

**The optimisation of stope leaching: a laboratory
investigation into the extraction of uranium from a
low-grade ore**

A thesis submitted for the Degree of Master of Philosophy

By

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Abstract

Nuclear power continues to make an important contribution to energy production in many countries around the world. Uranium mining is the first step in the production cycle of nuclear power. In order to enable low-grade uranium ore bodies to be developed as economically viable resources, low input mining techniques, such as stope leaching, are gaining interest. This thesis presents the results of research undertaken into the optimisation of stope leaching from a low-grade uranium ore.

Stope leaching was simulated in the laboratory by submitting crushed ore samples to successive saturated (flooding) and unsaturated (rest period) cycles. Experiments were carried out over a 52 week period using seven different protocols. The effects of rest period and lixiviant composition on uranium extraction rates were investigated. Rest period was varied by flooding at weekly, twice weekly, 2 weekly and 4 weekly intervals. Four different lixiviants were investigated, tap water, Fe(III) sulfate, a nutrient solution and recycled leachate.

Maximum uranium extractions over 52 weeks were: 57.7% for Fe(III) sulfate lixiviant with a 2 week rest period and 57.4% for tap water with a 4 week rest period. The introduction (via the lixiviant) or development (via oxidation of accessory pyrite) of low pH and Fe(III) and sulfate-rich interstitial water is thought to have provided conditions conducive to uranium oxidation and dissolution. The 4 week rest period is considered to have provided sufficient time for microbially assisted pyrite oxidation to develop similar conditions in the interstitial water as were provided by the addition of a Fe(III) sulfate lixiviant. All other protocols lead to less than 35% uranium extraction. Shorter rest periods did not allow time for sufficient pyrite oxidation to occur and the addition of a nutrient solution buffered pH which did not favour uranium dissolution. These findings have significant implications for low-grade uranium recovery by demonstrating that extraction achieved through the use of costly oxidising agents can be attained, in the same time frame, by using tap water and decreasing the number of cycles.

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1 Introduction

The demand for energy worldwide is ever increasing as the population continues to rise and the economies of less-developed countries (LDC) expand. Despite this the majority of the world energy market is dependent on non-renewable, but low cost fossil fuels (Yuksel and Kaygusuz, 2011). The terms “Renewable Energy” and “Sustainable Energy” are often used interchangeably; however, the term sustainable energy has a much broader application and can include renewable sources as well as non-renewable sources. Renewable sources of energy include hydro, solar, wind, tidal and geothermal power as well as the use of biofuels. Although nuclear power is considered to be a non-renewable energy source, as there is a finite supply, it is sustainable due to its ability to provide energy without environmental detriment (WNA, 2011a). As the demand for sustainable energy resources continues to grow, nuclear power is being utilised by many countries and governments. According to the World Nuclear Association (WNA) (2013) around 13% of the world’s electricity is generated using nuclear energy and this is set to increase in the future as a number of countries have announced nuclear energy targets including China, the United States, Japan, Russia and India (IEA, 2011).

Uranium mining is the first step in the production chain of nuclear power. Over half (53%) of the global uranium is produced by 4 countries; Kazakhstan, Canada, Australia and America (Yan et al, 2011) and production is very concentrated: the largest five uranium mines account for 43% of the global uranium production (WNA, 2011b). In 2010, 78% of the global uranium consumption was provided through mining of new or primary

sources while the remaining 22% was gained from secondary sources such as civil stockpiles, re-enriched depleted uranium tailings, decommissioned nuclear weapons and reprocessed natural and enriched uranium (Conde and Kallis, 2012). As the global grade of uranium mineral deposits are decreasing more inputs (energy, water, labour, capital) are required for extraction and more waste is produced (Prior et al, 2012). Thus the interest in low energy, low cost mining techniques is increasing as low-grade uranium deposits are being explored as viable resource options.

1.1 Thesis aims

The overall aim of this work was to identify the factors which influence the release rate of uranium from a low grade ore during stope leaching. This includes exploring areas of time and leaching frequency as well as the effect of different types of lixiviant. Stope mining was of particular interest as a low energy mining option and the test protocols were designed around a proposed mining method of stope flood leaching every 2 weeks.

The objectives were to undertake 1 year column leaching experiments on low-grade uranium ore to determine the following:

- i. to undertake a study on the effect of rest period on uranium extraction, including a two week control protocol, a double flush protocol, a weekly flush protocol and a 4 weekly flush protocol;
- ii. to investigate how the presence of Fe(III) sulfate influences extraction rates;
- iii. to determine whether the use of a nutrient solution has a positive effect on the uranium dissolution process
- iv. to identify the effects of recycling the leachate.

1.2 Organisation of the thesis

Chapter 2 – Literature review: This chapter presents literature concerning geological classifications of uranium, the chemistry of uranium extraction, uranium mining techniques and factors relating to the dissolution of uranium.

Chapter 3 – Methodology: This chapter describes the analytical techniques used during the test work and experimental protocols developed for this investigation.

Chapter 4 – Results: The results of the 1 year column leaching experiments are presented including the water quality parameters and the U, Fe and SO₄ release for each protocol.

Chapter 5 – Discussion: The data presented in the results is discussed in this chapter along with discussion of the methodology.

Chapter 6 – Conclusions: This chapter summarises the conclusions reached during this thesis and gives suggestions for further work which could improve the understanding of uranium oxidation and extraction for this ore.

2 Literature review

This literature review chapter serves to introduce and discuss the many factors that influence and control the extraction of uranium from its ores. Due to the multitude and varying aspects associated with uranium mining and extraction, the discussion of uranium minerals was focused on non-carbonate uranium minerals.

The occurrence of uranium with different designated geological classifications are described along with the significance of primary and secondary ore deposits. Next the associated mineralogy of uranium is presented and the importance of thorough mineralogical investigation highlighted. Uranium valence states and the chemistry of uranium dissolution is addressed and the need for oxidation from U(IV) to U(VI) is shown.

Mining techniques employed for the extraction of uranium are presented and the relative advantages and disadvantages of each technique are discussed. The growing interest in low grade ore mining is explored with a focus on the method of stope leaching.

Finally interacting factors, relating to the dissolution of uranium, are explored. There is a focus on the presence of an oxidising agent and the area of bioleaching, the use of a nutrient medium to enhance bacterial growth and the effect of rest period and leach frequency on uranium extraction.

2.1 Uranium geology, mineralogy and geochemistry

It is widely acknowledged that uranium is abundant in the Earth's crust, with an average concentration of 0.0003 – 0.0004%, making it more abundant than gold, silver and mercury and about equal to tin (Cordfunke, 1969). In nature uranium is never found in an elemental state and there are well over one hundred known uranium minerals as it readily forms chemical combinations with other elements. Uranium occurs in nature as a mixture of the isotopes ^{238}U , ^{235}U and ^{234}U (Table 2.1) and was discovered in 1789 by M. H. Klaproth.

Table 2.1 Naturally occurring isotopes of uranium. (Adapted from Cordfunke, 1969)

Isotope, mass	Atomic percentage	Half-life, years
238	99.276 ± 0.0005	$4.51 \cdot 10^9$
235	0.718 ± 0.0005	$7.09 \cdot 10^8$
234	0.0056 ± 0.0001	$2.35 \cdot 10^5$

During his lifetime Klaproth was unable to isolate the metal itself but did isolate the nitrate, sulfate and acetate of uranium as well as the potassium and sodium uranates. In 1841, the French chemist, E. M. Peligot became the first to prepare uranium as a metal as well as document some of the elements more important properties. Until the discovery of radioactivity by Becquerel (1896) the research into uranium as an element was of a purely academic nature and until 1942 no mining operations were carried out primarily for the production of uranium. (Cordfunke, 1969; Grainger, 1958)

2.1.1 Geology

There is some disagreement within the literature about the classification of uranium ore deposits. Older literature, such as Cordfunke (1969) and Grainger (1958), only distinguish between uranium ore as either primary or secondary ore deposit types. They express primary minerals as those deposited from molten rock within the earth's crust appearing

predominately as pegmatites, formed during terminal stages in the solidification of an acid magmatic intrusion. They go on to describe secondary ore deposits produced from the primary minerals as a result of weathering or hydrothermal action which leads to a wide range of secondary minerals. Secondary minerals are often brightly coloured as a consequence of the oxidation of uranium that takes place in the transition from a primary to a secondary ore deposit, for example U(VI) minerals are bright yellow in colour. Although Cordfunke (1969) offers more detail about secondary uranium deposits, explaining the three types of deposit that are found in Canada (conglomeratic, veins and pegmatitic) there is no further explanation and no other deposit types are mentioned.

The International Atomic Energy Agency (IAEA) in their 1993 report *Uranium Extraction Technology* classifies uranium resources with two systems: the geological environment in which they occur, and the level of confidence that they exist combined with the recovery economics of the resource. The majority of the world uranium resources can be assigned to one of the 15 deposit types laid out by the IAEA. The resources are assigned depending on their geological setting and arranged in descending order according to their approximate economic significance. The geological types are presented in Table 2.2, a brief description of the deposits has also been included.

A report by Lally and Bajwah (2006) about the uranium deposits of the Northern Territory in Australia described the IAEA classification scheme as “far from ideal, since it does not account for different geological settings of deposits formed by the same overall process”. Therefore they created a new designation scheme, with broader groupings, which incorporated the IAEA uranium deposit classifications but also accounted for the uranium mineralisation processes interpreted to be involved in their formation (Table 2.3).

The geology of a uranium deposit plays a significant role in the mineralisation of the deposit and the subsequent uranium oxidation state and extractability (Geometallurgy).

Thus, from a mining point of view the IAEA Technical report No. 359 (1993) states that uranium ore bodies can be roughly classified into two categories:

- a) Sedimentary ore bodies – present as subhorizontal layers of varying thickness from tens of centimetres to tens of meters.
- b) ‘Vein type’ ore bodies – often subvertical, with similar thickness variations to those found in sedimentary ore bodies.

2.1.2 Mineralogy

The mineralogy of any resource is of paramount importance due to the role that it plays in determining the extraction and recovery method of the mineral being investigated (IAEA Technical Report, 2000). The ‘availability’ of a mineral for extraction is influenced by the mineralogy and includes:

- The grinding requirements to expose (liberate) the mineral of interest;
- The potential for any physical improvement in the mineral concentration of the ore, also known as beneficiation;
- The preferred lixiviant system (e.g. acidic, alkaline dependent upon the gangue materials) and potential level of reagent consumption;
- The probable composition and concentration of the leach liquor.

These factors are also known as the processing factors which are influenced by the mineralogy of the ore (IAEA Technical Report, 1990).

Of all the known minerals in the earth’s crust, approximately 5% contain uranium as an essential structural constituent (Mandarino, 1999). According to the International Atomic Energy Agency (IAEA Technical Report, 1990) there are at least 185 different uranium minerals which have been identified in the literature. These included oxides, silicates,

Table 2.2 Geological deposit type as designated by IAEA

Deposit type	Description	Deposit type	Description
1 Unconformity related deposits	Occurs spatially close to major erosional unconformities. Ores in some of these deposits contain additional elements such as As, Ni, Mo and traces of Au.	9 Volcanic deposits	Strata bound and structure bound concentrations of uranium in acid volcanic rocks. Uranium is usually associated with Mo, F, etc.
2 Sandstone deposits	Mainly contained in sedimentary rocks that were deposited under fluvial or marginal marine conditions. Deposits can contain Mo, Se, Cu and V, which are occasionally recovered as by- or co-products.	10 Surficial deposits	Broadly defined as uraniferous sediments, usually very young to recent age that have not been deeply buried and may have been calcified to some degree. Additional environments included in this deposit type are peats, bogs and karst caverns plus pedogenic and structural fills.
3 Quartz pebble conglomerate deposits	Deposits are restricted to Lower Proterozoic rocks, formed under oxygen deficient conditions.	11 Metasomatite deposits	Uranium concentrations in metasomatites commonly intruded by microcline granites.
4 Vein deposits	Uranium minerals fill fissures, cracks, breccias etc. in the rock. The uranium is generally associated with other elements, such as Ag, Ni, Co, Bi, Fe and Mo. As a consequence of the variable geometric dimensions of the deposits there can be significant dilution of the ore mined.	12 Metamorphic deposits	Deposits generally occur in metasediments and/or metavolcanics, usually without direct evidence of post-metamorphic mineralisation
5 Breccia complex deposits	Developed in Proterozoic continental regimes during anorogenic periods. Uranium mineralisation occurs immediately above granitic basement complexes and is sometimes associated with Cu, Ag and Au.	13 Lignite	Generally classified as an unconventional uranium resource, occurs in lignites, and in clay and/or sandstone immediately adjacent to lignites.
6 Intrusive deposits	Includes those deposits associated with intrusive or anatectic rocks of different chemical compositions.	14 Black shale deposits	Also considered as an unconventional resource, low concentrations of uranium and other elements occur in black shale.
7 Phosphorite deposits	Deposits contain low concentrations of uranium in fine grained apatite. Usually uranium recovery is as a by-product dependent on the production of phosphoric acid.	15 Other types of deposits	All other deposits which cannot be classified under another heading.
8 Collapse breccias pipe deposits	Occurs in circular vertical pipes filled with down dropped rock fragments. Other elements which can be present are Mo and Ag.		

Table 2.3 Geological deposit designation as classified by Lally and Bajwah (2006)

Uranium transport/ precipitation conditions	Deposit type
Surface processes / syn- sedimentary	Surficial deposits
	Quartz pebble conglomerate deposits
	Phosphorite deposits
	Lignite
	Black shale deposits
Diagenetic	Sandstone deposits
Diagenetic-hydrothermal?'	Unconformity related deposits
	Vein deposits
	Collapse breccias pipe deposits?
Magmatic-hydrothermal	Breccia complex deposits
	Volcanic deposits
	Metasomatite deposits
	Vein deposits
	Intrusive deposits
Metamorphic-hydrothermal	Metamorphic deposits

The '?' is thought to indicate uncertainty of the authors regarding the designation of a deposit. (Adapted from Lally and Bajwah, 2006)

phosphates, sulfates, carbonates and molybdates; however, it is rarely possible to ascribe the whole uranium content of an ore to a specific uranium mineral and often the ore is found to be a mixture of minerals. Additionally, techniques used for chemical analysis only report the total uranium content of a mineral and do not indicate the fraction of uranium which can be recovered economically. In cases where it is uneconomical to extract the uranium, uranium bearing minerals are described as refractory; indeed in some rocks more than 80% of the uranium can be refractory.

There are many references which provide details of the structural and chemical diversity of uranium bearing minerals, including *Bowell et al (2011)*; *Mandarino et al (1999)*; IAEA Technical Report No. 313 (1990) and IAEA Technical Report No. 284 (1988). Table 2.4 provides the mineral names and chemistry of important ore grade uranium minerals. The minerals have been grouped together according to their mineral type as this can have a significant effect on the reagent requirements when leaching uranium ores.

2.1.2.1 Valency states of uranium

Langmuir (1997) explains that uranium is found in a number of oxidation states; 4+, 5+ and 6+. Of these oxidation states, uranous [U(IV)] and uranyl [U(VI)] are the most important in nature. Uranium (IV) and uranium (VI) can also be referred to as tetravalent and hexavalent uranium respectively. *Bowell et al (2011)* explains that amongst metallic ore elements uranium is unusual, as significant portions of the ore can host uranium in different valencies. Typically uranium (IV) minerals occur as primary minerals and require oxidation in order for dissolution of the mineral and liberation of the uranium into solution to occur. Although uranium (VI) minerals can be found in some primary ores they are more often found in secondary ores as a result of alteration and oxidation of primary

Table 2.4 Chemistry of important ore grade uranium minerals (Adapted from Bowell et al (2011) and IAEA Technical Report (1990))

Mineral	Formula
Oxides	
Fourmarierite	$\text{Pb}(\text{UO}_2)_4\text{O}_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$
Pitchblende*	Amorphous UO_2
Schoepite	$(\text{UO}_2)_4\text{O}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$
Uraninite*	UO_2
Urano-Iron Oxides*	Fe-U-oxide
Molybdates	
Umohoite	$(\text{UO}_2)\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
Phosphates	
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$
Meta-autunite	$\text{KCa}(\text{H}_3\text{O})_3(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_4 \cdot 6\text{-}8\text{H}_2\text{O}$
Phosphuranylite	$(\text{H}_3\text{O})_3\text{KCa}(\text{UO}_2)_7[\text{O} \text{PO}_4]_4 \cdot \text{H}_2\text{O}$
Saléeite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
Torbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{-}12\text{H}_2\text{O}$
Vanadates	
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1\text{-}3\text{H}_2\text{O}$
Francevillite	$(\text{Ba,Pb})(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$
Metatyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{-}5\text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{-}8\text{H}_2\text{O}$
Silicates	
Coffinite*	$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
Sklodowskite	$\text{Mg}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$
Uranophane	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Niobates-Tantalates-Titanates (multiple oxides)	
Betafite	$(\text{Ca,U})_2(\text{Nb,Ti})_2\text{O}_6\text{OH}$
Brannerite*	$(\text{U,Ca,Y,Ce,La})(\text{Ti,Fe})_2\text{O}_6$
Davidite	$(\text{La,Ce})(\text{Y,U,Fe})(\text{Ti,Fe})_{20}(\text{O,OH})_{38}$
Unknown	
Boltwoodite	$\text{HK}(\text{UO}_2)\text{SiO}_4 \cdot 1.5\text{H}_2\text{O}$
Margaritasite	$(\text{Cs,K,H}_3\text{O})_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$
Orthobrannerite	$\text{U}_2\text{Ti}_4\text{O}_{12}(\text{OH})_2$

* Primary and secondary mineral phases found in the material used in this study.

ore bodies, these minerals are readily soluble and thus require less ore pre-treatment (Bowell et al, 2011; Langmuir, 1997).

2.1.2.2 Common minerals found with uranium

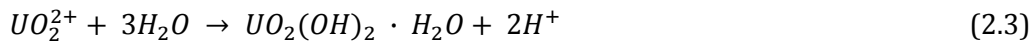
As shown in Table 2.4 there are various other elements which are commonly associated with uranium bearing minerals. Brannerite group minerals display complex chemistry and uranium can be found associated with thorium, titanium, rare earth elements, iron and alkaline metals (Bowell et al, 2011). Copper, magnesium, potassium and sodium are often found with uranium minerals whilst gold, yttrium or rare earth elements found with uranium can result in a low grade ore body being viewed as an economically viable resource (Sapsford et al. 2012; Kimberley et al. 1980; Macnaughton et al. 1999; Lottering et al. 2008).

2.1.3 Geochemistry

The oxidation state of uranium strongly influences its solubility and mobility; U(VI) complexes are much more soluble and mobile than U(IV) complexes which generally need to be oxidised before dissolution can occur (Luo et al. 2007).

U(VI) complexes are readily solubilised in acidic solutions forming a uranyl cation (Equation 2.1) (Macnaughton et al. 1999). Under mildly acidic conditions the uranyl cation will, in the presence of sulfate, form a soluble uranium-sulfate complex (Equation 2.2). If the solution containing the uranyl cation has a higher pH (pH 5 – 6 or greater) hydrolysis is favoured and an insoluble precipitate is formed (Equation 2.3) (Tomažič et al, 1969; Kirishima et al, 2004; Sapsford et al. 2012).





The extraction of uranium described in Equation 2.1 – 2.3 does not involve any oxidation but is simply the dissolution of U(VI) from a solid state into a soluble form. The pH of the solution is key to the solubilisation of U(VI) which is favoured by acidic conditions and alkaline conditions (especially in the presence of dissolved carbonate).

U(IV) mineral phases require an initial oxidation stage in order to solubilise the uranium (Langmuir, 1997). Where pyrite is present it can be oxidised *in situ* producing Fe(II). This in turn can be oxidised to Fe(III) which acts to oxidise U(IV) according to Equation 2.4 (Ring, 1980).



Once U(IV) has been oxidised to U(VI) the same chemical processes occur as described by Equations 2.1, 2.2, or 2.3, depending on the solution pH. Fe(III) is regenerated by oxidation of Fe(II) – discussed in section 2.4.1.1.

2.2 The deposit being investigated for this study

Areas of the Elliot Lake district of Ontario, Canada were mined extensively from 1956 to 1996 by Rio Algom and Denison Mines (Campbell et al., 1987; Downes, 1967). During this time the cut-off grade for the Denison Mine was 0.4kg U/t (0.04%). In total 138, 500 tonnes of uranium metal was produced from the Elliot Lake deposits with an average grade of about 0.09% U₃O₈ (Cox et al. 2012).

The site for the Eco Ridge Mine, an ore sample of which is being investigated for this project, lies 11 km east of the City of Elliot Lake, Ontario, Canada. Although it forms part of

the Elliot Lake area no mining or waste disposal has occurred in the proposed Eco Ridge mine site (Cox et al. 2012). On site, the uranium deposit has been determined to be contained within quartz-pebble conglomerate beds and exists in two distinct zones. The proposed mine is located at the south outcrop of the uraniferous conglomerate beds of the Quirke Syncline and the uraniferous quartz-pebble conglomerates are enclosed within quartzite beds (Cox et al. 2012; Campbell et al., 1987).

2.2.1 Elliot Lake area geology

The Elliot Lake district lies within the Southern Province of the Canadian Shield, which includes the clastic sequence referred to as the Huronian Supergroup, deposited in the Early Proterozoic. The source rocks are believed to be pegmatic granite located to the north of the area. Uranium was released from the uranium-rich granitic rocks due to the effect of weathering. It was subsequently transported to the site as uraninite, resulting in paleoplacer (detrital) deposits being formed (Cox et al. 2012; McMillan, 1977). McMillan (1977) categorises the Elliot Lake district as a detrital deposit, formed as secondary concentrations, which occurs in three 'zones', termed the Quirke, Nordic and Pronto. This categorisation is corroborated by Kimberley, et al. (1980) who reported that the Middle Precambrian atmosphere was compatible with purely physical concentration of tetravalent (U(IV)) uranium minerals.

The Elliot Lake deposits occur in pyritic quartz-pebble conglomerates, within an envelope of gangue (a poorly sorted, coarse-grained feldspathic quartzite matrix) (Downes, 1967). The ore body was deposited in palaeo-stream channels along with pyrite and other heavy minerals. Uraninite and brannerite are the main ore minerals. The Quirke zone occurred when the Huronian rocks folded to form a shallow, gently folded syncline, which generally dips from 10° to 40° and is about 1.5 by 7 miles in size. There is some disagreement about the direction of the Quirke zone; Cox et al. (2012) documents that the Quirke Syncline is westward plunging whereas McMillan (1977) reports that the Quirke zone dips south.

Uranium grade increases with increasing pyrite content and pebble size with pebble size decreasing ‘downstream’ in the channels (Cox et al. 2012; McMillan, 1977). Downes (1967) reports that the ratio of pebbles to matrix is approximately 2:1 and the matrix consists principally of quartz, sericite, feldspar, chlorite, pyrite, pyrrhotite, with the uranium bearing minerals brannerite, uraninite and monazite, and minor amounts of coffinite, pitchblende and uranothorite. The uranium bearing minerals present in the Elliot Lake have been summarised in Table 2.5.

Table 2.5 Mineralogy of the ore used for this study (As per Cox et al. (2012), adapted from Bowell et al. (2011) and IAEA Technical Report (1990))

Mineral	Formula
Uraninite	UO ₂
Brannerite	(U,Ca,Y,Ce,La)(Ti,Fe) ₂ O ₆
Pitchblende	Amorphous UO ₂
Coffinite	U(SiO ₄) _{1-x} (OH) _{4x}
Urano-Iron Oxides	Fe-U-oxide

Historical mining methods employed at the Elliot Lake deposits involved underground room and pillar techniques (also known as stope leaching) as the standard mining practice (Campbell et al. 1985). This technique is described in detail in section 2.3.3.

2.3 Methods of uranium mining

Uranium mining can be categorised as conventional mining or *in situ* mining, also known as *in situ* leaching. The term conventional mining covers open pit and underground mining methods (IAEA Technical Report, 2000). The mining technique chosen is usually based on the economics of the method once the cost of site development, mineral extraction, ore removal, safety precautions and environmental regulations have been taken into account (Hustrulid, 1996; IAEA Technical Report, 2000).

2.3.1 Conventional mining

Open pit mining, sometimes referred to as surface mining, is considered to be more efficient than underground mining owing to the fact that 95% uranium recovery is achievable (IAEA Technical Report, 2000). Other advantages include higher productivity, easier dewatering and safer mining conditions however; the environmental impact of open pit mining is great, often leaving scars on the landscape (Figure 2.1) or requiring a large amount of site restoration at the end of the project (IAEA Technical Report, 2000). The ore to waste stripping ratio is significant as it is a limiting factor for open pit mines and is directly related to the depth of a uranium deposit.



Figure 2.1 Aitik open pit copper mine, Sweden (courtesy of Geroni, J. N., 2009).

Although there is no fixed rule to determine which mining method to apply to a uranium ore body an IAEA Technical Report (1993) states that at deposit depths of 50 to 200m or more it becomes uneconomical to utilise open pit mining techniques and it is necessary to

adopt underground mining. Conventional underground mining requires the development of mine shafts for equipment to access the ore and the removal of the ore to the surface. As the volume of near-surface mineral resources becomes depleted, underground mining is predicted to account for an increased share in worldwide mineral production in the future (Lineberry, 1996). The geology and orientation of a deposit make a difference as to what type of mining technique is utilised. The application of underground mining to uranium ore has additional restrictions surrounding the excavation of radioactive material and it is necessary for mining methods to be adapted to address the health and environmental concerns which arise (IAEA Technical Report, 2000).

Both methods of conventional mining have high set up costs and require a large amount of infrastructure to be developed as there must be access for the vast quantities of mining machinery as well as process mill plants and storage areas for the ore prior to treatment and for the waste gangue material after the uranium has been extracted. As a result of this, depending on the grade of the ore it is not always economically feasible to mine any mineral using conventional techniques.

2.3.2 *In situ* leaching/*in situ* mining

In situ leaching (ISL) or *in situ* mining (ISM) as it is also known, offer advantages over conventional mining techniques because it eliminates the need for crushing, grinding and hauling systems. This in turn results in fewer workers on the mine site and safer operating conditions making the overall operation of the site far more economical. Another major advantage of ISL is that all operations are carried out underground and so disturbance at the surface is minimal (IAEA Technical Report, 2000; IAEA Technical Report, 1993).

In situ leaching (ISL or ISM) is defined by the IAEA Technical Report No. 359 (1993) as:

The ore is not moved from its geological setting. The leaching solutions are forced through the bed, usually in a horizontal direction. Typically vertical injection wells are used to inject the leaching solutions. The pregnant leach liquors are recovered by production wells and brought to the surface for processing.

Although ISL has potential as a low cost alternative for uranium extraction it is limited in its application (Rojas, 1987). ISL can only be carried out in a sandstone deposit, below the water table and the deposit must be confined by clay or another impermeable mineral. Recovery of uranium using ISL often involves the complex interaction of hydrology, mass transport and chemical kinetics and the interaction between the leaching solution and the gangue material must be minimal to avoid undesirable secondary reactions (Rojas, 1987; IAEA Technical Report, 1993). The necessary remediation and monitoring of an ISL site after mining has ended can be a costly activity and thus can represent a significant proportion of the overall mine expenditure as the process can take several years to accomplish (IAEA Technical Report, 2000).

There is some confusion in the literature about the exact definition of *in situ* mining (ISM). ISM is also described by Rojas (1987) as solution mining however, Schlitt et al (1996) in the SME Mining Engineering Handbook group solution mining in the chapter 'Surface and Hybrid Mining: Aqueous Extraction Methods' where there are two sub-sections with solution mining in the title, 'Solution Mining: Surface Techniques' and 'Solution Mining: *In Situ* Techniques'. They also state that, "*In situ* solution mining is a true mining technique" as opposed to the surface techniques which must be operated in conjunction with a method of conventional mining. The IAEA Technical Report No.359 (1993) does not mention ISL with the conventional mining techniques in 'Mining Technology', instead ISL is not mentioned until the chapter entitled 'Leaching'. Whereas the IAEA Technical Report No. 1174 (2000) discusses ISL in the 'Mining' section along with the conventional uranium mining methods.

2.3.3 Stope leaching

Stope leaching (U.S. Bureau of Mines, 1994) is a uranium mining method that was used historically to mine low grade uranium ore in the Elliot Lake area of Canada until production ended in 1983 (Campbell et al, 1985). This extraction technique can also be referred to as *in situ* stope leaching (Sand et al, 1993; Sapsford et al, 2012), in-place systems (Schlitt, 1996) and in-place leaching (Campbell et al, 1985; IAEA Technical Report, 1993). For the sake of consistency the term stope leaching will be used exclusively throughout the remainder of this thesis. Incidentally, similar to *in situ* leaching, the 1993 IAEA Technical Report No. 359 refers to stope leaching in the ‘Leaching’ section and not ‘Mining Technology’.

Schlitt (1996) describes the leaching technique as an “intermediate between surface heap and dump leaching and *in situ* mining”. The description seems apt as the ore is rubblised or broken up underground (hence *in situ*) and then leachate solution is either flooded into or continuously percolated over (hence surface heap and dump leaching) the rock. The pregnant leach solution whether produced through continuous percolation or flooding of the stope is collected at the base of the stope and pumped back to the surface for treatment. Often the ore is rubblised by blasting and therefore it is necessary to remove a portion of the rock, approximately 20% - 30%, for surface extraction (Sand et al. 1993). A diagram of the stope leaching operation at Ilba Mine, Romania has been shown in Figure 2.2.

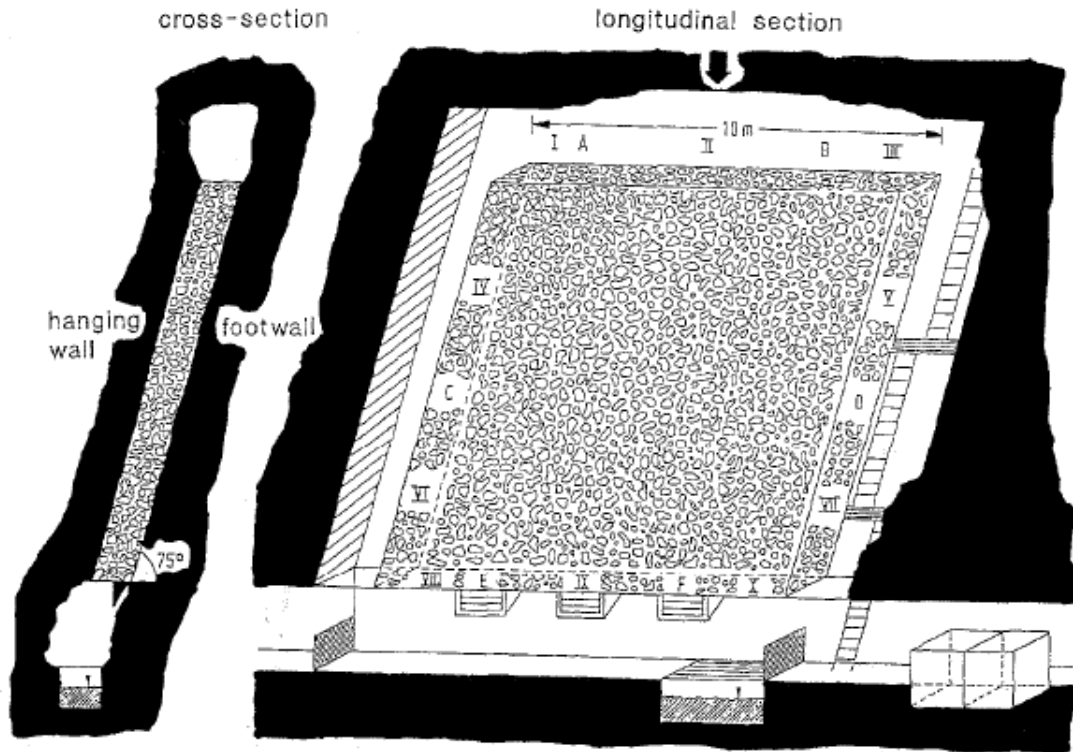


Figure 2.2 Ore body of the *in situ* stope leaching at Ilba Mine, Romania (Sand et al. 1993)

Stope leaching has been used on a number of mine sites in the past to extract uranium; according to Schlitt (1996) however, the extraction of copper seems to have been the most successful application for this process. As with all leaching activities the process is very site specific and acidic, alkaline or inoculated leaching solutions can offer a means to increase extraction at relatively low costs. Sand et al (1993) found that through the use of an inoculum, leaching of the ore body occurred without any lag phase. Low cost bacterially assisted stope leaching of uranium in Canada in 1984 was possible because of the pyrite content of the ore (5 – 7%) which provided an energy source for the bacteria (Campbell et al, 1987; IAEA Technical Report, 1993).

The particle size of the blasted or rubblised ore plays a significant role in extraction rates from stope leaching. Downes (1967) observed that the extraction of uranium reduced significantly as the particle size of the ore being leached increased. He predicted however,

that by increasing the duration of leaching it would be possible to raise the amount of uranium extracted and hypothesised that it was possible because the bacteria present in the mine water was able to penetrate into the particles of ore (Ghorbani et al. 2011; Liddell, 2005; Lizama et al. 2005).

The difficulty in getting a uniform distribution of leach solution throughout the broken rock mass within a stope has been highlighted by Schlitt (1996) and Sand et al (1993). Sand et al (1993) observed that a considerable part of the ore within a stope can remain unleached, with satisfactory leaching only occurring in the upper fraction of the broken rock mass causing a reduced metal output. There is also the potential for preferential flow paths problems similar to those experienced in heap leaching and, on a much smaller scale, humidity cell testing (Sapsford et al. 2009; Schlitt, 1996). Suggested methods to improve recovery are improved ventilation, stope flooding (as used by Denison mines) and, in extreme cases, injection wells being drilled from the surface (Schlitt, 1996; Sand et al, 1993).

As the worldwide ore grade of uranium continues to diminish stope leaching could offer an alternative to the other, more energy and resource intensive, extraction options. The optimisation of the duration of the leach and investigations into the best leaching solution could make slope leaching a viable option for some low grade ore deposits.

2.4 Controls on leaching

There are numerous interacting factors which affect the rate of leaching metals from their ore. These controls have varying levels of significance depending on the mineral of interest. The interactions of these factors are complex and cannot be assumed to be independent of each other; the mineral composition along with the environmental and operational factors must be taken into account (Muñizo et al, 1995a). Table 2.6 and Table

2.7 provide a summary of the different factors which have an effect on the rate of leaching; they are not to be considered an exclusive list.

This study focuses on the factors known to affect the rate of extraction. As the outline of the project was to investigate the optimisation of the rate of extraction of a low grade ore the following areas were focused on: the presence of an oxidising agent, rest period between leaching and a source of nutrients. The specifics of these areas will be explored in more detail in the rest of this chapter.

2.4.1 Use of a reagent to enhance extraction

The use of an acid or alkaline reagent to enhance the dissolution of uranium from its ores is a widely used technique in the mining industry (Mackay and Wadsworth, 1958). Uranium is commonly solubilised commercially, as U(VI) (Equation 2.2), with sulfuric acid (H_2SO_4) or sodium carbonate (Na_2CO_3)/sodium bicarbonate (NaHCO_3). The type of reagent used depends on the nature of the uranium mineral. Alkaline leaching with either Na_2CO_3 or NaHCO_3 is considered to be a more economical means of uranium extraction where the ore contains more than 7-9% of carbonates due to the excessive acid consumption experienced with high carbonate ores (IAEA Technical Report, 1993).

Table 2.6 Factors affecting the rate of uranium extraction (Part I)

Factor	Referenced in	Factor	Referenced in	Factor	Referenced in
Presence of an oxidant	Mackay and Wadsworth (1958); Downes (1967); Derry et al (1977); Ring (1979); Ring (1980); IAEA Technical Report (1993); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Moon-Sung et al (1999); Sand et al (2001); Moon-Sung et al (2005); Lottering et al (2008); van Hille et al (2010); Norgate and Jahanshahi (2010); Sapsford et al (2012); Abhilash and Pandey (2013)	Inoculation with bacteria	Derry et al (1977); Campbell et al (1985); IAEA Technical Report (1993); Sand et al (1993); Muñizo et al (1995c); Moon-Sung et al (2005); van Hille et al (2010); Norgate and Jahanshahi (2010); Abhilash and Pandey (2013)	Particle size of ore to be leached	Downes (1967); Derry et al (1977); IAEA Technical Report (1993); Muñizo et al (1995b); Moon-Sung et al (2005); Norgate and Jahanshahi (2010); Ghorbani et al (2011); Abhilash and Pandey (2013)
Temperature	Downes (1967); Derry et al (1977); Ring (1979); Ring (1980); Campbell et al (1985); IAEA Technical Report (1993); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Muñizo et al (1995c); Macnaughton et al (1999); Sand and Gehrke (2006); Lottering et al (2008); Rucker et al (2009); Ghorbani et al (2011); Abhilash and Pandey (2013)	Solution pH	Mackay and Wadsworth (1958); IAEA Technical Reports (1993); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); van Hille et al (2010); Ghorbani et al (2011); Sapsford et al (2012); Abhilash and Pandey (2013)	Flow Rate (inc. pressure leaching)	Mackay and Wadsworth (1958); Ring (1980); IAEA Technical Report (1993); Muñizo et al (1995a); Muñizo et al (2010)
Leach duration	Mackay and Wadsworth (1958); Downes (1967); Ring (1980); Campbell et al (1985); IAEA Technical Report (1993); Muñizo et al (1993); Muñizo et al (1995a); Lottering et al (2008); Padilla et al (2008); van Hille (2010); Norgate and Jahanshahi (2010); Ghorbani et al (2011); Sapsford et al (2012)	Ore Mineralogy (inc. bulk composition and mode of occurrence)	Ring (1979); Ring (1980); IAEA Technical Report (1993); Muñizo et al (1995a); Macnaughton et al (1999); Sand and Gehrke (2006); Lottering et al (2008); Reynolds et al (2010); Bowell et al (2011)	Source of nutrients for bacteria	Downes (1967); McCready et al (1986); Campbell et al (1985); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Sand and Gehrke (2006)
Precipitation of other metals/gangue	Derry et al (1977); McCready et al (1986); Campbell et al (1985); IAEA Technical Report (1993); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); van Hille et al (2010); Ghorbani et al (2011); Sapsford et al (2012); Abhilash and Pandey (2013)	Rock characteristics/ Permeability	IAEA Technical Report (1993); Munzo et al (1993); Muñizo et al (1995a); Munzo et al (1995c); Schlitt (1996); Rucker et al (2009); Norgate et al (2010); Ghorbani et al (2011)	Operational factors	Muñizo et al (1995a); Lizama et al (2005); Lottering et al (2008); Norgate and Jahanshahi (2010); Ghorbani et al (2011); Sapsford et al (2012)
Redox potential (Fe^{3+}/Fe^{2+} ratio)	Ring (1979); Ring (1980); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Muñizo et al (1995c); Macnaughton et al (1999); Lizama et al (2005); van Hille et al (2010); Ram et al (2011); Sapsford et al (2012); Abhilash and Pandey (2013)	Presence or concentration of pyrite	Campbell et al (1985); IAEA Technical Report (1993); Muñizo et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Sand et al (2001); Lizama et al (2005); Bowell et al (2011)	Oxygen availability	IAEA Technical Report (1993); Muñizo et al (1995a); Muñizo et al (1995b); Muñizo et al (1995c); Sand and Gehrke (2006); Ghorbani et al (2011)

Table 2.7 Factors affecting the rate of uranium extraction (Part II)

Factor	Referenced in	Factor	Referenced in	Factor	Referenced in
Aeration of stope/heap	Campbell et al (1985); Muñizo et al (1993); Sand et al (1993); Muñizo et al (1995a); Muñizo et al (1995b); Muñizo et al (1995c)	Agglomeration of stope/heap	Rucker et al (2009); Ghorbani et al (2011); Kodali et al (2011)	Hight and/or width of stope/heap	Muñizo et al (1995a); Lizama et al (2005); Padilla et al (2008)
Pore space in stope/heap (inc. void ratio, percolation of solution, preferential flow)	Downes (1967); Sand et al (1993); Rucker et al (2009); van Hille et al (2010); Ghorbani et al (2011)	Irrigation frequency	Campbell et al (1985); IAEA Technical Report (1993); Muñizo et al (1995c)	Solid-liquid and gas-solid interactions	Liddell (2005); Lizama et al (2005); Ghorbani et al (2011)
Type of gangue material	Ring (1980); Reynolds et al (2010); Bowell et al (2011); Ghorbani et al (2011)	Method of stope/heap construction	IAEA Technical Report (1993); Muñizo et al (1995c); Rucker et al (2009)	Pulp density	Downes (1967); Ring (1980); Abhilash and Pandey (2013)
Electrochemical interactions (inc. galvanic interactions)	Macnaughton et al (1999); Sand et al (2001); Sand and Gehrke (2006); van Hille et al (2010)	CO ₂ availability	IAEA Technical Report (1993); Muñizo et al (1995b); Sand and Gehrke (2006)	Presence of organic compounds	Muñizo et al (1995a); Bowell et al (2011)
Extracellular polymeric substances (EPS)	Sand et al (2001); Tsuneda et al (2003); Sand and Gehrke (2006); van Hille et al (2010)	Humidity	Muñizo et al (1995b); Sand and Gehrke (2006); Ghorbani et al (2011)	Type of bacteria	Muñizo et al (1993); Muñizo et al (1995b)

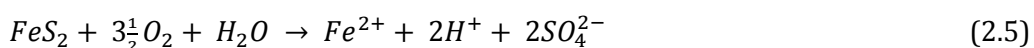
Although the addition of an acid or alkaline reagent works well to extract soluble U(VI) from simple uranium oxides and compounds, no oxidation is taking place. Insoluble U(IV) still requires oxidation for dissolution to occur (Equation 2.4) (Ring, 1980). As touched on briefly in section 2.1.3 the oxidation of U(IV) to U(VI) requires a source of O₂ or other oxidising agent. As pyrite is known to be present in the ore in the Elliot Lake region the chemistry and effect of this mineral shall be described in more detail.

2.4.1.1 Pyrite oxidation

The oxidation of pyrite contributes to the extraction of uranium in three ways;

1. It adds sulfuric acid (H_2SO_4) to the interstitial water lowering the pH of the solution. This favours U(VI) solubility and reduces the amount of insoluble uranium hydroxide precipitates formed (Equation 2.3).
2. It increases the concentration of sulfate (SO_4^{2-}) in the interstitial water. This also increases the solubility of U(VI) through formation of soluble uranium-sulfate complexes (Equation 2.2).
3. It can, in the presence of Fe(II) oxidising microbes, increase the concentration of Fe(III) in the solution which oxidises U(IV) to U(VI). This results in more uranium being mobilised overall and a higher extraction rate (Equation 2.4).

The oxidation of pyrite can be achieved through direct and indirect mechanisms (Suzuki 2001). During the direct process, oxygen is the oxidant in the first stage of the reaction (Equation 2.5) which produces sulfate and lowers the pH. The Fe(II) is then oxidised to Fe(III) (Equation 2.6) (Sand et al. 2001).

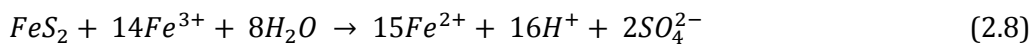




If the oxidation of Fe(II) to Fe(III) takes place in circumneutral pH solution, hydrolysis and precipitation of Fe(III) ions occur (Equation 2.7) preventing further indirect oxidation of pyrite (Equation 2.8) (Pham et al. 2006).



Under acidic conditions (pH < 5) Fe(III) is soluble and remains in solution (Pham et al. 2006). This increase in Fe(III) in solution, from (Equation 2.6), leads to further pyrite oxidation by the indirect mechanism (Equation 2.8). The oxidising action of Fe(III) ions proceed to oxidise the sulfur component of the pyrite (Sand et al. 2001).



The oxidation of pyrite by Fe(III) has a greater impact on lowering the pH of the solution and also increases the concentration of SO_4^{2-} present, thus increasing the solubility of U(VI).

Oxidation of Fe(II) to Fe(III) is highly dependent on the pH of the solution, as is shown in Figure 2.3 and Figure 2.4. Below pH 3 the oxidation rate is independent of the solution pH but becomes increasingly pH dependent between pH 3-5. From pH 5 onwards the rate of Fe(II) oxidation increases 100 fold every time pH increases by 1 point over the circumneutral range.

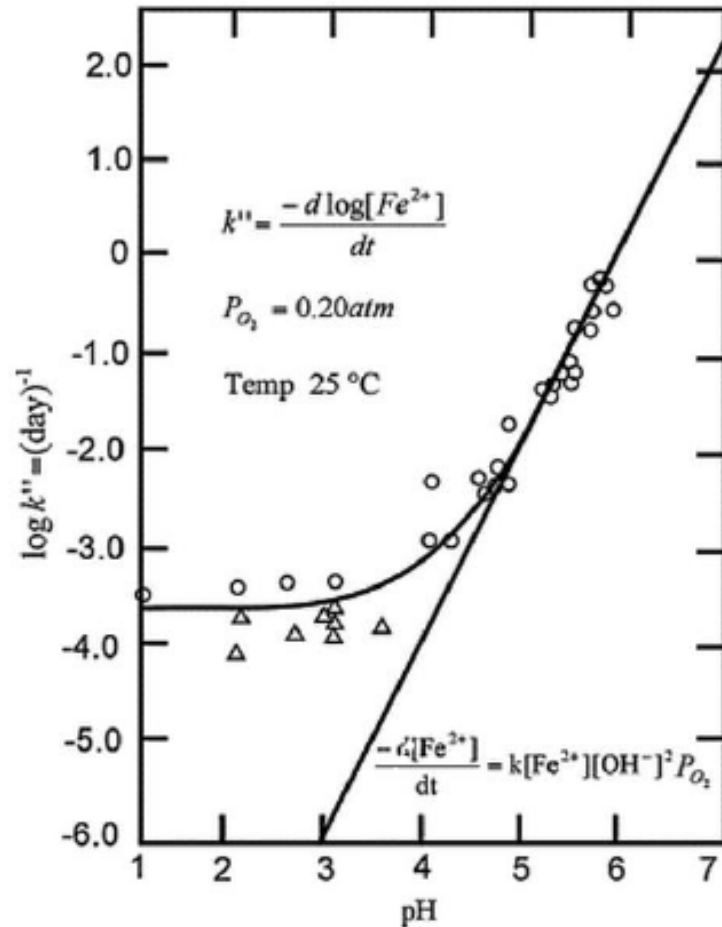


Figure 2.3 Effect of pH on rate of Fe(II) oxidation. Reproduced from Singer and Stumm (1970)

The presence of acidophilic microorganisms at low pH ($\text{pH} < 5$) have been found to catalyse the Fe(II) oxidation rate. In fact, at low pH, bacterial oxidation rates can be 10^5 to 10^6 times faster than abiotic oxidation rates (Kirby et al, 1999). In order to further understand the role that microorganisms play in the dissolution and extraction of uranium, and the subsequent implications for this study, the occurrence, environment and limitations of bioleaching have been investigated.

2.4.1.2 Bioleaching

It is thought that for hundreds of years the presence of microorganisms has been aiding the leaching of metals from sulfide minerals in engineered systems without any realisation

that they played any role in the extraction process (Suzuki, 2001). Campbell et al (1987) recorded how Denison Mines, in the Elliot Lake region of Canada, sometimes used to wash down completely mined stopes with mine water. Although no concerted or carefully engineered approach was taken towards this process, it was recognised that it increased uranium extraction. In the early 1960s the phenomenon of bacterial assisted leaching was first identified and explained and since then there has been continued and increasing interest (Campbell et al., 1987; McCready et al., 1986; Muñoz et al., 1995a; Suzuki, 2001).

Bioleaching essentially catalyses the leaching of uranium by regenerating the Fe(II) to Fe(III) (Figure 2.3 and Figure 2.4), thus creating the chemical conditions necessary for uranium oxidation (Muñoz et al., 1995a; Suzuki, 2001).

It is now widely accepted that, in nature, a combination of different acidophilic iron and sulfur compound-oxidising species are involved in the process of pyrite oxidation (Muñoz et al., 1995b; Sand and Gehrke, 2006). The principle microorganisms involved in the bioleaching of uranium ores are (Muñoz et al., 1995a; Sand and Gehrke, 2006):

- *Acidithiobacillus ferrooxidans* (formally *Thiobacillus ferrooxidans*)
- *Acidithiobacillus thiooxidans* (formally *Thiobacillus thiooxidans*)
- *Leptospirillum ferrooxidans*

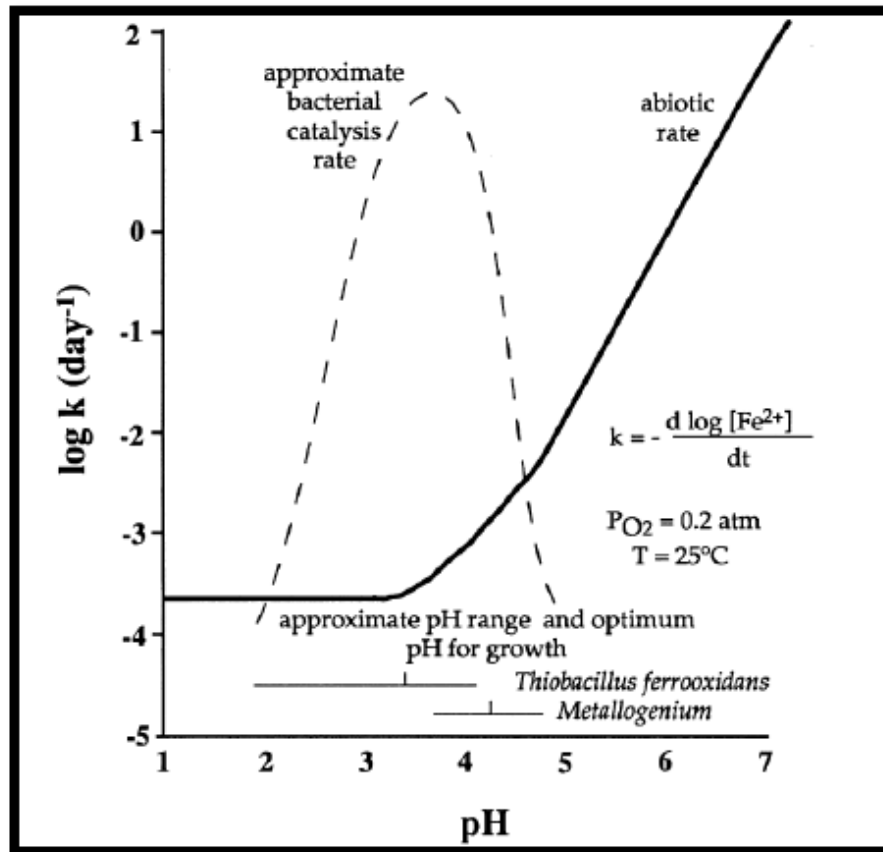


Figure 2.4 Schematic plot showing Fe(II) oxidation rates under abiotic and biotic conditions, against pH. From Kirby and Brady (1998).

McIntosh et al (1997) list the requirements for a bacterial population to survive and grow as:

1. Water
2. A source of energy (for various metabolic functions)
3. A source of carbon (for production of various cell components)
4. A source of trace elements (for production of specific components)
5. Favourable environmental conditions (temperature, Eh and pH)

During uranium bioleaching, in the presence of pyrite, the bacteria gain their energy from the oxidation of Fe(II) to Fe(III) or reduced sulfur compounds or both (Guay et al., 1976).

Water is present in any bioleaching operation and carbon and trace elements can often be

derived from the ore itself (Derry et al., 1977). The optimum environmental conditions for microorganisms' growth and survival vary depending on the bacterial present, see Table 2.8. However Sand and Gehrke (2006) state that as long as water is available, and the temperature does not exceed 116°C, bioleaching will occur.

Table 2.8 Main microorganisms involved in uranium bioleaching (Adapted from Muñoz et al., 1995a)

Microorganism	Characteristic	Oxygen requirement	pH (optimum)	T(°C) (optimum)
<i>Acidithiobacillus ferrooxidans</i>	Oxidise: Fe ²⁺ , S ⁰ , U ⁴⁺ , Cu ⁺ , Se ²⁺ , Thiosulfate, Tetrathionate, S ⁼	Aerobic	1.2 - 6.0 (2.5 - 2.8)	5 - 40 (28 - 35)
<i>Acidithiobacillus thiooxidans</i>	Oxidise: S ⁰ , Thiosulfate, Tetrathionate	Strict aerobic	0.5 - 6.0 (2.0 - 3.5)	10 - 40 (28 - 30)
<i>Leptospirillum ferrooxidans</i>	Oxidise: Fe ²⁺ , Pyrite	Aerobic	1.5 - 4.5 (2.5 - 3.0)	20 - 40 (30)

Temperature is mentioned in relation to uranium extraction in much of the literature (see Table 2.6). Muñoz et al. (1995a) refer to temperature as, “one of the variables that has the most influence on the metallic extraction process”, but it is important to consider that both biological and purely chemical extraction rates increase with temperature (McIntosh et al., 1997). Often temperature is varied during laboratory scale experiments in order to optimise the rate of extraction. The common bacterial species present for uranium extraction, *A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans*, are optimised at temperatures around 30°C (Table 2.8). In a mining environment however, it is costly to regulate the temperature during extraction and it is necessary to be aware of seasonal variations in temperature. Campbell et al. (1987) alluded to this effect and suggest that rest periods between flood leaching cycles should be scheduled to avoid the adverse effect that temperatures less than 12°C have on iron oxidation rates.

Redox potential is another factor which is regularly referred to in the literature regarding the optimisation of uranium extraction rates (see Table 2.6). The measurement of the ratio of Fe(II)/Fe(III) is important as it gives an indication of the rate of pyrite oxidation within the stope or heap. A higher Eh value indicates more oxidising conditions which is indicative of a thriving bacterial population.

For the majority of bacteria which solubilise sulfide minerals the optimum growth conditions occur at pH 2 to 3.5 (McIntosh et al., 1997). The low pH necessary for microbial leaching to occur is an important factor in uranium extraction as the mine water used for leaching most often enters the mine at near neutral pH. The time that it takes for the optimum microbial environment to occur is known as the 'lag phase' (Figure 2.5). It is an induction period where the bacterial culture adapts to a new environment and is an important consideration whilst trying to optimise the extraction rate in the presence of bacteria (Muñizo et al., 1995c). During the lag phase any bacteria present is maturing but not able to divide. Once the exponential phase is started the number of new bacteria growing is proportional to the present cell population because the number of cells doubles with each consecutive time period. The stationary phase occurs due to a growth limiting factor such as lack of nutrients.

There are two main options discussed in literature to remove the 'lag phase' – inoculation with naturally occurring strains of bacteria and the addition of ferric sulfate (Fe(III) sulfate) to the lixiviant. Sand et al (1993) found that through the use of an inoculum, leaching of the ore body occurred without any lag phase.

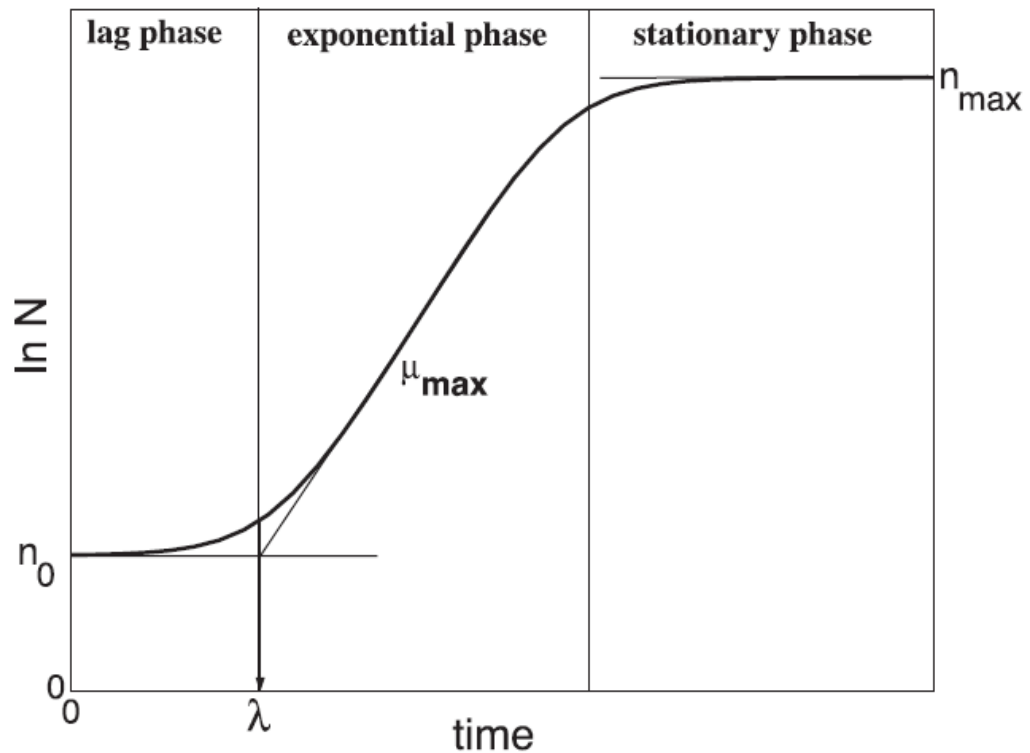


Figure 2.5 Typical microbial growth curve at constant temperature (from Swinnen et al. 2004). n_0 initial population density; n_{max} maximum population density; μ_{max} maximum specific growth rate; λ lag parameter

2.4.1.3 Addition of Fe(III) sulfate

During the assisted dissolution of uranium with bacteria there are two major reactions taking place simultaneously; the oxidation of pyrite, assisted by Fe(III), to produce an acidic Fe(II) sulfate lixiviant (equation 2.8) and the chemical leaching of uranium by the Fe(III) and sulfate (equation 2.4) (Derry et al., 1977; McIntosh et al., 1997). It is significant that both of these chemical processes require a supply of Fe(III), thus the rate of Fe(III) regeneration is the limiting step in the dissolution of uranium (Guay et al., 1976). At the beginning of a leach cycle the availability of Fe(III) ions would be low considering the chemical rate of reaction at neutral pH. To facilitate an increased rate of uranium extraction Fe(III) sulfate is often used commercially to reduce the amount of acid consumed during leaching (Ring, 1980).

The benefits of Fe(III) sulfate addition at different concentrations are covered extensively in literature (Derry et al., 1977; Dwivedy and Mathur, 1995; Guay et al., 1976; McIntosh et al., 1997; Sand et al., 2001). The ideal concentration of Fe(III) ions however, has not been agreed on. Derry et al. (1977) found that a concentration of 12g/L of Fe(III) resulted in the most successful uranium extraction rate, 96% uranium extracted over 10 days, although it was necessary to maintain the temperature at 50°C to obtain this rate of dissolution.

Similarly, during an investigation into extraction from a uraninite ore, Ring (1980) found that Fe(III) concentrations of 10g/L and 15g/L achieved 96.7% and 96.6% uranium extraction respectively at 40°C over a period of 20 hours. It is interesting to note that in the study carried out by Ring (1980) a test was carried out under the same leaching conditions (40°C for 20 hours) without the addition of any Fe(III) ions. This test also achieved 96.7% uranium extraction. Ring (1980) concluded that, for ores containing principally uraninite, the addition of Fe(III) ions only increased the initial rate of uranium dissolution and not the overall extraction.

Sand et al. (2001), in their study into the role that extracellular polymeric substances (EPS) play in bioleaching, found that Fe(III) ions are of pivotal importance for the attachment of cells onto the surface of pyrite. They also observed that the Fe(III) ions are vital to ensure the initial steps in the oxidation of metal sulfides thus, for bioleaching to begin, a sufficient amount of Fe(III) ions in solution is necessary. A threshold concentration value of $\geq 0.2\text{g/L}$ Fe(III) ions was required before the rate of pyrite oxidation was raised above negligible. The method of increasing the Fe(III) ion concentration was not found to be of importance and could be achieved via natural chemical oxidation or artificial supplementation. Subsequently, the addition of 0.5g/L Fe(III) ions was sufficient to instigate the leaching of pyrite without a lag phase. This advancement is of vital importance in the study of extraction from low grade ores, as it has

significant implications regarding reagent consumption and the time necessary for extraction to take place.

2.4.2 Source of nutrients

Along with an energy source, a source of trace elements to stimulate bacteria growth has been investigated. The importance of nutrient availability to a microbial population, and its ability to enhance the dissolution of metals, was first observed in the 1940's when investigating the bacteria present in leachate of acid mine drainage (AMD – also known as acid rock drainage (ARD)). It was found that these bacteria could be grown in a synthetic medium with simple inorganic salts and ferrous sulfate (Leathen et al., 1956). The composition of the nutrient solution suggested by Leathen et al. (1956) is presented in Table 2.9. It was concluded that the concentration of ammonium ions were the essential source of nitrogen to the bacteria and that nitrates did not appear to be necessary for growth of bacteria to occur (Leathen et al., 1956).

Silverman and Lundgren (1959) proposed an alteration to the nutrient solution recipe suggested by Leathen et al. (1956), their modified '9K' solution is given in Table 2.10. The reason for modification was to increase the growth rate of the bacteria, thought to be limited by the original medium. Silverman and Lundgren (1959) reported a substantial increase in the cell count using the 9K medium, with cell counts ranging from 2 to 4 x 10⁸ cells per mL as opposed to 7 x 10⁶ cells per mL using the medium of Leathen et al. (1956). They also found that aeration was necessary in order to ensure an adequate supply of O₂ and CO₂, for rapid bacteria growth.

Table 2.9 Composition of nutrient medium suggested by Leathen et al. (1956).

Components		Concentration (g)
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	0.15
Potassium chloride	KCl	0.05
Magnesium sulfate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.50
Dipotassium hydrogen phosphate	K_2HPO_4	0.05
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	0.01
Distilled water	-	1000mL
<i>Energy source</i>		
Ferrous sulfate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.0mL of a 10% (w/v) solution

Table 2.10 Composition of 9K nutrient medium suggested by Silverman and Lundgren (1959).

Components		Concentration (g)
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	0.30
Potassium chloride	KCl	0.10
Magnesium sulfate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.50
Dipotassium hydrogen phosphate	K_2HPO_4	0.50
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	0.01
Distilled water	-	to 700mL
Sulfuric acid	10N H_2SO_4	1.0 mL
<i>Energy source</i>		
Ferrous sulfate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	300mL of a 14.47% (w/v) solution

There has been some discussion since the publication of Silverman and Lundgren (1959) about whether the quantities of nutrients suggested for the 9K medium is excessive and a more conservative amount would suffice. There is evidence to suggest that the 9K medium contains excessive quantities of phosphate, magnesium and ammonium and can lead to the accumulation of salts. This accumulation can result in the precipitation of

jarosites and hydroxysulfates which are insoluble and hamper further solubilisation (Campbell et al., 1987; McCready et al., 1986; Muñoz et al., 1995b).

McCready et al. (1986) infer that, as *A. ferrooxidans* are found in indigenous mine waters, they can survive and grow under nutrient-limited conditions. They concluded that it is necessary to develop leaching nutrient medium on a site-by-site basis as the chemistry of the ores and the various water sources utilised to prepare the medium is so site specific. These findings are supported by Muñoz et al. (1995b) who observed better uranium extraction rates with a medium of dilute salts (0.06g/L $(\text{NH}_4)_2\text{SO}_4$; 0.06g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 0.02g/L K_2HPO_4 ; 0.02g/L KCl; no $\text{Ca}(\text{NO}_3)_2$ was included) than traditional 9K medium, thus concluding that the ore itself contained sufficient nutrients for the growth of bacteria. They add that although the 9K medium provided the best conditions for bacterial growth it did not result in the best rate of metals extraction because of the precipitation.

2.4.3 The effect of time on leaching

Throughout the literature there is a wide range of time frames used during extraction testing, varying from hours to years (see Table 2.6 and Table 2.7). The majority of studies investigate the maximum extraction possible in the minimum amount of time and thus factors such as lixiviant composition, inoculation with bacteria, temperature and particle size are varied to identify their respective effects. In order to show the maximum recovery achievable, samples are often finely ground to create the best liberation conditions and are agitated to ensure even and consistent contact between the ore and leachate. Studies also often involve continuous percolation of the leachate solution which requires flow monitoring and continuous supply. Problems exist, however, when applying small scale research extraction methods to industrial size mining operations. The development of low maintenance, low cost operations (such as stope leaching) are of vital importance, especially where low grade ores are concerned. Additionally, when processing low grade

ores, requirements for high temperature, intensive grinding or expensive reagents will make any mining operation impossible.

The duration of leaching, including the ‘rest period’ between leaching cycles, is of interest for stope leaching mining operations as mine water is often used to wash down the stope (Campbell et al., 1987; Downes, 1967; Sand et al., 1993). Flooding of the stope was found to be beneficial to extraction by Derry et al. (1977) as it achieved better solid-liquid contact. Although Campbell et al. (1987), Downes (1967) and Sand et al. (1993) all mention the periodical circulation of the stope with mine water (not continuous, as implemented in many small scale studies) there does not appear to be any systematic approach applied to determine the optimum frequency of its application. If the frequency of the leachate flush could be optimised, in other words the optimum ‘rest period’ between the circulation cycles could be identified, then it may be possible to improve recovery rates at no extra cost. As Campbell et al. (1987) state:

“Uranium in mine water was virtually free as it involved no mining costs, no additional pumping costs and can be treated in the existing mill.”

With the continued interest in extraction from low grade ores, any increase in uranium extraction, due to the optimisation of ‘rest period’ duration, would have significant implications for the future growth of stope leaching and mining as a whole.

2.5 Summary

The many complexities related to the extraction of uranium have been identified throughout the literature. The immense variety of uranium ore geology and mineralogy has been studied and the subsequent effects on extraction discussed. Mining methods employed to extract uranium have been summarised, with particular interest in the techniques which were applicable to low grade ores. Numerous factors which influence

the dissolution of uranium have been outlined with a focus on the presence of bacteria, the presence and effect of pyrite, the addition of Fe(III) ions, the use of a nutrient medium and the effect of time on extraction.

3 Methodology

The characterisation, particle size distribution and analytical techniques employed to determine the elements present in the ore material are outlined in this chapter. The test design and procedure are also covered in detail, including the collection of laboratory parameters and leachate sample analysis.

3.1 Materials

3.1.1 Sample collection

Six drill core samples, weighing a total of approximately 40kg were delivered to Cardiff University in September 2009. The samples of low-grade uranium ore (typically 5-10kg quarter core sections) were collected from the Elliot Lake mine site, Ontario, Canada. All samples were stored at room temperature in a dry environment.

3.1.2 Size reduction, homogenisation and riffing

The six drill core samples were passed through a large jaw crusher individually before being homogenised by passing the material through a large spinning cone riffler three times. Once homogenised the total sample, of approximately 40kg, was further reduced through a small jaw crushers and then a gyratory crusher, achieving a grain size of 100% passing 1cm.

The bulk homogenised sample was riffle split using a large 35-200(250) riffle box to produce a sample of 20kg. This subsample was subsequently split using the same riffle

box into eight subsamples of approx. 2.2kg. These were finally passed through the riffle box to obtain two samples of 1kg \pm 0.5g each which formed one set of duplicates for the test procedure. This was repeated on each of the remaining 2.2kg samples until 16 samples were produced. (ASTM Standard, D6323-12e1)

3.2 Mineralogical and geochemical characterisation

Before carrying out any extraction experiments it is required to establish the grade of the desired element contained within the ore. The grade refers to the content of the marketable end product in the material (Wills, 1997), and indicates the maximum amount of an element which could ever be extracted from that sample.

The grade of an ore is most often expressed as a percentage and can be calculated using Equation 3.1, e.g. nickel grade 600ppm could be written as 0.06% nickel ore.

$$x_{\%} = \frac{x(ppm)}{10000} \quad (3.1)$$

The grade of the ore, before any extraction or beneficiation (through removal of the gangue fraction) of the desired mineral has taken place, is commonly referred to as the head grade.

Despite the head grade of an ore being of great importance it is often difficult to determine with accuracy. This is due in part to the heterogeneous nature of many rocks, the presence of many different primary and secondary mineral phases and the presence of gangue material. Wills (1997) describes gangue material as the commercially worthless material that surrounds, or is closely mixed with, a wanted mineral in an ore deposit. As the mineral grade of the ore decreases the gangue material plays a much larger role in the extraction mechanics and makes head grade analysis more difficult.

The method of determining the element content of an ore is known as an assay. The head grade of a low-grade ore is harder to establish because the mineral of interest is distributed more sparsely in the ore and so it is more likely that the assay results are inconsistent. This process is further hampered by the small sample size used for many established assay methods as it must be large enough for the influence of individual grains on sample composition to be insignificant. The size of sample needed for it to be considered homogeneous depends on the grain size and the larger the grain size, the greater the mass of sample needed for digestion (Ramsey, 1997).

For this study the assay was determined using a variety of methods in order to more accurately establish the head grade.

3.2.1 Digestion methods and ore grade analysis

The bulk homogenised sample was used to carry out multiple head assays to determine the uranium head grade. All of the whole rock analysis was done on samples that had been split riffled, following the method described in section 3.1.2, to ensure samples were as representative of the gross original sample as possible. So as to determine the uranium content of the head grade it was beneficial to get whole rock analysis carried out using a variety of techniques at several different laboratories.

3.2.1.1 In house microwave digestion

In house microwave digestion was carried out on an Anton PAAR, Multiwave 3000 on 3 'grab' samples taken from a representative powdered sample. Approx. 0.01g of sample (accurately known) was used, collected as a grab from a representative powdered (<75µm) sample. This was placed into a PTFE liner in a ceramic vessel, with 2mL of analytical grade 47.51% Hydrofluoric acid (HF) and left overnight. 6mL of aqua regia solution (1:1 ratio of analytical grade 32% Hydrochloric acid (HCl) and 70% Nitric acid (HNO₃)) was then added and the containers were placed into the microwave. The

microwave was run on the HF100-16 program with the following stages; 10 minutes to reach 1400 watt (200°C), power is maintained for 30 minutes and then allowed to cool for 15 minutes.

To neutralise the HF, 12mL of analytical grade 4% Boric acid (H_3BO_3) was added to the sample (6mL boric per 1mL HF) and then run in the microwave. This stage is known as complexation and program MF100-8 was used following the boric acid addition. The stages were; 5 minutes to reach 900 watt (150°C), power is maintained for 20 minutes and then allowed to cool for 15 minutes. Once out of the microwave the PTFE caps were washed out with deionised water (DI) and the solution collected into a beaker. Next the content of the PTFE liner was poured into the beaker and the liner rinsed with DI. Solution from the beaker was transferred into a grade A, 50mL volumetric flask then topped up to 50mL with DI. This solution was used for analysis.

3.2.1.2 ICP-MS analysis

Analysis of the head grade digest solution was carried out on an ICP-MS at Aberystwyth University on an Agilent 7700x ICP – Mass Spectrometer (ICP-MS), with 7700 Series MassHunter software. The instrument was calibrated with a series of mixed multi-element standards (5µg/L, 10µg/L, 20µg/L, 50µg/L, 100µg/L) at both the beginning and end of each batch of analysis. The multi-element standard is made up with single element solutions. A blank sample of 2% HNO_3 in Milli-Q deionised water (18.2 MΩ/cm) was included with each batch of samples.

A fixed volume/concentration of an internal standard (usually Te) is added to each sample to check for instrument drift throughout analysis. Following analysis the results were checked to ensure standards were within 10% of the values expected and that there was no noise in the wavelength. The following trace elements were analysed: U, Th, Ce, Y, La, Pr, Nd, Yb, Dy, Sm (but only U results are reported here).

3.2.1.3 Acid digestion ALS South Africa

Four acid “near-total” digestion was carried out on three representative samples at an external certified laboratory (accredited to International Standards, ISO/IEC 17025:2005 and ISO 9001:2008), ALS South Africa. The term “near total” is used because, depending on the sample matrix, not all of the elements are quantitatively extracted. Three different representative powdered samples were provided to ALS SA. 0.25g of sample was digested with a perchloric, nitric, hydrofluoric and hydrochloric acids mixture. Following this the remaining solution was topped up with dilute hydrochloric acid and analysed. ICP-Mass Spectrometry (ICP-MS) and ICP-Atomic Emission Spectrometry (ICP-AES) were used to analyse the solution so as to report the widest possible concentration range. 48 elements plus Rare Earth Elements (RRE) - 60 elements in total - were analysed for: Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr, Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm, Yb (but not all elements are reported here).

3.2.1.4 In house lithium tetraborate fusion

Lithium borate digestion was carried out in house on 6 samples, collected as ‘grab’ samples from a representative powdered sample of head grade material. For the procedure 0.25g of sample was weighed into a platinum crucible and 0.6g lithium borate flux 50-50 (50% $\text{Li}_2\text{B}_4\text{O}_7$ - 50% LiBO_2) was added to the powdered material. A small amount of lithium iodide (5 drops) was then added to the mixture and placed into a CLAISSE M4 FLUXER analyser. The crucibles are heated over a propane flame at 1000°C for 3 minutes, after which the fusion melt is tipped into a receptacle beaker with 50mL of 2% HNO_3 and left to cool for 10 minutes. Following cooling, the platinum crucible is placed in the receptacle beaker with the melt solution and heated on a hotplate at approx. 70°C for 20 minutes, to ensure that no residue remains. The solution is transferred into a 100mL volumetric flask and topped up with deionised water before being analysed. The solutions were analysed on an Inductively Coupled Plasma - Optical Emission

spectroscopy (ICP-OES) and the following elements were analysed for: Al, Ca, Fe, K, Mg, Na, U, V.

3.2.1.5 Lithium metaborate fusion, ALS Seville

One representative sample of powdered head grade material was sent for analysis by lithium borate digestion at ALS laboratories, Seville (accredited to International Standards, ISO/IEC 17025:2005 and ISO 9001:2008). Although lithium metaborate fusion is a whole rock digestion method some base metal oxides and sulfides may not be completely decomposed. Therefore results for Ag, Co, Cu, Mo, Ni, Pb and Zn are unlikely to be quantitative by this method. The procedure involved a prepared sample (0.2g) being added to lithium metaborate flux (0.9g), mixed well and fused in a furnace at 1000°C. The resulting melt was cooled and dissolved in 100mL of 4% HNO₃/2% HCl₃ solution, and then analysed by ICP-MS. The following elements were analysed for: Ag, Ba, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr (but not all are reported here).

3.2.2 Determination of sulfur content

A LECO SC-144DR analyser was used to determine the sulfur content of the whole rock sample. Eight representative powdered samples were analysed for total sulfur (TS) and eight more were analysed for speciated sulfur (SS). The sulfur content is reported as a percentage by the computer and the software used is Version 1.34. Run time for each sample is 240 seconds and the temperature of the furnace chamber is 1297°C. Conditioning and calibration of the LECO is done with different standards depending on the concentration of sulfur present in the sample. For the initial sample the expected sulfur content is usually unknown and thus the lower reference material is used.

If the sulfur content of a sample is <5% the low sulfur reference material is used for calibration. Low sulfur reference material is a sulfur in coal material with a sulfur content

of 1.14% (+/- 0.05%). A reference sample is run before each batch of samples to standardise the machine. If the reference material does not give the expected reading of 1.14%, no further samples are analysed until the problem can be resolved. When a sample is analysed and >5% sulfur is detected, the machine is recalibrated with a high sulfur reference material of zinc sulfide, 32.91% (+/- 0.05%).

TS is determined by weighing 0.35g of sample into a nickel boat, which is then transferred inside a ceramic container of the same shape and size. The ceramic boat is placed into the oven chamber and run for 240 seconds. Sulfur content is reported and recorded. SS is analysed by first reacting 0.35g of sample with 10mL of 2M HCl in a 60mL plastic container, at room temperature, overnight. The acid solution is then filtered using a 300 mesh, glass fibre filter. Both the particulate material collected on the filter and the filter itself are folded and put into a nickel boat. Following the same procedure as TS the sulfur content of SS was reported and recorded.

Measurement of SS content provides the analyst with an indication of the type of sulfur present in the sample. If sulfur content is the same for TS and SS then sulfur is present as sulfide in the sample however, if no sulfur is detected following SS analysis it can be assumed that it is present in sulfate form. A sample may contain both sulfate and sulfide compounds, demonstrated by different TS and SS measurements.

3.2.3 X-Ray Diffraction

X-ray diffraction (XRD) analysis was used to establish the mineral phases present in the whole rock sample. This was done using a Philips PW3830 x-ray generator and X'Pert Industry software Version 1.1. The high tension (HT) current was set to 35kV and 40mA and was reached by increasing the kV and mA in increments of 5. Representative powdered samples were used for analysis and were compacted into the sample holder before being slid into the holder clip ready for XRD. The door to the sample chamber was

sealed, the shutter position selected (always position 2 on the CLEER machine) and the x-ray shutter opened. The XRD machine was then set-up via the X'Pert Industry software, with the parameters outlined in Table 3.1, and left to run the scan.

Table 3.1 X'Pert Industry scan parameters

Scan	
Type	Continuous
Start angle ($^{\circ}2\ \text{Theta}$):	5
End angle ($^{\circ}2\ \text{Theta}$):	80
Step size ($^{\circ}2\ \text{Theta}$):	0.02
Time per step (seconds):	0.5
Total time:	13 min 16 sec
Number of steps:	3751

Following the completion of the scan, a diffractogram was produced and X'Pert Highscore Plus software Version 2.0 was used to search for phases present in the sample. This was done by utilising the database to match the peak position on the diffractogram to the most likely mineral phase. The software issued a list of mineral phase candidates, in descending order of likelihood, from which the best matches were selected. When interpreting the diffractogram of XRD measurements it is important to use background knowledge of the material and experience to determine which phases are present.

3.2.4 X-Ray Fluorescence

X-ray fluorescence was carried out using an Olympus Innov-X portable XRF, model X-5000. During analysis the XRF was used to provide a quick analysis of the elements present in powdered whole rock samples. Representative powdered samples were analysed on the Soil 3-Beam mode and the elements analysed were as follows: Ag, As, Au, Ba, Bi, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, Ge, In, K, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Th, Ti, U, V, Zn, Zr (only U, Fe and S are reported here, the other elements analysed are reported in Appendix H). Each x-ray beam was run for 90 seconds and the XRF analyser was standardised before

every batch of samples and then every 15 samples. The unit is factory calibrated and is sent for re-calibration every 12 to 15 months.

3.3 Particle size distribution

Dry sieving took place, following BS 1796-1:1989, to determine the particle size distribution (PSD) of the head grade and residue samples using a vertical stacking machine sieve. Riffle splitting was carried out to ensure samples for PSD were representative of the bulk sample. Two sets of sieve nests were used during the protocol to ensure that no attrition occurred during sieving, aperture sizes 4000 μm , 2000 μm , 1180 μm , 500 μm and 250 μm , 150 μm , 63 μm were used for sieve nest 1 and sieve nest 2 respectively. 250g of head grade material and test residue material was used to determine the PSD. Each sample was sub-divided into 125g to ensure the sieve nests were not overloaded. As the sample was found to contain a lower proportion of $-500\mu\text{m}$ particles, the remainder from both 125g samples passed through sieve nest 1, to the receiver pan, were combined to be passed through sieve nest 2.

Sample were introduced at the top of the sieve nest and distributed evenly across the top sieve surface. A tight fitting lid was used to contain the entire sample. Shaking duration was 15 minutes for sieve nest 1 and 12 minutes for sieve nest 2. After the required time the sieves were separated and the oversize sample contained was collected and weighed. This was done by inverting the sieve onto a clean sheet of brown paper and gently taping the side. Any near mesh particles were removed by brushing the underside of the gauze gently with a nylon brush. To avoid cross contamination the sieves were wiped clean with acetate between uses.

3.4 Laboratory equipment and experimental design

The proposed stope leaching extraction procedure was an important aspect of the experimental design process; stope leaching was described in detail in section 2.3.3 of the

literature review. The proposed stope leaching process involved the flooding of underground chambers, using groundwater, followed by draining and aerating for a period of 2 weeks. This cycle would then be repeated. The drained solution would be collected and taken to a surface processing facility where solvent stripping and uranium extraction was carried out.

3.4.1 Ground water chemistry

The groundwater chemistry of the mine site under investigation was provided by Dey (2010) prior to test development. This data was used to decide whether it would be necessary to use an artificial mine water solution to mimic *in situ* conditions. A comparison between the average element concentrations, pH and conductivity in the ground water, tap water and deionised water are presented in Table 3.2.

Table 3.2 Water chemistry of mine site ground water, tap water and deionised water.

Element (ppm)	Ground water	Tap water	Deionised water
Aluminium	0.014	<LOD	<LOD
Calcium	23.330	50.012	<LOD
Iron	<LOD	0.011	<LOD
Potassium	-	1.916	0.003
Magnesium	2.67	6.043	<LOD
Sodium	-	13.879	<LOD
Uranium	0.003	0.069	<LOD
Vanadium	<LOD	0.010	<LOD
pH (S.U)	7.99	8.07	7.42
Conductivity ($\mu\text{S}/\text{cm}$)	215.80	317.00	0.97

Based on these values it was decided that tap water was the best substitute for the mine water because it provided similar pH, conductivity and element conditions. Deionised

water was not considered to be a suitable substitute for mine water as it was the most different in composition, especially the conductivity measurement. Therefore, tap water was used as the standard flood solution for all tests, not including any with modified solution compositions.

3.4.2 Experimental design

In order to determine the optimal leach program for the ore body a series of 7 tests were developed. These were based on the factors previously discussed (see tables 2.6 and 2.7, chapter 2) and were primarily concerned with the effect of time between leaches and lixiviant composition on the extraction rate.

Seven protocols were developed with variations in rest period, total number of cycles and lixiviant composition. Each test had an initial flood volume of 750mL and each subsequent flood volume was 500mL. Cells were flooded for 24 hours each cycle and the flood solution was introduced all at once by up-flow percolation so as to prevent air bubbles and the formation of preferential flow pathways. For the purpose of these tests the term *FLOOD* refers to the 24 hour period when the cell is completely saturated. *REST PERIOD* signifies the time when the cell is unsaturated and *CYCLE* denotes the entire time from when the cell is flooded until the next time it is flooded. The test protocols are summarised in Table 3.3.

Control

The Control test aimed to simulate the proposed *in situ* conditions of the proposed protocol as closely as possible (flood for 24 hours using ground water; drain; aerate for 2 week rest period). It was not a control test in the traditional sense of being a blank; instead it was designed to act as a reference point against which the modified testing protocols could be compared.

Table 3.3 Summary of testing protocols

Leaching protocol	Flood leach	Number of cycles	Rest period	Notes
Control	Tap water	27	13 days	
Double flush†	Tap water	54	12 days	Two flush per cycle
Weekly†	Tap water	53	6 days	
4 weekly†	Tap water	14	27 days	
Nutrient*	Nutrient solution	27	13 days	
Ferric*	Fe ₂ (SO ₄) ₃	27	13 days	0.5g/L Fe ₂ (SO ₄) ₃ at pH 3.5
Recycle*	recycled water	27	13 days	Use of previous week leachate

† rest period varying protocols * lixiviant varying protocols

For this reason one flood followed by draining was carried out every cycle with a rest period of 13 days. Tap water was used for the flood and a fresh batch of tap water was used for each cycle. The purpose of this test was to indicate the achievable uranium extraction rate that could be achieved at the mine site using the intended process and see how the modified protocols compare.

3.4.2.1 Rest period protocols

Time is recognised as a contributing factor to any mineral extraction process (see Table 2.6; leach duration). Any reduction in the time needed for extraction to take place is considered to be process optimisation. Therefore a series of tests were devised using tap water as a lixiviant to investigate the effect that the rest period between cycles has on extraction rates. The protocols are summarised in Table 3.3.

Double flush

The Double flush test involved two successive flood periods of 24 hours. The rest period was 12 days. This test was designed to determine whether all the leached uranium was removed from the cell in the first flush or whether a significant proportion could be extracted during the second flush.

Weekly

The Weekly flush test had the shortest cycle of all the protocols with 6 days rest period. It was introduced to investigate the possibility of reducing the number of cycles necessary to get optimum extraction rates. If a greater amount of uranium was extracted weekly than bi-monthly then it could be feasible to reduce the overall process time.

4 weekly

Similar to the Weekly test the 4 weekly protocol was established to see whether an increase in exposure time of the crushed rock to the lixiviant solution could lead to an increase in uranium extraction, again resulting in the overall reduction of time needed for extraction. It had fewer total cycles than the other protocols and the longest rest period of 27 days.

3.4.2.2 Lixiviant protocols

The lixiviant used for the flood solution can have a significant effect on the level of minerals that are extracted (see Table 2.6; Presence of an oxidant, solution pH, source of nutrients). It has been widely discussed in the literature (Table 2.6) that microbial activity plays a major role in the leaching of base and precious metals from mineral resources so the following tests aim to utilise this extraction mechanism. If a change in lixiviant leads to a significant reduction in the lag-time before uranium extraction occurs then this could have a considerable impact on the total time required for the extraction process to take place. Each of the following tests had a 13 day rest period, and the same number of total cycles in line with the control test.

Nutrient

As microbes will grow naturally in humidity cells (Sapsford et al, 2009), and it is assumed that their activity will not be oxygen limited, nutrients were added to the flood solution of

the nutrient protocol in an attempt to accelerate their growth. A liquid medium of nutrient solution was used from Leathen et al. (1956), shown in Table 3.4. The original process suggested by Leathen involved a number of autoclaving stages however these were not implemented for this solution as it was not considered practical or representative of the in situ procedure if there was no bacteria present at the start of the tests. The original nutrient medium required the addition of an energy source, ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), this was excluded for these tests because the effect of Fe(III) sulfate on uranium extraction was being investigated by a different protocol and there were concerns that the protocols would be too similar. Tap water was used instead of distilled water as it was considered uneconomical to develop a process which required a large amount of distilled water to be used on site for flood solution.

Table 3.4 Composition of nutrient medium, adapted from Leathen et al. (1956).

Components		Concentration (g)
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	0.15
Potassium chloride	KCl	0.05
Magnesium sulfate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.50
Dipotassium hydrogen phosphate	K_2HPO_4	0.05
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	0.01
Tap water	-	1000mL

Ferric

The addition of Fe(III) sulfate and its influence on microbial activity has also been discussed in literature (see Table 2.6, chapter 2). Its addition to the flood solution was included in the lixiviant protocols so that a comparison might be possible between the effect of adding nutrients or iron(III) sulfate. Sand et al. (2001) suggested 0.5g/L $\text{Fe}_2(\text{SO}_4)_3$ as a suitable concentration to encourage microbial growth due to the aided attachment of bacteria to mineral surfaces. Thus, it was used as the flood solution for the Ferric protocol.

Recycle

The purpose of the test using recycled leach solution was to observe any build up of minerals extracted and see if they subsequently aided the extraction of uranium from the ore. It was also considered worth investigating whether there was a point at which the recycled lixiviant became saturated and could no longer extract any more elements. For the initial flood tap water was used and the solution was recycled for every other cycle. Tap water was used to top the volume back up to 500mL.

All tests were run in duplicate with the test set up shown in Figure 3.1.



Figure 3.1 Annotated photograph of cells

3.4.3 Cell construction

The tests were carried out in Perspex cells containing 1kg of crushed rock with $d_{50} \sim 4\text{mm}$. The cells were originally designed to be used for humidity cell tests (Sapsford et al, 2009) and are 94mm in diameter x 200mm height. They have a Perspex base plate with drilled

holes for sample drainage, there is also a small sealed chamber beneath the base plate with two Perspex tubes attached, illustrated in Figure 3.2. 500mL of solution was sufficient to cover 1kg of rock in the cell.

The flood solution was introduced to the cells via a reservoir located above them (Figure 3.1); the head of water was sufficient to fill the cells so no pump was required. A diagram of the system is provided in Figure 3.2. The flood solution was introduced to the cell through the Perspex tube attached to the side of the base chamber by opening valve 1, ensuring that valve 2 was closed during flooding (Figure 3.2). It was also important to check that valve 1 to the duplicate cell was closed so that the solution only flooded the cell it was intended for. Flooding took ~ 1 minute. Following the 24 hour flood period the solution in the cell was drained through a Perspex tube at the bottom of the base chamber and collected for analysis by opening valve 2 (Figure 3.2). The leachate was allowed to drain for 5 minutes before valve 2 was sealed.

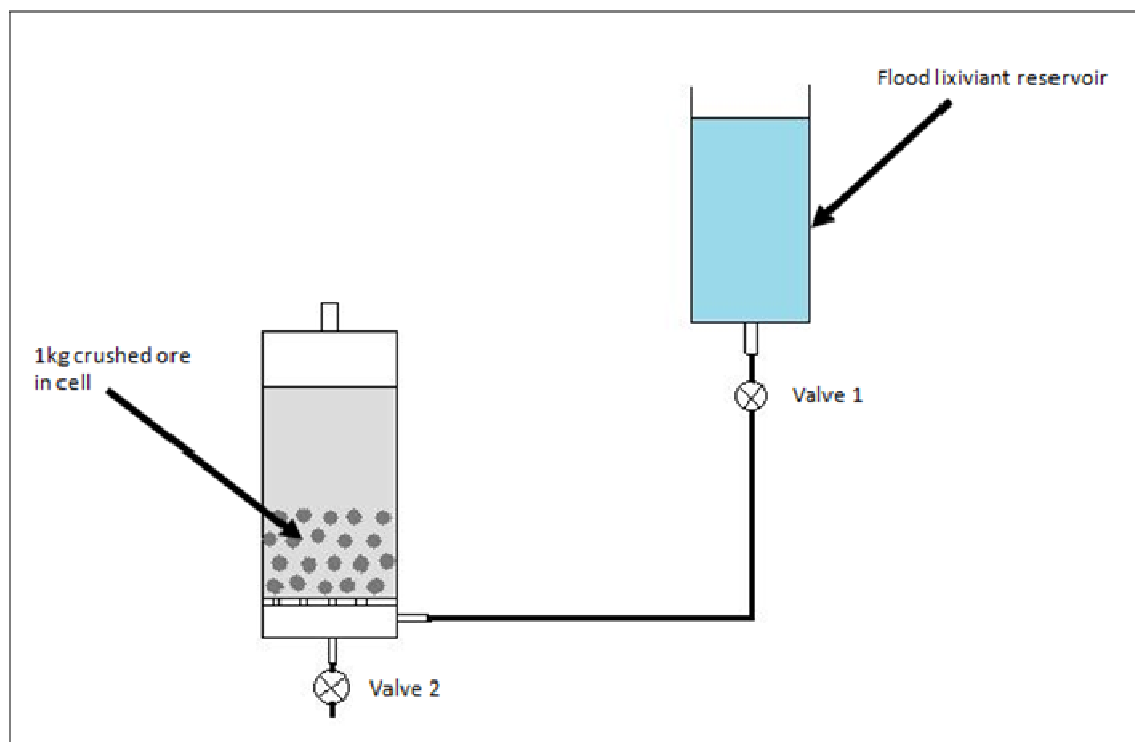


Figure 3.2 Representation of Perspex cell adapted from Sapsford et al. (2009).

Although the mining process proposed for stope leaching will include aeration of the rock after flushing, aeration was not used during the test work because, due to the small quantity of sample, it was felt that it would make the sample too dry. The protocols with longer than 6 days rest period were thought to be most at risk of drying out even at a low air flow rate. Evaporation from 1kg of material in a cell, following flooding with 500mL of tap water, was measured over 28 days to determine the amount of solution lost. In total 9mL of solution evaporated and data can be found in Appendix G. The cells were not considered to be oxygen deficient because they were not sealed and the lids had a tube through which air could pass.

3.4.4 Temperature monitoring

Laboratory temperature was monitored for the duration of testing using two temperature data loggers (HI 141AH Hanna Instruments) simultaneously. Temperature ($\pm 0.4^{\circ}\text{C}$) was measured and logged every 2 hours. HI 141AH Hanna Instruments are factory calibrated.

3.4.5 Cell loading procedure

The cells were loaded with approximately 1kg of material onto a 80micron nylon mesh (open area 32%). The mesh was included to reduce the volume of fines lost from the cell and prevent the base plate becoming blocked. The material was left undisturbed to avoid the separation of particles and removal of air void space.

3.4.6 Leaching procedure

Each cell was flooded with 500mL of tap water or previously specified lixiviant by opening valve 1 (Figure 3.2). An initial flood of 750mL was used in order to allow for solution being retained in the air voids in the sample. The flood solution was introduced from the bottom of the cell, rather than the top, to avoid the development of preferential flow pathways and reduce the likelihood of air bubbles and sample disturbance.

The flood period for each cell was 24 hours (as suggested by the proposed mine process). The leachate was drained into 500mL conical collection flasks by opening valve 2 (Figure 3.2). All cells were flushed fortnightly, except for the two cells that were flushed weekly and every 4 weeks.

3.4.7 Duration of experiments

All of the cells ran for 52 weeks. The reasons for this were mainly practical; as it was considered that a sufficient amount of data had been collected. It was also felt that 1 year was an adequate time frame to determine the long term effects of the different protocols. It is important to note that the number of weeks the cells were run for does not correspond with the number of cycles.

3.4.8 Solution treatment

pH, conductivity and relative reduction potential were all measured using a Mettler Toledo SevenMulti™ S40 unit. The solution parameters were measured and recorded immediately after the leachate was collected. All probes were calibrated prior to use each time they were used.

Solution pH was measured using a Mettler Toledo InLab® Expert Pro pH probe with an integrated temperature probe. The pH probe was calibrated using commercial buffer solutions (pH 4 and pH 7) before each set of measurements.

A Mettler Toledo LE703 general purpose conductivity probe was used for all conductivity measurements. It was calibrated using a 1413 μ S/cm standard solution.

The Oxidation Reduction Potential (ORP/Redox) was measured using a Mettler Toledo LE510 redox probe with a platinum pin. The electrode was standardised using a reference solution to measure an offset value for the probe. The measurement was taken and

recorded as relative reduction potential (Rel.mV) to account for the reference offset. For discussion and results the ORP values measured were adjusted for standard hydrogen electrode (SHE). From time to time observations on the test cells, leachate, precipitation etc. were recorded when deemed necessary.

3.4.8.1 Treatment of lixiviant

Before being added to the cell the pH, conductivity and volume of each lixiviant solution were measured. pH and conductivity were measured following the procedure described in 3.4.8. Blank samples of tap water, nutrient solution and iron (III) sulfate solution were collected for analysis every cycle after 24 weeks.

3.4.8.2 Treatment of leachate

Once collected the volume of leachate was measured by weight (assuming 1000g = 1000mL) and recorded. The pH, temperature, conductivity and relative reduction potential (Rel.mV) of the solution were measured using the same SevenMulti™ S40 unit, as described in section 3.4.8.

The alkalinity of the leachate was determined using a HACH 16900-08 Digital Titrator with a 1.600N (H₂SO₄) titration cartridge. For the titration 50mL of sample was used and deionised water made the solution up to 100mL. A Bromcresol Green – Methyl Red powder pillow was used as the indicator.

Two filtered samples of 30mL and 10mL were collected for analysis using a syringe and a CHROMACOL 0.45µm cellulosic nitrate filter tip (30-SF-45(CA)). These were then analysed via ICP-OES and ion chromatography (IC) to determine the concentration of dissolved elements. In order to preserve the ICP-OES sample it was acidified with 100µL of 10% HNO₃. A 30mL sample was also collected for Fe(II) analysis on the spectrophotometer. These were acidified and frozen for future use.

3.4.9 Testwork completion procedure

After the final drain the cells were disconnected and weighed individually with their contents. They were dried at 40°C until the contents were completely dry (3 days). The cells and contents were weighed to obtain the dry weight and then the contents were removed, bagged and stored for later analysis. The empty cells were weighed so that the wet and dry sample weight could be calculated. The duplicate samples were combined to make one residue sample.

3.5 Leaching programme

A summary of the leaching programme followed during this study can be found in Table 3.5.

Table 3.5 Summary of leaching programme

Leaching protocol	Rest period	Flood leach	Number of cycles
Control (A)	13 days	Tap water	27
Control (B)			
Double flush† (A)	12 days	Tap water	54
Double flush† (B)			
Weekly† (A)	6 days	Tap water	53
Weekly† (B)			
4 weekly† (A)	27 days	Tap water	14
4 weekly† (B)			
Nutrient* (A)	13 days	Nutrient solution	27
Nutrient* (B)			
Ferric* (A)	13 days	Fe ₂ (SO ₄) ₃	27
Ferric* (B)			
Recycle* (A)	13 days	recycled water	27
Recycle* (B)			

† rest period varying protocols * lixiviant varying protocols

3.6 Analysis of leachate

The samples collected throughout the testing schedule were analysed for cation and anions present in the leachate. All leachates were analysed within 3 days of collection and were stored in refrigerated conditions (<4°C) prior to analysis.

3.6.1 Cation analysis

The leachate samples were analysed in-house using a Perkin Elmer Optima 2100™ DV, ICP-Optical Emission Spectrometer (ICP-OES), with WinLab32 Windows software. The instrument was calibrated with 3 standards (10mg/L, 1mg/L, 0.1mg/L) prior to each batch of samples that was analysed. A 28 element standard and a uranium single element standard were used for calibration; the standards were freshly made each week. A blank sample, of 2% HNO₃ was included with each batch of samples analysed.

Following analysis the results were checked to see that there was no noise in the wavelength and that the standards were within 10% of the values expected. If the standards had drifted an adjustment was made and the data was reprocessed. The following cations were analysed based on initial data analysis: Al, Ca, Fe, K, Na, Mg, Si, U, V.

3.6.2 Anion analysis

In-house ion chromatography (IC) analysis was carried out on a DIONEX ICS-2000 Ion Chromatography System, with Chromeleon Windows software. Sulfate (SO₄), Fluoride (F) and Chloride (Cl) standards were made from 1000ppm solutions using deionised water of 18.2mΩ purity. The three standard strengths used were 100mg/L, 10mg/L and 1mg/L for SO₄ and 50mg/L, 5mg/L and 0.5mg/L for both F and Cl. New standards were created every 3 weeks.

The calibration standards, blank and leachate samples were measured into 5mL vials for analysis. New vials were used for each batch of analysis and the vials were disposed of

after use. Analysis for SO₄, F and Cl took 6 minutes per sample. Following analysis the element peaks of each sample were checked to ensure that they were clear and clean. If any peaks were suspected of drifting test strips were used to confirm the peak. For SO₄ Quantofix® Sulfate, 200-1600mg/L test strips were used and for Cl HACH QuanTab® test strips 30-600mg/L were used.

3.6.3 Quality control and quality assurance (QA/QC) of leachate analysis

To ensure that the in house uranium analysis by ICP-OES was accurate it was necessary to have as many samples as possible analysed on a different instrument. Composite samples combining the duplicate cell leachates were analysed externally on an ICP-MS. Details of this procedure can be found in Appendix F.

3.7 Cell residue analysis

After the completion procedure had been followed (section 3.4.9) the composite protocol residues were analysed following the same procedures described in section 3.2.1. Riffle splitting was carried out as per section 3.1.2 to ensure that samples were representative. The residues were analysed in house using the three acid “near total” microwave digest and a sample of each residue was sent for external lithium metaborate fusion analysis.

3.8 Spectrophotometric method

As per Geroni (2011) the Fe(II) concentration in leachate samples was measured spectrophotometrically using 2,2'-bipyridyl as the complexing agent. The samples were analysed on a Hitachi U1900 spectrophotometer at 520 nm absorbance. The full method and calibration curve used can be found in Appendix B.

3.9 Summary

The methods used to reduce and sample a representative portion the original bulk sample were presented along with the subsequent mineralogical and chemical characterisation techniques carried out to determine the uranium head grade. Experiment protocol design was explained and seven tests were developed: Control, Double flush, Weekly, 4 weekly, Nutrient, Ferric and Recycle. Treatment of leachate following each cycle was detailed and the QA/QC for uranium concentration was explained.

4 Results

The results of the extraction optimisation trials are summarised in this chapter. The results are presented and the discussion of these results can be found in Chapter 5. The test time is presented in weeks in order to keep presentation uniform and to enable easy comparison between the different test parameters.

The majority of results presented in this section are an average of the duplicate test cells A and B, where this is not the case it has been specified. For ease of comparison, analysis carried out on the leachate and residue material has been grouped into rest period leaching protocols (Control, Double flush, Weekly and 4 weekly) and lixiviant leaching protocols (Control, Nutrient, Recycle, Ferric). The Control test results are presented with both groups but will only be discussed once.

4.1 Mineralogical and chemical characterisation

4.1.1 Head grade material characterisation

Prior to beginning leaching experiments it was necessary to characterise the material to determine the elemental content of the ore. Head grade characterisation was carried out in a number of laboratories using several whole rock digestion techniques. The merits of the different methods and quantity of samples analysed are discussed in Chapter 5 (section 5.1.1).

Two acid digestion techniques were used. Table 4.1 shows the uranium, iron and sulfur content of the head material determined following ‘Four acid “near-total” digestion’ (Chapter 3, section 3.2.1.3). The assay was carried out at an accredited external lab (ALS – South Africa). ‘Three acid “near-total” microwave digestion’ analysis was carried out in house at Cardiff university (section 3.2.1.1) and the solution was analysed by ICP-MS at Aberystwyth university (section 3.2.1.2) (Table 4.2).

Table 4.1 ‘Four acid “near-total” digest’ analysis on head grade material (ALS – South Africa).

Head Grade	Uranium	Iron	Sulfur
	ppm	%	%
	361	2.76	2.63
	386	3.02	2.86
	421	2.85	2.73
Average	389	2.88	2.74

Table 4.2 ‘Three acid “near-total” microwave digestion’ analysis on head grade material (In house – Cardiff University).

Head Grade	Uranium
	ppm
	365
	392
	417
Average	391

Fusion analysis was used as an alternative whole rock assay technique. Lithium metaborate fusion was carried out on one sample at an accredited external lab (ALS – Seville) (section 3.2.1.5), and the uranium content determined as *421ppm*. In house lithium tetraborate fusion (section 3.2.1.4) results are shown in Table 4.3

Table 4.3 Lithium tetraborate fusion analysis on head grade material.

Head Grade	Uranium ppm
	419
	453
	474
	435
	466
	441
Average	448

Table 4.4 shows the uranium, iron and sulfur content of the head grade material determined by x-ray fluorescence (XRF). XRF does not require whole rock digestion, the samples were pulverised in a tema mill to <75 μ m (Chapter 3, section 3.2.4). The range of detection for uranium, iron and sulfur, using portable XRF, are ± 6 (ppm), ± 0.04 (%) and ± 0.06 (%) respectively. Detection ranges were provided by the XRF during the analysis.

Table 4.4 Portable XRF analysis on head grade material

Head Grade	Uranium ppm	Iron %	Sulfur %
	365	3.56	2.00
	365	3.56	1.99
	368	3.52	1.97
Average	366	3.55	1.99

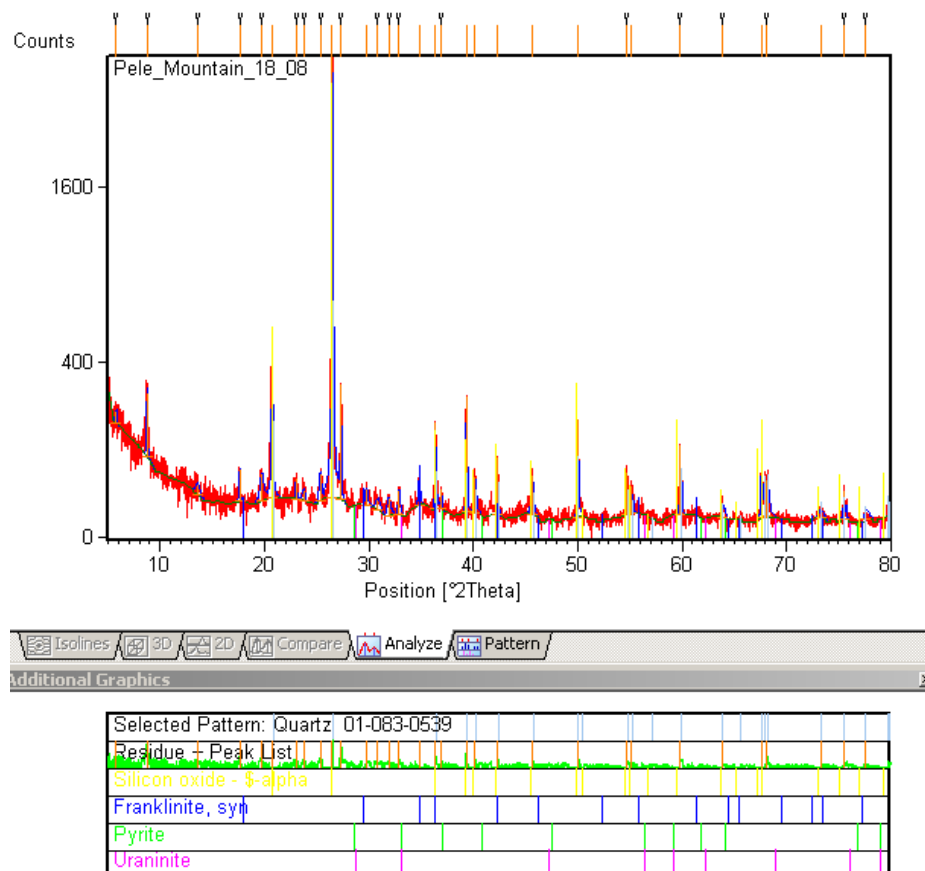
4.1.2 Sulfur content of head grade material

The sulfur content of the head grade material was determined by LECO induction furnace analysis (section 3.2.2) and the total sulfur and speciated sulfur content were measured. Results are provided in Table 4.5. Speciated sulfur indicates the type of sulfur present in the sample. As the total sulfur and speciated sulfur concentrations were found to be almost equal this indicates that all the sulfur in the material is present as sulfides.

Table 4.5 Total and speciated sulfur content of head grade material

Head Grade	Total sulfur	Speciated sulfur
	%	%
	2.25	2.16
	2.13	1.92
	2.10	2.16
	1.78	2.05
	2.17	2.50
	2.20	2.32
	2.24	2.16
	2.16	1.84
Average	2.13	2.14

As iron is the only element present in the ore in concentrations higher than 0.02% (see Appendix J) it is most likely that the sulfides are present as pyrite in the ore. This is corroborated by XRD analysis which identified pyrite as one of the main mineral phases present in the head grade material (Figure 4.1).

**Figure 4.1 XRD diffractogram identification of mineral phases.**

4.1.3 Particle size distribution of head grade material

Particle size distribution (PSD) analysis was carried out on a representative 250g of the head grade material (Figure 4.2) as described in Chapter 3 (section 3.3). It is evident that the ore crushing procedure has resulted in a large particle size distribution ($d_{50} \sim 4\text{mm}$, $d_{10} \sim 1.18\text{mm}$), however the majority of ore was in the $>1180\mu\text{m}$ size fraction.

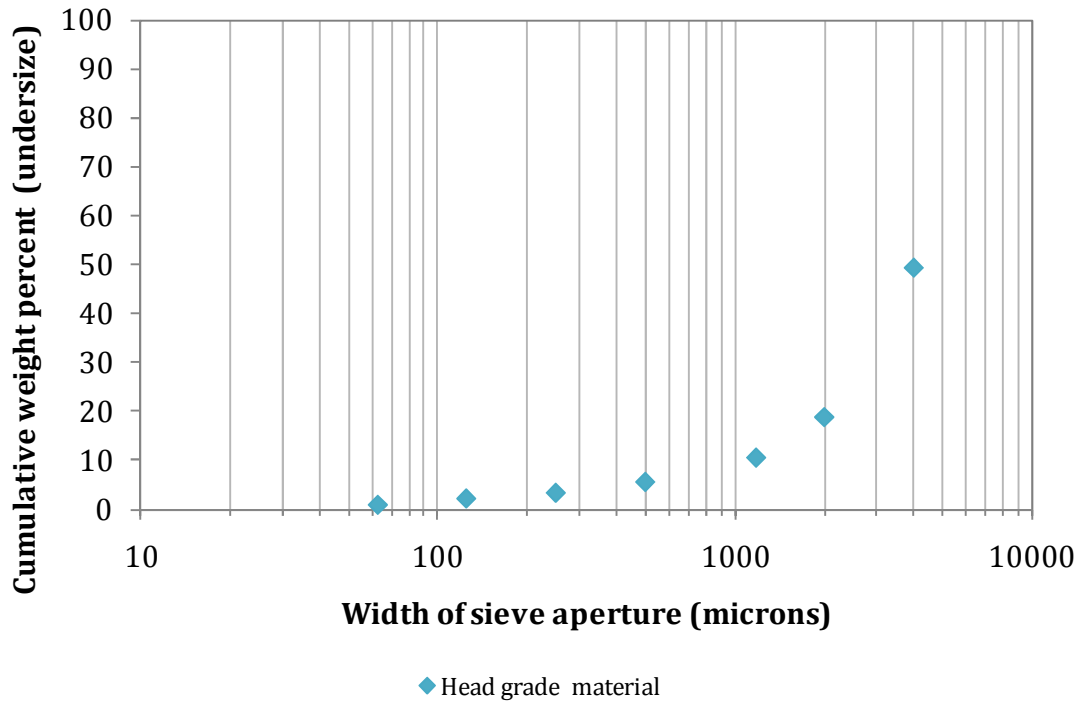


Figure 4.2 Particle size distribution, cumulative % undersize for head grade material

4.1.4 Residue material characterisation

Characterisation analysis was carried out on all residue samples following the completion of leaching test work. The concentration of elements in the residue samples is of interest so that, combined with the total leachate data, the reconstituted head grade of the material can be calculated (see discussion, section 5.1.3). The residues of the duplicate cells, for each leaching protocol, were combined for all of the post test physical and chemical

characterisation procedures. The head grade analysis, as presented in section 4.1 has been included with the residue results to provide an indication of the effectiveness of the different protocols.

Whole rock digestion was carried out on the combined duplicate residue samples using the ‘three acid “near-total” microwave digestion’ technique (see section 3.2.1.1) followed by ICP-MS analysis. The digested residue results are presented in Table 4.6 (the head grade material results from Table 4.2 have been included for comparison).

Table 4.6 ‘Three acid “near-total” microwave digestion’ on residue material

Sample	Uranium ppm	Sample	Uranium ppm
Head grade	365	Control	255
	392		257
	417		253
Average	391	Average	255
Double flush	308	Nutrient	262
	380		251
	332		248
Average	340	Average	254
Weekly	297	Ferric	197
	328		180
	314		181
Average	313	Average	186
4 weekly	180	Recycle	201
	165		211
	177		162
Average	174	Average	191

Three acid digestion results show that the 4 weekly protocol resulted in the greatest uranium extraction when compared with the head grade material. Addition of Fe(III) sulfate and recycled lixiviant were the second and third most effective extraction methods according to the three acid microwave digestion technique respectively. The Double flush and Weekly leaching protocols were less effective than the Control test, with the Double flush protocol being the least effective overall.

Portable XRF analysis (see section 3.2.4) was also carried out on the residue samples. The concentration of uranium, iron and sulfur are summarised in Table 4.7. Analysis was done in triplicate and the values averaged. According to the XRF analysis on the residue materials the 4 weekly leaching protocol was the most successful method to extract uranium. There was a 177ppm reduction in the concentration of uranium compared to the head grade material. Only the Recycled and 4 weekly leaching protocols extracted more uranium than the Control protocol did. The Weekly leach protocol showed the greatest reduction in iron concentration when compared to the head grade material, closely followed by the 4 weekly protocol. The lowest concentration of sulfur was also measured during the Weekly leaching test residue.

Comparison of the two techniques used to characterise the residue material shows a difference in the concentration of uranium remaining in the material. Although both techniques found that the 4 weekly leaching protocol lead to the greatest reduction in uranium, there is no agreement of the effectiveness of the remaining tests. As the material used for this test work is a low grade uranium ore it is considered to be heterogeneous and therefore can be difficult to characterise (Ramsey, 1997). This is discussed in more detail in Chapter 5 (section 5.1).

Table 4.7 Portable XRF analysis on residue material

Sample	Uranium		Iron		Sulfur	
	ppm	%	%	%	ppm	%
Head grade	365	3.56	3.56	2.00	314	3.14
	365	3.56	3.56	1.99	316	3.17
	368	3.52	3.52	1.97	315	3.16
Average	366	3.55	3.55	1.99	315	3.16
Double Flush	397	3.00	3.00	1.92	343	2.78
	397	3.00	3.00	1.91	343	2.77
	397	3.00	3.00	1.90	343	2.77
Average	397	3.00	3.00	1.91	343	2.78
Weekly	357	2.68	2.68	1.62	341	3.09
	359	2.67	2.67	1.64	340	3.08
	352	2.65	2.65	1.63	339	3.07
Average	356	2.67	2.67	1.63	340	3.08
4 weekly	249	2.77	2.77	1.82	286	2.81
	248	2.77	2.77	1.84	286	2.80
	250	2.76	2.76	1.81	284	2.79
Average	249	2.77	2.77	1.82	285	2.80
Average	343	2.78	2.78	1.73	343	2.77

4.1.5 Particle size distribution of residue material

Particle size distribution analysis was conducted on the post-test residue material using the same technique as for the head grade material (Chapter 3, section 3.3). For ease of comparison, the variable duration leaching results and the variable lixiviant leaching results have been presented in different figures. The head grade material has been included in each figure for easy comparison.

Figure 4.3 shows the PSD of the different rest period protocols. The +4000 μm size fraction shows the greatest variation, with a greater proportion of the 4 weekly and Control residue material being retained than the protocols which experienced more regular flush frequencies. This trend continues as the sieve aperture decreases until the +125 μm sieve size. For the variable lixiviant PSD in Figure 4.4, there is a noticeable difference between the amounts of Ferric and Recycle residue material retained in the sieves and the Nutrient residue. As the sieve aperture decreases the range between the cumulative weight percent and the different post-test residues also decreases.

As the particles were dry sieved the variation in the cumulative weight percent, seen for the rest period protocols (Figure 4.3), was initially thought to be caused by cementation of fines particles as a result of drying during the longer rest periods (Control and 4 weekly). However, as a similar variation is evident during the lixiviant protocols (Figure 4.4) cementation is thought to be an unlikely explanation because the rest period was the same for all of the lixiviant protocols. As over 50% of the particles typically remained in the largest sieve aperture (+4000 μm) the variation was then thought to be a result of 'blinding' however, if this was the case it would have occurred for all of the samples including the head grade. Therefore it is most likely that the variation is a result of experimental error as a result of only one head grade sample being sieved.

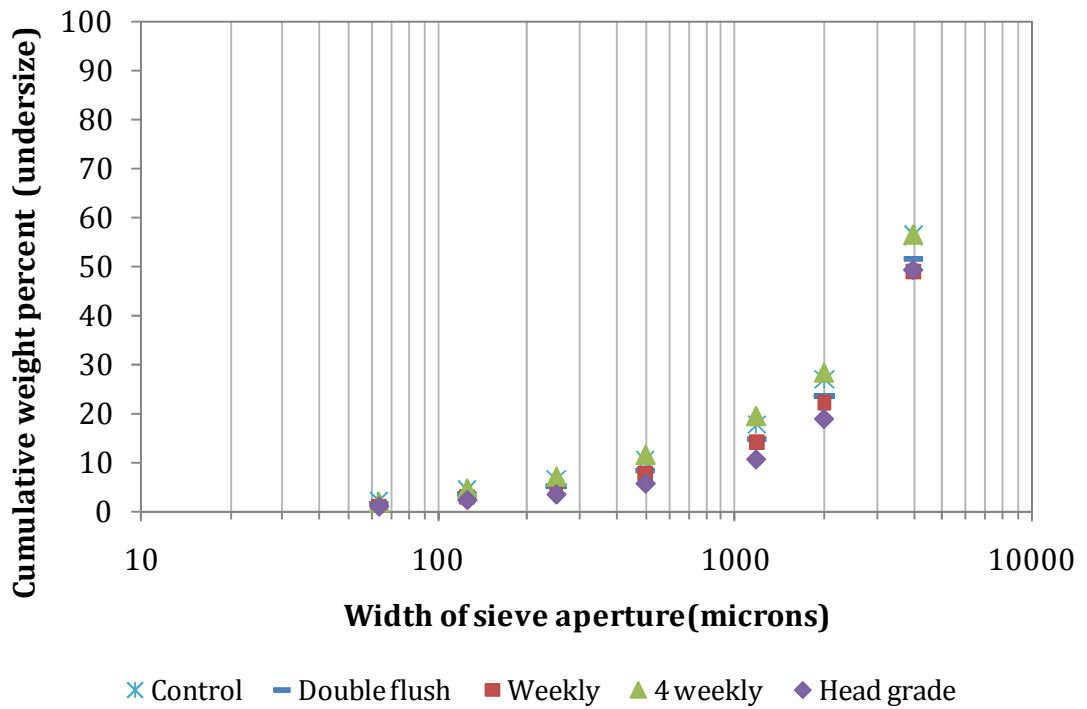


Figure 4.3 Particle size distribution, cumulative % undersize for rest period protocols residue material

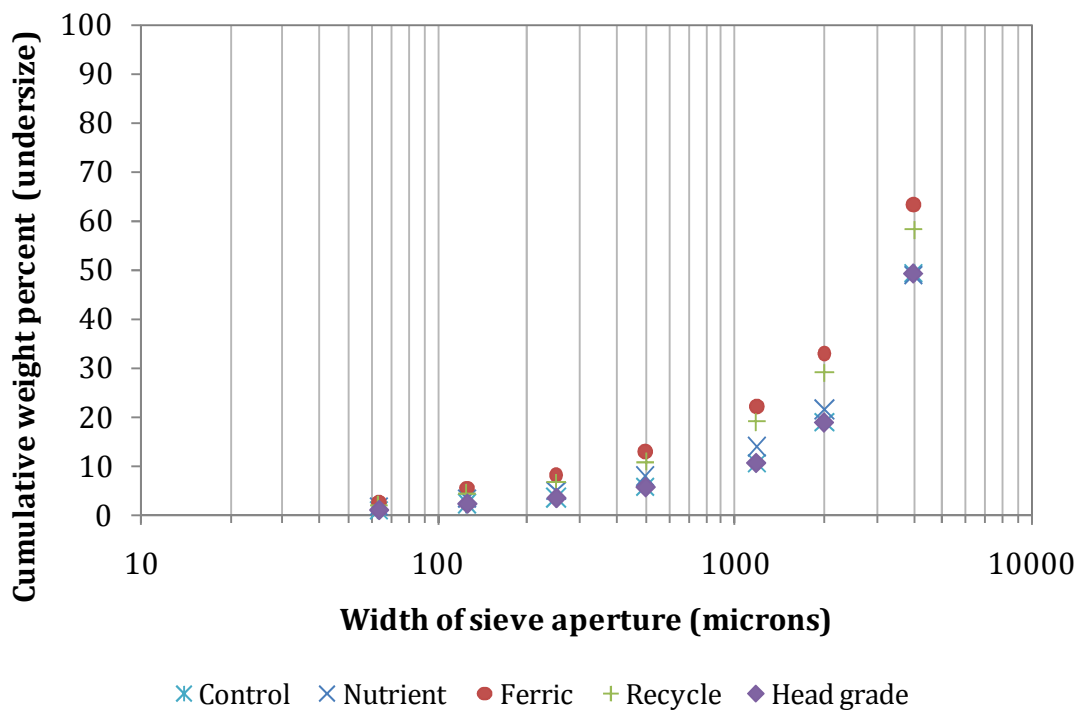


Figure 4.4 Particle size distribution, cumulative % undersize for lixiviant protocols residue material

4.2 pH of feed and leachate solutions

The pH of all solutions going in to and out of the cells was measured and the values recorded. Results are shown in graphical form. The pH of the feed solution is shown first (Figure 4.5 and Figure 4.6), followed by the leachate pH measurements (Figure 4.7 and Figure 4.8). For ease of comparison between the different tests the rest period protocols and the lixiviant protocols have been presented in different figures. In each figure graph (a) is the Control test so that all results can be compared with the Control test. Any observations on the Control test will only be mentioned once with the rest period protocols figure to avoid repetition. Conductivity readings are not presented but given in Appendix D.

The pH of individual cell data is differentiated by the solid line for cell A and the dashed line for cell B. For the Double flush test results presented in graphical form, the initial flush of week 0 is represented by a symbol because the preliminary point is lost on the line graph. Cell A is represented by a dash shape (–) and cell B is represented by a cross (X).

4.2.1 Cell feed solution pH

The pH of the feed solution for all of the rest period protocols is shown in Figure 4.5. Tap water was used as the feed solution for each of the tests and although the graphs seem to be showing a great deal of variation in the pH of the feed solution the maximum variation is 1.3pH over the course of 52 weeks.

The pH of feed solution for cells A and B of the Control test are shown in Figure 4.5(a). The average change in pH of the feed solution is 1.2 pH units. A similar pattern can be observed for the feed solution pH of the Double flush test, shown in Figure 4.5(b), except there is a drop in pH at week 20 (cycle 22) which did not occur during the Control test. The mean difference in pH is less than 1.2 pH unit. When compared to the Control test (Figure 4.5 (a)) the Double flush pH measurements follow a similar pattern and much of

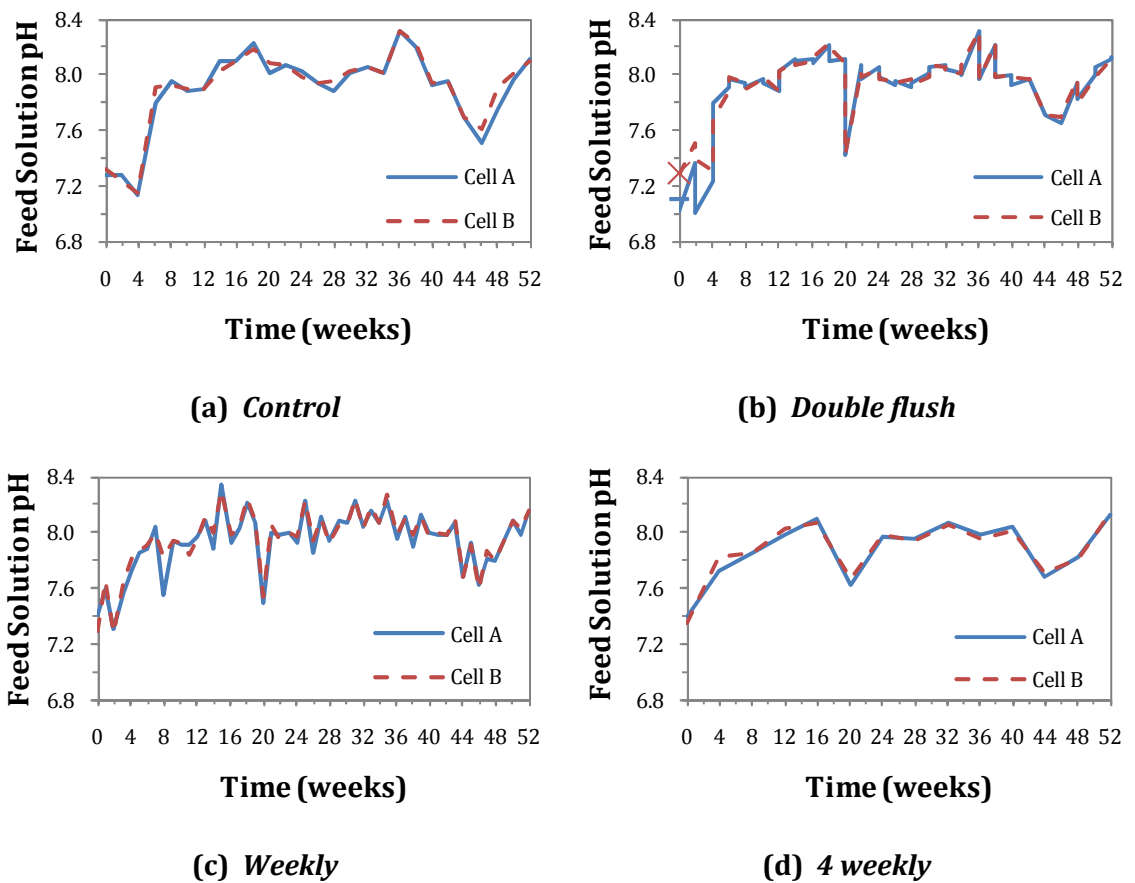


Figure 4.5 pH of cell feed solution for rest period optimisation trials.

(a) Control - pH of feed solution from cells A and B. (b) Double flush - pH of feed solution from cells A and B. (c) Weekly - pH of feed solution from cells A and B. (d) 4 weekly - pH of feed solution from cells A and B.

the variation from the Control test occurs during the second flush of the week, this is thought to be due to the way the feed solution was stored. Figure 4.5(c) shows the data for the Weekly flush test. With the exception of the low pH measurement at week 20 the pH of the Weekly flush test follows the trend observed for the Control test. There is more fluctuation of the pH between weeks which is also attributed to the way that the tap water was stored. The pH of the feed solution for the 4 weekly flush test is shown in Figure 4.5(d). At week 0, cycle 1 the pH is similar to the initial feed solution of the other rest period protocols. Comparison of Figure 4.5(a) and Figure 4.5(d) shows that there is a similarity in the pH measured for the tests with an oscillation of the pH values, starting low around pH 7.4 and concluding at week 52 with over pH 8.0. The mean change in pH was less than 1 pH unit overall.

Figure 4.6 contains the graphical representations of the feed solution pH of the lixiviant protocols. Figure 4.6(a) is the same as Figure 4.5(a) and shows the pH of the Control cell feed solution. Figure 4.6(b) is the pH measurements of the Nutrient solution lixiviant and was measured every 2 weeks in line with the flush cycles. The average initial pH was 7.23 and the pH varied from a low of 6.95 (week 6, cycle 4) and a high of 8.12 (measure on week 14, cycle 8 and week 15, cycle 9) throughout the test period. At week 10, cycle 6 the maximum variation between the duplicate cells occurred, a difference of 0.21 between cell A and cell B. Of the variable lixiviant test protocols the pH of the Nutrient feed solution was the highest and displayed the most similarities with the Control cells. This is due to the absence of Fe(III) sulfate in the nutrient mixture and the use of tap water instead of deionised water. This is discussed in more detail in Chapter 5, section 5.4.6.

The pH of the feed solution for the Recycle protocol is shown in Figure 4.6(c). Throughout the test duration the pH of the Recycle feed solution decreased from pH 7.26 (average) at week 0, cycle 1 to pH 2.87 at week 52, cycle 26. There was a low pH measurement taken on week 20, cycle 11; pH 2.44 and pH 2.61 for cell A and cell B respectively. Overall the pH

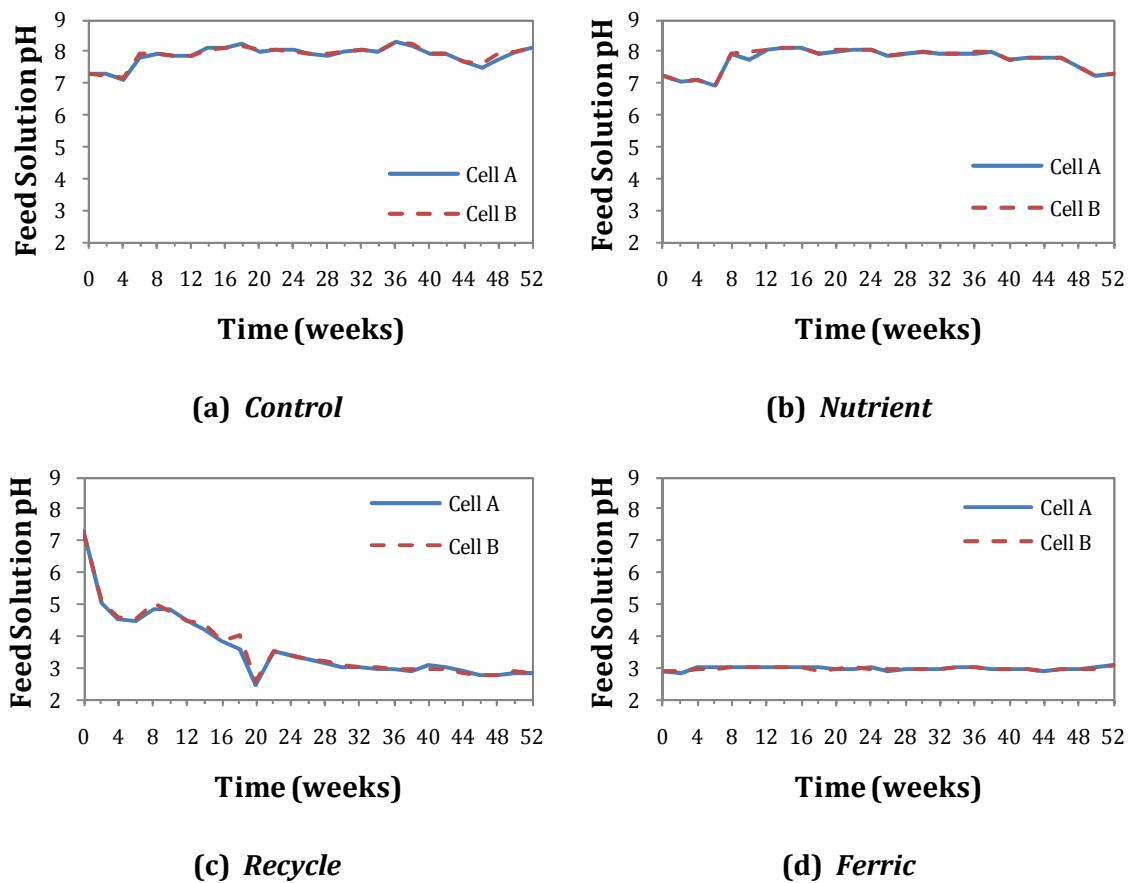


Figure 4.6 pH of cell feed solution for lixiviant protocol optimisation trials.

(a) Control - pH of feed solution from cells A and B. (b) Nutrient - pH of feed solution from cells A and B. (c) Recycle - pH of feed solution from cells A and B. (d) Ferric - pH of feed solution from cells A and B.

decreased by 4.4 pH units and this is thought to be due to the $[H^+]$ associated with sulfate and Fe(III) in the recycle solution.

Of the three lixiviant solutions, Fe(III) sulfate had the lowest initial pH at pH 2.93 (Figure 4.6(d)). It also varied the least over the 52 weeks, with a range of 0.21. The largest variation between cell A and cell B occurred at week 18, cycle 10 and week 26, cycle 14 both with a difference of 0.1 pH.

4.2.2 Cell leachate solution pH

The pH of the leachate solution collected from the test cells are presented in graphical form in Figure 4.7 and Figure 4.8. Their presentation is the same as in the previous section; the Control cell (a) is present in both figures and for the Double flush test results the initial flush of week 0 is represented by a symbol because the preliminary point is lost on the line graph. Cell A is represented by a dash shape (–) and cell B is represented by a cross (X).

After an initial 24 hours of leaching the pH of the Control cell was 5.11, over 2 pH units less than the feed solution pH. In Figure 4.7(a) it can be seen that the pH increases sharply for the second cycle, a trend that can be seen for all of the tests shown in Figure 4.7, although it is less pronounced for the 4 weekly protocol (Figure 4.7(d)). This initial pH decrease followed by an increase is believed to be a result of the highly reactive fine grain material which is present during the first flush. After the fines have been removed in the first leach solution the interstitial water which remains needs time to react with the rock.

Of the four test protocols which had tap water as the feed solution only the 4 weekly protocol showed a significant decrease in the leachate pH. Over the course of 52 test weeks the pH of leachate dropped from an initial average value of pH 4.91 to a final

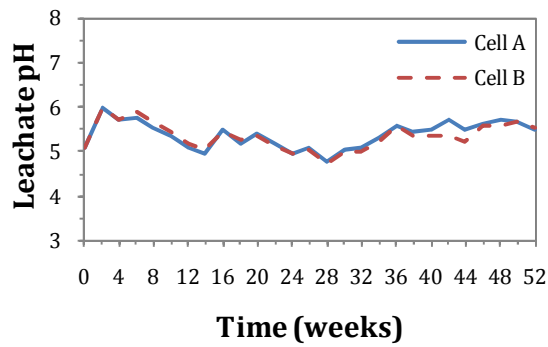
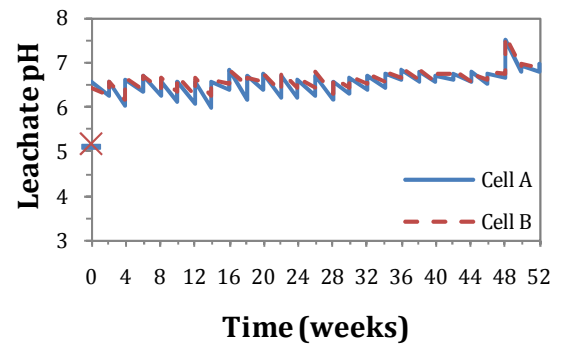
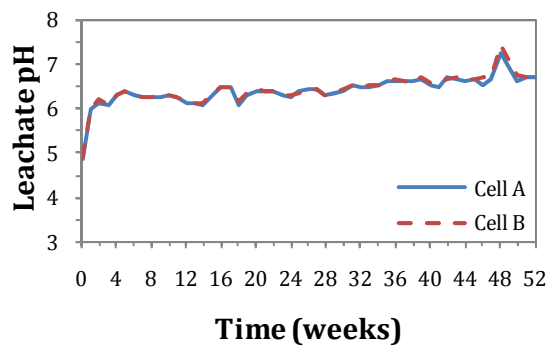
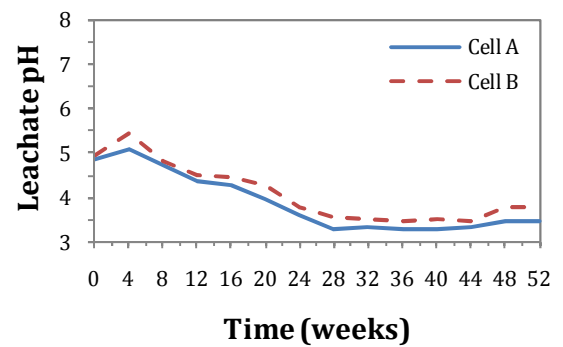
(a) *Control*(b) *Double flush*(c) *Weekly*(d) *4 weekly*

Figure 4.7 pH of cell leachate for rest period optimisation trials.

(a) Control - pH of leachate solution from cells A and B. (b) Double flush - pH of leachate solution from cells A and B. (c) Weekly - pH of leachate solution from cells A and B. (d) 4 weekly - pH of leachate solution from cells A and B.

average value of pH 3.62 (Figure 4.7(d)). In contrast, the other cells with tap water feed solution had final pH values higher than the leachate pH collected after week 0, cycle 1. The Double flush protocol had an average initial leachate measurement of pH 5.15 and a final average leachate value of pH 6.97 (Figure 4.7(b)). A similar observation can be made for the Weekly flush test where initial and final average pH values of 4.88 and 6.74 were measured respectively (Figure 4.7(c)). The final pH measurement for the Control test was pH 5.52 (average). Leachate pH values fluctuated, neither steadily increasing or decreasing, during the Control, Double flush and Weekly flush protocols. This effect was most pronounced for the Double flush test (Figure 4.7(b)) displayed a 'spiky' plot profile.

Differences in the lixiviant protocol (Figure 4.8) resulted in very different leachate pH plot profiles to those seen for the rest period protocols. For two of the three protocols, addition of Fe(III) sulfate (Figure 4.8(d)) and Recycled leachate solution (Figure 4.8(c)), the pH of the leachate dropped over the 52 testing weeks. Only the Nutrient lixiviant protocol (Figure 4.8(b)) showed an increase in the leachate pH rising from an average pH 4.04 at week 0, cycle 1 to pH 6.03 at week 52 (cycle 27). This is thought to be a result of buffering and is explored in Chapter 5, section 5.4.6.

The Recycle leachate, which had tap water as feed solution for week 0, showed a decrease in pH after the second cycle – an opposite response to the leachate pH observed for all of the other protocols which used tap water. This suggests that the ions present in the leachate could be beneficial to maintaining a lower pH necessary for uranium extraction, as discussed in the literature. However, at week 4 (cycle 3) the pH of the leachate increased for one cycle before steadily decreasing to a final average pH of 2.79.

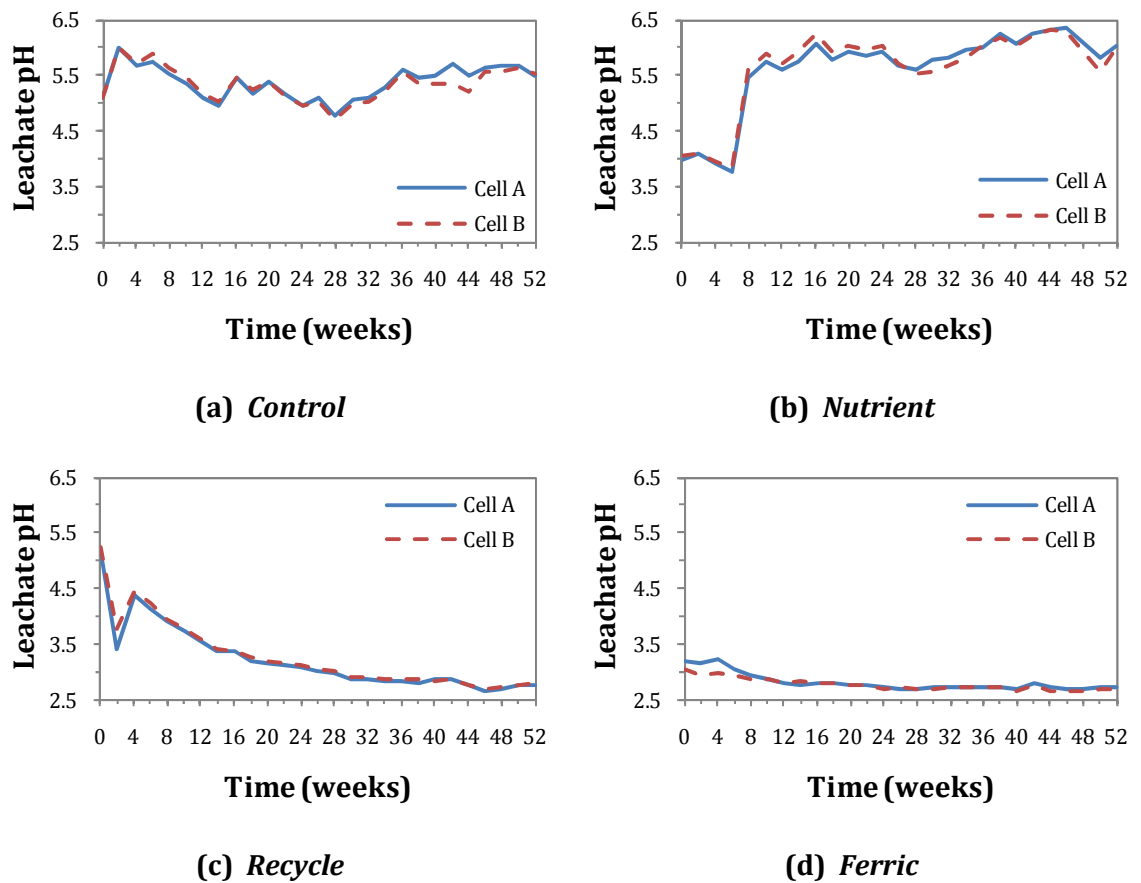


Figure 4.8 pH of cell leachate for lixiviant protocol optimisation trials.

- (a) Control - pH of leachate solution from cells A and B. (b) Nutrient - pH of leachate solution from cells A and B. (c) Recycle - pH of leachate solution from cells A and B. (d) Ferric - pH of leachate solution from cells A and B.

Fe(III) sulfate addition (Figure 4.8(d)) presents the smallest variation in leachate pH measurements. This trend was also observed for the feed solution pH and is thought to be due to the consistent pH of the feed solution. The pH of the Fe(III) sulfate leachate was initially greater than the feed solution pH until week 6 (cycle 4), indicating buffering by the test material and development of optimum leaching conditions. Variation between the A and B duplicate cells was greatest for the Fe(III) sulfate leachate compare with the other leaching protocols, reaching a maximum of 0.23 pH units at week 2 (cycle 3). By week 8 (cycle 5) the leachate pH showed a lot less variance and stayed that way until the end of the test work.

4.3 Redox potentials (Eh values)

Figure 4.9 and Figure 4.10 contain the results of redox measurements (corrected to Eh versus Standard Hydrogen Electrode (SHE)) taken of the leachate solutions and are presented in mV. As before, the results are split into duration variable protocols (Figure 4.9) and lixiviant variable protocols (Figure 4.10) and the data from the Control cell is presented in each figure as graph (a). Symbols ((-) for cell A and (X) for cell B) identify the initial flush for the Double flush protocol.

The highest redox conditions occurred in the 4 weekly (Figure 4.9(d)), Recycle (Figure 4.10(c)) and Ferric (Figure 4.10(d)) protocols. An Eh-pH diagram has been presented in the discussion (Chapter 5, Figure 5.3) along with the suggested uranium speciation.

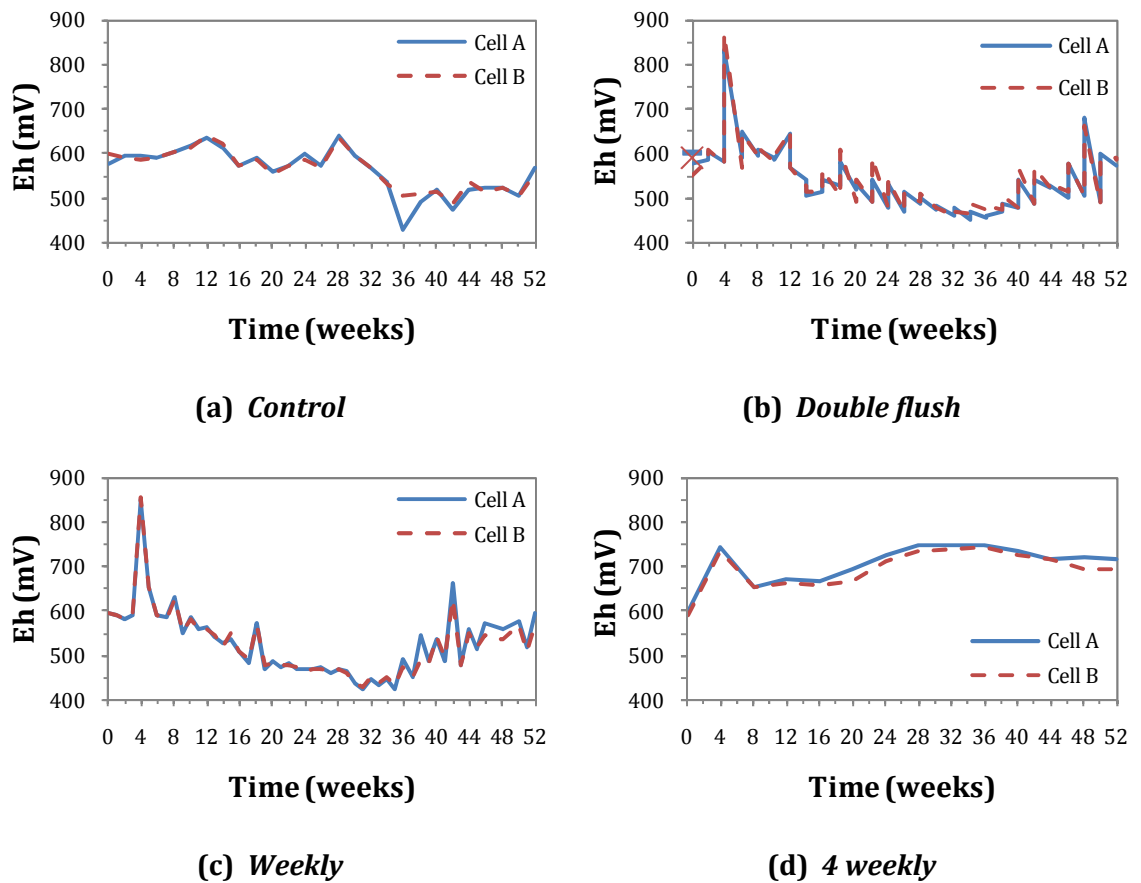


Figure 4.9 Eh of cell leachate solution for rest period protocol optimisation trials.

- (a) Control - Eh of leachate solution from cells A and B. (b) Double flush - Eh of leachate solution from cells A and B. (c) Weekly - Eh of leachate solution from cells A and B. (d) 4 weekly - Eh of leachate solution from cells A and B.

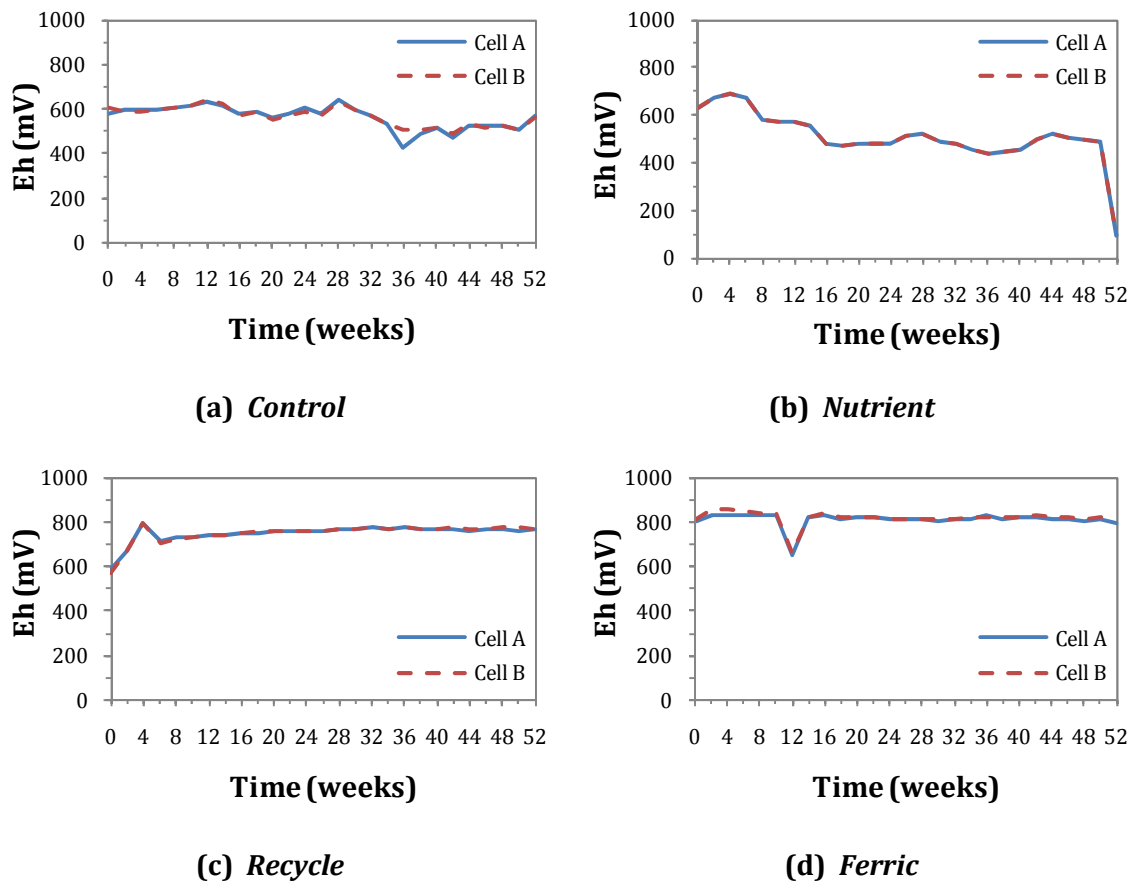


Figure 4.10 Eh of cell leachate solution for lixiviant protocol optimisation trials.

- (a) Control - Eh of leachate solution from cells A and B. (b) Nutrient - Eh of leachate solution from cells A and B. (c) Recycle - Eh of leachate solution from cells A and B. (d) Ferric - Eh of leachate solution from cells A and B.

4.4 Release rate of dissolved solids from cells

Throughout the test work samples of the feed and leachate solutions were collected and analysed to determine the dissolved solid concentrations. All samples were filtered unless otherwise stated (Chapter 3, section 3.4.8.2). Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) analysis (Chapter 3, section 3.6.1) was used to determine the cations in solution and the anion concentration was determined by Ion Chromatography (IC) analysis (Chapter 3, section 3.6.2). The results are presented in the same format as they have been earlier in this chapter, with the rest period protocol results grouped separately to the lixiviant protocol results. The different elements are presented individually and the interactions between them are considered in the discussion chapter (Chapter 5). Element extraction is presented as mg/kg/cycle and cumulative extraction has not been considered here. Lines have been used in graphs for presentation clarity and have not been ‘smoothed’.

4.4.1 Release rate of uranium from cells

Uranium release from all of the cells decreased over the duration of the test work, the results are presented in Figure 4.11 and Figure 4.12. For the rest period leaching protocols (Figure 4.11) the Control protocol (Figure 4.11(a)) and the 4 weekly flush protocol (Figure 4.11(d)) are the experiments which extracted the most uranium.

Protocols with flush cycles more frequent than the Control test (2 weeks); the Double flush (Figure 4.11(b)) and Weekly flush (Figure 4.11(c)) extracted a comparatively negligible amount of uranium. Following an initial extraction of 17.5 mg/kg and 30.5 mg/kg for the Double flush and Weekly flush protocols respectively, the amount of uranium extracted per cycle drops considerably to an average of 0.9 mg/kg/cycle and 0.6 mg/kg/cycle for the Double and Weekly flush respectively. This corresponds to the leachate pH for the Double (Figure 4.7(b)) and Weekly (Figure 4.7(c)) flush protocols as the circumneutral pH measured would lead to unfavourable uranium extraction conditions.

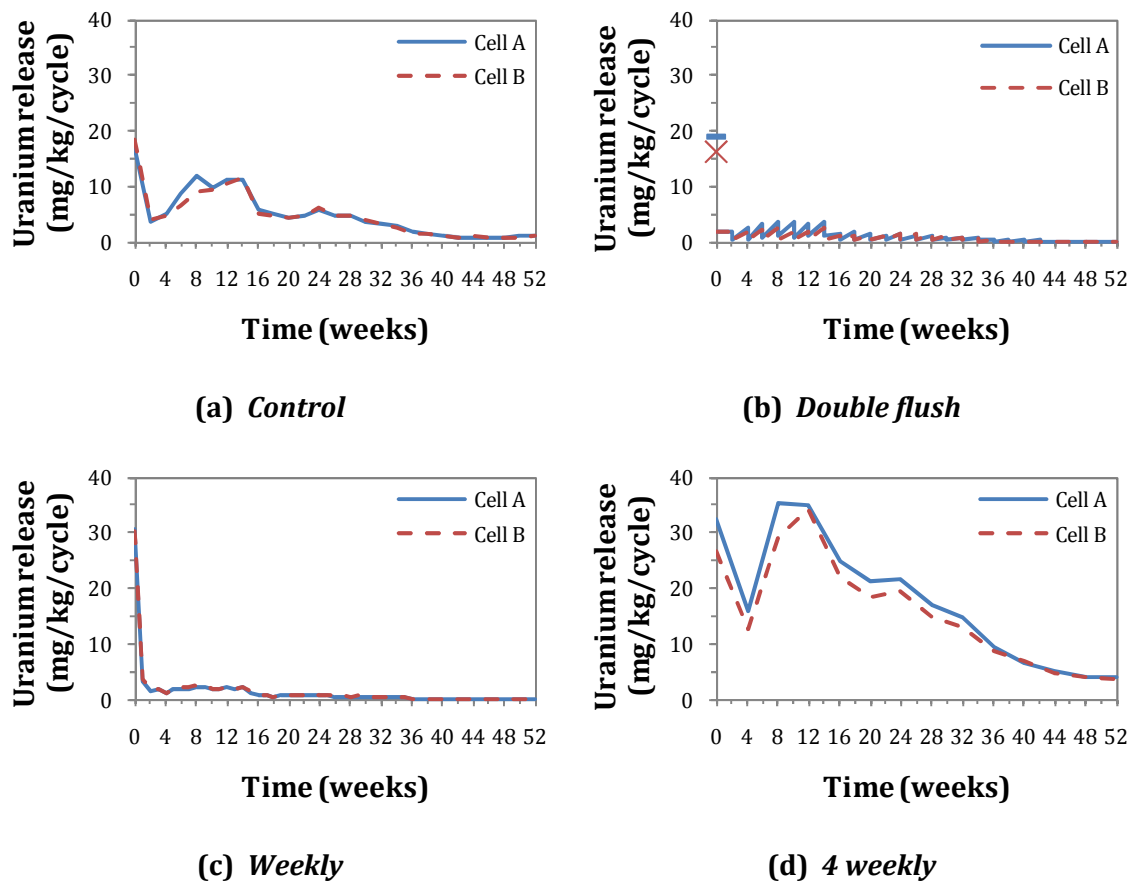


Figure 4.11 Uranium release rate per cycle for rest period optimisation trials.

(a) Control - Uranium release rate per cycle from cells A and B. (b) Double flush - Uranium release rate per cycle from cells A and B. (c) Weekly - Uranium release rate per cycle from cells A and B. (d) 4 weekly - Uranium release rate per cycle from cells A and B.

The 4 weekly flush protocol was more effective than the Control test for extracting uranium. Similar to the other rest period protocols, the amount of uranium leached by both the Control and the 4 weekly test, dropped after the initial flush from 17.7 mg/kg to 3.8 mg/kg for the Control protocol and 29.6 mg/kg to 14.4 mg/kg for the 4 weekly protocol. Uranium release for both tests improved again after the initial dip however, the Control protocol never extracted more than had been achieved for the initial flush whereas the 4 weekly protocol increased beyond the initial extraction concentration.

The longer rest period had a measurable effect on the amount of uranium extracted per cycle. Along with the decrease in leachate pH (Figure 4.7(d)) the increase in duration led to an increase in uranium extracted, probably due to the more optimum uranium extraction conditions created by the increase in H⁺ ions. This is referred to in Chapter 5, section 5.4.2.

Of the lixiviant protocols the addition of Fe(III) sulfate (Figure 4.12(d)) was the only one which produced better uranium release compared to the Control test. Although the Recycled leachate displayed a higher release concentration per cycle on initial inspection of results (Appendix C), the uranium concentration is cumulative because the solution is recycled therefore, once adjusted, the release rate was lower than that measured for the Control test (Figure 4.12(c)). Addition of Nutrient solution as a lixiviant (Figure 4.12(b)) appears to have had a detrimental effect on the release of uranium into solution. After a promising initial extraction, the uranium release per cycle reduced to below the limit of detection (0.11 mg/kg) by week 16, cycle 9, possible reasons for this are discussed in Chapter 5, section 5.4.6.

Unlike all the other test protocols the Fe(III) sulfate lixiviant did not display the same substantial decrease in uranium release. Although the release of uranium did reduce it was a much steadier decline. Around week 44, it can be observed that the concentration of

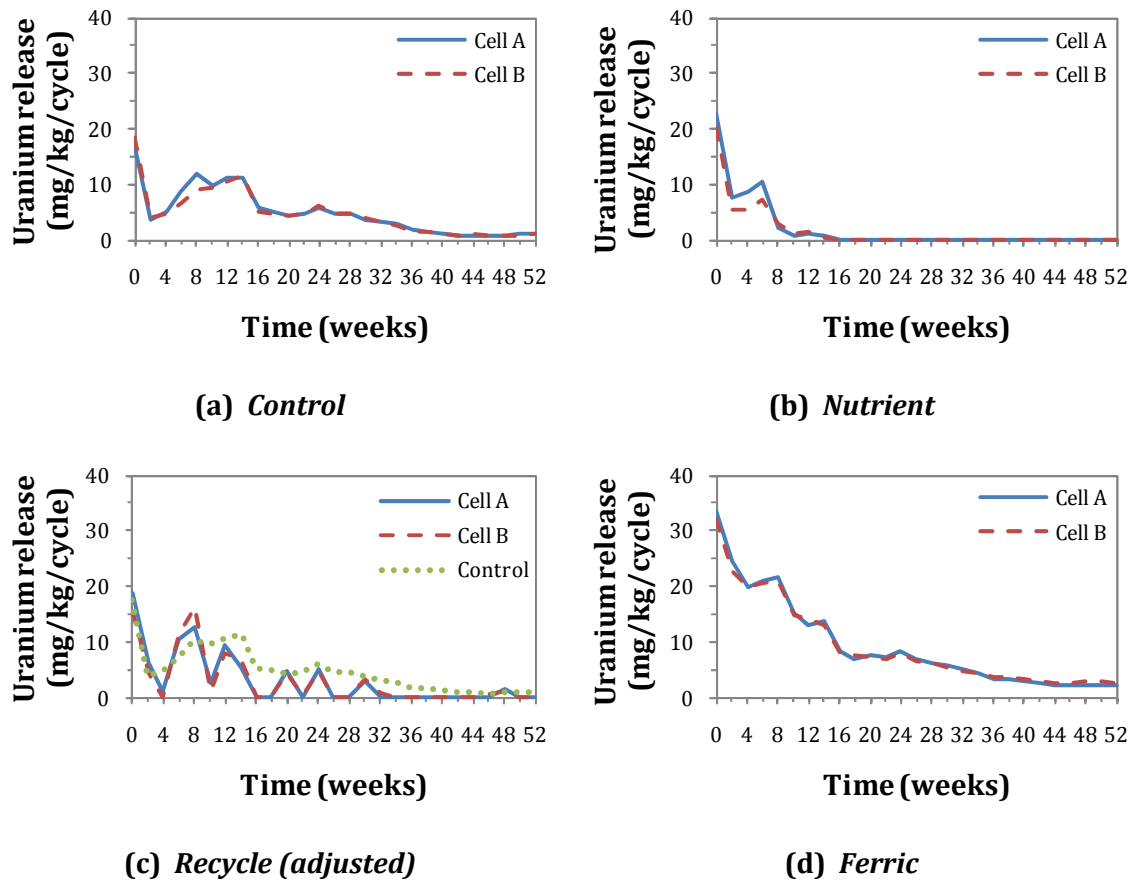


Figure 4.12 Uranium release rate per cycle for lixiviant protocol optimisation trials.

(a) Control - Uranium release rate per cycle from cells A and B. (b) Nutrient - Uranium release rate per cycle from cells A and B. (c) Recycle (adjusted) - Uranium release rate per cycle from cells A and B. (d) Ferric - Uranium release rate per cycle from cells A and B.

uranium released per cycle for the Control, 4 weekly flush and Fe(III) sulfate lixiviant protocols starts to stabilise. What is clear, is that there is a similar uranium release rate for the 4 weekly rest period and the Fe(III) sulfate protocols. This is significant because it could reduce the need for an oxidant leading to lower mining costs and thus optimising the process; this is discussed further in Chapter 5, section 5.5.

4.4.2 Release rate of iron from cells

Release of iron into the leach solution was varied across the different test protocols. The iron release results are presented in the same format as the uranium release results with the rest period protocols and the lixiviant protocols presented separately, Figure 4.13 and Figure 4.14 respectively. In addition to the adjusted Recycle leachate figure (Figure 4.14(c)) the data for the unfiltered Ferric protocol samples (Figure 4.14(e)) are also presented for comparison to the filtered results.

Similar to uranium release in section 4.4.1, iron release in some of the experiments quickly fell close to the limit of detection (0.003 mg/kg). Both the Double flush protocol (Figure 4.13(b)) and Weekly flush protocol (Figure 4.13(c)) released very little iron following the initial flush cycle. With initial release concentrations of 13.9 mg/kg (Double flush) and 23.2 mg/kg (Weekly), the average concentration from cycle 2 onwards was 0.04 mg/kg (Double flush) and 0.06 mg/kg (Weekly) per cycle. This lack of iron in the leachate is thought to be because of the Fe solubility occurring in the pH conditions.

The Control test (Figure 4.13(a)) and the 4 weekly test (Figure 4.13(d)) displayed very similar plot profiles despite the different rest duration lengths. Following the iron release from the initial 24 hour flood, 12.0 mg/kg and 23.0 mg/kg respectively for the Control and 4 weekly test, the iron concentration dropped very low (0.1 mg/kg and 1.0 mg/kg respectively) before recovering to a varied extent. The maximum amount of iron released

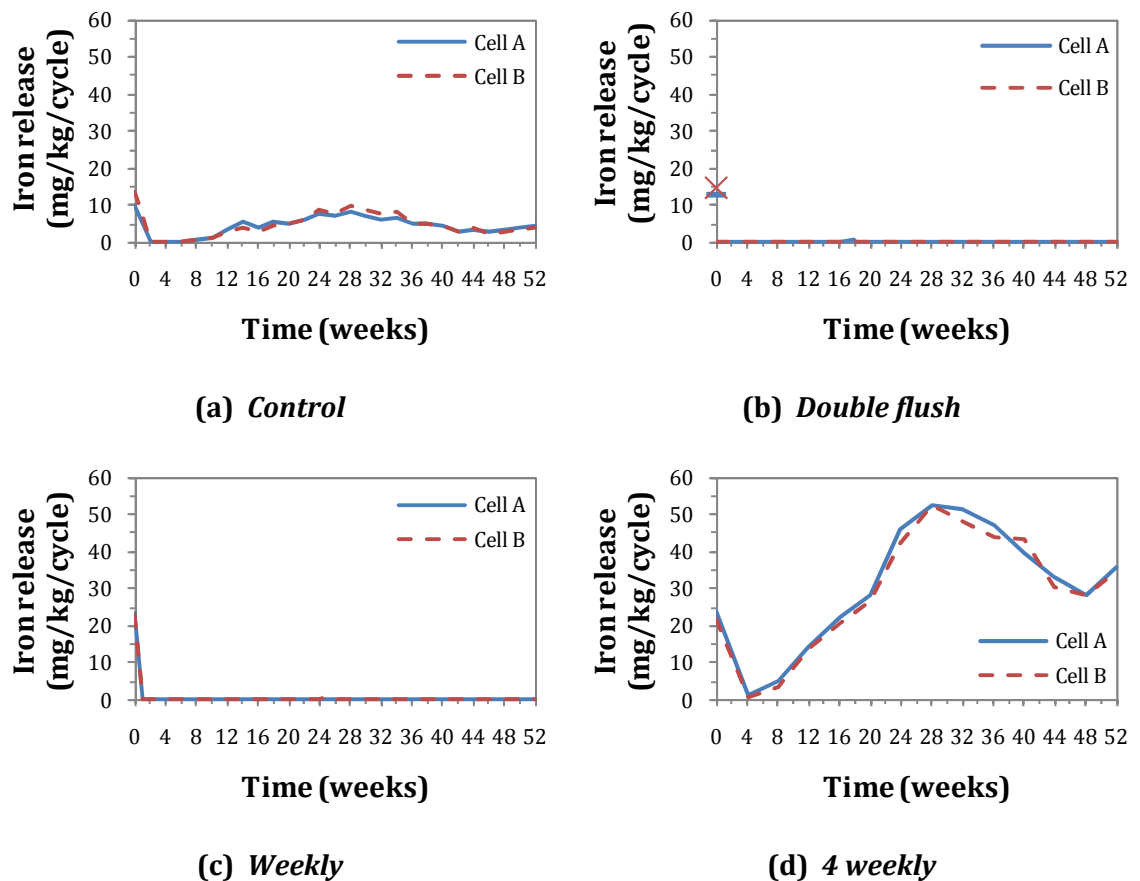


Figure 4.13 Iron release rate per cycle for rest period protocol optimisation trials.

(a) Control - Iron release rate per cycle from cells A and B. (b) Double flush - Iron release rate per cycle from cells A and B. (c) Weekly - Iron release rate per cycle from cells A and B. (d) 4 weekly - Iron release rate per cycle from cells A and B.

during one cycle, after the initial cycle, was 9.1 mg/kg for the Control and 52.3 mg/kg for the 4 weekly protocols. Interestingly, both of these maximum releases occurred on week 28. The similarity in plot profiles (release rate decreasing and then starting to increase again) could be down to the temperature of the laboratory and will be discussed later in section 4.6. The difference between the maximum iron released from the Control cell and that released from the 4 weekly cells is consistent with the release of uranium and the leachate pH. Once again the increased rest period for the cell and subsequent increase in contact time between the material and interstitial water appears to have been beneficial to the overall extraction, discussed in Chapter 5, section 5.5. It is interesting to note that despite the iron extraction per cycle increasing over the duration of the test work the uranium extraction does not follow the same trend.

The lixiviant protocols (Figure 4.14) had a similar effect on the release of iron as it did on the release of uranium into the leachate. Again the Nutrient solution (Figure 4.14(b)) had limited success extracting iron when compared to the Control and iron release was low following the initial cycle. The Recycle solution appeared to produce a steady increase in iron release (Appendix C) but once normalised to show the mg/kg released per cycle (Figure 4.14(c)) the iron release was sporadic.

As the use of Fe(III) sulfate as a lixiviant involved the addition of iron to the solution, it is no surprise that the highest iron concentrations were observed in the leachate from this test (Figure 4.14(d)). It is interesting however, to see that the concentration of iron measured is not constant and actually increases over time. This leads to the thought that oxidation of pyrite must be occurring as it is the only other source of iron in the ore material.

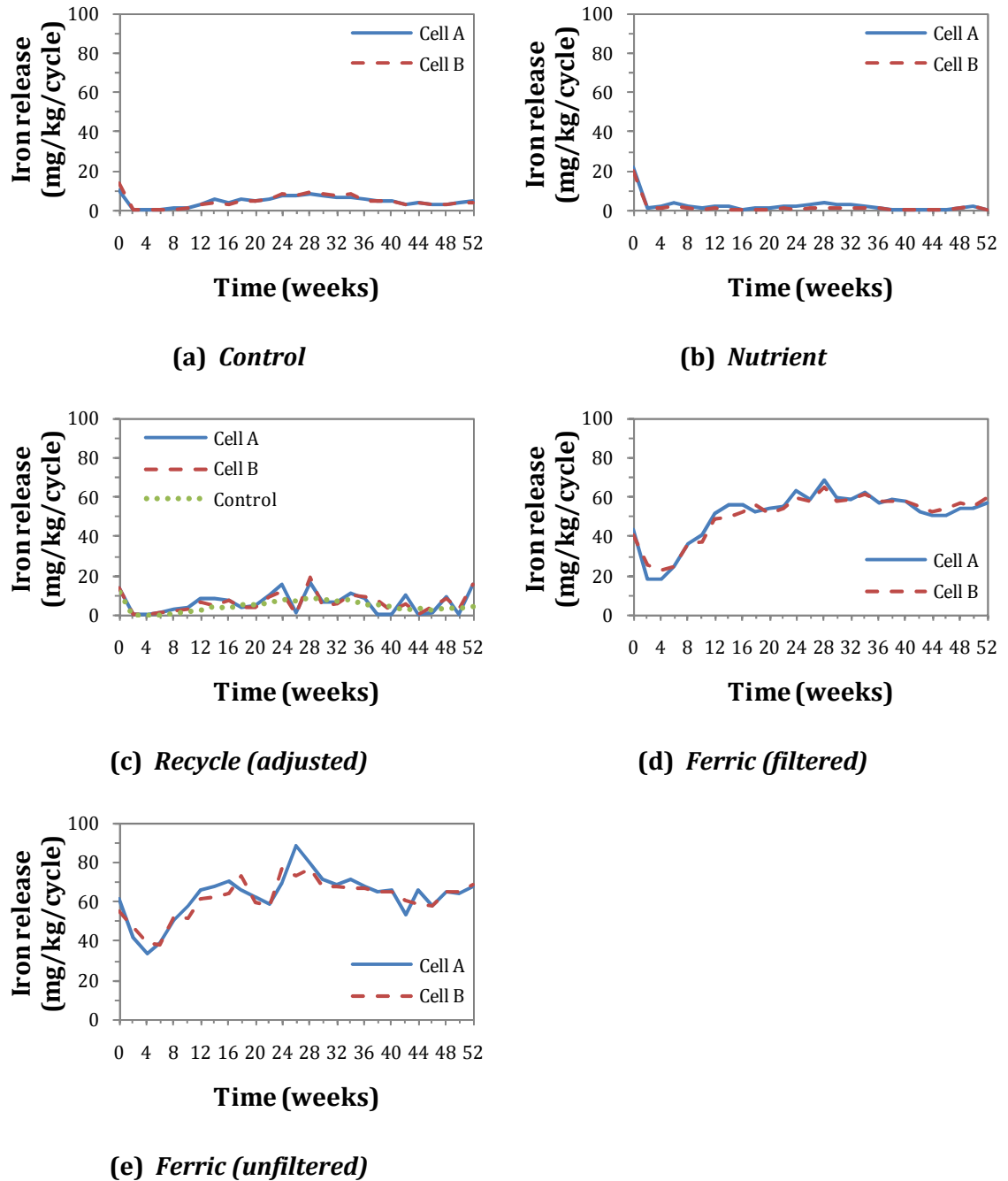


Figure 4.14 Iron release rate per cycle for lixiviant protocol optimisation trials.

(a) Control - Iron release rate per cycle from cells A and B. (b) Nutrient - Iron release rate per cycle from cells A and B. (c) Recycle (adjusted) Iron release rate per cycle from cells A and B. (d) Ferric (filtered) - Iron release rate per cycle from cells A and B. (e) Ferric (unfiltered) - Iron release rate per cycle from cells A and B.

Iron release rates from the filtered (Figure 4.14(d)) and unfiltered (Figure 4.14(e)) leachate are different, with a maximum concentration of 66.8 mg/kg (week 28, cycle 15) and 76.7 mg/kg (week 24, cycle 13) iron released over one cycle respectively. The difference in iron concentration between the filtered and unfiltered leachate samples indicates that there must have been some solids or precipitates that contained iron. It is likely that the leachate became saturated with iron and thus started to precipitate, some of which would have been wash out with the leachate and analysed in the unfiltered sample.

4.4.3 Release rate of sulfate from cells

The release of sulfate was similar to that of iron and uranium and showed varied levels of success depending on the testing protocol. Sulfate release is linked to the oxidation of pyrite and thus higher extraction was only seen in the cells which also solubilised iron and, subsequently uranium. As pyrite has the chemical equation FeS_2 , sulfur is present in a molar ratio of 2:1 (S:Fe).

Double flush (Figure 4.15(b)) and Weekly flush (Figure 4.15(c)) protocols resulted in the least amount of sulfate being released for the duration variable tests. Other than the Weekly test which had one singular peak of 210 mg/kg on week 31 (cycle 32), both tests followed the same pattern as previously presented. Initial release measurements of 216 mg/kg and 240 mg/kg for the Double flush and Weekly flush tests respectively, followed by average releases of 42 mg/kg per cycle for both. The Double flush displayed a 'spiky' plot profile the same as was observed for uranium release.

For both the Control (Figure 4.15(a)) and the 4 weekly flush (Figure 4.15(d)) tests the initial flood resulted in the maximum concentration of sulfate released throughout the duration of the test work, 233 mg/kg and 255 mg/kg respectively. Although the sulfate release measured for the 4 weekly protocol leachate increased again after a dip at week 4 (cycle 2), the release for the Control test remained below 107 mg/kg/cycle. The amount of

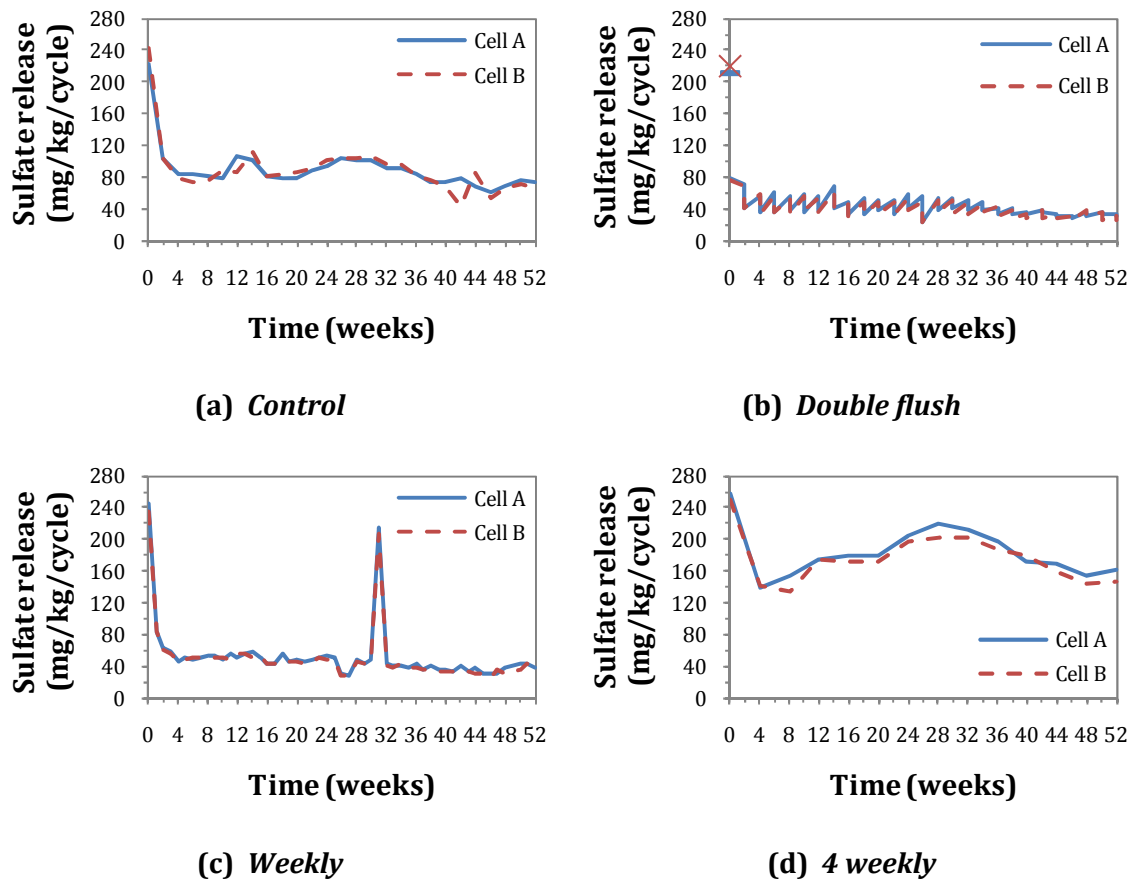


Figure 4.15 Sulfate release rate per cycle for rest period protocol optimisation trials.

(a) Control - Sulfate release rate per cycle from cells A and B. (b) Double flush - Sulfate release rate per cycle from cells A and B. (c) Weekly - Sulfate release rate per cycle from cells A and B. (d) 4 weekly - Sulfate release rate per cycle from cells A and B.

sulfate and iron released by the 4 weekly flush protocol most probably lead to the higher uranium dissolution experienced with this test. It is thought that through the increased contact time between the interstitial water and ore material conditions conducive to extraction were able to develop, discussed in more detail in Chapter 5, section 5.4.2.

For the lixiviant protocols (Figure 4.16), both the Nutrient (Figure 4.16(b)) and Ferric lixiviant (Figure 4.16(d)) solutions had sulfate added. Ammonium sulfate and potassium sulfate were present in the Nutrient solution and Fe(III) sulfate was used for the Ferric solution, thus the graphical sulfate results are not fully representative of the sulfate released from the ore material. Although sulfate in solution is beneficial for uranium dissolution, to form soluble uranium-sulfate complexes, other conditions are also necessary such as low pH and an oxidant which was not the case for the Nutrient protocol. On the other hand, these conditions did occur for the Ferric protocol because of the addition of Fe(III) sulfate.

Release of sulfate from the Recycle solution test initially appears to have the highest sulfate release rate out of all of the test protocols, reaching a high of 532 mg/kg (Appendix C). However, when the adjusted Recycle protocol results (Figure 4.16(c)) are checked the release rate is considerably lower, with a maximum release of 206 mg/kg/cycle during the initial cycle, and an overall release rate which was much lower than the Control protocol. This possibly indicates precipitation of sulfate, discussed in Chapter 5, section 5.4.5.

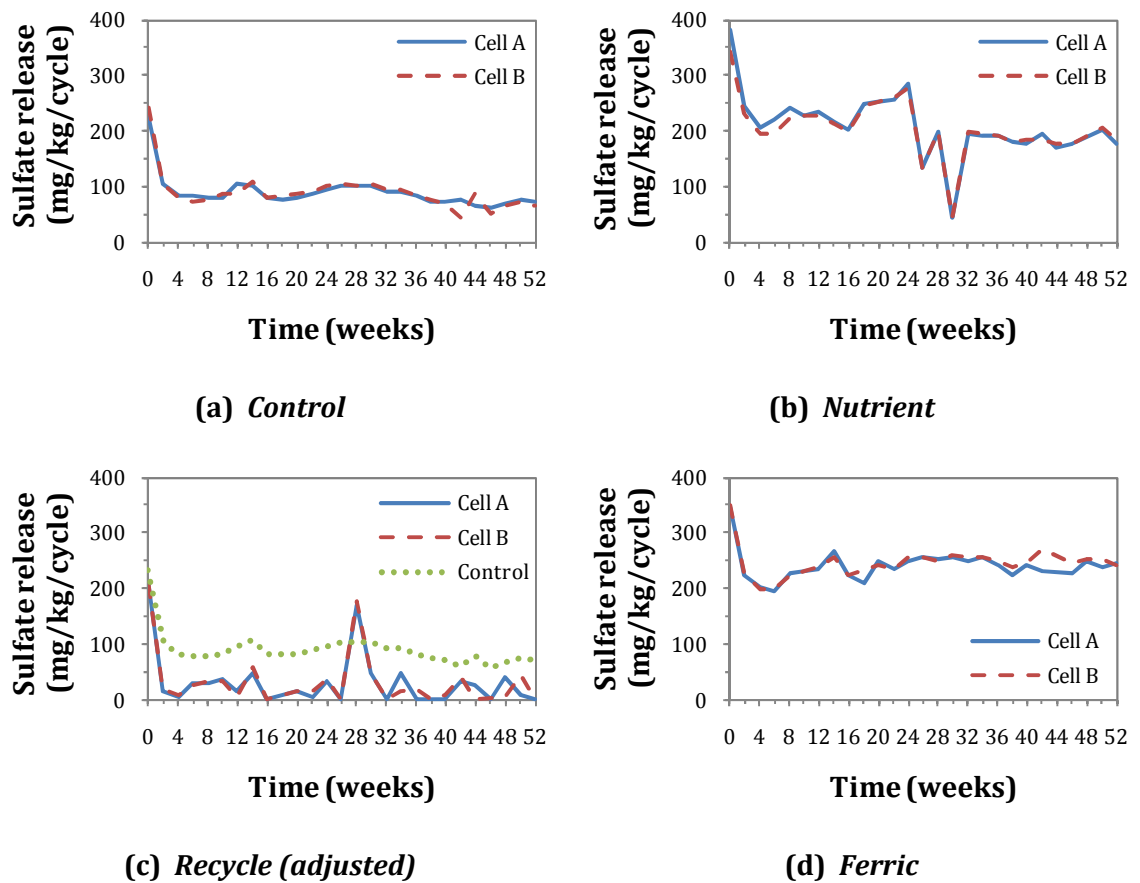


Figure 4.16 Sulfate release rate per cycle for lixiviant protocol optimisation trials.

(a) Control - Sulfate release rate per cycle from cells A and B. (b) Nutrient - Sulfate release rate per cycle from cells A and B. (c) Recycle (adjusted) - Sulfate release rate per cycle from cells A and B. (d) Ferric - Sulfate release rate per cycle from cells A and B.

4.4.4 Release rate of the minor species from cells

The other elements that were analysed for on a regular basis have been summarised below. These were Aluminium (Figure 4.17), Calcium (Figure 4.18), Potassium (Figure 4.19), Magnesium (Figure 4.20), Sodium (Figure 4.21), Vanadium (Figure 4.22), Silicon (Figure 4.23), Fluoride (Figure 4.24) and Chloride (Figure 4.25). Complete data can be found in Appendix (C) and were not included in this results chapter as they were released from cells at rates much lower than for U, Fe and SO₄.

It can be summarised that the 4 weekly and Ferric protocols show higher releases compared to the other test protocols. Despite the low pH of the Recycle protocol there was also low corresponding release for all elements. Vanadium release was low for all protocols regardless of leachate pH. Release of magnesium and potassium appeared high for the Nutrient protocol however; these were present in the lixiviant and not a result of leaching.

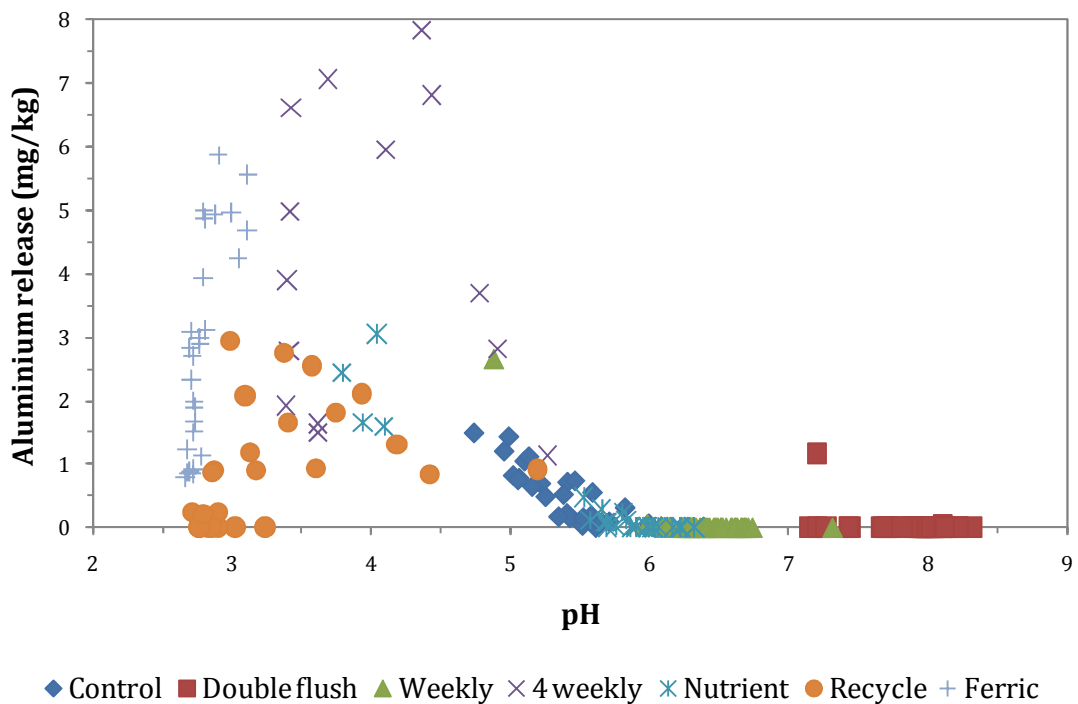


Figure 4.17 Aluminium release vs. pH scatter plot for all protocols.

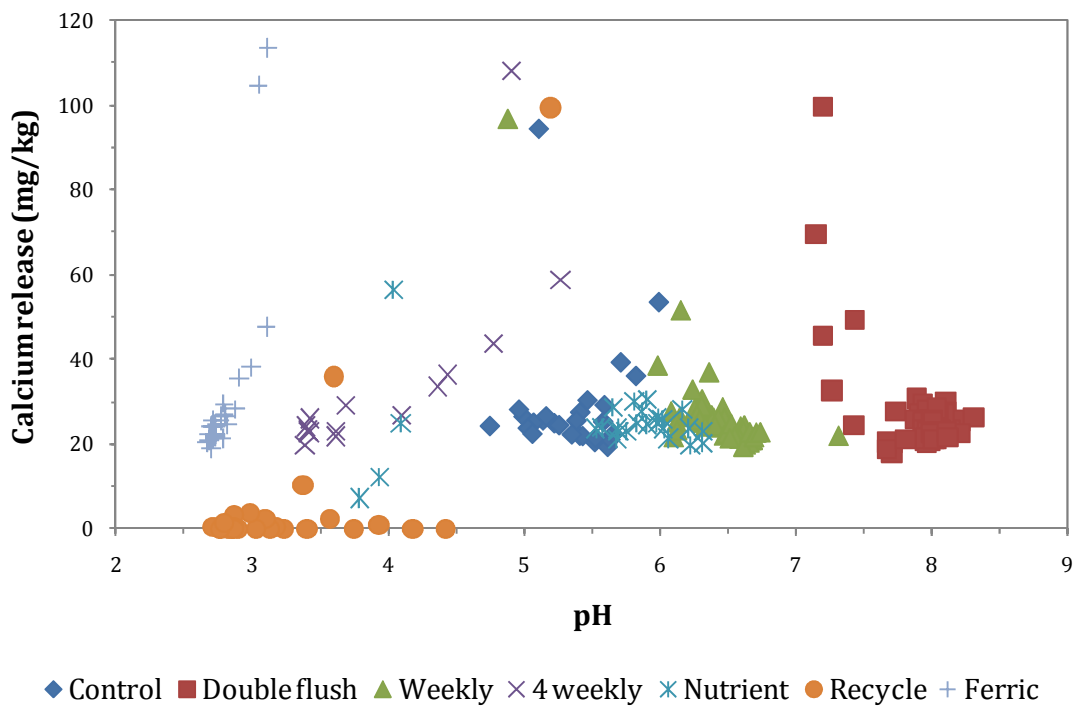


Figure 4.18 Calcium release vs. pH scatter plot for all protocols.

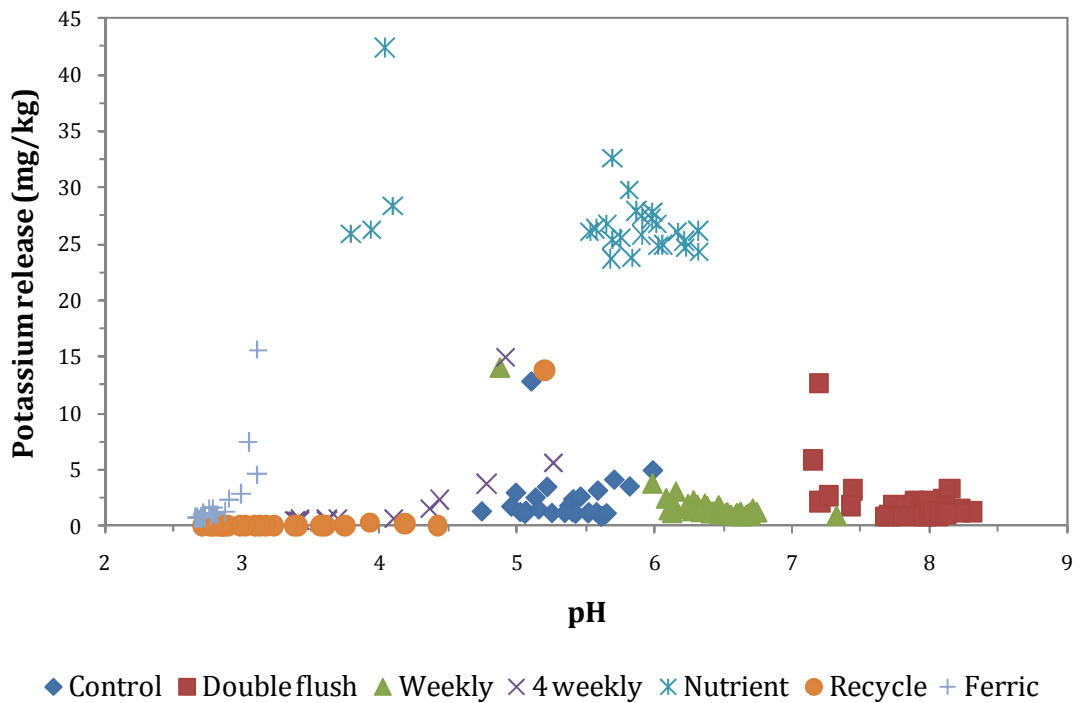


Figure 4.19 Potassium release vs. pH scatter plot for all protocols.

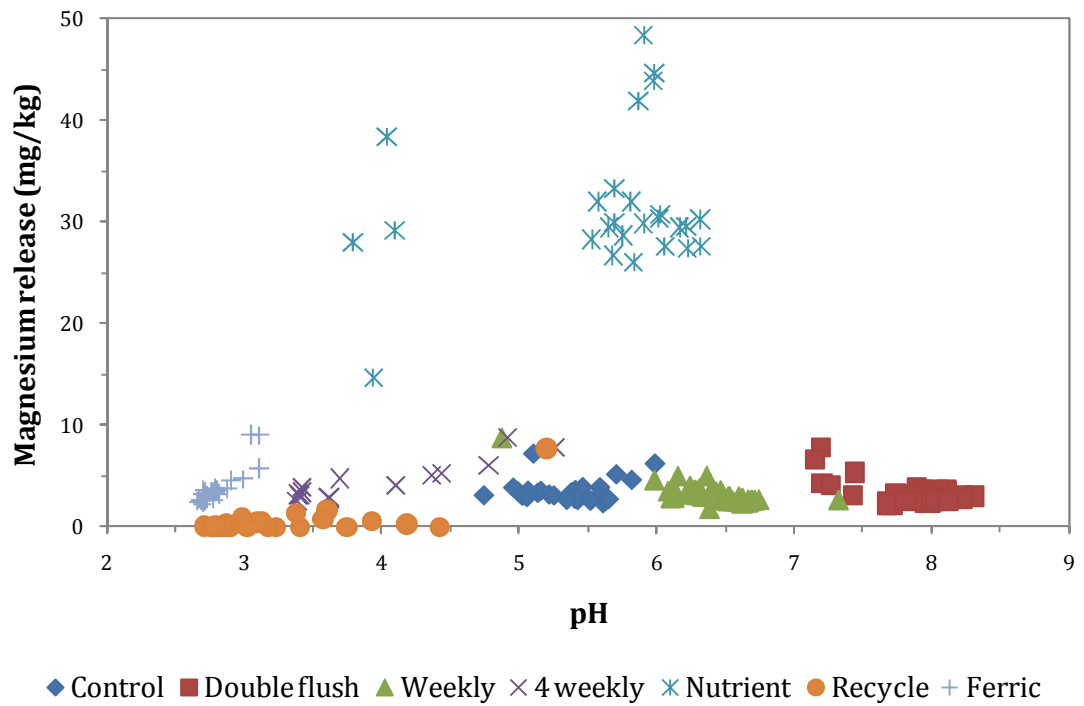


Figure 4.20 Magnesium release vs. pH scatter plot for all protocols.

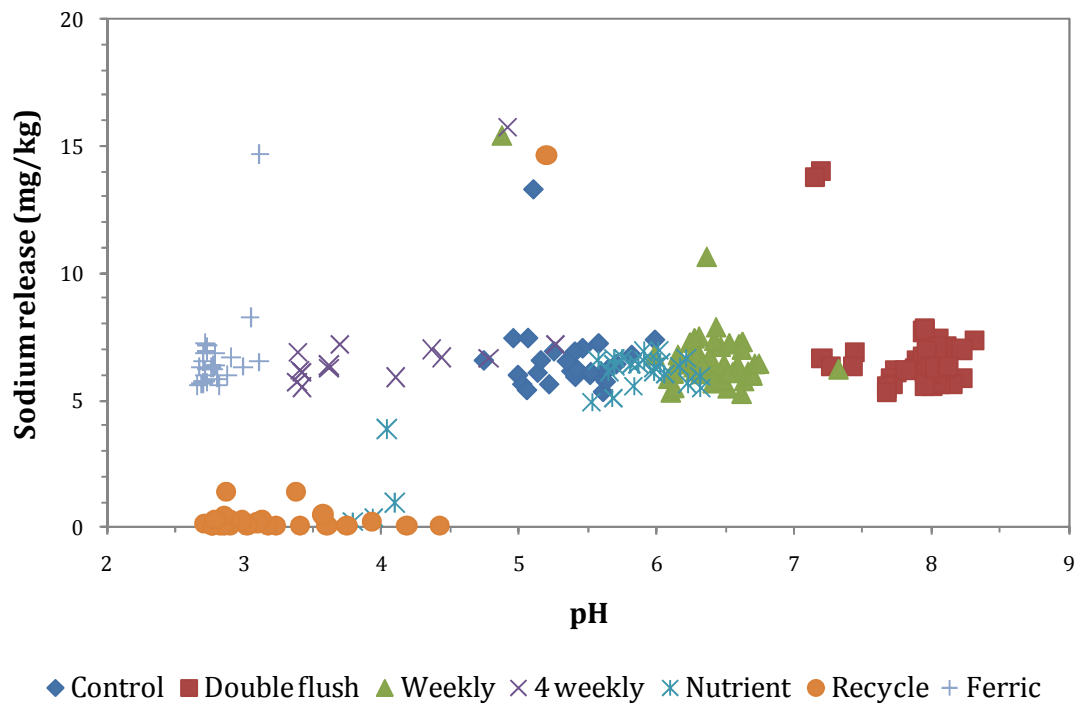


Figure 4.21 Sodium release vs. pH scatter plot for all protocols.

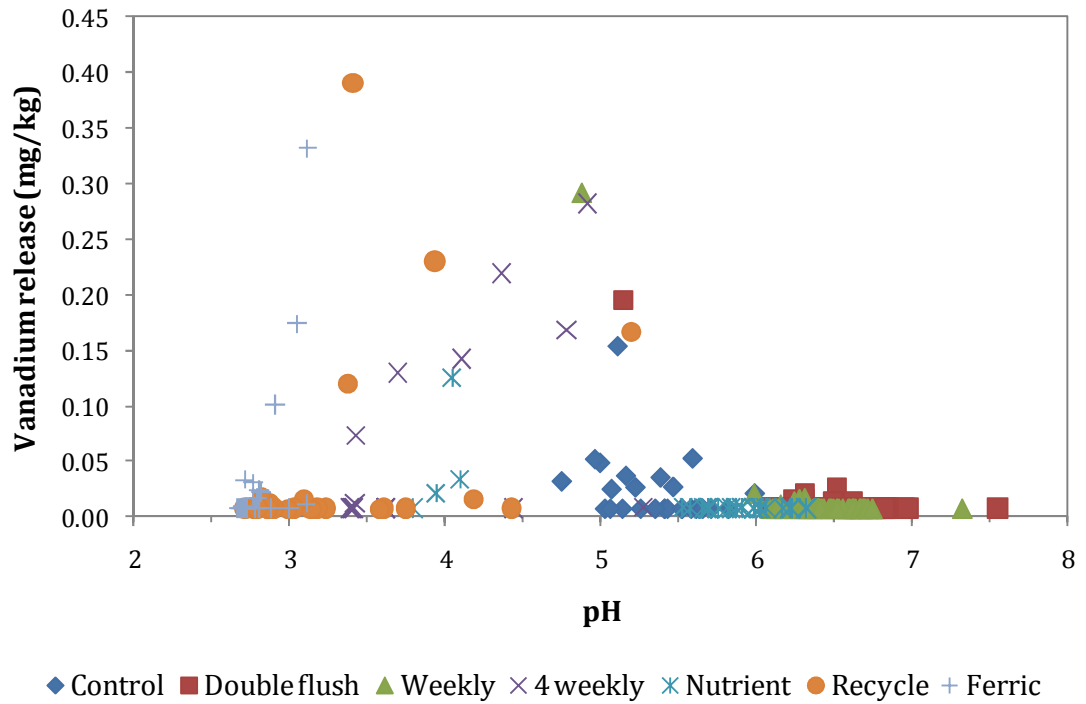


Figure 4.22 Vanadium release vs. pH scatter plot for all protocols.

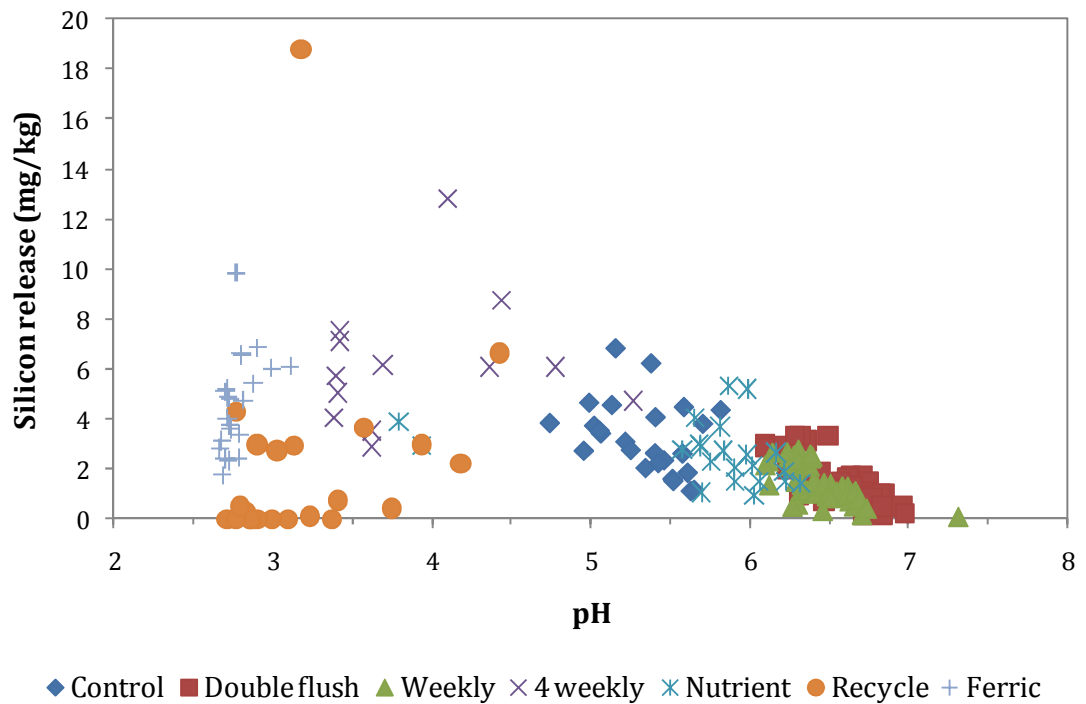


Figure 4.23 Silicon release vs. pH scatter plot for all protocols.

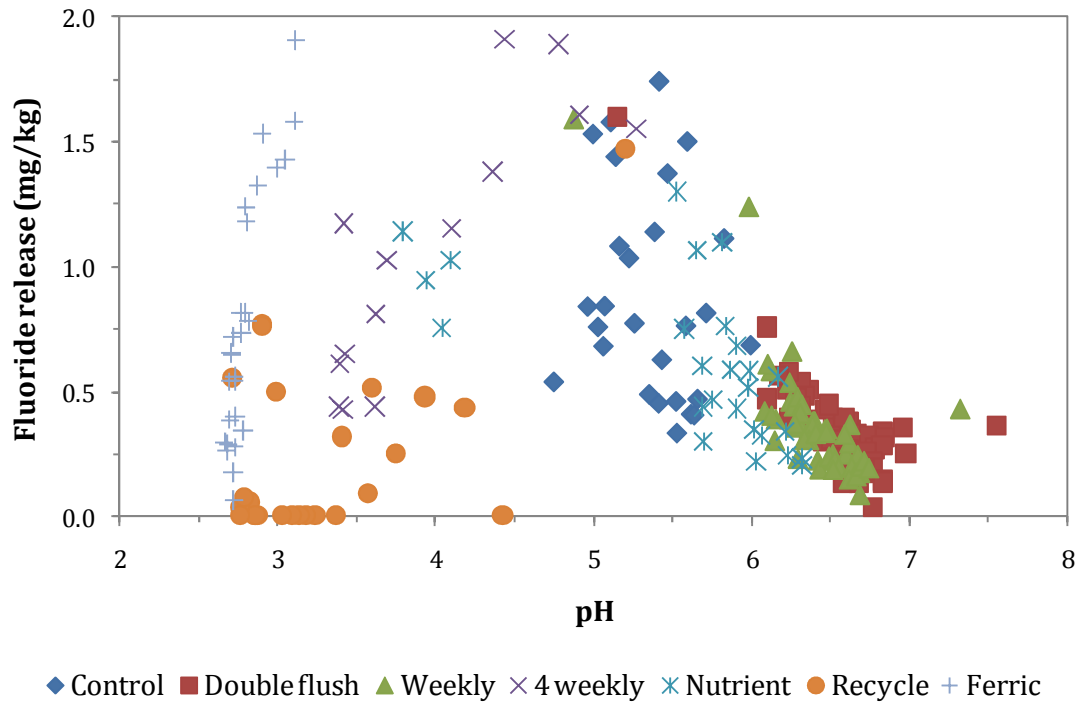


Figure 4.24 Fluoride release vs. pH scatter plot for all protocols.

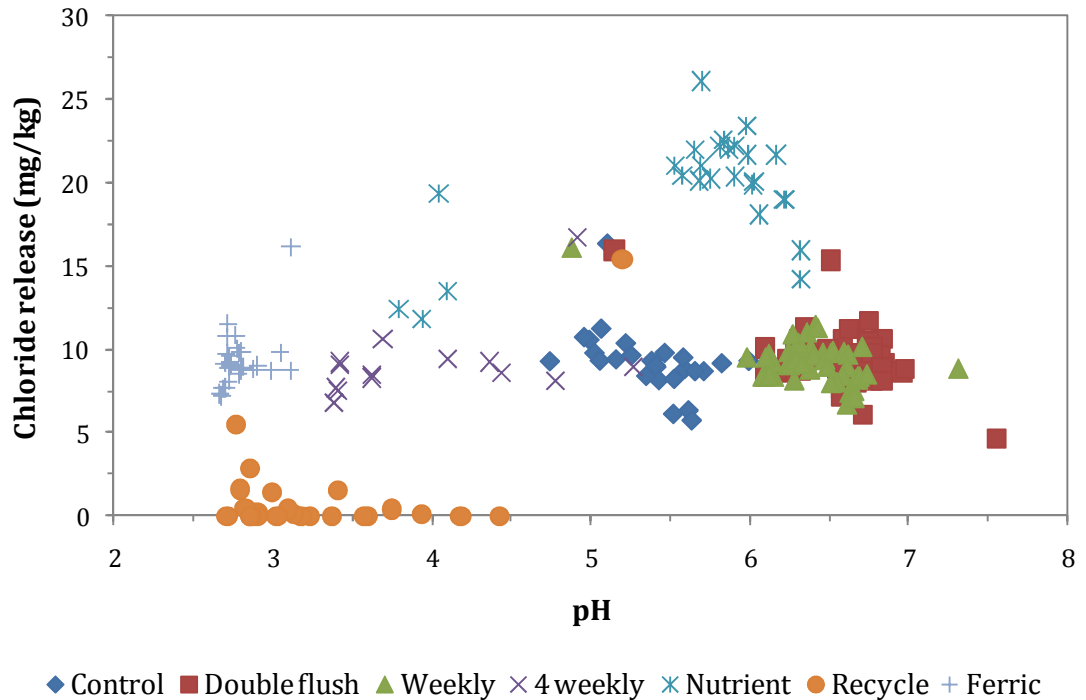


Figure 4.25 Chloride release vs. pH scatter plot for all protocols.

4.5 Water retention in cells

For the initial leach cycle all cells contained 1kg of dry, crushed ore material, were flooded with an initial 750mL of solution and left for 24 hours. Tap water was used for the Control, Double flush, Weekly flush, 4 weekly flush and Recycle protocols and Fe(III) sulfate and Nutrient solution for the Ferric and Nutrient lixiviant protocols respectively. 500mL was used for all subsequent leach cycles (except for week 0, cycle 2 of the Double flush protocol which had a second leach with 750mL tap water). Figure 4.26 shows the volume of solution retained in each cell (average volume of cell A and cell B), the mean volume of retained solution is shown by the dashed line.

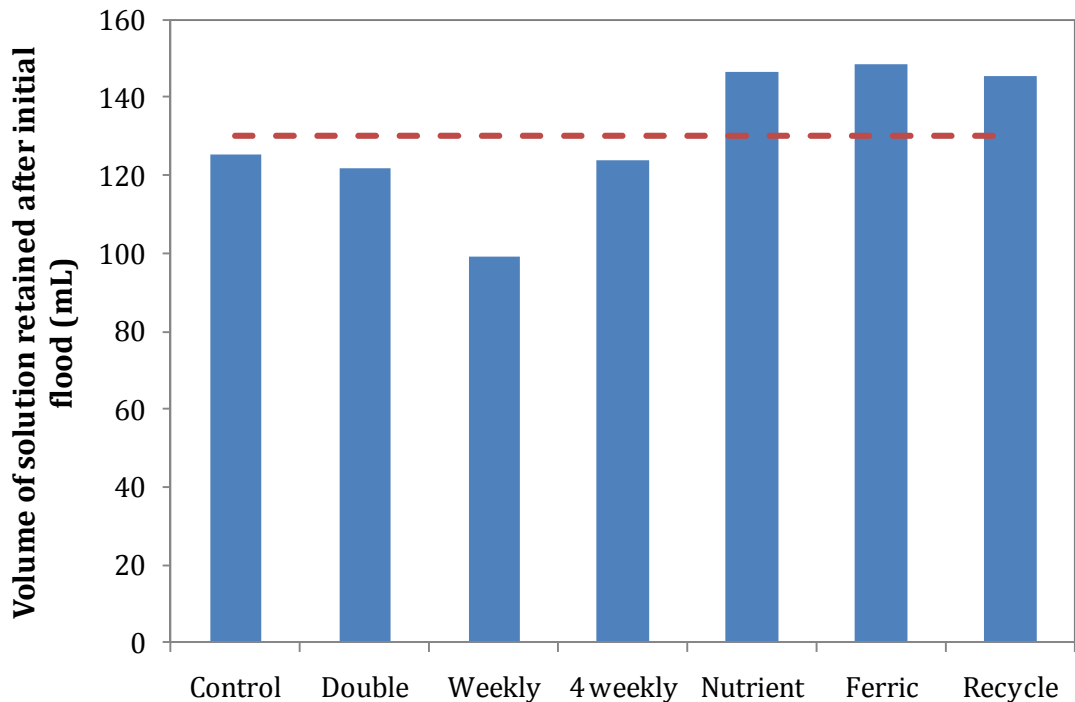
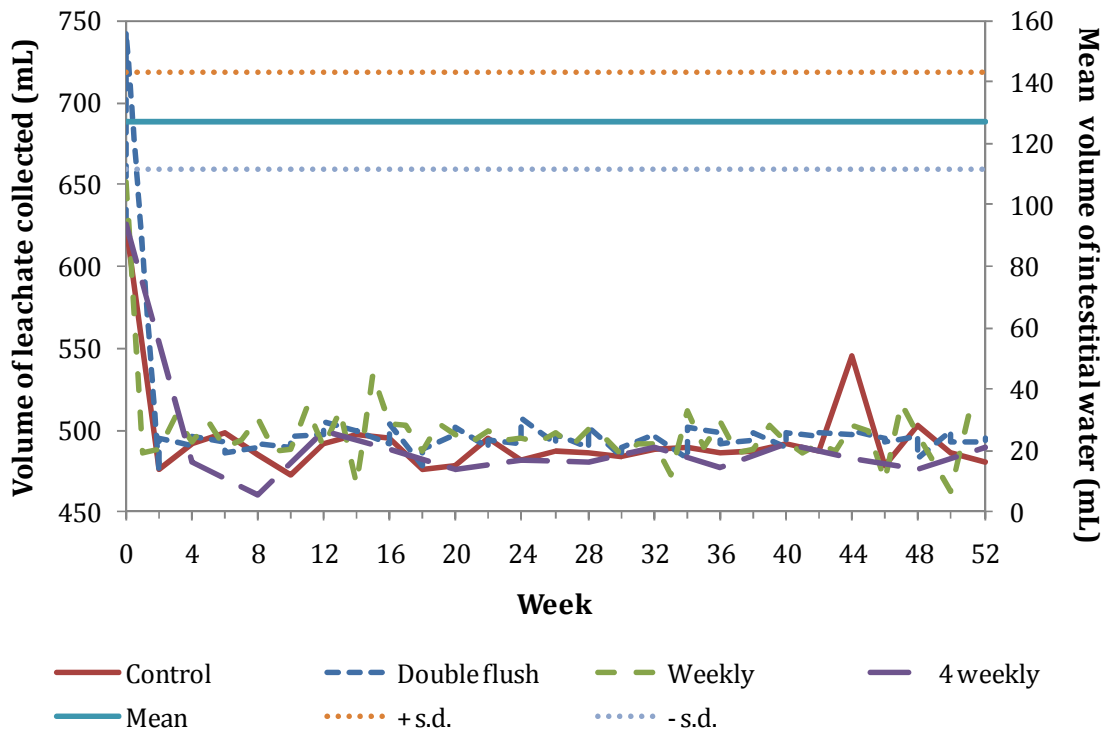


Figure 4.26 Volume of solution retained (mL) by cells after the initial flood. Dashed line indicates mean solution retained by all cells.

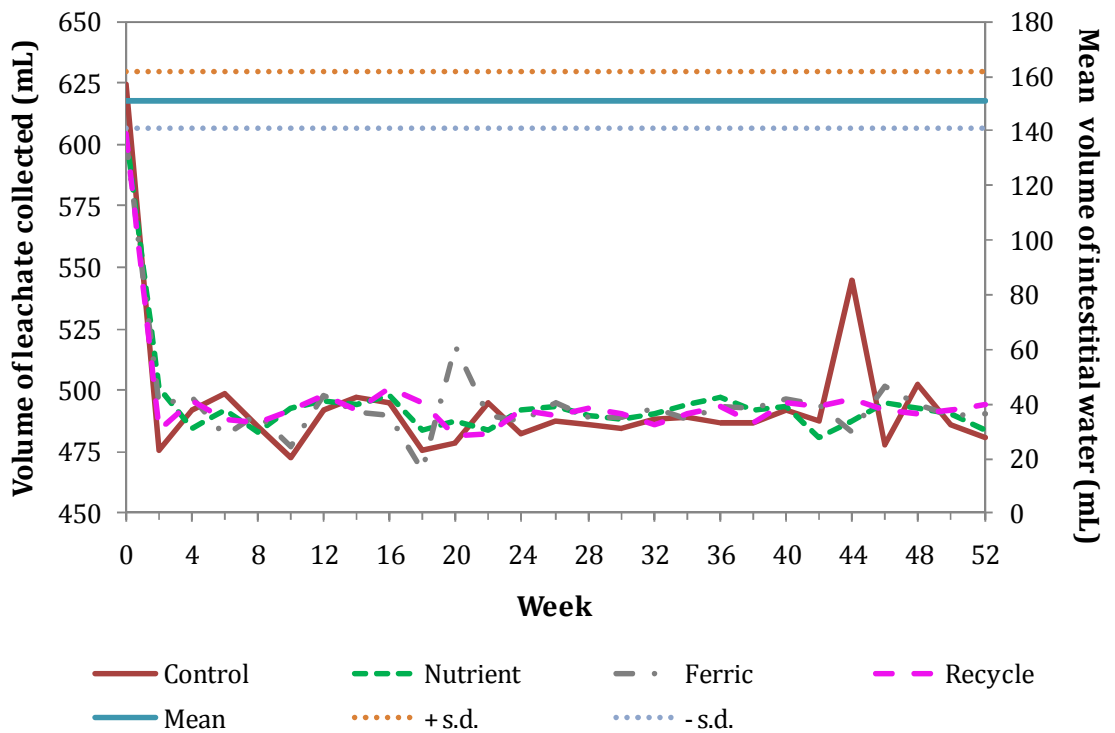
The volume of solution retained after the initial flood cycle is important because without it the water retention of the cells, after each flood, cannot be calculated nor the concentration of elements present in the interstitial water. The cells of the lixiviant

protocols retained more solution than the rest period protocol cells. This is thought to be a coincidence and not connected to the lixiviant composition as the initial flush solution for the Recycle protocol was also tap water.

Figure 4.27(a) and (b) show the volume of solution collected after each cycle. The test protocols have been separated into rest period protocols and lixiviant protocols to prevent the figures from becoming too cluttered. After the initial flood, the volume of leachate collected became quite constant, normally between 500mL and 450mL. Occasionally more than 500mL of leachate was collected but this was often following a cycle where more of the leachate had been retained in the cell. Overall the volume varied by less than 100mL from cycle to cycle. The mean volume and standard deviation of interstitial water have been included on the figures for completion.



(a) Rest period protocols



(b) Lixiviant protocols

Figure 4.27 Volume (mL) of leachate collected after each leaching cycle for cells.

(a) Volume of leachate collected for variable duration cells. (b) Volume of leachate collected for variable lixiviant cells.

4.6 Temperature in laboratory

The temperature in the laboratory was monitored throughout the 52 weeks of test work. There were two temperature loggers and measurements were taken every 2 hours, the data presented in Figure 4.28 has been converted to the mean weekly temperature. The temperature of the laboratory environment was of interest for two reasons; firstly because temperature is known to have an effect on the release and oxidation rates of minerals and elements and secondly to ensure that a comparison could be made between conditions on the mine site and conditions in the laboratory.

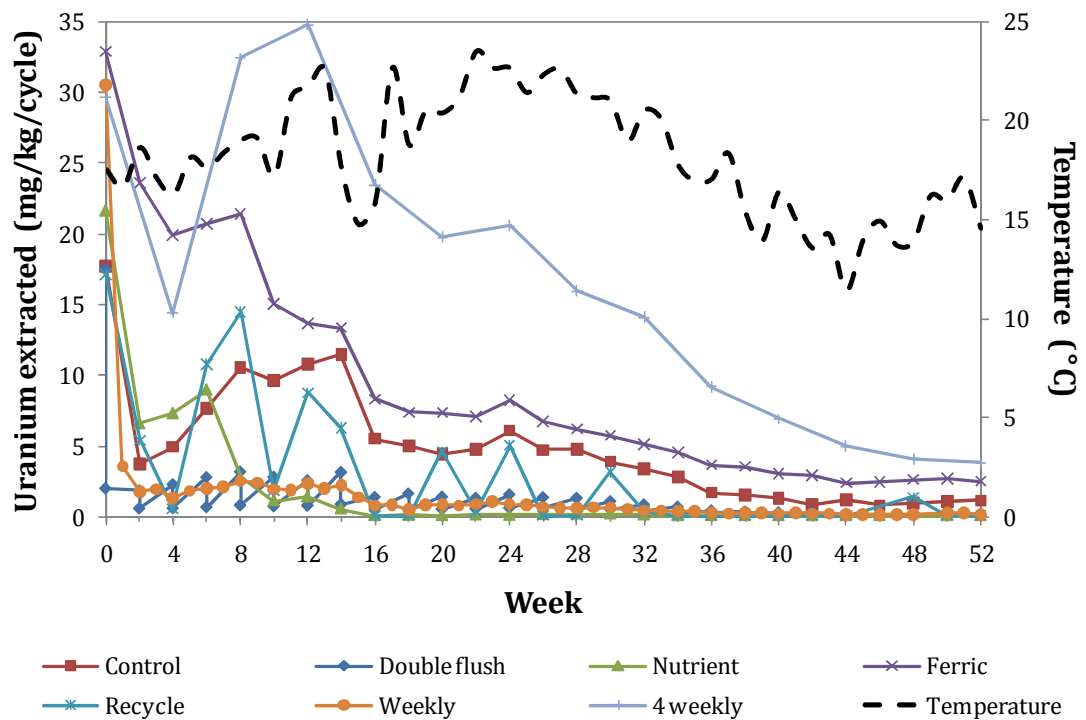


Figure 4.28 Mean weekly laboratory temperature (°C) measurements and uranium extraction over the leaching duration

A fluctuation of temperature between a low of 13.5°C (week 42) and a high of 23.5°C (week 22) can be seen. This variation is thought to be attributed to seasonal temperature fluctuations and central heating in the building.

4.7 Summary

It can be summarised from this chapter that the addition of Fe(III) sulfate as a lixiviant and the duration of a 4 week rest period lead to the most successful uranium release rates in comparison to the Control protocol. A combination of the low pH, high Fe release and high SO₄ release lead the creation of optimum uranium dissolution conditions which will be discussed in Chapter 5.

5 Discussion

The aim of this chapter is to discuss the results presented in Chapter 4 and to suggest possible mechanisms at work during the extraction process. The chapter will also incorporate discussion about the methodology used and any improvements which could have been made.

For ease of discussion the duplicate test cells are referred to as single cells. Each test parameter cell was run in duplicate. At any point where the discussion is explicitly referring to the differences between the duplicate cells it has been made clear. Otherwise both of the cells (cell A and cell B) have been referred to as a single cell. The structure of this chapter is similar to the methodology and results with the material characterisation being presented first followed by an examination of the test protocols.

5.1 Mineralogical and geochemical characterisation

5.1.1 Head grade analysis

A summary of the methods used for head grade analysis is presented in Table 5.1, along with the uranium concentrations. It can be seen from the table that there are significant variations in the analytical techniques, detection limits and sample weights for digestion. XRF (X-ray fluorescence) analysis, which does not require digestion, has been included for comparison purposes.

Table 5.1 Uranium concentration in head grade material.

Analysis method	Laboratory	Description	Approx. sample weight (g)	Detection limit (mg/kg)	Uranium (mg/kg)	Mean (mg/kg)
Four Acid "Near Total" digest - Multi-element method	ALS South Africa*	HF-HNO ₃ -HClO ₄ acid digestion, residue topped up with dilute HCl and analysed by ICP-MS & ICP-AES.	0.2500	0.1 - 10000	361 386 421	389
Three Acid "Near Total" microwave digest - ICP-MS Multi-element method	Digestion - Cardiff Uni Analysis - Aberystwyth Uni	HF-HNO ₃ -HCl acid digestion, residue topped up with deionised water, analysed by ICP-MS.	0.1000	0.00001	365 392 417	391
Lithium Metaborate Fusion	ALS Seville*	Sample added to lithium metaborate flux and fused in a furnace at 1000°C. Melt dissolved in 100mL of HNO ₃ /HCl solution and analysed by ICP-MS.	0.2000	0.05 - 1000	421	421
Lithium Tetraborate Fusion	Cardiff Uni	Sample added to lithium tetraborate flux and fused in a furnace at 1000°C. Melt dissolved in 50mL of HNO ₃ solution and analysed by ICP-OES.	0.2500	0.1	419 453 474 435 466 441	448
Portable XRF (Olympus Innov-X, X-5000)	N/A	Sample analysed on Soil 3 Beam setting and each reading was taken 3 times and an average recorded.	N/A	+/- 6 ppm	365 365 368	366

* external accredited facilities

For each of the digestion procedures presented in Table 5.1 the uranium content was determined from separate samples, digested individually and then analysed. These separate samples were representative of the bulk head grade sample and were produced following the split riffle method described in section 3.1.2. Samples were given different identification codes to ensure analysts were 'blind' to their similarity. Each representative 5g sample was milled to a fine powder and a 'grab' of that sample was digested according to the designated procedure. For XRF analysis the three uranium concentrations presented were triplicate analysis of the same sample.

The uranium content of the head grade samples varied considerably depending on the type of analysis used to determine the mineral content. The "*near-total*" digestion methods showed good correlation; with less than 1% percent difference between the average uranium content of the two methods. There is a 60ppm (15%) and 52ppm (13%) difference (percent difference) between the maximum and minimum uranium values for the four acid and three acid microwave digestion respectively. Fusion digestion techniques also showed good correlation with 6% percent difference between the mean uranium content of the in house analysis and the single external analysis. The percent difference between the maximum and minimum uranium concentrations was less for the fusion digestion method than for the acid digestion methods at 12%. Finally the percentage difference between the two digestion techniques is 10.8% which, considering the variety of samples and methods is considered to show good correlation between the digestion techniques overall.

No statistical inferences can be drawn from the single sample analysed externally using lithium metaborate fusion as there is no way of telling whether the concentration measured is within the normal population distribution. The reported value is within 1.4 standard deviations of the mean in house uranium lithium tetraborate fusion digestion value and within 1.3 standard deviations of the acid digestion techniques. As the

individual uranium concentration, determined by lithium metaborate fusion, falls within ± 2 standard deviations of the mean of the other digestion methods, the accuracy of the measurement can be assured with some confidence (Gill and Ramsey, 1997).

XRF analysis was included because it is a quick and cost effective mode of analysis which can analyse a large quantity of samples in a relatively short amount of time. The average XRF uranium concentration was within $\pm 20\%$ and $\pm 10\%$ percent difference of the mean uranium concentration measured by the fusion digest and acid digest techniques respectively. Due to this variance between the digestion and XRF techniques, the XRF data will not be used extensively to discuss the total uranium extraction achieved by the different test protocols and will only be discussed relative to itself in future sections.

Having considered the results from the various methods of head grade analysis the uranium head grade, for the rest of this discussion, is going to be taken as 390ppm. This was decided as the acid digestion techniques demonstrated the greatest correlation to each other. Overall, sizeable differences in head grade values can occur during analysis depending on the technique used and the number of samples analysed. Discretion is needed when handling data and to this end the reconstituted head grade of the samples will be determined and discussed in section 5.1.3.

5.1.2 Residue analysis

Following the completion of the leaching test work the residue material from the cells was dried and analysed as described in section 3.7. A summary of the uranium concentration remaining in the residues is given in Table 5.2.

Table 5.2 Uranium concentration in residue material.

Test protocol	Lithium metaborate fusion*	Three Acid "Near Total" microwave digest - ICP-MS Multi-element method				Portable XRF (Olympus Innov-X, model X-5000)			
	mg/kg	mg/kg			Mean	mg/kg			Mean
Control	338	255	257	253	255	314	316	315	315
Double flush	465	308	380	332	340	397	397	397	397
Weekly	373	297	328	314	313	357	359	353	356
4 weekly	268	180	165	177	174	249	248	250	249
Nutrient	341	262	251	248	254	343	343	343	343
Ferric	266	197	180	181	186	341	340	339	340
Recycle	275	201	211	162	191	286	286	284	285

* external accredited facility

There is a lack of consensus between the different techniques in relation to the uranium content of the residues and which leaching protocol was most effective. The mean three acid digest results showed that the least uranium remained in the 4 weekly protocol residue. The order of protocol effectiveness, according to the acid digest was: 4 weekly > Ferric > Recycle > Nutrient > Control > Weekly > Double. The XRF analysis on the residue material agrees with the three acid digest to an extent as it also found the 4 weekly protocol to have the lowest concentration of uranium remaining and the Double flush protocol to have the highest. That is where the similarity ends however, and the effectiveness of the protocols according to XRF is as follows: 4 weekly > Recycle > Control > Ferric > Nutrient > Weekly > Double. Finally the fusion digestion measured the Ferric protocol as the most effective as it had the least uranium remaining in the residue, it also found the Double flush protocol to be the least effective protocol. The effectiveness of the testing protocols according to fusion digestion are: Ferric > 4 weekly > Recycle > Control > Nutrient > Weekly > Double.

It is obvious that analytical variation experienced during the head grade analysis also occurred during the residue analysis. To get an idea of the amount of uranium extracted by each protocol, according to the whole rock analysis, extraction percentages have been

presented in Table 5.3. The uranium extractions calculated from the residue material not only vary across the different analysis methods but they do not correlate with the total uranium extracted from the leachate (summarised in Table 5.4).

Table 5.3 Uranium leached during test protocols according to whole rock analysis.

Test protocol	Lithium metaborate fusion*		Three Acid "Near Total" microwave digest - ICP-MS Multi-element method		Portable XRF (Olympus Innov-X, model X-5000)	
	mg/kg	%	mg/kg	%	mg/kg	%
Control	83	20	135	35	51	14
Double flush	N/A	N/A	50	13	N/A	N/A
Weekly	48	11	77	20	10	3
4 weekly	153	36	216	55	117	32
Nutrient	80	19	136	35	23	6
Ferric	155	37	204	52	26	7
Recycle	146	35	199	51	81	22

* external accredited facility N/A - analysis disparity

Table 5.4 Cumulative uranium extraction over 52 weeks.

Leaching protocol	Cell A	Cell B	Mean
	mg/kg	mg/kg	mg/kg
Control	135	130	133
Double flush	72	58	65
Weekly	78	82	80
4 weekly	249	220	234
Nutrient	56	47	51
Ferric	254	253	254
Recycle*	40	47	43

* Recycle data cumulative in design

The analysis disparity for the Double flush protocol occurred because the residue analysis (Table 5.3) detected more uranium present in the residue than in the head grade material. As this is not possible it is clear that an analytical and/or sampling error has occurred during the head grade and/or residue analysis.

As there was only one sample of material analysed for each test protocol using the lithium metaborate technique it is not possible to rely on the concentration of either the head grade or residue analysis. Although every attempt was made to ensure that each sample was representative it is not possible to gauge the accuracy of the results without a larger sample size. XRF analysis was carried out in triplicate on the same powdered sample and although the residue results show very good correlation it only confirms that the XRF provides precise analysis. The accuracy of the analysis can not be assured without comparing the results to a certified external analysis. As this is not possible, the XRF analysis will only be used in future sections when being compared relative to itself.

The acid digest technique gave the best leached uranium results (determined using residue analysis, Table 5.3) when compared to the actual concentration of uranium leached in solution from the cells. Solution leachate analysis was within 10% percent difference when QA/QC was carried out (Appendix F) and thus is considered to be accurate. The greatest discrepancy between the leached uranium determined by whole rock analysis and the measured leachate was seen for the Nutrient and Recycled test protocols. Both protocols leached less uranium in solution than was calculated by the digest data. Despite this difference, the three acid microwave digest residue analysis was more consistent overall.

By analysing the mineralogical and characterisation data it is evident that there are discrepancies in the residue analysis just as there were for determination of the head grade of the material. For the purpose of this study the three acid microwave digestion

data will be used for future discussion and comparison of the protocols because the method was the most accurate (within 1% percent difference) compared to external analysis. This has also been done for consistency, so that throughout the discussion whole rock analysis is considered relative to the same technique.

5.1.3 Reconstituted head grade

Due to the differences between the amount of uranium that was actually leached in solution and the amount that was leached according to the whole rock analysis there is an advantage in calculating the Reconstituted Head Grade (RHG). The RHG determines the head grade of the material put into each of the cells by back calculation, using the residual uranium content of the cells and the cumulative extraction values (Equation 5.1)

$$\text{Reconstituted head grade} = \text{concentration in column residue} + \text{cumulative extraction over 52 weeks} \quad (5.1)$$

Once the RHG of the samples was calculated it was possible to determine the relative percent extraction achieved by each cell and thus compare the effectiveness of each leaching protocol. The RHG of the cells are presented in Table 5.5.

The majority of the RHG was within $\pm 12\%$ percent difference of the head grade (390 mg/kg). The samples used in the Nutrient and Recycle protocol cells were observed to have RHG uranium concentrations considerably lower than those determined by whole rock digestion. Having reviewed the whole rock digestion procedure during this section this disparity is believed to be down to the number of samples used for the initial head grade analysis. With hindsight a larger sample size would have been appropriate and it is recommended that in the future at least 5 samples are analysed.

Table 5.5 Reconstituted head grade of cells (based on three acid microwave digest).

Leaching protocol	Cell A	Cell B	Mean
	mg/kg	mg/kg	mg/kg
Control	391	385	388
Double flush	413	399	406
Weekly	391	395	393
4 weekly	423	393	408
Nutrient	310	300	305
Ferric	440	439	439
Recycle	231	238	235

The reconstituted head grade values will be used as the head grade values during the remainder of this discussion (except section 5.2) so as to provide extraction percentages relative to the head grade of the material in each cell rather than the general bulk head grade.

5.2 Particle size distribution

The particle size distribution (PSD) of the head grade and residue samples were determined as described in the methodology (section 3.3). Separation of the head grade and test residue samples was achieved using dry sieving (BS 1796-1:1989). PSD whether determined through dry or wet sieve analysis, is greatly influenced by particle shape and texture (Fernlund et al. 2007). Ideally all particles would be spherical, as elongated or flat particles are affected by their orientation to the sieve mesh, which leads to blinding. Other causes of blinding are agglomeration of particles or fine particles sticking to the sieve mesh (Fuerstenau and Han, 2003). Dry sieving is not considered suitable for samples with a high proportion of particles $<37\mu\text{m}$ and it is advisable to employ a wet sieving technique to analyse the particle size (Fuerstenau and Han, 2003).

Before PSD analysis was carried out the samples were inspected to see how much the coarse particles were coated in fine material. The fine particles did not seem attached to the coarser particles and so wet sieving was not used. Two dry sieve 'test runs' with extra

head grade material were completed to determine the necessary period of shaking and the sieve mesh size, 15 minutes was found to be sufficient to separate the particles. A 20 μ m sieve was used originally but was considered unnecessary because only 0.11g (average) of the material was collected in the bottom pan. Subsequently a 63 μ m sieve was used as the smallest mesh size. The dry sieve 'test runs' along with all other PSD raw data can be found in Appendix I.

The weight and uranium content of the different size fractions are summarised in Table 5.6. Uranium was analysed by portable XRF (description in methods section 3.3.4) using powdered samples produced from the size fractions. Each sample was analysed in triplicate and the mean is presented. Portable XRF analysis is not the most accurate method to determine element concentrations in a sample, however it is quick (210 seconds per sample) and efficient. Thus the results presented in section 5.2.1 should be considered as an indication of where the uranium is concentrated and not an absolute measurement.

5.2.1 Uranium extraction

For each of the samples put through the nest of sieves, the smallest proportion (between 1-3%) of the total material passed through the 63 μ m aperture sieve to be collected in the bottom pan. On initial inspection of the results, despite the < 63 μ m size fraction containing the lowest weight percent, it seemed to contain the highest concentration of uranium for the majority of samples (Table 5.6). Once the uranium concentration was calculated however, by taking the contribution of each size fraction into account, the largest proportion of uranium was concentrated in the > 2000 μ m size fraction. This is illustrated in Figure 5.1.

Table 5.6 Summary of size fraction analysis on the head grade and residue material using the portable XRF.

Test	Sieve size range (µm)	Sieve fractions % wgt	Uranium (mg/kg)	Uranium (mg)	Test	Sieve size range (µm)	Sieve fractions % wgt	Uranium (mg/kg)	Uranium (mg)
Head Grade	+ 4000	50.79	207	105.2	4 weekly	+ 4000	43.55	265	115.5
	- 4000 + 2000	30.37	563	170.7		- 4000 + 2000	28.07	221	61.9
	- 2000 + 1180	8.23	447	36.7		- 2000 + 1180	8.85	266	23.6
	- 1180 + 500	4.94	430	21.2		- 1180 + 500	7.88	274	21.5
	- 500 + 250	2.20	492	10.8		- 500 + 250	4.43	216	9.6
	- 250 + 125	1.16	562	6.5		- 250 + 125	2.47	218	5.4
	- 125 + 63	1.28	557	7.1		- 125 + 63	2.81	218	6.1
- 63	1.02	750	7.6	- 63	1.93	292	5.6		
Control	+ 4000	43.69	289	126.0	Nutrient	+ 4000	51.23	328	167.6
	- 4000 + 2000	29.30	368	107.5		- 4000 + 2000	27.27	365	99.3
	- 2000 + 1180	9.19	309	28.3		- 2000 + 1180	7.60	298	22.6
	- 1180 + 500	7.48	285	21.3		- 1180 + 500	5.92	291	17.2
	- 500 + 250	3.90	270	10.5		- 500 + 250	2.96	344	10.2
	- 250 + 125	2.07	272	5.6		- 250 + 125	1.59	353	5.6
	- 125 + 63	2.36	261	6.1		- 125 + 63	1.83	378	6.9
- 63	2.01	475	9.5	- 63	1.60	860	13.8		
Double Flush	+ 4000	48.53	439	212.5	Ferric	+ 4000	36.83	405	148.8
	- 4000 + 2000	28.06	335	93.7		- 4000 + 2000	30.32	391	118.5
	- 2000 + 1180	8.57	347	29.7		- 2000 + 1180	10.68	232	24.7
	- 1180 + 500	6.50	386	25.0		- 1180 + 500	9.20	229	21.1
	- 500 + 250	3.20	359	11.5		- 500 + 250	4.89	210	10.2
	- 250 + 125	1.69	379	6.4		- 250 + 125	2.61	197	5.1
	- 125 + 63	1.94	374	7.2		- 125 + 63	2.95	184	5.4
- 63	1.52	725	11.0	- 63	2.52	255	6.4		
Weekly	+ 4000	51.09	291	148.4	Recycle	+ 4000	41.82	327	136.3
	- 4000 + 2000	26.68	462	123.1		- 4000 + 2000	29.27	276	80.5
	- 2000 + 1180	8.12	376	30.5		- 2000 + 1180	9.94	236	23.4
	- 1180 + 500	6.45	362	23.3		- 1180 + 500	8.11	226	18.3
	- 500 + 250	3.07	350	10.7		- 500 + 250	4.22	236	10.0
	- 250 + 125	1.60	354	5.7		- 250 + 125	2.24	217	4.9
	- 125 + 63	1.83	360	6.6		- 125 + 63	2.54	235	6.0
- 63	1.16	684	7.9	- 63	1.86	314	5.8		

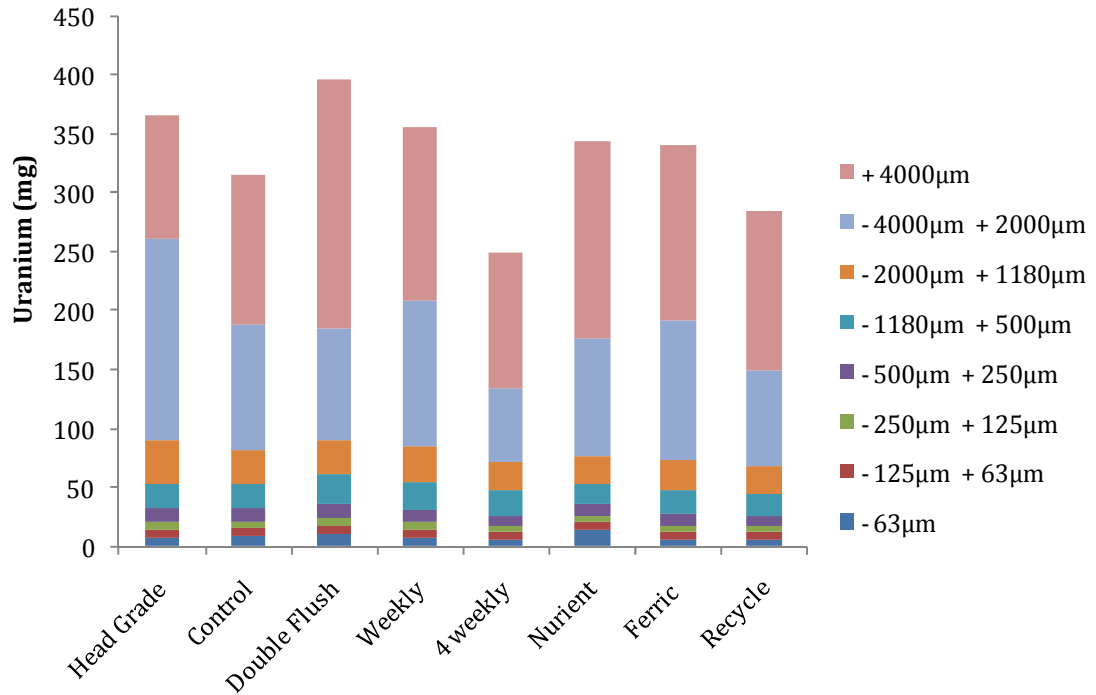


Figure 5.1 Contribution of each size fraction to the overall uranium concentration according to portable XRF analysis.

It can be seen from Figure 5.1 that any particles $< 2000\mu\text{m}$ do not contribute a large proportion of uranium to the total concentration because of the small volume of sample which was collected in the smaller sieves. It is feasible that a proportion of the finer particles were lost from the cells during the test period because any fines that were washed out of the cells with the leachate were not collected and returned to the cells. Although, by comparing the particle size distribution of the residues to the distribution in the head grade loss of fines does not seem to have been a significant problem and no great reduction in the volume of fines in the residues can be seen.

It is clear that the largest reduction in uranium concentration occurred in the $-4000\mu\text{m} + 2000\mu\text{m}$ size fraction. This would suggest that the coarse grains rather than the fine grains controlled the release of uranium. As the uranium was hosted in a quartz-pebble conglomerate deposit it is possible that the minerals containing the uranium required less

force to break than the quartz pebbles. Consequently a larger proportion of the uranium was exposed to the flood solution as it had a larger surface exposure on the exterior of the quartz pebbles. Lottering et al. (2008) highlighted the distinction between liberation and surface exposure with regards uranium extraction from a pebble-supported conglomerate (Figure 5.2). They found that uranium minerals exhibit high levels of surface exposure, despite low liberation from the gangue material, concluding that breakage of ore particles occurs near the uranium grains. This could have positive results for stope leaching, which often involves larger size fractions, as it suggest that coarser grinds can be tolerated for uranium leaching processes (Lottering et al, 2008). Work by Campbell et al. (1985), carried out on a low-grade uranium quartz-pebble conglomerate deposit, also supports this. They reported a minimum size fraction of $-5000\mu\text{m}$ in the stope and found that a large particle size was not detrimental to uranium extraction with extractions of 70% achieved. It should be noted that the temperature for the Lottering et al. (2008) and Campbell et al. (1985) studies was higher than for this study at $40^{\circ}\text{C} - 60^{\circ}\text{C}$ and 28°C respectively.

Wills (1997) comments that the gangue material associated with low-grade ores often can be liberated at coarser size fractions, suggesting that the low-grade ore is concentrated in the fine particles. Therefore it was expected that the uranium in the fine particles would be the first to be leached due to greater liberation and surface exposure of the minerals (Figure 5.2). This does not appear to have happened however, and there was very little reduction of uranium concentration in the fine particles (Figure 5.1).

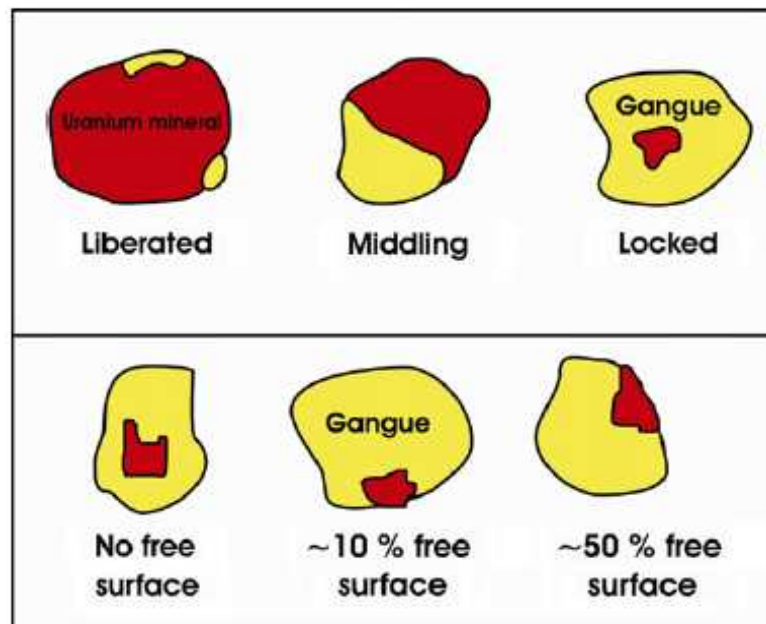


Figure 5.2 Distinction between liberation and surface exposure (Lottering et al. 2008)

A possible explanation is that the fine particles contained a high proportion of U(IV) which was unleached in the conditions created during this study. Brannerite is notoriously hard to extract due to its slow reaction kinetics (Lottering et al, 2008) and it is also possible that these minerals were concentrated in the fines.

The negligible changes in uranium concentration observed in the fine size fractions could also be affected by the surface exposure vs. liberation theory. Despite the increase in liberation, as a result of the smaller size fractions, there was also an increase in the concentration of gangue material leading to a 'dilution' of the uranium concentration. As a result the finer particles were largely un-reactive.

Particle size seems to have been a controlling factor for the extraction of uranium into solution and the $-4000\mu\text{m}$ to $+2000\mu\text{m}$ size fraction showed the largest difference in uranium concentration. There was not a measurable amount of uranium extracted from the finer particles which has been attributed to the presence of brannerite. As previously

discussed in section 5.1 the XRF analysis presented here is only being considered relative to itself and to this end, all future discussion about the optimisation of uranium extraction will only involve the reconsitued head grade.

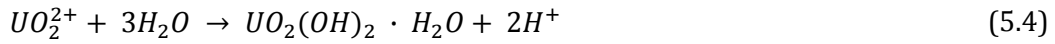
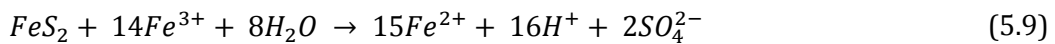
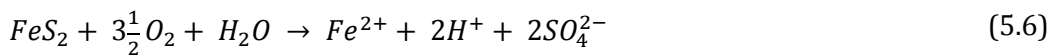
5.2.2 Effect of ore mineralogy on uranium leaching

The mineralogy of the ore presented in Chapter 2 (section 2.2.1, Table 2.5) has an influence on the uranium leaching requirements to extract uranium from the ore. As mentioned previously (section 5.2.1) the presence of brannerite can have a detrimental effect on the amount of uranium extraction due to its slow reaction kinetics (Lottering et al, 2008). Similarly Zhang et al (2003) found that the uranium release from brannerite was an order of magnitude lower than was measured for uraninite.

The leaching of U(VI) is likely to be preferential over other minerals present in the ore and U(IV) in uraninite is easily oxidised to U(VI) (Fayek et al, 1997; Macnaughton et al, 1999; Bowell et al, 2011). Coffinite, one of the major U(IV) minerals, can be difficult to extract because it usually occurs as very fine grain crystals and with large amounts of associated minerals (Deditius et al, 2008). In Figure 5.3 the pH and Eh values of the Ferric and 4 weekly protocols are on the boarder of the coffinite phase and thus it is thought that the oxidation and dissolution of coffinite was having an effect on the mobilisation of uranium into the leachate (Sapsford et al, 2012).

5.3 Uranium and pyrite oxidation chemistry

The chemistry involved in the dissolution of uranium and oxidation of pyrite is discussed in detail in Chapter 2, section 2.1.3 (uranium chemistry) and section 2.4.1.1 (pyrite oxidation). In order to aid the discussion the main chemical equations have been provided here for reference (Ring, 1980; Sand et al. 2001; Pham et al. 2006; Sapsford et al. 2012).

Uranium chemistry**Oxidation of pyrite****5.4 Controls on the extraction rates of uranium**

The effectiveness of the time and lixiviant protocols investigated to optimise the extraction of uranium from a low grade ore body cannot be observed until the total extraction by each of the tests is calculated. The total amount of uranium extracted during each test, except the Recycle leachate which is already cumulative, can be determined by calculating the cumulative extraction, Table 5.4.

As the samples used for this study are from a low grade ore body it has been prudent to establish the reconstituted head grade for each cell, section 5.1.3 and Table 5.5. Once the reconstituted head grade of the samples had been calculated it was possible to calculate the percent extraction achieved in each cell and thus compare the effectiveness of each leaching protocol. The percent of uranium extracted during the 52 weeks of test work are presented in Table 5.7.

Table 5.7 Percent of uranium extracted from the reconstituted head grade of the cells.

Leaching protocol	Cell A	Cell B	Mean
	%	%	%
Control	34.7	33.8	34.3
Double flush	17.5	14.6	16.1
Weekly	20.0	20.7	20.4
4 weekly	58.9	55.8	57.4
Nutrient	18.2	15.5	16.9
Ferric	57.8	57.6	57.7
Recycle	17.3	19.6	18.4

There is much literature published on the extraction of uranium and the expected recovery rates using different methods and techniques, as discussed in the literature review (Table 2.6 and Table 2.7). The volume of solution retained in the interstitial water of the cells was consistent for the duration of the test work following the initial flood (see Results, Figure 4.26 and Figure 4.27). The temperature measured within the laboratory varied over the 52 weeks from a high of 23.5°C and a low of 13.5°C (see Results, Figure 4.28). These fluctuations are within the optimum temperature range for the microorganisms described in Chapter 2, section 2.4.1.2: Bioleaching (Table 2.8). The total extraction rates achieved during this body of work, as presented in Table 5.7, do not match the suggested extraction rates presented in the literature, e.g. 90% (Lottering et al. 2008); 81% (McCready, 1986); 80% (Moon-Sung et al. 2005). The following sections will discuss possible reasons why the extraction rates were limited and whether they could be improved in any way.

The chemical reactions summarised in section 2.1, play a significant role in the rate of uranium extraction. Table 5.8 presents a summary of the mean and final pH and Eh measurements recorded for each of the test parameters and Figure 5.3 is the Eh-pH diagram based on the leachate chemistry. Table 5.9 summarises the total extraction and mean extraction rates of dissolved uranium, sulfate and total iron. The mean extraction rate was calculated using data from cycle 1 onwards; cycle 0 was omitted from the

calculation because the initial flush cycle produced higher than average concentrations thought to be because of the fine particles. A reminder of the flush protocols has been provided in Table 5.10. The tests have been discussed in descending order, based on the percent of uranium extracted.

Table 5.8 Summary of pH and Eh values of leaching protocols.

Leaching protocol	Leachate pH		Leachate Eh (mV)*	
	Mean	Final	Mean	Final
Control	5.4	5.5	564	561
Double flush	6.6	7.0	542	579
Weekly	6.4	6.7	527	581
4 weekly	4.0	3.6	700	705
Nutrient	5.6	6.0	507	92
Ferric	2.8	2.7	815	808
Recycle	3.3	2.8	748	767

* Corrected to Standard Hydrogen Electrode (SHE)

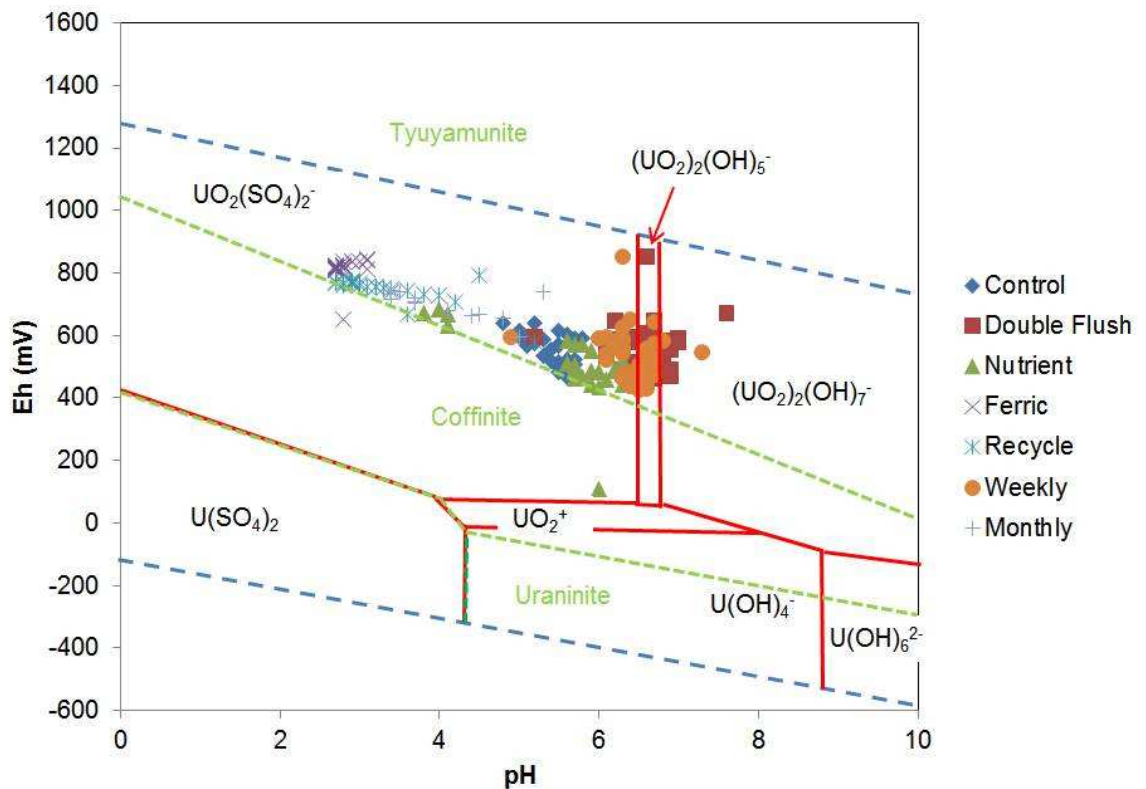


Figure 5.3 Eh-pH diagram indicating uranium speciation and common mineralogy, based on leachate chemistry for test protocols (from Sapsford et al. 2012).

Table 5.9 Summary of mean and total elemental extraction after 52 weeks.

Leaching protocol	Uranium [†]		Sulfate* [†]		Iron* [†]	
	Mean	Total	Mean	Total	Mean	Total
	mg/kg/cycle	mg/kg	mg/kg/cycle	mg/kg	mg/kg/cycle	mg/kg
Control	4.4	133	84.7	2435	4.36	125
Double flush	0.9	65.3	42.0	2442	0.03	15.7
Weekly	1.0	80.0	48.1	2693	0.08	27.2
4 weekly	16	234	174	2523	30.4	419
Nutrient	1.1	51.4	194	5407	1.29	54.5
Ferric	8.5	254	226	6223	51.1	1371
Recycle	1.0	43.3	11.9	502.5	5.14	142

* Mean and total values have not been adjusted for SO₄ or Fe added to the lixiviant. † dissolved

Table 5.10 Summary of variations in leaching protocols.

Leaching protocol	Flood leach	No. of cycles	Rest period	Notes
Control	Tap water	27	13 days	
Double flush[†]	Tap water	54	12 days	Two flush per cycle
Weekly[†]	Tap water	53	6 days	
4 weekly[†]	Tap water	14	27 days	
Nutrient*	Nutrient solution	27	13 days	Adapted '9K salts'
Ferric*	Fe ₂ (SO ₄) ₃	27	13 days	0.5g/L Fe ₂ (SO ₄) ₃ at pH 3.5
Recycle*	recycled water	27	13 days	Use of previous week leachate

[†] rest period varying protocols * lixiviant varying protocols

5.4.1 Ferric

As the most effective leaching parameter, the addition of Fe(III) sulfate provided the optimum conditions for the dissolution of uranium. As a result of the 0.5g/L of Fe(III) sulfate, three main processes occurred;

1. The pH of the lixiviant was acidic before being introduced to the cells which achieved two things. It provided the H^+ ions for dissolution of U(VI) (Equation 5.2) and also provided an acidic environment which favours the solubility of uranium rather than precipitation (Equation 5.4).

2. As well as lowering the pH of the lixiviant, the addition of 0.5g/L of Fe(III) sulfate provided SO_4^{2-} . This increased concentration of SO_4^{2-} ions in solution meant that, following either the dissolution of U(VI) (Equation 5.2) or the oxidation of U(IV) to U(VI) (Equation 5.4), the solubility of U(VI) was increased compared to the situation where little SO_4^{2-} was present.
3. The use of Fe(III) sulfate in solution would also have had a significant effect on the oxidation of U(IV) to U(VI). The increase in the amount of Fe(III) in solution would have contributed to the rate at which the oxidation occurred (Equation 5.5).

The relatively high concentration of Fe(III) ions in solution lead to increased Eh (see Results, section 4.3). An increase in the redox potential of the solution leads to an increase in the oxidation rate of U(IV) and pyrite (Lizama et al. 2005). The redox potential of the Ferric protocol leachate was found to be higher than the other cells, the highest value observed for all the leaching protocols (Table 5.8), providing conditions conducive to U(IV) oxidation and U(VI) dissolution. Figure 5.3 shows that the Ferric leachate Eh-pH values are concentrated in the soluble uranium-sulfate complex region of the diagram thus confirming that protocol provided optimum uranium leaching conditions.

5.4.2 4 weekly

The extraction rate observed in the 4 weekly flush cell was almost as high as in the Ferric cell, Table 5.9. This is despite lower total concentrations of self-generated sulfate and iron being recovered during the 4 weekly protocol than during the Ferric protocol (Total 4 weekly sulfate: 2523mg/kg, total 4 weekly iron: 419mg/kg and total Ferric sulfate: 6223mg/kg, total Ferric iron: 1371mg/kg). The reduction of pH and extraction of iron and sulfate would suggest similar extraction mechanisms as discussed for the Ferric cell, mainly the oxidation of pyrite.

The reduction in leachate pH to a mean value of pH 4 was substantial, as the mean pH of the feed solution was pH 8. In order for the pH of the leachate to be sufficiently low for uranium and iron precipitation (Equation 5.4 and 5.8) to be avoided there must have been a large source of H^+ ions. The only chemical reaction providing this is the indirect oxidation of pyrite by Fe(III) (Equation 5.9) and thus is considered to be the dominating reaction.

Indirect oxidation of pyrite involves numerous Fe(III) ions so there must have been a significant amount of oxidation of Fe(II) produced from Equation 5.5, 5.6 and eventually 5.9. The oxidation from Fe(II) to Fe(III) can be catalysed by the presence of bacteria (Kirby et al, 1999; Sand et al, 2001). It is likely that the longer rest period provided sufficient time for the lag period (see Chapter 2, section 2.4.1.2) to be passed and bacteria colonies to become established. The increase in Fe(III) in solution following pyrite oxidation (Equation 5.9) also lead to oxidation of U(IV) to U(VI) (Equation 5.5) and the subsequent decrease in pH ensured that uranium remained in solution (Equation 5.3).

The conditions of the 4 weekly protocol leachate were measured to be oxidising compared to the other leaching protocols (Table 5.8). The Eh values measured were similar to those within the Ferric cells and the high Eh is believed to have increased the dissolution of uranium. Figure 5.3 shows that the 4 weekly Eh-pH values are clustered in the soluble uranium-sulfate area of the diagram, close to the Ferric leachate. Furthermore the release of Aluminium and Silicon (Figure 4.17 and Figure 4.23 respectively) show similarities between the 4 weekly and Ferric protocols. This supports the assumption that similar conditions developed within the 4 weekly cells as were provided by the Ferric lixiviant.

The suggestion that pyrite oxidation was prevalent in the 4 weekly cell is supported by the higher concentrations of total iron and sulfate in solution compared to the Control test, Table 5.9. Although the oxidation of pyrite, dissolution of U(VI) and oxidation of U(IV) to

U(VI) will have occurred simultaneously in the cell, the pH of the solution is thought to have been the controlling factor in the extraction process.

5.4.3 Control

The Control test gave the third highest extraction rate of uranium confirming that it is possible to optimise the suggested in situ stope leaching mining process. On inspection of summary Table 5.8 it is clear that the pH and Eh values have decreased with respect to the influent water however, the pH never dropped below pH 5. As a consequence of this, the concentration of H^+ ions in solution would have remained relatively low compared to the Ferric addition and the 4 weekly flush cells, not creating the optimal conditions for uranium solubility.

This assumption that the rate of pyrite oxidation was lower for the Control test was initially thought to be supported by the decrease in iron extraction seen for this test. However, the total extraction of sulfate in solution was 2435mg/kg, only 100mg/kg less than for the 4 weekly flush indicating that a similar rate of pyrite oxidation was taking place. As the dissolved iron extraction rates were much lower in the Control cell than the 4 weekly flush (125mg/kg and 419mg/kg respectively) it is believed that the iron formed insoluble precipitates due to $pH \sim 5$ (Equation 5.8). The limited supply of dissolved iron in solution significantly reduced the cycling of Fe(II) and Fe(III) in the system (Equation 5.7). Without the oxidation to Fe(III), and subsequent increase in H^+ ions (Equation 5.9) the pH of the solution remained at $\sim pH 5$. This pH created more favourable conditions for the formation of insoluble uranium hydroxide precipitates (Equation 5.4) than soluble uranium sulfate ions (Equation 5.3). Conditions within the cells are likely to have been approaching more oxidising conditions according to the Eh-pH diagram (Figure 5.3) with some uranium forming soluble uranium-sulfate complexes and some forming insoluble precipitates.

For the Control test it can be concluded that a number of conditions affected the total uranium extracted. The dominating control on the extraction rate was the solution pH as it resulted in the precipitation of iron out of solution and prevented the optimum conditions for uranium extraction from developing.

5.4.4 Weekly

The Weekly flush test was thought to be inhibited by the pH conditions within the cell, similar to the Control test. Although the Weekly protocol extracted more sulfate overall than the Control test, 2693mg/kg and 2435mg/kg respectively, the mean sulfate extraction over the 52 weeks was lower. Dissolved iron concentration in the Weekly cell however was lower than in the Control cell; mean: 0.08mg/kg and cumulative total extracted: 27mg/kg. This is thought to be a result of the flush frequency

As the pH of the leachate was > pH 6, the high sulfate and low iron concentrations indicate that pyrite oxidation was occurring but the iron was forming insoluble precipitates (Equation 5.7). The Eh-pH measurements for the Weekly cell confirm this showing that conditions in cell were in the insoluble hydroxyl range (Figure 5.3). Subsequently, less uranium was extracted due to the condition discussed for the Control cell. This combination of circumneutral pH and low iron concentration meant that conditions were not favourable for uranium dissolution.

5.4.5 Recycle

The pH and Eh conditions for the Recycled leachate, summarised in Table 5.8, suggest that similar extraction rates seen with the addition of Fe(III) sulfate and a 4 weekly flush cycle could be expected. Additionally the uranium speciation on the Eh-pH diagram (Figure 5.3) indicated that the uranium dissolution would be similar to that achieved by the Ferric and 4 weekly protocols however, this was not the case. Despite the mean pH being maintained at pH < 3.4 and the Eh indicating highly oxidising conditions the mean uranium extraction

was 1mg/kg per cycle. The same can be observed for the release of minor species, Figure 4.17 – 4.25 (Chapter 4, section 4.4.4) where the Recycle protocol consistently resulted in the lowest release rates despite low pH. If the extraction was not being limited by the pH conditions or the oxidation potential it suggests that there was another controlling mechanism at work.

The total sulfate extraction measured for the Recycled leachate was much lower than all the other test parameters at 503mg/kg. Iron extraction on the other hand was relatively high – the third most effective protocol for cumulative iron extraction. The presence of iron indicates pyrite oxidation despite the lack of sulfate thus it is thought that the low sulfate and uranium extraction was because the solution was recycled for each flush leading to saturation with respect to uranium and Rare Earth Element-sulfate secondary minerals (Sapsford et al. 2012, Fig. 2., Appendix A). Once the solution was saturated dissolution of uranium was inhibited despite the pH and Eh conditions being suitable for extraction. Thus the controlling factor for the Recycled leachate test is thought to be the saturation of the solution with respect to uranium-sulfate complexes.

5.4.6 Nutrient

The addition of nutrients to the cell lixiviant was expected to increase the concentration of uranium extracted because nutrients are widely acknowledged to increase microbial populations (section 2.4.2, literature review). However, the extraction rates achieved by the addition of nutrients to the lixiviant were poor when compared to all other test protocols other than the Double flush protocol (Table 5.7). Figure 4.19 (Potassium), Figure 4.20 (Magnesium) and Figure 4.25 (Chloride), which display high release rates for the Nutrient protocol are not a result of leaching but were present in the lixiviant. The pH and Eh of the leachate from the Nutrient cell were found to be higher and lower respectively than that reported for the Control cell as illustrated in Figure 5.3; both of these occurrences create unfavourable conditions for the extraction of uranium.

The higher levels of sulfate in solution are a result of the ammonium sulfate ($(NH_4)_2SO_4$) and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) added as part of the nutrient solution and are not evidence of pyrite oxidation. Dipotassium hydrogen phosphate (K_2HPO_4) present in the nutrient solution is likely to have provided some buffering capacity to the lixiviant, removing H^+ ions from solution. Although the mean Nutrient pH was similar to the Control (Table 5.8) the lower uranium extracted per cycle (Table 5.9) shows that it is likely that the pH in the Control cell fell faster than in the Nutrient cell because there was less buffering.

The buffering experienced the adapted '9K salts' is thought to be a result of the modified recipe used to create the solution. The standard '9K salts' recipe includes the uses of an energy source, hydrated Fe(II) sulfate ($FeSO_4 \cdot 7H_2O$). This energy source was not included in the Nutrient solution for this test work as it was thought that it would make the Nutrient solution too similar in composition to the Ferric protocol (Chapter 3, section 3.4.2.2). With hindsight, the hydrated Fe(II) sulfate should have been included in the Nutrient solution recipe in order to create the correct pH conditions for the acidophilic microorganisms to thrive.

5.4.7 Double flush

The Double flush resulted in similar leachate pH and Eh values measured for the Weekly flush protocol, summary Table 5.8. However, the total concentration of uranium and iron extracted from the ore were less than was seen for the Weekly and Control tests, summary Table 5.9. Cumulative sulfate extraction was similar to the Weekly and Control protocols (Double: 2442mg/kg, Weekly: 2693mg/kg, Control: 2435mg/kg) but the mean sulfate extracted over the 52 weeks was lowest for this test (Double: 42mg/kg, Weekly: 48mg/kg, Control: 85mg/kg) showing that pyrite oxidation was taking place.

The mean pH for Double flush test was > pH 6.5 at which it is likely that iron precipitates were forming (Equation 5.8), similar to the Control and Weekly flush protocols. The majority of leachate measurements are confined within the $(UO_2)_2(OH)_5^-$ speciation phase in Figure 5.3 confirming the likelihood of precipitation of any uranium that was solubilised. Therefore the controlling aspect for the dissolution of uranium in the Double flush cell is the same as for the Control and Weekly flush – the high pH of the leachate, as a result of limited Fe(II)/Fe(III) cycling (Equation 5.7) prevented favourable conditions for uranium dissolution (Equation 5.5) developing.

5.5 Effect of cycle length on extraction rates

The 4 weekly test protocol lead to the greatest improvement in extraction rates when compared to the Control (2 week), Weekly and Double flush protocols. In fact the 4 week cycle produced extraction rates comparable to the addition of Fe(III) sulfate, a known and widely used oxidant in the mining industry. This has important implications as it demonstrates that, for this ore body, it was possible to achieve extraction rates, comparable to the use of an oxidant but requiring just tap water (used as a ground water substitute) and fewer cycle interventions.

For all of the test protocols involving the use of just tap water the pH of the leachate, and subsequently the pH of the interstitial water, is believed to have been the controlling factor on the extraction rates, requiring the development of low pH (pH < 3) environments. Pyrite oxidation is evident in all of the cells regardless of the rest period length but only the 4 weekly protocol showed corresponding levels of dissolved iron.

The relative success of the 4 week cycle is thought to be as a result of less frequent flushing leading to a reduction in pH and a build up of Fe(III) in the interstitial water. By virtue of these processes the effect of lag time (Sapsford et al. 2009), thought to have been

instrumental in the low extraction rates observed in the other cycle length protocols, was removed.

5.6 Effect of lixiviant composition on extraction rates

The addition of Fe(III) sulfate to the cell lixiviant was the most effective test protocol, followed closely by the extended rest period. Of the various lixiviant compositions tested, the addition of Fe(III) sulfate was the only protocol that had a higher extraction rate than the Control cell. The use of Fe(III) sulfate as an oxidant to improve extraction rates is widely discussed in literature (Table 2.6) and so it is unremarkable that its use lead to increased extraction in this study. If anything the rate of extraction observed for this test work was less than was suggested possible in the literature (Ring, 1980; Macnaughton et al, 1999).

The 0.5g/L Fe(III) sulfate as used in this body of work is suggested by Sand et al. (2001) only as a concentration suitable for removing the lag time experienced by many microbial extraction activities. In order to drastically increase the uranium extraction rate a different Fe(III) sulfate dose would need to be considered, e.g. Ring (1980) found that Fe(III) sulfate concentrations of 10-15g/L produced uranium extractions of 96%. However, it was concluded that with ores containing refractory brannerite, both the initial and overall uranium extraction rate were reduced where high concentrations of Fe(III) sulfate were used (Ring, 1980).

The Nutrient protocol was affected by the buffering capacity of the lixiviant and the Recycle protocol resulted in saturation of the solution by secondary minerals.

5.7 Iron (II) concentration

The concentration of Fe(II) in solution was determined by spectrophotometer as described in Chapter 3, section 3.8 and Appendix B. The concentration of Fe(II) was

investigated for only the Control, Ferric addition and 4 weekly test parameters because it was felt that only the 4 weekly and Ferric cells had the potential for bacterial oxidation to be occurring due to the low pH achieved by the cells. The Control cell was included as a comparison. The results are summarised in Table 5.11. From the results presented in Table 5.11 it appears that there is very little Fe(II) present in any of the cells after week 0, as the values are below detection on the calibration curve.

Table 5.11 Summary of Fe(II) concentration in leachate

Control			Ferric			4 weekly					
Week	Total Fe	Fe(II)	Fe(III)	Week	Total Fe	Fe(II)	Fe(III)	Week	Total Fe	Fe(II)	Fe(III)
	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L		mg/L	mg/L	mg/L
0	11.99	0.51	11.49	0	42.34	1.25	41.09	0	22.97	1.18	21.78
2	0.08	bd	0.08	2	22.18	bd	22.26	4	0.97	bd	0.97
52	4.39	bd	4.39	52	58.33	bd	58.45	28	52.31	14.10	38.16
								52	35.08	bd	35.08

* bd - below detection

There are three possible explanations for the low levels of Fe(II) detected:

1. Bacterial oxidation of pyrite was occurring and therefore any Fe(II) in the system, as a result of either oxidation of U(IV) to U(VI) (Equation 5.5) or chemical oxidation of pyrite (Equation 5.6), was being converted to Fe(III) at a fast rate so no Fe(II) detected in the leachate.
2. All the uranium in the sample was present as U(VI) and so no Fe(II) produced during oxidation of U(IV) to U(VI) (Equation 5.5)
3. The samples were stored for too long in the freezer before analysis and were also acidified using NHO_3 and therefore the results can not be relied upon, as oxidation of Fe(II) to Fe(III) could have happened in the containers.

With many variables to consider the Fe(II) results should be regarded as inconclusive although high redox potentials (section 4.3) indicate high ratios of Fe(II)/Fe(III).

5.8 Summary

It can be concluded from the discussion during this chapter that the main controlling factor on the extraction of uranium was the pH of the interstitial water in the cell. Without a sufficiently low pH the oxidised U(VI) was unable to be solubilised without being precipitated. There is some indirect evidence that bacterial oxidation of pyrite had a role in the higher yielding protocols however, attempts to substantiate this hypothesis were inconclusive. Quantitative methods of uranium analysis were investigated and the importance of discretion when determining the mineral content of any sample was highlighted.

6 Conclusions

The objectives of the thesis are outlined below, along with the corresponding conclusions of the study:

- i. to undertake a study on the effect of rest period on uranium extraction, including a two week control protocol, a double flush protocol, a weekly flush protocol and a 4 weekly flush protocol;
 - o the duration of rest period had a measurable effect on the uranium extraction from the ore material. Increased flushing rate and multiple flushes decreased extraction whereas a less frequent flush rate yielded higher uranium extraction.
 - o higher uranium extraction during the 4 weekly protocol was attributed to overcoming the lag time as a result of the long rest period. Along with optimised uranium dissolution conditions created by the oxidation of pyrite and reduction in solution pH.
 - o the uranium extraction in the Control, Double flush and Weekly protocols was a result of limited Fe(II)/Fe(III) cycling and circumneutral pH conditions which prevented favourable conditions for uranium dissolution developing.

- ii. to investigate how the presence of Fe(III) sulfate influences extraction rates;
 - o addition of Fe(III) sulfate resulted in high uranium extraction because it provided low pH conditions, increased the concentration of SO_4^{2-} in solution and aided Fe(II) oxidation by providing a source of Fe(III) leading to a removal of lag time before optimal uranium dissolution conditions were created.
 - o in comparison to extraction rates given in literature the Ferric protocol was less successful than expected.

- iii. to determine whether the use of a nutrient solution has a positive effect on the uranium dissolution process
 - o the nutrient solution protocol did not aid uranium dissolution. This is thought to be down to the buffering capacity of dipotassium hydrogen phosphate and removing H^+ ions from solution.
 - o the absence of hydrated Fe(II) sulfate in the lixiviant resulted in circumneutral pH conditions which did not aid uranium dissolution.

- iv. to identify the effects of recycling the leachate.
 - o no benefits to recycling the leachate were identified. Low sulfate extraction was measured which, along with low uranium extraction, is thought to be a result of saturation of the recycled solution with uranium secondary minerals.

Fundamentally leaching of the ore was controlled by the lag time required to establish biogeochemical conditions favouring rapid pyrite oxidation, and thus provide an environment conducive for uranium dissolution. The addition of Fe(III) sulfate removed the lag time and so a higher initial uranium extraction was observed. Overall the uranium

extraction achieved by addition of Fe(III) sulfate and a 4 week rest period was the same which could have important implications in the mining industry.

6.1 Recommendations for further work

- Further experiments with different initial and overall rest periods could be investigated to determine whether the overall time required for uranium dissolution could be reduced. The experiments suggested are 1) a 4 week/2 week flood protocol to establish whether following the initial 4 week progression beyond the lag period a 2 week rest period would be sufficient to maintain the optimised extraction conditions in the interstitial water. 2) a 3 weekly and 5 weekly protocols to investigate whether the suspected bacteria are still in the exponential growth stage.
- The presence of bacteria in the leachate and interstitial water could be confirmed or disproven by further test work. If bacteria was proven to be present and the species determined, a greater understanding of the nutrient requirements and growth phase could be determined thus improving the overall quantity of uranium extracted.
- Thin resin sections of the head grade and residue material could be used to determine detailed mineralogy of the samples. This would benefit this study by establishing which minerals the uranium was being extracted from and whether it was being oxidised and then mobilised or just mobilised into solution.
- A pilot scale study could be developed to investigate the uranium extraction rates achievable in a scaled up stope leaching environment with a larger particle size. If a large scale system could be optimised the use of stope leaching in suitable ore bodies could become a standard extraction procedure for low-grade ore.

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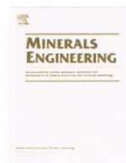
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Appendix A – Minerals Engineering paper

Sapsford, D. J., Bowell, R. J., Geroni, J. N., Penman, K. M., Dey, M., 2012. Factors influencing the release rate of uranium, thorium, yttrium and rare earth elements from a low grade ore. *Minerals Engineering* 39(0), pp. 165-172.



Factors influencing the release rate of uranium, thorium, yttrium and rare earth elements from a low grade ore

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ABSTRACT

This paper presents data from laboratory leaching of a mineralogically complex low grade ore containing uranium (U), thorium (Th), yttrium (Y), rare earth elements (REEs) and accessory pyrite. The study examines the influence of varying the leaching protocol on the rate of release of U, Th, Y and REEs. Leaching protocols were designed to simulate a range of heap/in situ stope leaching scenarios. Protocol variants included flushing frequency, leachate recycle, nutrient (9 K salts) addition and ferric sulphate addition to cells. Maximum extractions over 52 weeks were: 58% U, 50% Th, 36% Y and 45% of the REEs; observed in cells flushed fortnightly with a ferric sulphate lixiviant (0.5 g/l, pH 3.5). Flushing with tap water once monthly resulted in second highest observed extractions (57% U, 6% Th, 27% Y, 37% REEs) with the exception of Th, where the lower release was due to insufficiently low pH for Th mobilisation. Pourbaix plots indicate that redox potentials within the leaching system were buffered by coffinite dissolution. The high redox potentials, acidic pH and elevated sulphate concentrations required for metals dissolution were found to be a consequence of (a) direct addition of ferric sulphate as a lixiviant or (b) in situ generation of acidity and ferric sulphate via microbially-mediated oxidation of accessory pyrite. Generation and maintenance of acidic sulphate-rich interstitial water appear to control the dissolution of Th, Y and REEs in addition to U. The presented data highlight that significant U, Th, Y and REEs can be mobilised from rock materials by the addition of a ferric sulphate lixiviant, furthermore periodic flushing with water alone is sufficient to achieve similar release of U, Y and REEs where accessory pyrite is available in the reacting system. These findings have significant implications for recovery of valuable elements from low grade and marginal ores or materials previously considered as wastes.

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1. Introduction

The efficiency of leaching of elements such as uranium and Rare Earths (REEs) is a major factor in determining the economic viability of mining low grade ores. In cases where uranium concentration is too low to be economical to extract alone the recovery of REEs as a leaching by-product can boost profitability. Such ores may contain a variety of complex REE bearing mineral phases as well as uraninite and pitchblende and while the leaching kinetics of uraninite have been widely studied, the interrelationship between complex mineralogy, mineral liberation and leaching behaviour in low grade mixed ore deposits is not yet well defined and often site specific.

The processes which operators seek to maximise during mineral extraction operations by contrast need to be minimised with respect to natural weathering of waste rock piles which can lead to the release of uranium and other heavy metals into the environ-

ment with implications for eco-toxicity. Understanding the processes occurring within rock piles is therefore essential not only in terms of maximising the profitability of mining operations, but also in reducing their environmental impact over the long term.

1.1. Uranium chemistry

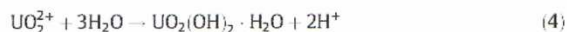
Uranium is most commonly found in the +4 oxidation state as UO₂ (uraninite and pitchblende being different crystalline phases with the same chemical composition). Hexavalent uranium is readily solubilised in acidic solution forming a uranyl cation (Eq. (1)) with tetravalent uranium requiring oxidation, often by Fe(III) liberated from accessory pyrite or added during leaching (Eq. (2)).



In sulphate systems a soluble complex is formed under mildly acidic conditions (Eq. (3)) with hydrolysis favoured above pH 5–6 resulting in the formation of an insoluble hydroxyoxide precipitate (Eq. (4)).

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1.2. Heap/stope leaching

Despite the increasingly widespread use by the mining industry of heap leaching for the recovery of uranium and other elements the method is still limited by low recoveries and long extraction times (Ghorbani et al., 2011). Similarly attempts to carry out heap leaching underground, so called in situ (or 'in-place') stope leaching (e.g. Campbell et al., 1987) incurs the same set of constraints. The processes controlling the rate of leaching range from the molecular scale such as diffusion of reacting species towards and away from the mineral surface to the transport of water, air and heat throughout the entire heap. It is widely recognised that in many heap/stope leach operations microbial catalysis of redox processes is an important factor in the liberating metals from their ores (McCready et al., 1986; Dwivedy and Mathur, 1995; Muñoz et al., 1995; Ghorbani et al., 2011). Bacteria such as *Acidithiobacillus ferrooxidans* which oxidise Fe(II) provide an important source of Fe(III) for reaction with and solubilisation of U(IV) (Eq. (2)). In order to encourage the growth and activity of these bacteria nutrients may be added to lixivants. Other options include the addition of acidic solutions or dosing with Fe(III) salts to encourage the chemical oxidation and dissolution of the metals present.

1.3. This study

The aims of this study were to determine the effects of varying the leaching protocol on the release of uranium, thorium, yttrium and REEs from a low grade uranium ore. This included the addition of nutrients and Fe(III) salts, variation in the length of the leaching cycle and recycling of the leachate to simulate the effects of variations in solute concentrations throughout a rock pile and recycling of lixivants.

2. Materials and methodology

2.1. Materials

A uranium-bearing quartz pebble conglomerate ore was used in this evaluation. The material was sourced from the Denison mine, Elliot Lake district of Ontario, Canada, where conventional uranium mineral processing has historically been combined with heap leaching and in situ stope leaching (Fisher, 1966; MacGregor, 1966; Campbell et al., 1987). The paleoplacer conglomerate is composed of quartz pebbles cemented by a matrix comprising fine-grained quartz, feldspar, and sericite with variable (5–25%) amounts of pyrite (Derry, 1960) and a wide variety of other heavy minerals. Uranium, thorium, yttrium and rare earth element-bearing minerals occur as both primary (detrital) phases and secondary alteration phases (see Table 1) within the cement matrix, with grain sizes ranging from 1 to 600 μm. Detailed descriptions of the mineralogy/textural descriptions of the quartz pebble conglomerate from this area and the geological setting can be found in Derry, 1960; Robertson and Steenland, 1960; Burton and Fralick, 2003.

2.2. Materials preparation and physicochemical characterisation

Approximately 50 kg of raw material was crushed through jaw and gyratory crushers and homogenised so that a final grain size of 100% passing 10 mm was achieved. Indicative experiments in the field has shown that blasting of similar material resulted in 28%

material passing 12.7 mm (Campbell et al., 1987) and as has been found in acid rock drainage prediction work (e.g. Price, 1997) most of the reactive surface area is concentrated in these smaller size fractions. A portion of the bulk homogenised material was then milled to <20 μm for determination of the head grade of U, Th, and the Rare Earth Elements (REEs) Ce, Y, La, Pr, Nd, Yb, Dy and Sm. Uranium assays were carried out by digesting 0.1 g samples of the finely milled material with 2 ml HF and 6 ml aqua regia (50 ml HCl and 50 ml HNO₃) in a microwave oven-digester. The resultant solutions were diluted to 50 ml and analysed by ICP-OES. Further chemical assays for thorium and REEs were carried out by an external laboratory. All assays were carried out in triplicate. Samples of the bulk material, and size fractions isolated by wet sieving (milled to ≈50 μm in a ring mill), were analysed by X-ray Diffraction (XRD) using a Philips PW1710 diffractometer in order to establish the dominant crystalline mineral phases.

2.3. Leaching experiments

The experimental setup was designed to mimic in situ stope leaching. In this process the leaching is conducted via flooding an underground heap of blasted rock (e.g. Campbell et al., 1987) with water for 24 h (this step is referred to here as a 'flood leach'). The heap material is then drained to unsaturated conditions with the rock remaining in contact with the residual interstitial water until the next flood leach (this step is referred to here as the 'rest period'). Water is then introduced to begin the next flood leach and this represents the completion of one cycle.

It was noted early on in the research that the process of cyclic flood leaching and rest periods is readily mimicked in so called humidity cell testing procedures which are routinely used for the assessment of ARD potential in mine wastes. It was therefore decided to adopt an experimental setup based on humidity cells to imitate the process of stope leaching.

The cells were constructed from Perspex cylinders of 100 mm in diameter. The crushed ore was riffled into representative 1 kg portions and loaded into the cells, the packed length of the columns was approximately 0.11 m. The material sat on a filter mesh which was supported by a perforated Perspex plate. Lixiviant was introduced rapidly from the bottom of the cell from the reservoir above under gravity, this was done for three reasons: (i) To prevent problems of 'air-locks' forming within the material and ensure effective contact between lixiviant and rock – this is a common problem in humidity cell procedures (Sapsford et al., 2009) and can lead to incomplete contact of the sample with water during the flood leach. (ii) Flood leaching in this fashion circumvents problems encountered with incomplete or unequal contact of all of the rock material with lixiviant caused by unpredictable flow paths during trickle leaching. (iii) In situ stope leaching commonly involves containment of material through stope walling of rubblized ore material and flooding of the ore rather than trickle irrigation as would occur in a standard heap leach. This reflects limitations in being able to construct suitable pipe and irrigation work underground in a confined stope (Campbell et al., 1987). Consequently a similar method was selected in this study that mimicked this approach used in the field. In total 14 of these cells were constructed and used for the experiments. The following steps were followed:

1. Dry crushed ore loaded into the cell.
2. Ore flood leached with 750 ml of lixiviant.
3. Ore left in contact with lixiviant for 24 h.
4. Reactor drained under gravity.
5. Ore left to react during rest period.
6. Steps 2–5 repeated for total of 12 months but using 500 ml of lixiviant.

Table 1
Principal minerals carrying uranium thorium and REEs.

Primary phases		Secondary alteration phases	
Thorium enriched uraninite	UO ₂	Coffinite	U(SiO ₄) _{1-x} (OH) _{4x}
Monazite (thorium rich)	{Ce, La, Y}PO ₄	Brannerite	UTi ₂ O ₆
Thorite	{Th, U}SiO ₄	Uraninite (thorium, REE poor)	UO ₂
Allanite	{Ca, REE}Al ₂ Fe(SiO ₄)(Si ₂ O ₇)O(OH)	Florencite	(REE)Al ₃ (PO ₄)(OH) ₆
		Xenotime	YPO ₄
		Uraniferous rutile or "leucocoxene"	'UO ₂ -Rutile'
		Silicified monazite	'Mz-Silicate'
		Very fine-grained intergrowth of pitchblende, pyrite and aluminium-rich silicate phase	'UO ₂ -Pyr-AISI-mix'
		Uraniferous pyrite	'UO ₂ -Pyrite'

Table 2
Variations in leaching protocols investigated.

Cell name	Rest period (weeks)	Flood leach	Notes
Control	2	1 × 500 ml tap water	
Double flush	2	2 × 500 ml tap water	
Nutrient addition	2	1 × 500 ml nutrient solution	Nutrients '9 K salts'
Ferric addition	2	1 × 500 ml Fe ₂ (SO ₄) ₃	0.5 g/l Fe ₂ (SO ₄) ₃ at pH 3.5
Recycle	2	1 × 500 ml recycled water	Use of previous weeks leachate
Weekly flush	1	1 × 500 ml tap water	
Monthly flush	4	1 × 500 ml tap water	

2.3.1. Variations in leaching protocol

Table 2 gives the protocol variations explored during the experiments. In total seven different protocols were investigated with each test carried out in duplicate. Variations were made with respect to both the length of the rest period (1 week, 2 week, 4 week) and the lixiviant used to carry out the leaching. In addition to tap water the effect of nutrient addition ('9 K salts'), oxidant addition (Fe₂(SO₄)₃ at 0.5 g/l) and recycling of lixiviants was tested.

2.4. Chemical analyses

The volume of leachate recovered after each flooding cycle was measured and recorded. The pH, temperature, conductivity and relative ORP (Rel.mV) were measured using a SevenMulti™ S40 unit, with calibration was carried out immediately prior to analysis. Alkalinity of the leachates was measured by titration with 1.6 N H₂SO₄ using a HACH 16900-08 Digital Titrator. The end point of the titration was determined by a colour change from green to pink using a bromocresol green methyl red indicator which corresponds to a pH of approximately 4.5.

Two samples were collected for analysis of metals by ICP-OES and sulphate by ion chromatography. Samples were filtered using a syringe and 0.45 µm cellulose nitrate filter tip. Samples collected for ICP-OES analysis were acidified with 100 µL of 10% HNO₃.

2.5. Test work completion procedure

After the final flush the cells were disconnected and weighed individually with their contents. The cells were then dried at 40 °C for 3 days and re-weighed. The duplicate samples were recombined, representative samples were riffled and milled to <20 µm and 0.1 g portions were taken for microwave digestion and analysis as described in Section 2.1. The results of these assays

Table 3
Elemental composition of head grade ore and reconstituted head grades (with standard deviation in parentheses).

Element	Head grade ore (mg/kg)	
	Head	Reconstituted head
U	391 (25.7)	359 (18.6)
Th	41.5 (12.6)	53.3 (25.6)
Ce	143 (14.6)	145 (18.6)
Y	32.3 (1.90)	34.8 (4.2)
La	102 (8.13)	103 (14.0)
Pr	19.0 (1.72)	19.1 (2.4)
Nd	65.1 (5.88)	69.9 (14.6)
Yb	4.96 (0.36)	4.72 (0.26)
Dy	16.1 (0.65)	21.1 (12.9)
Sm	13.6 (0.85)	14.7 (3.1)

for the column residues were then used in reconstituted head grade calculations for each of the columns according to Eq. (5) (see Table 3).

$$\text{Reconstituted head grade} - \text{concentration in column residue} + \text{total leached over 52 weeks} \quad (5)$$

3. Results

3.1. Material characterisation

The elemental composition of the head grade ore with respect to U, Th and REEs are shown in Table 2. Analysis by XRD demonstrated that the material was primarily composed of quartz with minor (2–5%) pyrite. The principal minerals carrying uranium, thorium and REEs can be split into primary phases and secondary alteration phases as shown in Table 1.

3.2. Leachate chemistry

Mean and final values recorded for pH for each of the leaching protocols are shown in Table 4. It can be seen that the lowest pH values and highest Eh values (most oxidising conditions) were observed for the ferric sulphate addition and the leachate recycle protocols. It should also be noted that pH and Eh showed a negative correlation with the length of the flushing cycle, i.e. more frequent flushing resulted in higher pH and less oxidising conditions. Addition of the nutrient appeared to buffer the pH of the system at around pH 6.

3.3. Element extraction

The results for the total extraction of U, Th and REE over the entire 52 week test are summarised in Table 5. The data shown in the table were calculated based on a reconstituted head grade value (Table 3) for each of the cells in order to minimise the errors that

Table 4
pH and Eh values for each of the leaching protocols investigated.

Protocol	Leachate pH		Leachate Eh (mV)	
	Mean	Final	Mean	Final
Control	5.4	5.5	561	561
Double flush	6.6	7.0	540	579
Nutrient	5.6	6.0	507	493
Ferric	2.8	2.7	821	807
Recycle	3.3	2.8	748	766
Weekly	6.4	6.7	526	580
Monthly	4.0	3.7	700	704

might be incurred using the average head grade composition. The addition of ferric sulphate resulted in the largest recoveries for the majority of the elements under investigation, with the double flush and weekly flushes giving the lowest recoveries. Nearly 58% of the U content of the ore was leached and 50% of the Th content. For the REEs Dy showed the greatest percentage leached at 76% (equivalent to 40 mg/kg) and Cerium the lowest at 16.3% (equivalent to 28.8 mg/kg).

Cumulative extraction of U and Th over time are shown in Fig. 1. It can be seen that for both U and Th the addition of ferric sulphate resulted in the most efficient leaching. By contrast recycling of the leachate resulted in the lowest overall U extraction, but the second highest overall Th extraction. Also of great interest (especially to the practical application of heap leaching/stope leaching) is the

observation that the second highest U, Y and REE extractions were from the cells leached on a monthly basis. Where pH remained above 4, regardless of the leaching protocols, thorium extraction was negligible.

Cumulative data for the leaching of Y and REEs are compared in Fig. 2. Similar patterns of extraction are seen for all of the elements with ferric sulphate addition and/or monthly flushing giving the highest overall percentage extraction in all instances. In the cases of La, Pr and Ce the recycled leachate gave the highest leaching rate between weeks 12 and 38, after which point results show decreasing concentrations of the elements suggesting precipitation. As with U and Th the double flush and weekly flush protocols showed the worst leaching performance for all elements.

3.4. Uranium leaching rate

Rates of U leaching in mg/kg/day, averaged over an entire cycle (U leaching rate = quantity leached/cycle length) for each of the leaching protocols are shown in Fig. 3. It can be seen that ferric sulphate addition produced the highest leaching rate by at least a factor of 3 over the first flushing cycle compared to any of the other protocols, reducing from a maximum of 1.7 mg/kg/day to a 0.18 mg/kg/day after 52 weeks. Leaching rate using the monthly protocol increased significantly over the first three cycles (12 weeks). By contrast U leaching rate was effectively zero after 12 weeks where recycled leachate was used.

Table 5
Total elemental extraction after 52 weeks (based on reconstituted head).

Leaching protocol	Uranium		Thorium		Yttrium		Total REE		Cerium		Praseodymium	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Control	41.9	163	0.10	0.02	18.8	6.41	26.3	223	9.70	15.6	10.6	2.02
Double flush	16.0	65.1	0.00	0.01	7.40	2.30	9.40	77.0	2.30	3.06	1.50	0.26
Nutrient	17.1	52.1	0.00	0.00	9.40	3.43	9.90	79.0	4.00	5.99	4.30	0.80
Ferric	57.7	253	49.9	44.6	35.9	14.4	45.2	452	16.3	28.8	20.5	3.91
Recycle	18.5	43.4	38.9	19.4	18.2	5.60	17.4	104	10.6	13.3	12.3	1.80
Weekly	20.4	80.1	0.00	0.01	8.10	2.60	12.4	93.0	3.00	3.56	2.60	0.41
Monthly	56.6	226	5.50	2.69	27.0	11.3	36.7	313	17.4	26.8	22.4	3.65
	Lanthanum		Neodymium		Ytterbium		Dysprosium		Samarium			
Control	13.4	13.34	21.2	17.5	10.3	0.49	10.4	1.67	20.3	3.33		
Double flush	3.60	3.27	2.90	1.77	2.80	0.13	3.00	0.46	4.00	0.52		
Nutrient	7.70	7.74	9.60	6.78	3.70	0.17	5.50	0.86	10.3	1.56		
Ferric	22.6	23.1	34.5	34.1	20.7	1.16	76.1	39.6	41.3	8.85		
Recycle	13.9	10.7	11.2	6.32	10.3	0.51	12.1	1.66	13.1	1.57		
Weekly	4.60	3.64	2.50	1.39	4.30	0.20	3.60	0.55	3.00	0.37		
Monthly	24.6	21.9	18.7	12.78	18.5	1.01	20.2	3.36	21.8	3.17		

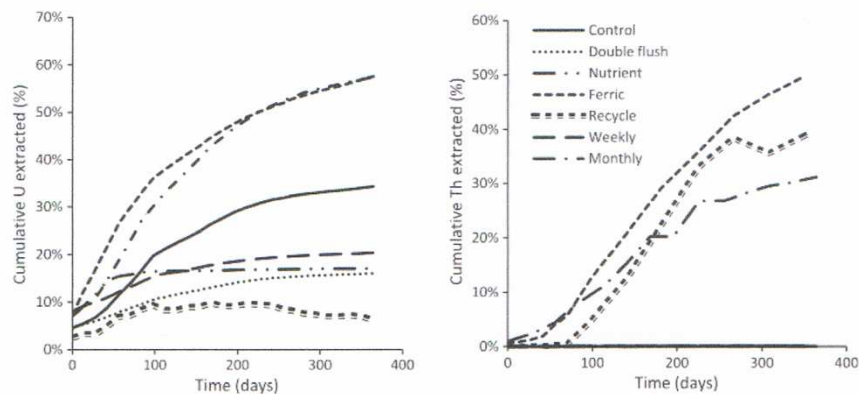


Fig. 1. Comparison of U and Th cumulative leaching for each of the protocols investigated.

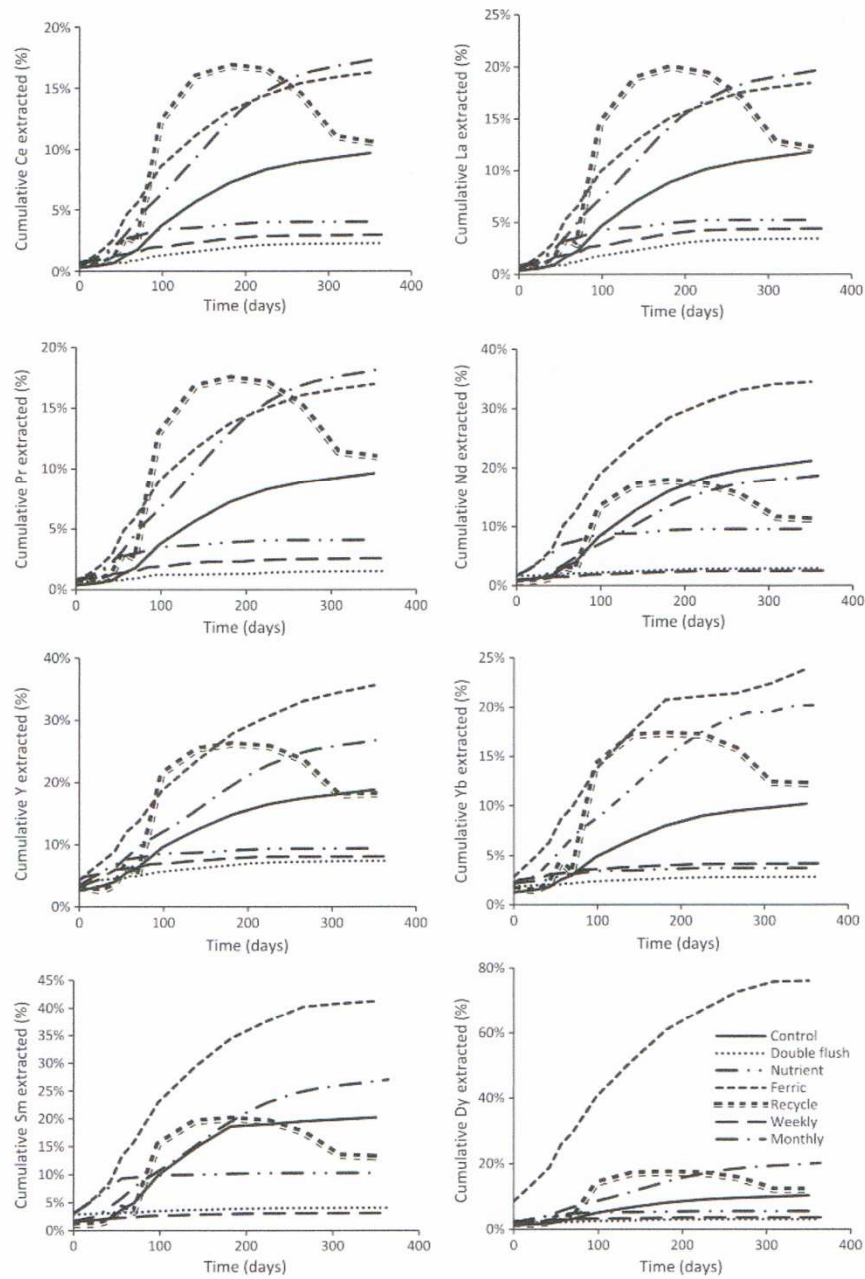


Fig. 2. Comparison of Y and REEs cumulative leaching for each of the protocols investigated.

4. Discussion

4.1. General controls on leaching

The dominant factors controlling leaching rate vary between the different elements investigated in this study. This is evidenced by the extent to which changing leaching protocol affects the quantities of each element extracted. In terms of their behaviours

U and Th may be considered separately, with Y and REEs exhibiting broadly similar characteristics.

4.1.1. Uranium

As discussed in Section 1.1 the rate of U leaching will depend on the proportion of the element available as the soluble U(VI) compared to the insoluble U(IV). The U extraction efficiency of the leaches was as follows: Ferric sulphate > Monthly flush >

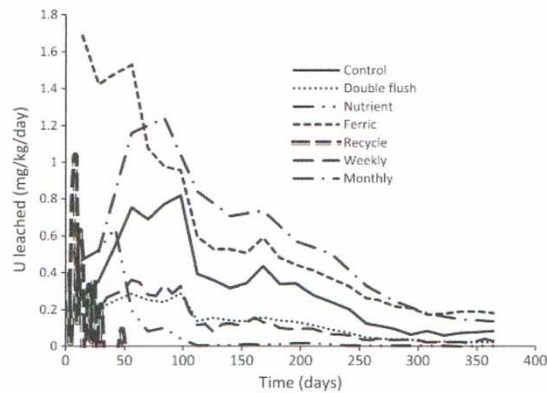


Fig. 3. Comparison of U leaching rate over time for each of the protocols tested.

Control > Weekly flush > Recycled flush > nutrient flush > double flush. For successful U leaching one of the critical factors will therefore be a sufficiently high Eh to cause U(IV) oxidation on the time-scale of the leaching protocol, hence the benefit of ferric sulphate addition – this sulphate-rich low pH lixiviant also serving to increase the solubilisation of U(VI) through formation of the $UO_2(SO_4)_2^{2-}$ complex (see Fig 4).

Of interest (particularly to commercial heap/stope leaching) is that with the exception of the nutrient/ferric addition, the other protocols were adding only tap water to the system, yet it can be seen especially in the case of the monthly flush that extraction of U, Y and REEs was almost as high as with the ferric sulphate addition. The authors suspect that microbial oxidation of the accessory pyrite in the system created favourable Eh/pH conditions and sulphate concentrations for extraction of U, Th, Y and REEs. The suggested mechanism is the establishment of acidophilic Fe(II) oxidising microbes in the system which rapidly recycle system Fe(II) to Fe(III) thus maintaining the high redox potential required to oxidise pyrite (releasing further Fe(II) for the microbes to process and sulphuric acid) (cf. Sapsford et al., 2009). The maintenance of high Eh (Fe(III)/Fe(II) dominated) serves to oxidise U(IV) and the low pH/high sulphate concentrations serve to solubilise U(VI), Th,

Y and REEs. The lengthening of the 'rest' period between flushes allows the posited microbial action to take best effect, this might be due to kinetic or mass transfer constraints such that leaching efficiency is increased as contact time with the high Eh/low pH interstitial water with the U, Th, Y, REE bearing phases increases. Another possible explanation is that more frequent flushing of the material flushes planktonic Fe(II) oxidising microorganisms from the system and hinders the establishment of a sessile microbial population. It is important to note that the addition of the ferric sulphate lixiviant will also promote the establishment of sessile microbial populations as shown by Sand et al. (2001). The low extraction efficiencies observed with the addition of a nutrient-rich lixiviant are due to the pH buffering effect of the solution.

It is also important to highlight that although the microbes are probably responsible for increases in redox potential, Fig. 4 clearly shows that the Eh is buffered by contact with coffinite bearing phases, and suggests that where coffinite had formed in the ores then this U(IV) appears easier to oxidise than the more refractory brannerite phase.

4.1.2. Thorium

The major controlling factor in the release of Th in these leaching tests is likely to be pH, with sulphate concentration having an important secondary role. Under the conditions in the leaching cells Th will be present as Th(IV), which, in the absence of dissolved sulphate forms the highly insoluble ThO_2 in aqueous systems above approximately pH 1.5 (Pourbaix, 1966). The addition of sulphate increases Th solubility by expanding stability region of the $Th_{1(a)}^{4+}$ ion through the formation of soluble $Th(SO_4)_2$ and $ThSO_4^{2+}$. The pH range over which Th is soluble increases as a function of sulphate concentration, though it remains insoluble at circumneutral and alkaline pH values (Kim and Osseo-Asare, 2012).

4.1.3. Yttrium and rare earth elements

As with Th, the oxidation state of Y and the REEs is unlikely to change during leaching and so Eh is not a factor of primary concern. In the case of these elements the major controlling factors are sulphate concentration and pH. REEs can form solid sulphate phases at high sulphate concentrations, indeed precipitation of REEs sulphate has been shown to be an effective step in their recovery from Monzanite digestate (Abreu and Morais, 2010). The effect of pH on the solubility of the sulphate complexes varies

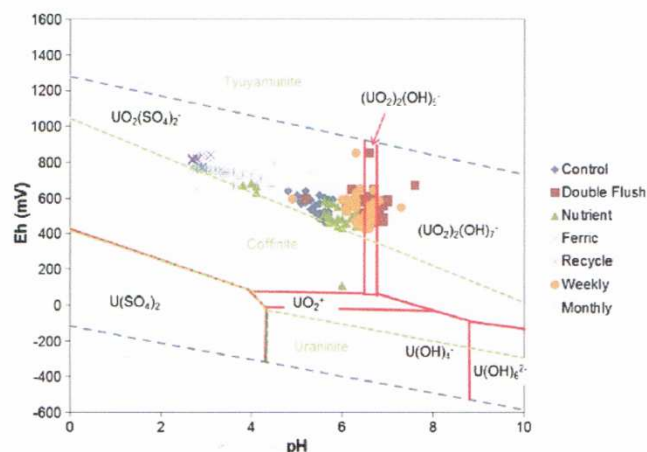


Fig. 4. Eh-pH diagram indicating uranium speciation and common mineralogy, based on the leachate chemistry for the seven leaching protocols tested.

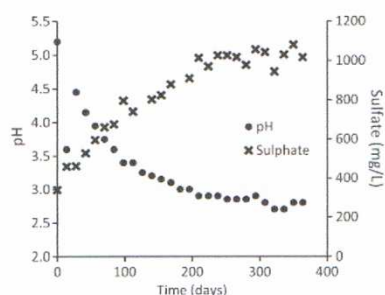


Fig. 5. Changes in pH and sulphate concentration over time for the recycled leachate.

between the different REEs and therefore will be of varying importance in determining leaching rate (Kim and Osseo-Asare, 2012).

4.2. Effect of lixiviant composition

Of the three different lixivants used (ferric sulphate dosed, nutrient dosed and recycled leachate), the ferric sulphate dosed lixiviant showed the best overall leaching properties with respect to both U and Th as well as Y and REEs. This lixiviant combined low pH with strong oxidising conditions and moderate sulphate concentration providing all of the conditions necessary to increase the solubility of the elements under investigation. Conversely the nutrient dosed lixiviant showed reduced leaching rates compared to the control experiment across all elements. In terms of the leachate chemistry the nutrient dosed lixiviant resulted in higher pH and lower Eh, most likely as a result of buffering by the 9 K salts. The low leaching rates can be accounted for by these relatively high pH values which would have favoured the formation of insoluble metal oxides and hydroxides.

The recycled lixiviant showed the greatest variation in its effect on leaching rate of the different elements. This can be explained in terms of the mechanisms by which the different elements are released into the leachate and the solubility of their sulphate complexes. In the case of U, higher concentrations within the ore relative to the other elements are likely to have resulted in saturation relatively early on in the experimental period. For Th however, increasing sulphate concentration and decreasing pH (see Fig. 5) over time led to increasing solubility.

For Y and the REE's the decreasing pH is likely to have resulted in increased solubility during the first half of the test work. Subsequent decreases in REEs concentration within the recycled leachate can be explained by the precipitation of solid $M_2(SO_4)_3$ phases as the concentration of sulphate increased (Kim and Osseo-Asare, 2012). An important alternative mechanism for reducing REE concentrations could be co-precipitation and/or adsorption onto Fe(III) oxyhydroxide precipitates generated in situ.

4.3. Effect of varying cycle length

With the exception of Nd, the 4 week cycle resulted in the greatest extraction rates compared to the 2 week or 1 week cycles, and was in many cases comparable to the extraction rates achieved with ferric sulphate addition to the lixiviant. Where no additional solutes are present in the lixiviant, leaching rates are largely dependent on the development of low pH, oxidising conditions within the pore water which arise as a result of accessory pyrite oxidation. Less frequent flushing allows for greater concentrations of dissolved Fe(III) to build up within the pore water, with an associated reduction in pH. Dissolved Fe(III) concentrations were up to

three orders of magnitude higher in the monthly flush leachate compared to the weekly flush leachate with average pH values of 4.0 and 6.4 respectively.

5. Conclusions

It has been shown that for a mineralogically-complex Elliot Lake ore up to 57% of uranium, 50% thorium, 36% yttrium and between 16% and 76% of REEs can be extracted by periodic flood leaching of the material. Mobilisation of U, Th, Y and REEs was due to the development of acidic conditions favouring the direct solubilisation of U(VI) and the Fe(III)-mediated oxidation of insoluble U(IV) to soluble U(VI), with the dominant control of U mobilisation being the dissolution of coffinite. Whilst the most effective leaching protocol used an acidic (pH < 3) and strongly oxidising (iron (III) sulphate) lixiviant (which resulted in maximum U, Th, Y and REE extraction) it was found that similar recovery of U, Y and REEs could be achieved simply by flushing the material once monthly with tap water. It was also found that the frequency of flushing has a significant effect on leaching efficiency. Less frequent flushing (monthly) resulted in an increase in the extraction efficiency of 2–4 times for the REEs and three times for U compared to more frequent (weekly) flushing. Longer periods between flushing allow for more pyrite oxidation, generating acidic Fe(III) rich conditions in situ. A nutrient-bearing lixiviant was found to buffer the leachate at a pH of around 6–8. This resulted in low leaching efficiencies as U(VI) is insoluble within the circumneutral pH range. Recycling of the leachates (a common strategy in water constrained mining environments) resulted in an overall reduction in U and REE extraction, probably as a result of the solution reaching saturation with respect to U(VI) over time. Overall this study demonstrates the importance of optimising the leaching protocol for in situ stope leaching and heap leaching for the economic viability of recovery of U, Th, Y and REEs from Elliot lake ore and similar ores. The study demonstrates that in the absence of reagent addition, optimising the leaching environment to promote microbial oxidation of accessory pyrite can lead to comparable recoveries of U, Y and REEs and in effect make the ore 'self-leaching'.

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Appendix B – Spectrophotometric method

The spectrophotometric method used to determine the Fe(II) concentration in chapter 3, (section 3.8) was as per Geroni (2011). The procedure was developed from Barnes (2008).

The Fe(II) concentration in samples was measured spectrophotometrically using 2,2'-bipyridyl as the complexing agent. A solution of 2,2'-bipyridyl was prepared by dissolving 2g of the solid in 100mL of 0.2M HCl. 2mL samples of aqueous Fe(II) (previously acidified with HNO₃ to prevent oxidation) were added to 5mL of ammonium acetate buffer (prepared according AWWA et al (1999)) containing 2 drops of the 2,2'-bipyridyl solution. A 2mL portion of the buffer containing the sample was then transferred to a 1.5mL semi-micro cuvette. The absorbance at 520nm was measured using a Hitachi U1900 spectrophotometer and compared to a calibration curve (Figure B1) determined against a solution of FeSO₄ standardised using a method adapted from a chemical oxygen demand test (AWWA et al (1999)) as used by Park and Dempsey (2005). Beer's Law was obeyed with Fe(II) concentration in the range 0.93-46.5mg/L (values determined from dilutions of Fe(II) secondary standard). Where initial concentrations of Fe(II) were found to be greater than 46.5mg/L the samples were diluted by 50% and the procedure for analysis was repeated. Further details of the calibration and precision and accuracy of the method are given below.

Preparation of Fe(II) secondary standard

All glassware was washed with 10% nitric acid followed by 18mΩ deionised water prior to use. An approximately 10mg/L (179mM) Fe(II) solution was prepared by dissolving 49.752g of Fe(II)SO₄·7H₂O in 2.6N H₂SO₄. The stock was stored in the fridge at 5°C in a tightly capped brown glass bottle. The exclusion of light (brown glass and darkness inside the fridge) prevents photo redox effects and the low pH retards aerial oxidation of the Fe(II). The stock solution was then calibrated using K₂Cr₂O₇ as described in AWWA et al (1999). The procedure is outlined here:

1. 3 x 25mL solutions of the K₂Cr₂O₇ primary standard (41.69mM) were added to 250mL conical flasks using a 25mL class B volumetric pipette.
2. Approximately 75mL of deionised water followed by 30mL of conc. H₂SO₄ (pipetted in 10mL aliquots) was then added, swirled and left to cool to room temperature in a fume cupboard.
3. The Fe(II) solution was diluted to 50% using 2.6N H₂SO₄ by pipetting 50mL into a 100mL class A volumetric flask and making up to the mark with the acid.
4. 3 drops of ferroin redox indicator were added to the cooled K₂Cr₂O₇ solutions (ferroin indicator was prepared according to AWWA et al (1999) by adding 1.485g 1,10-phenanthroline monohydrate and 0.695g Fe(II)SO₄·7H₂O to 100mL deionised water).
5. The K₂Cr₂O₇ solutions were then titrated with the 50% Fe(II) secondary standard through the orange/green transition (Cr₂O₇²⁻ to Cr³⁺) to the ferroin end point marked by a dark red colour.

Calibration of the spectrophotometer

The spectrophotometer was calibrated using a set of dilutions of the secondary Fe(II) standard. These were made from an initial 1 in 200 dilution which was then diluted by a further 10%, 20%, 30%, 40%, 50%, 70%, 80%, 95%, 96%, 97% and 98%. All dilutions were carried out using class A volumetric flasks and made up to the mark with 2.6N H₂SO₄.

All Fe(II) solutions were analysed by the method described at the beginning of Appendix B. A calibration curve was produced and a linear relationship ($R^2 = 0.9992$) with absorbance was observed over the range 0.93-46.5mg/L Fe(II). The relationship is given in Equation B.1 where [Fe(II)] is in mg/L and ABS_{520} is the absorbance of light at a 520nm wavelength (using a 10mm path length disposable polystyrene semi-micro cuvette). According to the manufacturer of the spectrophotometer, the photometric accuracy is +/- 0.002 ABS (0 – 0.5 ABS), +/- 0.004 ABS (0.5 – 1.0 ABS).

$$[Fe(II)] = 42.6 \times ABS_{520} \quad (B.1)$$

The calibration procedure to obtain the relationship between [Fe(II)] and ABS_{520} was carried out once at the beginning of the experimental period (Figure B1). Calibration of the spectrophotometer against a blank was carried out immediately prior to the analysis of any mine water samples. The blank was prepared by adding several drops of 10% HNO_3 to 10mL of deionised water. The mixture was then treated in the same way as the mine water samples as described at the beginning of Appendix B. The spectrophotometer was then calibrated such that the absorbance for the blank sample was taken to be zero.

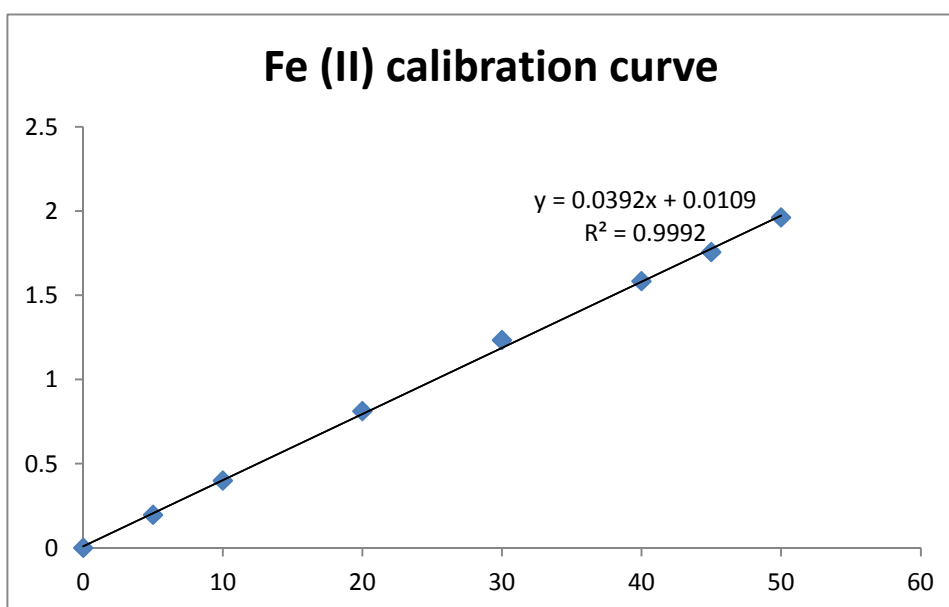


Figure B1 Fe(II) calibration curve.

The 2,2'-bipyridyl indicator was chosen as it had been used for a number of years to distinguish between Fe(II) and Fe(III) in natural waters (Heaney and Davison 1977). It is also used in Iron Cell Tests for the Merck Spectroquant® Photometers and is advocated in the testing of ground and surface waters, industrial and waste waters and drinking waters containing up to 50mg/L Fe(II) (www.merck-chemicals.com/photometry 2011).

Table B1 Concentrations of foreign substances in mg/L or % that interfere with 2,2' bipyridyl analysis

Al ³⁺	1000	Cu ²⁺	10 (250 ¹⁾)	Ni ²⁺	250	EDTA	2
Ca ²⁺	1000	F ⁻	100	NO ₂ ⁻	100	Surfactants ²⁾	1 %
Cd ²⁺	1000	Hg ²⁺	10	Pb ²⁺	1000	NaCl	5 %
CN ⁻	50	Mg ²⁺	1000	PO ₄ ³⁻	50	NaNO ₃	5 %
Co ²⁺	250	Mn ²⁺	1000	Polyphosphates	250	Na ₂ SO ₄	5 %
Cr ³⁺	500	MoO ₄ ²⁻	1000	SiO ₃ ²⁻	1000		
Cr ₂ O ₇ ²⁻	250	NH ₄ ⁺	1000	Zn ²⁺	1000		

Table B1 is reproduced from the 2,2' bipyridyl Iron Cell Test (www.merck-chemicals.com/photometry 2011) instruction manual from Merck showing the levels at which other ions start to interfere with Fe(II) determination where Fe(II) is in the range 0-25 mg/L.

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Appendices on disc

Appendix C – Minor element release

Raw data for Al, Ca, K, Mg, Na, V, Si, F and Cl release per cycle according to protocol followed.

Appendix D – Lab parameter raw data

Raw data for pH, Conductivity ($\mu\text{S}/\text{cm}$), Temperature ($^{\circ}\text{C}$), Volume of solution (mL) and Redox (Rel.mV) analysed per cycle for each protocol.

Appendix E – Feed solution blanks

Data for feed solution blanks; tap water, nutrient solutions and Fe(III) sulfate.

Appendix F – Uranium analysis Quality Assurance/Quality Control

Data for uranium analysis of leachate by in house ICP-OES and external ICP-MS.

Appendix G – Evaporation experiment

Data collected over 28 days to measure the total volume of solution that evaporated from a 1kg cell.

Appendix H – Portable XRF raw data

Data downloaded directly from the Olympus Innov-X portable XRF, model X-5000.

Appendix I – Particle size distribution raw data

Weight of head grade and residue material retained in each sieve.

Appendix J – Head grade analysis from ALS SA data

Head grade analysis data from accredited external laboratory.