697 mV vs. SHE at temperatures of 35 °C–40 °C, though the precise E_h value required depends on the source of the ore, and leaching can take place acceptably with a lower E_h value (Ring, 1979). Leaching at potentials greater than 890 mV vs. SHE often increases the initial rate of extraction but the overall rate and ultimate recovery are not improved.

Comprehensive studies conducted on the influence of Fe^{3+} and Fe^{2+} on UO_2 dissolution under commercial processing conditions were carried out by Laxen (1971) and Nicol et al. (1975). Laxen

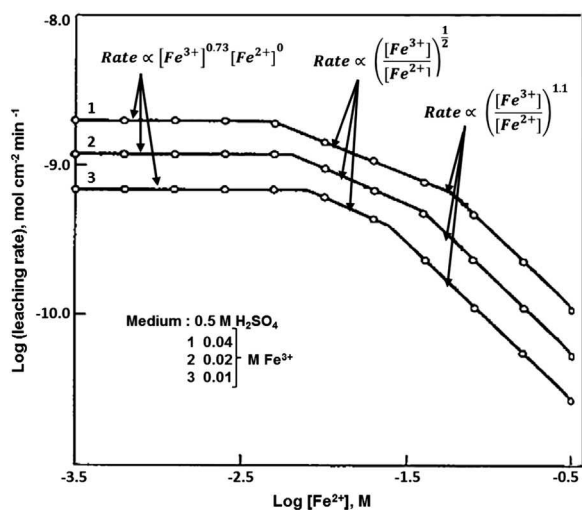


Fig. 7. Effect of concentration of Fe^{2+} on rate of leaching of UO_2 by Fe^{3+} in sulfuric acid at 25 °C (sintered UO_2 sample). Copyright permission received from Nicol et al. (1975). License No: 3496700273957.

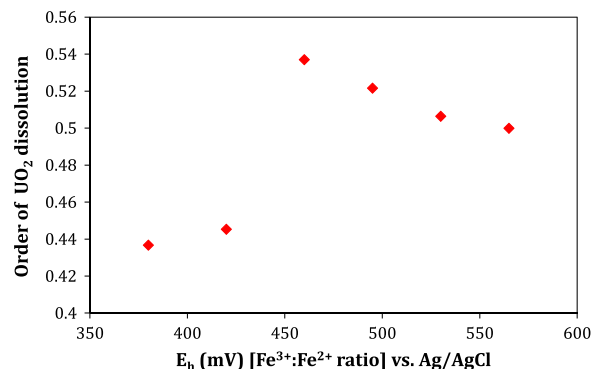


Fig. 8. Order of UO_2 dissolution with respect to Fe at different E_h s. Copyright permission received from Ram et al. (2011a). License No: 3485090244632.

(1971) investigated the influence of $[\text{Fe}^{3+}]$, $[\text{Fe}^{2+}]$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on the dissolution of synthetic UO_2 between 15 °C–35 °C whilst Nicol et al. (1975) explored the influence of Fe^{2+} concentration on the dissolution of a sintered pellet of synthetic UO_2 at different concentrations of Fe^{3+} . The main findings from the two studies were that the UO_2 dissolution rate increased with an increase in $[\text{Fe}^{3+}]$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Results from Nicol et al. (1975) are shown in Fig. 7.

More recently, investigations on the relationship between the UO_2 dissolution rate and $[\text{Fe}]$ at six different solution E_h s by Ram et al. (2011a) revealed a high dissolution rate dependency on $[\text{Fe}]$ at higher E_h (≥ 657 mV–762 mV vs. SHE), whilst at lower E_h (≤ 617 mV), $[\text{Fe}]$ had a significantly lower influence on the UO_2 dissolution rate under the conditions used (Ram et al., 2011a) (Fig. 8). The order of dependence on $[\text{Fe}]$ was in the range of 0.44–0.54 for the conditions used. The dependence of the UO_2 dissolution rate on total iron concentration was essentially linear over a wide $[\text{Fe}]$ range at a solution E_h of 657 mV (Temp – 50 °C, $[\text{H}_2\text{SO}_4]$ – 0.15 M, Fe^{3+} 1.1×10^{-4} to 4.2×10^{-3} ; Fe^{2+} 3.2×10^{-4} to 1.8×10^{-2} M, Fe_{TOT} 4.2×10^{-4} to 2.4×10^{-2} M). The effect of $[\text{Fe}^{2+}]$ on the rate of UO_2 dissolution at four different fixed ferric iron concentrations showed very similar trends. At low ferric iron concentrations, $[\text{Fe}^{2+}]$ had only a minor effect on the rate of UO_2 dissolution; whereas with increasing $[\text{Fe}^{2+}]$ at constant $[\text{Fe}^{3+}]$, a linear decrease in dissolution rate was observed (Fig. 9) (Ram et al., 2011a).

Studies have also been conducted on the addition of Fe^{3+} directly into a leach system to improve overall extraction efficiencies through increasing both E_h and the total iron available for reaction with the U^{4+} . Jansen van Rensburg (2014) reported an increased total uranium extraction after 13 h ($T = 35$ °C, $\text{pH} = 1.6$, %Solids – 70, U – 0.24 g/L, Uraninite – 77.5%, Uranophane – 20.5%) with an increase in total iron concentration for all tested E_h set points (650–850 mV vs SHE).

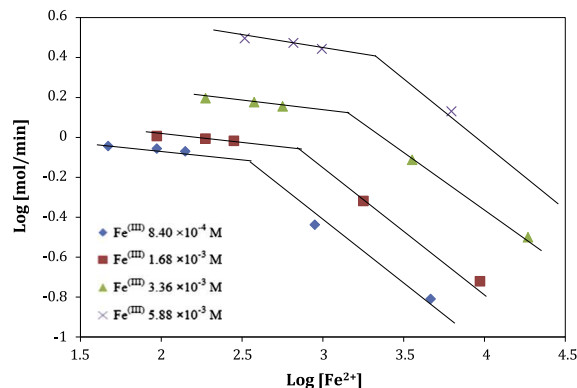


Fig. 9. Log UO_2 dissolution rate vs. $[\text{Fe}^{2+}]$ at four fixed Fe^{3+} concentrations. Copyright permission received from Ram et al. (2011a). License No: 3485090244632.

3.2. Leaching of natural uraninite and synthetic uraninite

Several studies have been conducted on the dissolution of naturally occurring uraninite ores (Casas et al., 1998; Eary et al., 1986; Finch and Ewing, 1992; Bautista, 1995; Grandstaff, 1976; Ring, 1979; Janeczka and Ewing, 1992b; Laxen, 1965; Lottering et al., 2008; Mackay and Wadsworth, 1958; Macnaughton et al., 2000; Turos et al., 1996). The results obtained from the aforementioned studies are highly varied, which is most likely due to one or more of the following: significant differences in composition between the uraninites; gangue mineralogy; and degree of liberation. Some of the key studies are reviewed below.

Numerous investigators (Abdelouas et al., 1999; Eary et al., 1986; Galichon et al., 1977; Munoz et al., 1995a) have conducted simple column leaching experiments with ores containing uraninite to determine rates of uranium extraction. In these studies, reaching unequivocal determinations of the relative importance of the chemical factors which control dissolution rates of the uraninite, compared to morphological factors which control the leachable uranium content of the ore, have been impeded by the complex nature of the reactions occurring between the natural ores and the leach solutions. Ring (1979) conducted sulfuric acid leaching studies of uraninite-dominated ores from a number of Australian deposits (Ranger, Nabarlek and Jabiluka). All three ores were all readily amenable to conventional sulfuric acid leaching ($T = 35\text{--}40\text{ }^{\circ}\text{C}$, $16\text{--}24\text{ h}$, $\text{pH} = 1.5\text{--}2.0$, $E_h = \sim 716\text{ mV}$ and acid addition $37\text{--}55\text{ kg/t}^{-1}$ ore) with variations in temperature and pH having the most influence in determining the most suitable leaching conditions. The presence of refractory uranium minerals, which were not leached under conventional conditions, limited uranium extraction to $90\text{--}96\%$ (Ring, 1979). Ring also examined a uranium-rich copper tailings concentrate from the Olympic Dam deposit containing uranium in both uraninite and brannerite. The extraction of uranium from this ore required leaching at $55\text{ }^{\circ}\text{C}$ and a redox potential of $\sim 890\text{ mV}$ vs. SHE (Ring, 1979).

Macnaughton et al. (1999, 2000) conducted studies examining the influence of acid strength, Fe^{3+} concentration, redox potential and temperature on the dissolution of uranium in three Roxby Downs copper tailings residues ($1.6\text{ g/L U}_3\text{O}_8$). Uranium leaching behaviour under leach conditions ($\text{pH} = 1.5$, $T = 55\text{ }^{\circ}\text{C}$, $55\text{ wt.}\%$ solids and $1.5\text{ kg/t}^{-1}\text{ NaClO}_3$) was characterised by a very rapid initial dissolution ($>60\%$ dissolution after $\sim 15\text{ min}$) that slowed down significantly after $\sim 80\%$ dissolution. The slow uranium leaching rate above $\sim 80\%$ extraction was attributed to the presence of the refractory uranium-bearing minerals coffinite and brannerite as well as poorly liberated uraninite. In all cases, uranium extraction increased with acidity and temperature and had a complex co-dependence on Fe^{3+} and redox potential. They also observed that the amount of acid consumed significantly varied across the three samples and attributed this to changes in gangue mineral abundances (mainly chlorite and fluorite).

Lottering et al. (2008) conducted acid leaching studies on three low grade uranium ores from the Vaal River region in South Africa. The average composition of uranium minerals in ores studied were (as total U) – uraninite ($\sim 85\%$), brannerite ($\sim 10\%$), coffinite ($\sim 2\%$), and U-phosphate ($\sim 0.2\%$). A maximum uranium dissolution of $\sim 90\%$ over 24 h was achieved using $[\text{H}_2\text{SO}_4] = 16.3\text{ kg/t}$, $T = 60\text{ }^{\circ}\text{C}$, $\text{MnO}_2 = 4\text{ kg/t}$ (pyrolusite containing 29.3% Mn and 36.5% Fe), and a pulp density of 1.55 . The unrecovered uranium was attributed to refractory brannerite. A doubling of the residence time and use of nitric acid did not show any improvement in overall uranium dissolution. Reagent consumption varied for the three ores as a result of changes in the gangue mineral content with chlorite found to be the major acid consumer (Lottering et al., 2008).

Ram et al. (2013c) conducted dissolution tests on two natural uraninite samples ($63\text{--}73\text{ wt.}\%$ U) under the following leaching conditions: $0.15\text{ M H}_2\text{SO}_4$, $50\text{ }^{\circ}\text{C}$, $E_h\ 657\text{ mV}$, $6.7 \times 10^{-3}\text{ M Fe}_{\text{TOT}}$. Both samples had lower extraction rates when compared to synthetic UO_2 . Decreasing the particle size, increasing temperature and increasing Fe_{TOT} all

resulted in an increase in the rate of uranium dissolution whereas changing acid concentration ($1.5\text{--}70\text{ g/L}$) and changing the E_h ($577\text{--}762\text{ mV}$ vs SHE) had a negligible effect. The changes in dissolution rates between the natural ores and the synthetic uraninite was attributed to lead impurities within the natural uraninites being preferentially leached and then re-precipitated as a sulfate (thus inhibiting further reaction) (Ram et al., 2013c).

The above studies on the leaching of natural uraninite produced mixed results primarily due to natural uraninites being chemically complex as a result of alteration, cationic substitution and radioactive decay processes (causing loss of crystalline structural integrity). Significant effects on uranium extraction may also be caused by process differences (i.e. T , pH , grain size etc.) as well as factors relating to the ore itself such as the associated gangue mineralogy and the degree of liberation. These effects are discussed in more detail in the following sections.

3.2.1. Effect of foreign ions released from gangue

The leaching of uraninite ores containing soluble gangue leads to the release of foreign species into the solution. The dissolution of gangue minerals influences the dissolution of uraninite via two main pathways; firstly, it can lead to a reduction in the acid concentration (by consuming acid) of the slurry (Ramadevi et al., 2012; Seidel, 1981; Tamrakar et al., 2010; Venter and Boylett, 2009); and secondly, the foreign ions released may influence the $\text{UO}_2/\text{UO}_2^{2+}$ oxidation/dissolution reactions.

There have been very few studies on the influence of foreign ions on UO_2 dissolution under conditions similar to those used in uranium minerals processing. Spitsyn et al. (1960) conducted studies on the effect of sulfate addition (as Na_2SO_4) on UO_2 dissolution under the following conditions; 1.5 g UO_2 in a $1\text{ L Fe}_2(\text{SO}_4)_3$ solution, $\text{pH} = 2.3$, $T = 20\text{--}70\text{ }^{\circ}\text{C}$ for 6 h . They observed an initial increase in the degree of oxidation of uranium with a $0.5\text{--}1.5\text{ wt.}\%$ Na_2SO_4 addition. However upon reaching a SO_4^{2-} concentration of 6.7% w/w, there was a substantial drop in the degree of oxidation. They proposed that this was due to either a change in the mobility of ions, the formation of iron complexes or formation of hydrolysed compounds of Fe^{3+} (Spitsyn et al., 1960). Laxen (1971) conducted studies on the effect of Cl^- , NO_3^- and SO_4^{2-} on the dissolution of UO_2 single crystals at $35\text{ }^{\circ}\text{C}$. At a concentration of 0.009 M Fe^{3+} , an increase in dissolution rate from 0.04×10^{-2} to $0.12 \times 10^{-2}\text{ (mg U) cm}^{-2}\text{ min}^{-1}$ was observed when 0.015 M Cl^- was added, however a similar amount of NO_3^- did not result in an improved dissolution rate. The effect of SO_4^{2-} (added as Na_2SO_4) showed that a 0.1 M SO_4^{2-} addition had a marked positive effect on uraninite dissolution. This was attributed to increasing concentrations of FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$ in the electron exchange involved in UO_2 dissolution (Laxen, 1971). Laxen (1971) also conducted studies on the effect of Mn^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} (which can leach from gangue minerals) on UO_2 dissolution and noted decreased rates of dissolution.

Nesmeyanova and Vikulov (1965) investigated the influence of NaI, NaF, NaBr and NaCl on UO_2 dissolution at 0.5 g UO_2 , $0.2\text{ M }[\text{H}_2\text{SO}_4]$, $T = 90\text{ }^{\circ}\text{C}$, and 0.01 g of halide salt. All four halides accelerated uranium oxidation by manganese dioxide and maximum dissolution occurred when F^- ions were added. This was attributed to complexation between U^{4+} and F^- (Nesmeyanova and Vikulov, 1965). Santos et al. (2006a) investigated the influence of Ca^{2+} , present as CaCl_2 on the anodic dissolution of Ca-doped uranium dioxide over the potential range of $240\text{--}740\text{ mV}$ (vs SHE). Ca^{2+} was found not to influence the conversion of UO_2 to $\text{U}^{4+}_{1-2x}\text{U}^{5+}_{2x}\text{O}_{2+x}$, but to suppress the subsequent formation of U^{6+} surface species which lead to the formation of a hydrated surface, $\text{UO}_3 \cdot y\text{H}_2\text{O}$. The addition of Ca^{2+} on the UO_2 surface was believed to inhibit uranium dissolution either via inhibiting the stabilisation of the cation precursor ($\text{UO}_2(\text{OH})_2$)_{ads} or by blocking the O^{2-} anion transfer reaction from the fuel surface (Santos et al., 2006a). Rey et al. (2008) studied the dissolution of UO_2 in the presence of PO_4^{3-} using a flow through reactor. For PO_4^{3-} concentrations of 10^{-4} , 10^{-5} and $10^{-6}\text{ mol dm}^{-3}$, dissolution rates were determined to

be: $1.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$, $6.7 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$, and $2.0 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively. Dissolution rates determined were found to be higher than determined for similar concentrations of carbonate (Rey et al., 2008).

Ram et al. (2013a) investigated the effect of Fe counter anions and demonstrated that the rate of UO_2 dissolution was highest when $\text{FePO}_4/\text{Fe}_3(\text{PO}_4)_2$ and $\text{Fe}(\text{NO}_3)_3/\text{FeO}$ salts were used. In comparison, UO_2 dissolution rates observed when $\text{FeF}_3/\text{FeF}_2$ was used were significantly lower than the rates in all of the other systems tested. Increasing F^- concentration however led to increases in the rate of UO_2 dissolution compared to increasing Cl^- , I^- and Br^- which had minimal effect on the rate of UO_2 dissolution. However, this increase was clearly not due to solution E_h as this decreased with increasing F^- concentration (as would be expected from F^- complexation of Fe^{3+}). The trends observed with increasing F^- concentration were most likely due to (i) changes in the types of $\text{Fe}^{3+}-\text{F}^-$ complexes present at the different F^- concentrations (and the subsequent differences in reactivity of these species) and/or (ii) F^- influencing the equilibrium position of reactions through complexing UO_2^{2+} , which in turn may lead to an increase in the rate of UO_2 dissolution (Ram et al., 2013a). With SO_4^{2-} addition, it was postulated that the decrease in rate and %dissolution that was observed with increasing SO_4^{2-} was most likely caused by the significant decrease in solution E_h that occurred preventing and/or slowing down the formation of the effective Fe^{3+} complexes. The positive influence of F^- addition discussed earlier was negated by the addition of SO_4^{2-} , NO_3^- and PO_4^{3-} . This was attributed to the addition of these anions competing with F^- to complex with the Fe^{3+} and adsorb onto the active sites of the UO_2 surface thereby reducing effective electron transfer between Fe^{3+} and UO_2 (Ram et al., 2013a).

Recently, Youlton and Kinnaird (2013) conducted batch acid tests (solid:liquid 1:1, P_{80} 75–212 μm , $T = 35\text{--}40^\circ\text{C}$, $\text{pH} = 0.97\text{--}2.02$, $E_h = 610\text{--}696 \text{ mV vs. SHE}$, $\text{U\%} 67.71\text{--}89.47$) to determine the influence of gangue mineralogy on uranium leaching. The major gangue minerals present were quartz, plagioclase, K-feldspar, muscovite, chlorite, illite, smectite, laumontite, calcite and pyrite. Only smectite was reported to have a significant negative influence on uranium dissolution which was attributed to reaction between dissolved U and the surface of the smectite.

3.2.2. Effect of substitutional impurities

Many uraninite leaching studies have focussed on the effect of externally sourced impurities on uraninite leaching (i.e. those originating from the dissolution of associated gangue), however there are limited experimental leaching studies focussed on the effect of intrinsic, substitutional impurities. The only studies we are aware of are those related to the effects main impurities in uraninite, Pb and Th (e.g. Finch and Ewing, 1992; Pearcy et al., 1994). According to Finch and Ewing (1992), the role of radiogenic Pb in the oxidation/corrosion behaviour of uraninite is profound with Pb-uranyl hydrates the most common product of oxidative alteration of Pb-bearing uraninites. The effect of highly acidic, oxidative environments on radiogenic Pb in uraninite is unknown. In a recent study Ram et al. (2014) synthesised uraninite containing up to 6 mol% Pb. Results demonstrated a reduced uranium dissolution rate compared to synthetic UO_2 . This was attributed to the formation of a lead sulfate precipitate layer at the surface of the uraninite, slowing down or blocking uranium release. Th-doped UO_2 dissolution studies reported on by Ram et al. (2014) demonstrated approximately 50% U dissolution over a leach period of 90 min under the following conditions; $T = 50^\circ\text{C}$, $[\text{H}_2\text{SO}_4] = 0.15 \text{ M}$, $\text{Fe}^{3+} = 120 \text{ mg/L}$, $\text{UO}_2 = 100 \text{ mg/L}$. The decrease in uraninite leaching from Th-doped UO_2 compared to unsubstituted UO_2 (86% U) under the same conditions was hypothesised to be due to; (a) increased stability and/or (b) the Th could be initially oxidised and mobilised from the structure to form either a secondary Th-bearing phase or passivation layer on the surface of the uraninite (Ram et al., 2014).

3.2.3. Effect of acid concentration

A principal requirement of acid sulfate leaching is the maintenance of a free acid concentration sufficient to keep uranium and ferric ions in solution without dissolving an excessive amount of associated gangue minerals. Maintaining the correct free acid concentration is also important to ensure that re-precipitation of the uranium does not occur. The rate of uranium extraction can be expected to increase with a decrease in pH and increase in free acid concentration.

Eligwe et al. (1982) found that %uranium extraction increased with a decrease in pH from 8 to 4 (over a 4 h leach). Mackay and Wadsworth (1958) reported that the UO_2 dissolution rate increased with increasing acid concentration to a limiting value above which the rate was independent of the acid concentration. Laxen (1971) conducted similar tests on synthetic UO_2 ($\text{Temp } 35^\circ\text{C}$, $\text{H}_2\text{SO}_4 = 3\text{--}40 \text{ g/L}$) and observed a slow increase in rate of dissolution with increasing acid concentration. Jansen van Rensburg (2014) reported that at Rossing Ore conditions ($\text{pH } 1\text{--}2$, $E_h = 617\text{--}697 \text{ mV vs. SHE}$; $\text{Fe}_{\text{TOT}} = 4\text{--}5.2 \text{ g/L}$, $\text{Temp} = 35^\circ\text{C}$, $\text{Solids} = 70\%$), at a terminal acid concentration of 1.2 g/L, uranium extraction decreased by 1.1%. Above an acid concentration of 1.5 g/L, the decrease in uranium extraction was found to be negligible.

Ram (2013) conducted leach experiments on synthetic UO_2 to examine the effect of pH over the range of 0.15–2.0 on dissolution kinetics. Experiments were run for 90 min at 50°C using an initial $[\text{U}^{4+}] = 100 \text{ mg/L}$, an initial $\text{Fe}^{3+}/\text{U}^{4+}$ molar ratio of 4:1 and an initial E_h of 657 mV vs SHE. Results indicated pH had a marginal effect with uranium dissolution declining slightly from ~85% to 82% as the pH was increased from 0.15 to 2.0. These results were in agreement with previous work by Santos et al. (2006b) and Casas et al. (1998) who predicted that the corrosion rate of UO_2 varies with pH over the range of 2–5, but was independent of pH for more acidic conditions. Casas (1998) attributed this to a change in surface coverage by the protonated complex $(\text{UO}_3\text{H})^+$. Nicol et al. (1975) noted that the effect of solution pH on UO_2 dissolution was insignificant below pH 3. Similarly Celeda and Lara (1965) observed no significant change in dissolution rate below pH 2, whilst above pH 2 there was a rapid drop in the dissolution rate due to the hydrolysis of ferric ions to polymerised products.

3.2.4. Effect of temperature

Increasing temperature improves uranium extraction from uraninite (Merritt, 1971). Arden and Beaumont (1950) demonstrated a strong dependence of UO_2 leaching on temperature. They observed a uranium extraction of 16% at 8°C compared to 90% with an increase in temperature to 26°C . Analysis of the data obtained for the tests conducted at varying temperatures with respect to the kinetics of the dissolution process showed that the dissolution of UO_2 most closely followed first order kinetics. Eligwe et al. (1982) and Roshani and Mirjalili (2009) both reported an increase in uranium extraction with an increase in temperature, but at the expense of increased acid consumption. This was attributed to an associated increase in the dissolution of gangue minerals at higher temperatures. Ring (1979) also noted a slight increase in uranium extraction with temperature at the expense of a significant increase in acid consumption — a 50°C leach temperature required 25 kg/t more sulfuric acid than a 40°C leach temperature in order to maintain the pH at 1.5.

Ram (2013) conducted experiments on the dissolution of synthetic UO_2 to examine the effect of temperature on the dissolution kinetics ($\text{temp } 35\text{--}95^\circ\text{C}$; initial $[\text{U}^{4+}] = 100 \text{ mg/L U}$, initial $\text{Fe}^{3+}/\text{U}^{4+} = 4:1$, $\text{H}_2\text{SO}_4 = 15 \text{ g/L}$, particle size $< 75 \mu\text{m}$). observed a significant increase in the extent of uranium dissolution from 33% to 100% over 1.5 h as the temperature was increased from 35 to 95°C (Fig. 10). Analysis of the data showed that the dissolution of UO_2 most closely followed first order kinetics. The activation energy was calculated to be 15.2 kJ/mol with an Arrhenius parameter of 53.6.

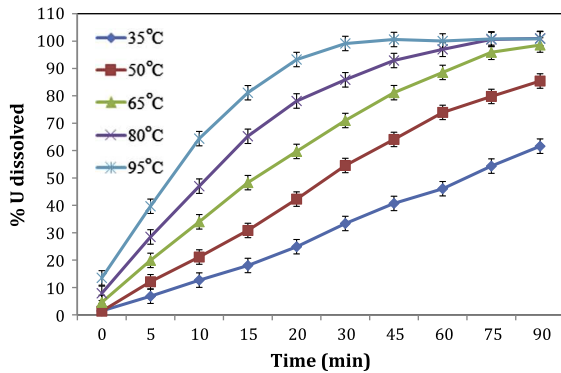


Fig. 10. Percentage U dissolved versus time with varying temperature (35 °C, E_h 637 mV (vs. SHE); 50 °C, E_h 657 mV (vs. SHE); 65 °C, E_h 677 mV (vs. SHE); 80 °C, E_h 697 mV (vs. SHE); and 95 °C, E_h 717 mV (vs. SHE)). Copyright permission received from Ram (2013).

3.2.5. Effect of grain size, liberation, metamictisation and pulp density

The grain size and occurrence of uraninite in an ore are major factors in the leaching performance. Typically uraninite can occur in several size fractions within ore material and its distribution may be heterogeneous in terms of grain size and mineral associations. The accessibility of leaching fluids to uraninite grains is dependent on uranium mineral liberation and fracture formation, which in turn is dependent on the crushed particle size. Where uraninite is coarse (e.g. above 150–200 μm) and forms a significant portion of the matrix, it is relatively simple for leaching process fluids to contact the uranium-bearing phase and thus solubilise uranium. In many uranium ores however, the uraninite is locked inside another mineral (e.g. hematite, clay matrix or carbonates). In this instance, if the gangue phase is not reactive with respect to the leaching solution and there is no leaching conduit to the uranium phase such as a cleavage plane or fracture, then the uraninite will remain unaffected by the process solution.

Grandstaff (1976) noted that the variation in uranium dissolution rate with respect to surface area was first order ($T = 23^\circ\text{C}$, ambient air, distilled water). Roth et al. (2006) observed that the experimental rate constants were inversely proportional to the particle size at constant activation energy (particle size fractions studied included <20 μm , 20–41 μm , 41–72 μm and >72 μm) (Fig. 11). Ram (2013) investigated the effect of particle size on the dissolution of uranium from uraninite using synthetic UO_2 . They noted an increase in uranium dissolution with a decrease in particle size – the increased surface area to volume ratio allowed better reaction between the leach solution and the uraninite. In a follow-up study using natural uraninite samples, Ram et al. (2013c) examined the effect of three different particle size ranges at $T = 50^\circ\text{C}$, $[\text{H}_2\text{SO}_4] = 0.15\text{ M}$, $\text{Fe}^{3+}/\text{U}^{4+} = 4:1$. Results indicated that decreasing the particle size from 75–38 μm to <20 μm resulted in an increase in uranium dissolution from 71% U to 78% U over 1.5 h. It

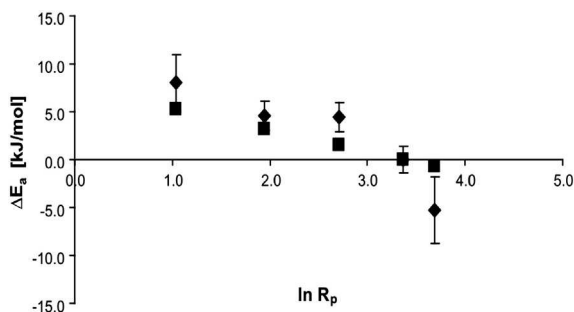


Fig. 11. Experimental (♦) and theoretical (■) relative activation energies for the reaction between UO_2 and MnO_2 plotted for four size fractions of UO_2 powder (>72 μm ; 41–72 μm ; 20–41 μm and <20 μm). Copyright permission received from Roth et al. (2006). License No: 3485091179596.

was unclear however whether the difference was due solely to the particle size effect or partially due to the liberation of trapped uraninite and other U-bearing mineral species encapsulated within gangue mineral phases (Ram et al., 2013c).

Alteration and metamictisation of uraninite, due to radioactive decay, has been investigated previously (Deditius et al., 2007; Finch and Murakami, 1999; Janeczek and Ewing, 1991, 1992b). It has been reported that UO_2 does not undergo metamictisation (Permar and McDonnell, 1980). This is consistent with X-ray diffraction studies on natural uraninite minerals by Ram et al. (2013b) which showed that the UO_2 in samples from three different locations were predominantly crystalline (heating of the samples under inert conditions did not lead to any significant increase in the intensity of the UO_2 diffraction lines hence indicating no significant amount of metamict UO_2 in the samples). However, there are well documented radiation effects that have been observed for natural uraninite at the atomic scale, such as an increase of the unit cell parameter (Janeczek and Ewing, 1991; Turos et al., 1996). Janeczek et al. reported isolated areas of amorphous material may form at the grain boundaries of uraninite, and there may be chemical segregation (e.g., Pb) along the grain boundaries (Janeczek et al., 1996). The aforementioned radiation damage may have an influence on the dissolution of natural uraninite that contains substituted Pb. No direct studies on this have however been reported in the literature.

For economic purposes, pulp density is generally maximised as far as possible in a slurry leaching process as less acid and oxidant are required to obtain required set point concentrations, equipment sizing is affected by ore flow rate and the degree of agitation required to maintain coarse particles in suspension is affected at lower pulp densities. Jansen van Rensburg (2014) conducted studies on the influence of pulp density and reported an increase in uranium extraction with lower pulp densities of 70% solids compared to 75% solids over 13 h (U concentration – 0.24 g/L, pH – 1.6, E_h – 647 mV vs. SHE, Temp 35 °C, $\text{Fe}_{\text{TOT}} = 4\text{ g/L}$). However variation in results on the effect of pulp density on uranium extraction (Demopoulos, 1985; Lottering et al., 2008; Roshani and Mirjalili, 2009) further illustrates the complex nature of uranium leaching and how different variables interact with each other to result in different rates of uranium extraction.

3.2.6. Effect of other uranium bearing minerals

As previously discussed other uranium minerals apart from uraninite are typically present in uraninite bearing ore bodies. The influence of associated uranium bearing minerals such as brannerite (UTi_2O_6), coffinite (USiO_4) and betafite ($(\text{Ca,U})_2(\text{Nb,Ti,Ta})_2\text{O}_7$) on the dissolution of uraninite are also important to consider as they may encapsulate uraninite, and to a lesser extent consume acid and oxidant. Encapsulation of uraninite in the aforementioned minerals would significantly hinder the rate of dissolution of the locked in uraninite as these minerals are not readily leached under the conditions used to leach uraninite. For example studies conducted by Charalambous et al. (2014) on the dissolution of natural brannerite under conditions commonly used to leach uraninite showed that leaching of brannerite was extremely slow under these conditions (between 10 and 15% U dissolved in 1.5 h: Initial U – 100 mg/L; $[\text{H}_2\text{SO}_4] = 0.15\text{ M}$, $E_h = 797\text{ mV}$, $\text{Fe}^{3+} = 3\text{ g/L}$).

4. Alternative acid sulfate leach processes

Other techniques, outside of tank based leaching processes, are also employed to leach uraninite bearing ores including heap leaching, in-situ leaching and pressure leaching. There are a number of pros and cons associated with the different leaching processes apart from the mineralogy of the ore itself, including engineering and scale. The above processes involve both acid and alkaline leaching; however the current review focuses on the major leaching processes that involve acid leaching of uraninite.

4.1. Pressure leaching

Although pressure leaching is primarily used to extract uranium from refractory uranium minerals, such as brannerite and betafite, it can also be used to extract uraninite from refractory host matrices (silicates, titanates) (I.A.E.A. et al., 2006). Pressure leaching involves leaching under high pressure in reaction vessels. The reaction proceeds at temperatures above the boiling point of water, thus creating a vapour pressure inside the vessel. Oxygen is injected under pressure and is used as an oxidant. The higher capital cost required for pressure leaching is offset to some degree by the lower operating costs, which are reduced as no addition of reagents is required. Under such high-temperature and high-pressure conditions, under suitable pH conditions, iron, aluminium, calcium, magnesium etc., form precipitates of hydrated oxides or sulfates which further assist in the formation of free acid and reduce the overall consumption of acid (Bovey and Stewart, 1979; Demopoulos, 1985).

Pressure leach operations have been successfully employed in Canada, South Africa and the U.S.A. (Boydell and Viljoen, 1982; Demopoulos, 1985; I.A.E.A. et al., 2006; James, 1976; Kondos, 1989; Lyaudet et al., 1987; Seidel et al., 1993). At Key Lake mill in Saskatchewan, Canada, severe conditions were required to achieve a high recovery of uranium as the uraninite was encapsulated in a quartz matrix (Kondos, 1989). The ore was leached in a first stage for 2 h at a temperature of 50 to 70 °C, followed by leaching in a second stage with 60 to 100 g/L H₂SO₄ in a series of up to ten autoclaves (3.3 m diameter). The leach vessels were operated at 70 °C and a pressure of 650 kPa for up to 6 h (Kondos, 1989). A process for the pressure leaching of South African ores at elevated temperatures, with air as oxidant, which resulted in the decomposition of pyrite in the ore to ferric sulfate and sulfuric acid, was successfully demonstrated in the 1950s (James, 1976).

4.2. Microbial leaching

Microbial leaching processes for treating uranium ores arose from the need to develop economically viable processes for processing low grade ores (Ehrlich, 1997, 2001; Munoz et al., 1995a,b). The basic chemistry of the chemical leaching with sulfuric acid described earlier also holds for microbial leaching however the key difference is that the rate controlling step involves the ability of microorganisms to dissolve sulfide minerals also present in the uranium deposit. It has been established that the rate of dissolution of sulfide minerals (e.g. pyrite) is considerably accelerated by the use of specific microorganisms (Harrison, 1984; Rawlings, 2002; Rohwerder et al., 2003). These microorganisms can also enhance the oxidation of elemental sulfur, ferrous ion, sulfite ion, and thiosulfate ion. They derive energy for their growth and metabolic functions through oxidation of the sulfides although any ore that does not contain sulfide minerals will require the addition of ferrous sulfate or pyrite for the bacterial activity to occur (Merritt, 1971; Munoz et al., 1995b). The major leaching mechanism which operates during microbial leaching of uraninite is the indirect (non-contact) leaching (Olson et al., 2003). The uraninite dissolution is mediated by the dissolution of sulfides by ferric sulfate originating from the microbial oxidation of Fe²⁺ compounds present in accessory minerals. The micro-organisms need not be in contact with the ore surface to ensure a continuous supply of ferric ions at a suitable concentration, thus facilitating a higher dissolution rate.

$MS + Fe_2(SO_4)_3 = MSO_4 + 2FeSO_4 + S^0$ where M is a bivalent metal.

The process of dissolution of uraninite is thus brought about by the combined actions of the iron-oxidising bacteria reacting with contained sulfides in the ore resulting in them being converted to ferric sulfate and sulfuric acid, both of which serve as leaching agents. The continuous oxidation of recycled acidic ferrous sulfate leach solution through bacterial involvement is a key step in the process.

The effectiveness of microbial uranium dissolution depends on a number of factors including; the properties of the micro-organisms, uraninite chemistry, presence of sulfides, particle size, water availability, temperature, pH, redox potential, oxygen/carbon dioxide supply, and presence of toxic substances (Abhilash and Pandey, 2013; Abhilash et al., 2010; Bhatti et al., 1997; Munoz et al., 1995a). The effectiveness of the bioleaching process also depends on the nature of the host rock. When the host rock is alkaline it is probable that precipitates will be formed which will hinder the natural percolation of the leaching liquid through the heap. This will lower the uranium yield because some pockets of ore won't be attacked. On the other hand, when the host rock is acidic, as in the case of sandstone, the acid consumption by the rock will remain low and the process of uranium dissolution will be favoured. Another important aspect of the host rock is the amount of nutrient available for bacteria. The host rock should supply at least sufficient minerals for the long-lasting growth of the microorganism (Munoz et al., 1995b).

Munoz et al. (1995a) studied the bio leaching of a uranium ore. It was found that presence of pyrite was ideal for bacterial growth. The variables having the most influence on the leaching were pH and temperature. A range of pH tests (1.5–3) determined that a pH of 2.5 was optimal. The temperatures investigated (15–45 °C) determined that a temperature of 35–40 °C was ideal for bio leaching. *Thiobacillus ferrooxidans* seemed to be the most important for bioleaching. Ore alteration played an essential role in the uranium dissolution process. Munoz et al. (1995a) also identified, that the composition and granulometry of the ore, play an important role in its solubilisation and in the percolation of the leaching liquid, respectively. Dwivedy and Mathur (1995) reviewed various physico-chemical parameters, such as the biomass availability of CO₂, particle size, mineralogy of the ore and pulp density influence on the bioleaching rates of uraninite. It was concluded that the pyrite associated with uranium and other sulfide minerals is oxidised to acid ferric sulfate by the *Ferrobacillus* group of bacteria. Mehta et al. (2011) conducted large scale bioleaching trials (using 100 kg and 2 tonne columns). The results obtained showed a maximum recovery of 69% U in 60 days. Guay et al. (1976) investigated the microbiological leaching of low-grade uranium ore using a pure strain of *T. ferrooxidans*. The highest uranium extraction rate derived in this study (57.1 mg/L/day) was realised with a 40% pulp density suspension containing 9.0 g/L of ferrous ion. The highest yield (100%) was obtained with a 5% pulp density suspension (initial mean particle diameter: 0.64 mm) and without addition of iron after ten days of treatment.

4.3. Heap leaching

Hydrometallurgical processing via heap or in-situ leaching, offers an alternative processing route for the treatment of low-grade ores that are difficult and possibly uneconomic to treat using conventional pyrometallurgical technology. The choice between the two methods depends on the amount and location of the low grade ore. In heap leaching the ore is mined and then piled over a collection system. Leach solutions are distributed over the upper surface of the heap and passed downwards through the bed of the ore. The bed may be run-of-mine (ROM) ore or coarse, crushed and agglomerated material (Fig. 12a). Heap leaching has long been an attractive option for the recovery of base and precious metals due to its low capital and operating expenses (Taylor, 2009). Other advantages include reduced crushing/grinding costs, simplified solid/liquid separation, and the lack of a large tailings dam. These advantages apply to the heap leach recovery of uranium, as well.

Uniformity of the distribution of the leaching solution is probably the primary variable for most heap leaching operations, but other factors can also be important (Lunt et al., 2007). Heap leaching is more dependent upon the mineralogy of the ore than conventional agitation leaching operations because of the lower temperatures and the coarser particle size. The distribution of the uranium minerals in

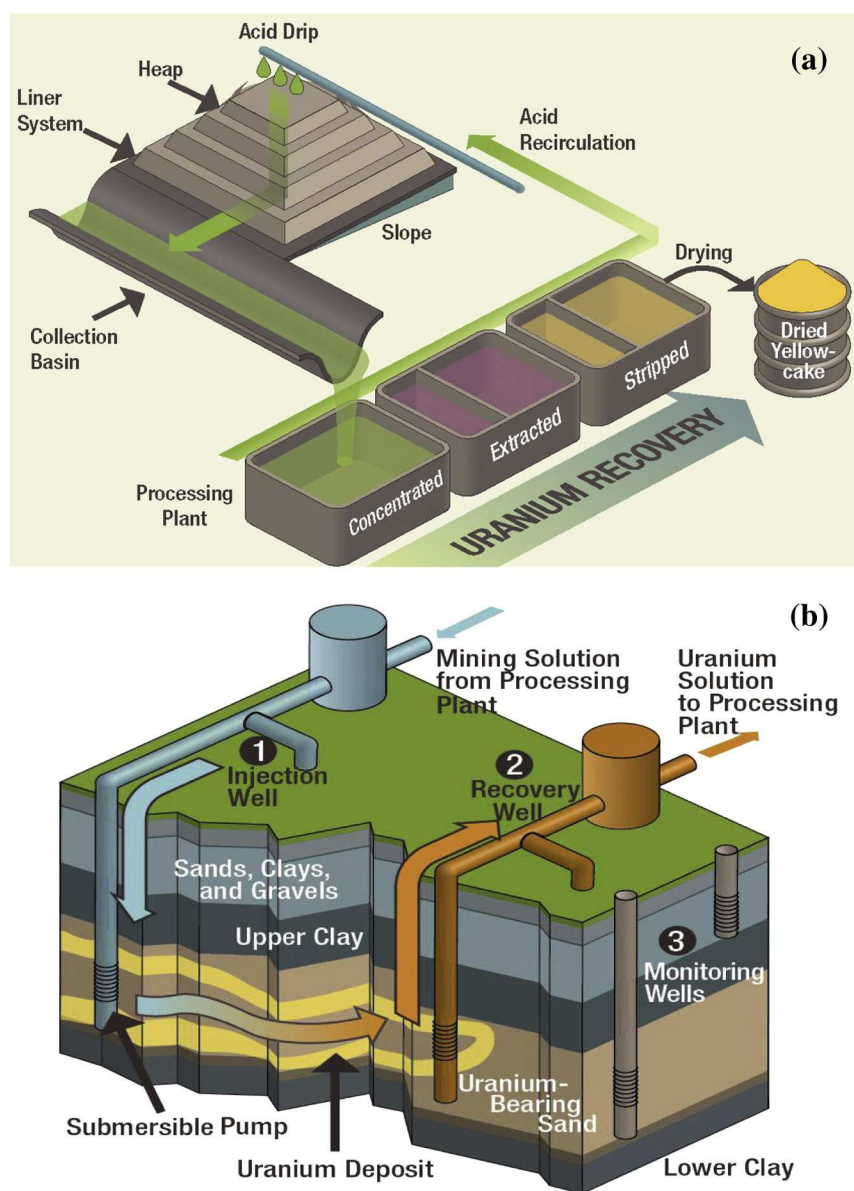


Fig. 12. (a) A typical heap leach setup process; (b) A typical in-situ leach process. Copyright permission received from the Nuclear Regulatory Commission (2013) – <http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1350/>.

the ore must be considered. The type of gangue mineralogy may also be a critical factor (Ding et al., 2013; Ghorbani et al., 2011). Heap leach studies have been employed in Argentina, Canada, France, Spain and Australia (Dhawan et al., 2013; I.A.E.A. et al., 2006; Júnior, 1993; Lunt et al., 2007; Padilla et al., 2008; Seidel et al., 1993). Júnior (1993) investigated the dissolution of uranium ore (0.08% mainly as uraninite), in laboratory and pilot scale. Experiments at semi-pilot scale (particle size – <10 cm, weight – 3 t, H_2SO_4 : 10–100 g/L, $t = 90$ days) and pilot scale (particle size – <10 cm, weight – 850 t, pH – 1.8, $t = 90$ days, irrigation rate – $15\text{--}20 \text{ L h}^{-1} \text{ m}^{-2}$, Fe^{3+} – 5–14 g/L) showed uranium extractions of ~50%. However a complementary sulfuric acid attack, after the bacterial leaching phase, was necessary in order to reach the level (Júnior, 1993).

4.4. In-situ leaching

In-situ leaching (ISL) is usually a chemical process applied to lower grade uraninite-containing ores too deep to justify mining and transportation (Gardner, 1967; Larson, 1978). With ISL, low-grade uranium

deposits (up to 0.1% U_3O_8) can be extracted (Benes et al., 2001). In either the acid or alkali leaching method, fortified groundwater is pumped into the aquifer via a series of injection wells where it migrates through the aquifer leaching the uranium bearing host sand on its way to appropriately placed extraction wells where pumps extract the pregnant leach solution to the surface. Once the solution is returned to the surface, the uranium is recovered in much the same way as in any other uranium minerals processing plant (Fig. 12b).

The principal advantage of ISL in processing low grade ores is that liquid is moved rather than rock. Disturbance at the surface is therefore minimised and environmental impact is further reduced as the tailings associated with conventional mining and milling plant operations are eliminated (Benes et al., 2001). The major disadvantage of the ISL process lies in lower recoveries and risk of groundwater contamination due to uncontrolled infiltration of the leach solution into ground water. ISL can only be applied in situations where the geology is favourable (i.e. permeable sand or sandstones, confined above and below by impermeable strata, and which are below the water table) (Mudd, 2001). In-situ leaching has been employed in the U.S.A. and Russia and recently

in Australia and Kazakhstan (Lunt et al., 2007). Examples of in-situ studies include (Benes et al., 2001; Bommer and Schechter, 1979; Eary and Cathles, 1983; Gardner, 1967; Liddell and Bautista, 1994, 1995a,b; Tweeton and Peterson, 1981).

5. Conclusions

The current review investigates the dissolution of uraninite and compiles information that could contribute to improvements in leaching of this important primary uranium mineral (i.e. improvements in processing efficiency, reduction of waste, conservation of energy & water, and reducing environmental impacts) not withstanding variations in individual ore types across multiple deposits. Specific aspects of uraninite that have been investigated to date include its structure, occurrence and composition, the effects of a number of solution parameters on the dissolution (stability) of synthetic and natural uraninite, and the influence of uraninite composition on dissolution. Studies conducted to date have clearly shown the influence (or lack of influence) of factors such as temperature, acid concentration and particle size on dissolution over a range of conditions. The influence(s) of solution E_h and total Fe concentration, which have been investigated using a range of conditions, are however not as well established, and therefore are worthy of further investigation, particularly with regards to their influence on dissolution rates. Based on what has been reported in the literature, the optimum conditions for leaching of uraninite bearing ores are: a temperature range of 35–60 °C, pH = 1.5–1.8, H_2SO_4 concentration of 15–50 g/L, pulp densities ranging 35–65% w/v solids, residence time between 6 and 8 h, Fe_{TOT} concentration higher than 2 g/L (provided the molar ratio of $Fe^{3+}:U^{4+}$ remains higher than 4:1) and an E_h of over 750 mV vs. SHE. Based on the literature reviewed the influence of foreign ions in leach slurries should also be considered when conducting leaching of uraninite. For example it has been shown that certain foreign ions (i.e. fluoride and sulfate) can improve uranium leach efficiencies under certain conditions whilst having a negative impact under other conditions.

The combined effects of chemical modifications (structure, oxidation, alteration and gangue mineralogy) likely explains the differences often recorded in leaching studies of natural uraninite-bearing ores and makes it essential to consider unique processing conditions for different uraninite ore bodies in order to optimise the extraction of uranium. Therefore it is essential that before any extraction process is considered, detailed ore characterisation studies of pre- and post-leach residues are very important to fully understand the interrelationship between chemistry, mineralogy (ore and gangue), mineral liberation and potential leaching behaviour of uranium.

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