

Leaching behaviour and the solution consumption of uranium-vanadium ore in alkali carbonate-bicarbonate column leaching

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Abstract

Although heap leaching using sulfuric acid was introduced to the uranium industry in the 1950s, sodium carbonate-bicarbonate (alkaline) heap leaching of low-grade Ca-carbonate-rich uranium ores has recently gained popularity. This study presents the results of two column tests on a calcrete-type uranium-vanadium (carnotite) ore using a mixture of sodium carbonate and bicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) as the leach solution. This data was kindly supplied by Toro Energy Ltd. The experimental data comprised physical-chemical leach information and two different irrigation rates (10 and 20 L/hr.m²). The experimental data indicated that the carnotite ore with high calcium carbonate (CaCO_3) can be leached effectively using the alkaline leach solution. The increase in the irrigation rate increased the uranium and vanadium extraction and decreased their concentration in the effluent.

The column leach data was therefore fitted to a simplified first-order kinetic model using two approaches, a general form and a second based on the reagent consumption per unit mass of the initial valuable species (U and V). As reagent consumption is a key economic factor in the heap leaching process, having a kinetic leaching model incorporating reagent consumption would provide useful techno-economic information. In this regards a new leaching index of (β) is also introduced. Both approaches of the first order kinetic model provide a good agreement with the column testing data.

Key words: uranium-vanadium, carnotite ore, alkaline heap leaching, calcrete type uranium, kinetic modelling.

1. Introduction

Heap leaching is extensively applied to extract copper and gold from their respective ores. Heap leaching was introduced to the uranium industry in the 1950s by the Portuguese to extract uranium from low grade uranium ores (Scheffel, 2002). The environmental concerns, low grades and low commodity prices made heap leaching unattractive since there were still large amounts of high grade uranium ore globally available at that time. As the high grade uranium ores have been consumed, many countries have turned to heap leaching (Taylor, 2013; Scheffel, 2010; Taylor, 2007; Carlsson and Büchel, 2005; Scheffel, 2002; Shakir et al., 1992). Taylor (2009) described how heap leaching for uranium is increasing in popularity, initially using acid-leach technology, but with future projects aiming to use alkaline leaching on low-grade calcium carbonate-rich ores. Heap leach studies were carried out in Argentina, Trekkopje in Namibia, Canada, France, Spain and Australia (Dhawan et al., 2013; Padilla et al., 2008; Lunt et al., 2007; I.A.E.A. et al., 2006; Júnior, 1993; Seidel et al., 1981). Alkaline leaching is used when the ore contains a high calcium carbonate (calcite) and magnesium carbonate (dolomite) content. Future uranium heap leach projects will benefit from the experience gained from copper and gold heap leaching, including strong acid cures, heap building techniques and operating strategies.

Currently several new projects are progressing to recover uranium from carbonate deposits (Sole et al. 2011; Gillman, 2010; Lunt et al., 2007). At present, commercial operations have utilized sulphuric acid leaching including those at Ranger in Australia, Rössing in Namibia and Somaïr in Niger, while the first commercial use of alkaline leaching started to operation in 2012 at Areva's Trekkopje mine in Namibia. A series of pilot scale alkaline heap leaching trials have been conducted on high acid consuming ores in Hungary (Czegledi, 1980), in China (Taylor, 2013; Taylor, 2007; Li et al. 2006) and in western Namibia (SRK Corporation 2010). Calcrete type uranium deposits known as Yilgarn craton uranium are found in Western Australia covering a big part of the country (Figure 1). The advantages of the alkaline leaching process include higher selectivity and a lower corrosivity than acid leaching. Carbonate leaching of uranium ores offers the possibility of using binders, such as Portland cement, when agglomeration of fines is needed (Lottering et al., 2008; Taylor, 2007).

The objective of this study is to investigate the alkaline leaching of a uranium-vanadium ore in the course of heap leaching and evaluate two simplified first-order kinetic models—a general form and a second based on the reagent consumption per unit mass of the valuable species. In this paper, the physico-chemical dynamics during leaching in terms of pH-Eh window and irrigation rate are investigated.

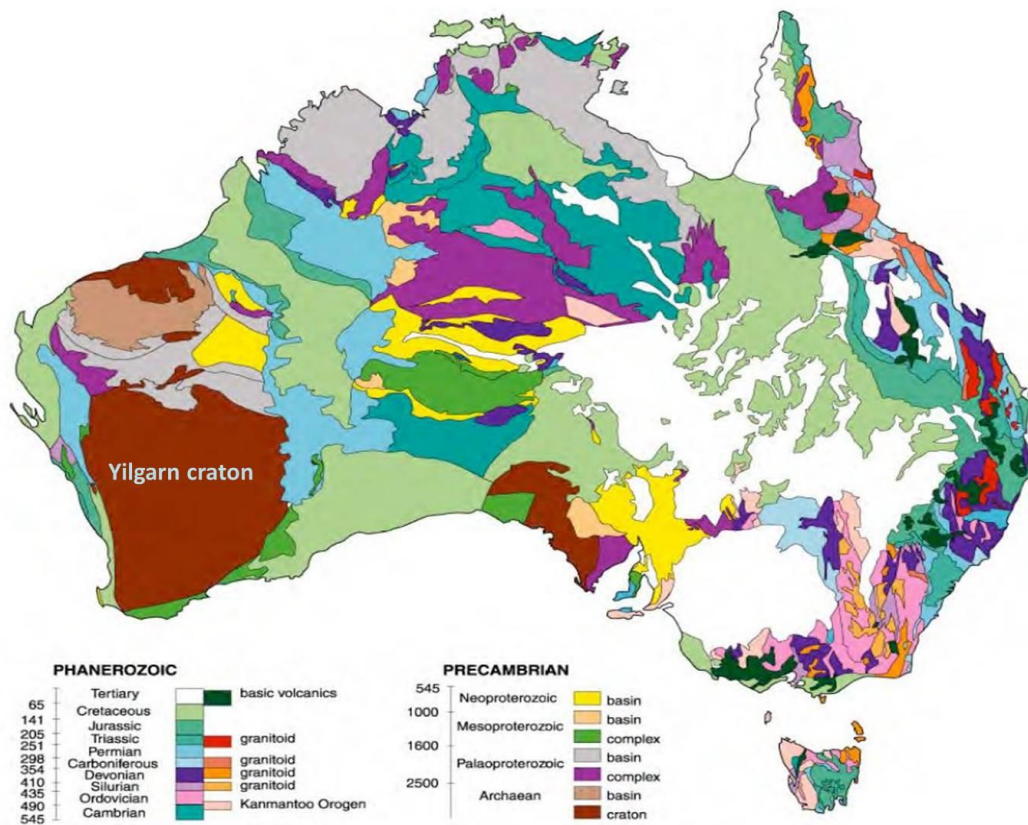


Figure 1: Basic geological regions of Australia, with the Yilgarn craton highlighted (adapted from Pownceby and Johnson, 2014 and Kreuzer et al., 2010).

2. Materials and methods

2.1 Ore sample

The leaching trials were conducted on a calcrite-hosted uranium deposit obtained from Wiluna, Western Australia. The deposit, owned by Toro Energy Ltd, is located 30 kilometres south of the mining town of Wiluna (Figure 2). Table 1 shows the X-ray fluorescence (XRF) analysis of the sample used in this study. The ore contains significant quantities of CaO and MgO and some MnO. The presence of Cl, S and P are noticeable and relate to halite (NaCl), possibly small amounts of alum (KAl(SO₄)₂) and gypsum (CaSO₄·2H₂O), and apatite (Ca₅(PO₄)₃F), respectively. High resolution Electron Probe Micro-Analysis (EPMA) undertaken at CSIRO Australia showed that carnotite (K₂(UO₂)₂(VO₄)₂·3H₂O) was the only uranium mineral and it was intricately associated with dolomite and to some extent with magnesium aluminium silicates (Pownceby, et al., 2011; Aral, 2010). Well-defined, submicron (<150 µm) carnotite grains were observed embedded into the host mineral grains. Some discrete liberated carnotite grains were also observed. The quantitative spot analysis of dolomite and magnesium aluminium silicate showed the absence of uranium and vanadium in their crystal lattice (Aral, 2010).

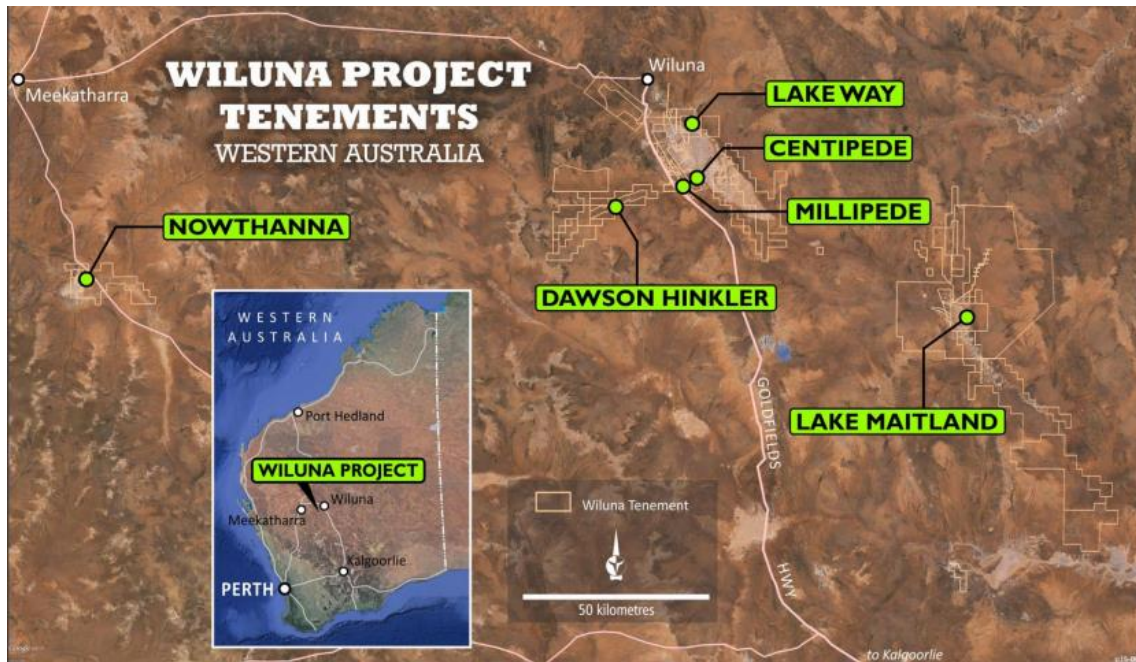


Figure 2: Wiluna Mine Location (Toro Energy, 2015).

Table 1: Chemical composition of the calcrete type uranium ore sample determined using XRF method.

Composition	Amount (wt. %)	Detection limits
TiO ₂	0.157	0.005
Fe ₂ O ₃	1.785	0.005
MnO	0.153	0.005
Al ₂ O ₃	3.268	0.005
SiO ₂	35.401	0.005
MgO	26.626	0.010
CaO	28.593	0.005
K ₂ O	0.679	0.005
Na ₂ O	1.891	0.010
Cl	1.921	0.010
S	0.262	0.005
	Amount (mg/dm³)	
Uranium (U)	540	10
Vanadium (V)	162	10
Thorium (Th)	14	10
Sum (wt. %)	100	-

Detailed Quantitative X-ray Diffraction (QXRD) (Aral, 2010) identified the general mineralogical assemblage and more specifically determined a variety of clay minerals in both ore samples. The mineralogy of the ore sample was mainly dominated by dolomite and clay minerals. Clay minerals were swelling (smectite) and non-swelling (kaolin) types.

The smectite type clays identified were beidellite- $\text{Na}_{0.5}\text{Al}_2(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}(\text{OH})_2$; nontronite- $(\text{Na}_{0.3}\text{Fe}^{3+}.2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2)$; montmorillonite $(\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}.(\text{OH})_2$; saponite- $(\text{Ca}/2,\text{Na})_{0.3}(\text{Mg},\text{Fe}^{2+})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$. Palygorskite $(\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ and sepiolite $(\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2)$ were also present. Trace amounts of sulphate minerals were also identified, namely gypsum and a Sr-rich barite. The main mineralogical composition of the ore sample is given in the Table 2.

Table 2: The main mineralogical composition of the ore sample as determined by QXRD (Aral, 2010).

Mineral	Quartz	Kaolin	Smectite*	Albite	Feldespar**	Calcite	Dolomite	Halite
Amount (wt. %)	9	7	15	3	2	<1	63	1

* 1M muscovite, illite-montmorillonite and montmorillonite are reported as smectite

** Microcline or Orthoclase

2.2 Leach experiments

The column leaching tests were conducted by a third party using subsamples from the calcrete ore type. The leaching tests were carried out in two PVC columns 100 mm in diameter and 1 m in height. The columns were loaded with 12.263 kg of the uranium ore sample. Preliminary metallurgical tests using the bottles and columns were performed to assess and optimize the effect of the physical and chemical parameters. The influence of particle size on the efficiency of uranium leaching was studied using three size fractions of $d_{80}=9$ mm, $d_{80}=11$ mm and $d_{80}=13$ mm. No evident influence of particle size on the metal leaching efficiencies was observed (data not shown). The ore sample with $d_{80}=11$ mm was selected for this study taking into consideration the need for a 6-to-1 (or higher) column diameter to ore particle size ratio to minimize undue wall effects. A 1 mm stainless steel screen with a glass wool felt on top covered the drain plate, before loading the ore in the column to prevent fine grained material from migrating and plugging the recirculation pump. Another felt was placed on top of the ore, after loading the column, to assist the even distribution of the extraction reagent.

In the beginning, column tests were irrigated in closed cycle within the columns with a mixed sodium carbonate and bicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) solution. Concentration and the ratio of the leaching reagent were selected based on the previous studies of the alkali carbonate-bicarbonate leaching of uranium-vanadium through the literatures (Hunter, 2013; Lunt et al., 2007) and also were based on the results of preliminary tests performed in this study.

When the pH value of the pregnant leach solution (PLS) increased above 10, the leach columns were operated in continuous mode. Sodium carbonate and bicarbonate were analytical-grade reagents (AR) and the solution was prepared using distilled water. A comparative summary of the column leach tests conditions is given in Table 3.

Table 3: A summary and comparison of the column leach tests conditions.

Column number	Leaching conditions					
	Column size	Ore sample weight (kg)	Moisture in Column (%)	Retained solution in column (l)	Reagent	Irrigation rate L/(hr.m ²)
					Composition and Concentration (gpL)	
A	1 m high and 10 cm in diameter	12.263	21.8	3.4	Na ₂ CO ₃ (40 gpL)	10
B			20.8	3.2	+ NaHCO ₃ (2.55 gpL)	20

The leaching lasted for 190 days in one column (column A) with an irrigation rate of 10 L/ (hr.m²) and 142 days for the other column (column B) with the irrigation rate of 20 L/ (hr.m²) at ambient temperature of (16-25) °C. Leaching time was chosen through the preliminary experiments and based on the characteristics of the ore e.g. type of mineralization, particle size and leaching conditions. After 142 days of leaching in column B, about 84.8% of the uranium was recovered. At this point the extraction rates were very slow thus leaching was ceased. In column A, after 142 days of leaching the uranium extraction was about 72.5% so leaching was sustained up to 190 days in order to approach a comparable degree of extraction (82.4% vs 84.8%) with the lower irrigation rate of 10 L/ (hr.m²).

The pH, Eh (mV), U and V concentration in the effluent solution were measured each day. All pH measurements were performed using a Metrohm 704 pH meter and probe, which was calibrated at pH 7.0 and 10.0, each time before use. Oxidation reduction potential or Eh (mV) was determined against saturated calomel electrode (SCE) and the precision of the measurements was tested using a Crison standard redox solution having a potential of 468 mV at 25°C. Uranium and vanadium concentrations of the solution were determined using Inductively Coupled Plasma (ICP) Varian 730-ES, Optical Emission Spectrometer (OES). At the end of the tests, leached ore residues were air dried and weighed, and the uranium content of the solid residues was determined by XRF analysis.

3. Results and discussion

3.1 Chemical dynamics during leaching

Except for the small initial fluctuation in pH in response to the addition of leach reagent, the pH of the effluent in columns remained between pH 9.0 to 11.0 throughout the experiment (Figure 3). The change in reduction potential (Eh) with time is shown in Figure 4. After small changes at the beginning of the tests, Eh values then remained between (0-50) mV during the first 40 days of the experiment. From day

40 up to day 60, the Eh values ranged from (0 - (-50)) mV. After day 60, Eh values gradually increased to about 150 mV and remained stable between (150-200) mV thereafter, correlating with changes in the relative concentrations of dissolved ions and species which will be discussed in the following sections.

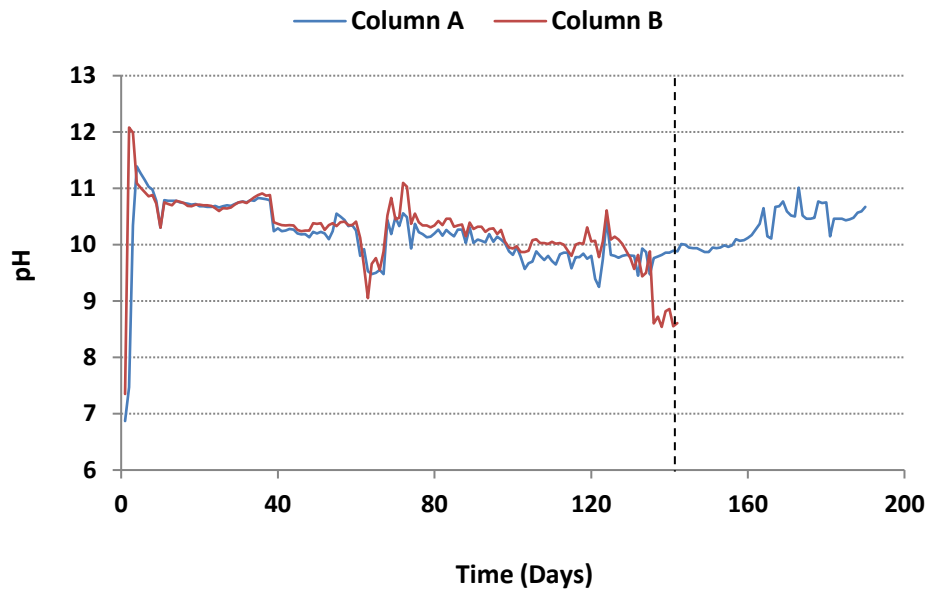


Figure 3: Variations in pH measurements against time. Data from PLS of Columns A and B.

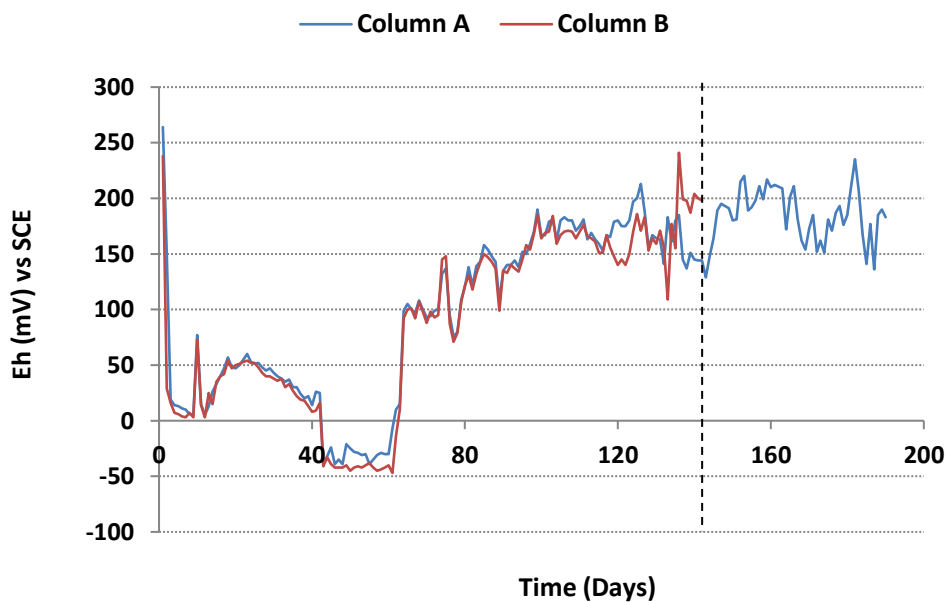


Figure 4: Variations in the measured redox potential (Eh) against time. Data from PLS of Columns A and B.

The similar measured values for redox potential and pH in columns indicated that the different irrigation rates does not affect the chemical dynamics during leaching, but influences the leaching kinetic and

consequently extraction rate (see Section 3.2). Eh-pH diagrams are useful tools for visualizing the stability areas of metal species in a solution depending on the solution's Eh and pH. Figure 5 shows the Eh-pH diagram of PLS for the column A. Although as it mentioned earlier in the section 2.2, Eh (mV) was determined against SCE, but for ease of comparison purposes it is converted against standard hydrogen electrode (SHE) and values are presented in Volts. The aqueous U(VI) carbonate system has been thoroughly studied (Kumar et al., 2011; Gorman-Lewis et al., 2008; Choppin, 2007; Morss et al., 2006; Sutton, 1999; Newton and Sullivan, 1985; Allard; 1983) and there is little doubt about the compositions of the three monomeric complexes of general formula $\text{UO}_2(\text{CO}_3)$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ present under the appropriate conditions as seen in Figure 6. In carbonate media, the uranium is converted to a series of carbonate complexes, UO_2CO_3 (maximum concentration at ca. pH 5), $\text{UO}_2(\text{CO}_3)_2^{2-}$ (maximum concentration at ca. pH 6.5) and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (maximum concentration at ca. pH 10 to 11), when the pH of the solution is increased. Comparison of the results presented in Figure 5 with Figure 6, indicates that $\text{UO}_2(\text{CO}_3)_3^{4-}$ is the main carbonate complex in the condition studied in this work.

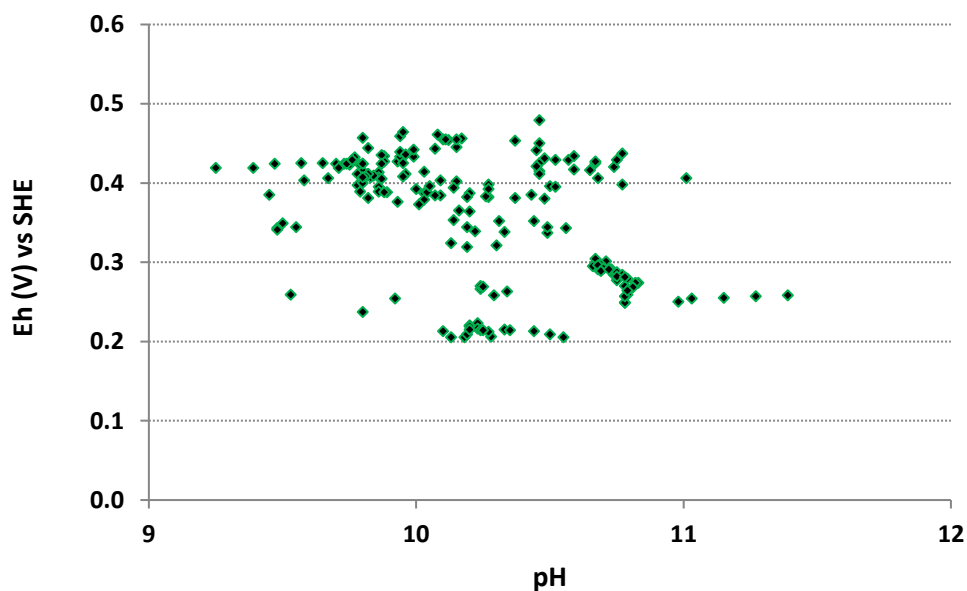


Figure 5: The relationship between Eh and pH for column A PLS.

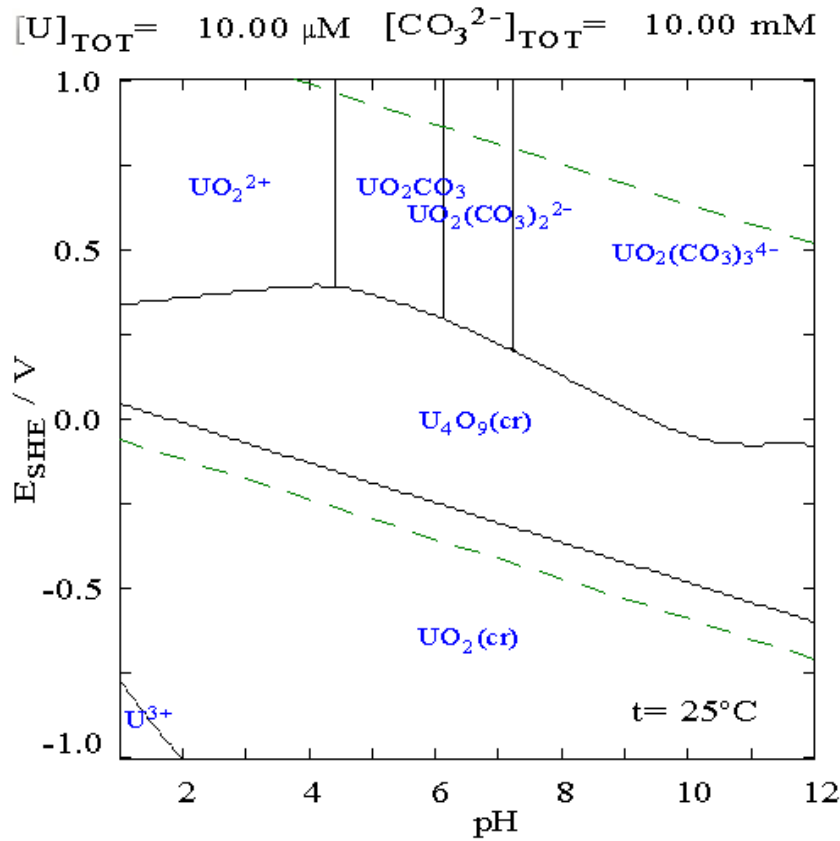
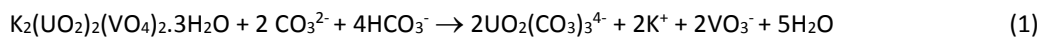


Figure 6: Eh-pH diagram (Pourbaix diagram) of uranium in carbonate media (Figure reprinted from Morss et al., 2006).

3.2 Uranium and vanadium extraction

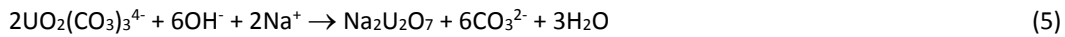
As it discussed earlier, the alkali leaching process is based on the ability of the hexavalent uranium to form highly soluble complexes in alkaline media. The major cations within the ore sample are Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The major anions are uranyl tricarbonatate $[UO_2(CO_3)_3]^{4-}$ or uranyl dicarbonatate $[UO_2(CO_3)_2]^{2-}$ as well as some chloride and vanadate. As it was mentioned in the Section 2.1, carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) was the only uranium mineral in the ore sample in this study. The main reaction for dissolution of carnotite as a complex vanadium-uranium in a carbonate-bicarbonate solution can be described as Equation 1 (Gorman-Lewis et al., 2008; Morss et al., 2006; Newton and Sullivan, 1985; Allard; 1983):



The alkaline reactants do not react in significant amounts with silicate and alumino-silicate minerals, which commonly occur in the uranium ores, including the sample used in this study. Therefore the reagent consumption is relatively low. The other minerals that consume carbonate-bicarbonate are the sulphide minerals, sulphates (gypsum, anhydride), phosphates and organic matter. Equation 2 and 3 show the reagent consumption for gypsum present in the ore sample:



The other economic advantage of using alkali carbonate is the viability of CO_3^{2-} to be regenerated through the following reactions:



The cumulative extraction trends of uranium into the leach liquors is illustrated in Figure 7 for leach columns A and B. Increasing the irrigation rate increases the uranium extraction rate, with 84.8% uranium recovered in column B with the irrigation rate of 20 (L/hr.m²) after 142 days. In comparison, 72.5% was recovered in column A with the irrigation rate of 10 (L/hr.m²) over the same time period.

The recovery curve corresponding to column B in Figure 7 shows very slow extraction rate after 80 % with very low uranium concentration in the PLS (Figure 8), therefore the leaching process stopped on day 142. This is mainly due to the two stages leach regimes where an initially fast leaching rate is followed by a slower constant rate period, typical leaching trend in the coarse ore particles (Ghorbani et al., 2013a). General trend of decrease in the uranium concentration presented in the Figure 8 is also mainly because of changes in the leaching stages from fast to slow (see section 3.2).

As Figure 7 shows, the leaching processing in the column A continued up to 190 days to monitor the effect of leaching time with the lower irrigation rate on the uranium recovery. Continuing leaching 48 days more in the column A, increased the recovery about 10 %, and the recovery reached 82.4%. Time period for process and solution consumption are two key techno-economic factors and play a key role in the process design and decision making steps. Further discussion about this has been given with a new leaching index of (β) in the section 3.4.

Although in this study two different irrigation rates were investigated, but there is an optimum irrigated rate up to that, the recovery will increase, but introducing solution reagent in the rate higher than that, in fact will decrease the PLS residence time and correspondingly more of the solution will pass through the column with little or no meaningful interaction with ore particles. The percolation rate of the fluids should be slow enough to provide sufficiently long-lived contact of the lixiviant with the ore particles to affect ore dissolution. (The optimum rate will be dependent on other factors such as the mineralisation and permeability of the heap.) Higher irrigation rate in the leaching process dilutes the uranium concentration in the effluent of column tests (Figure 8).

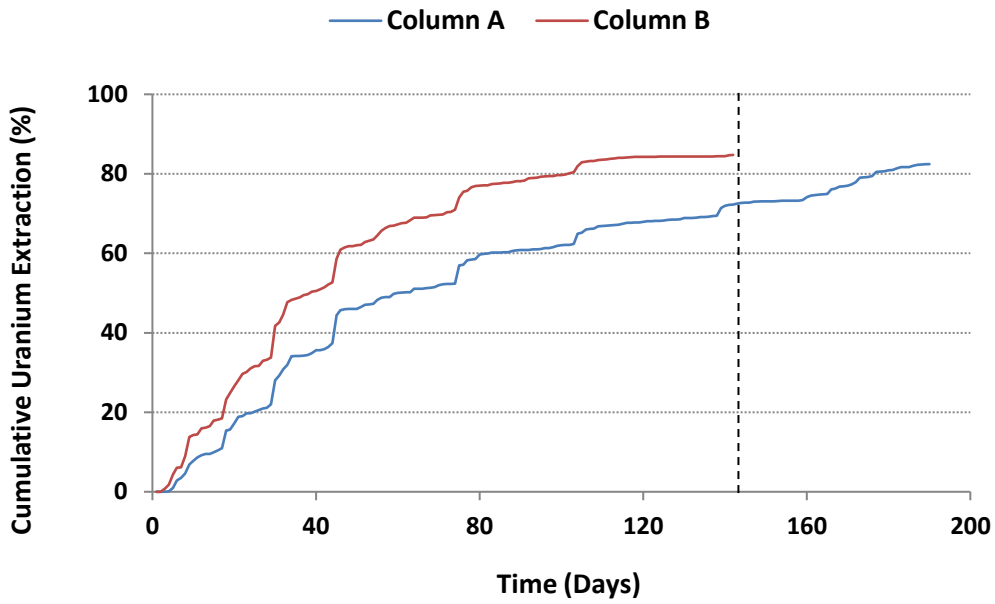


Figure 7: Cumulative uranium extraction rates against time for Columns A and B.

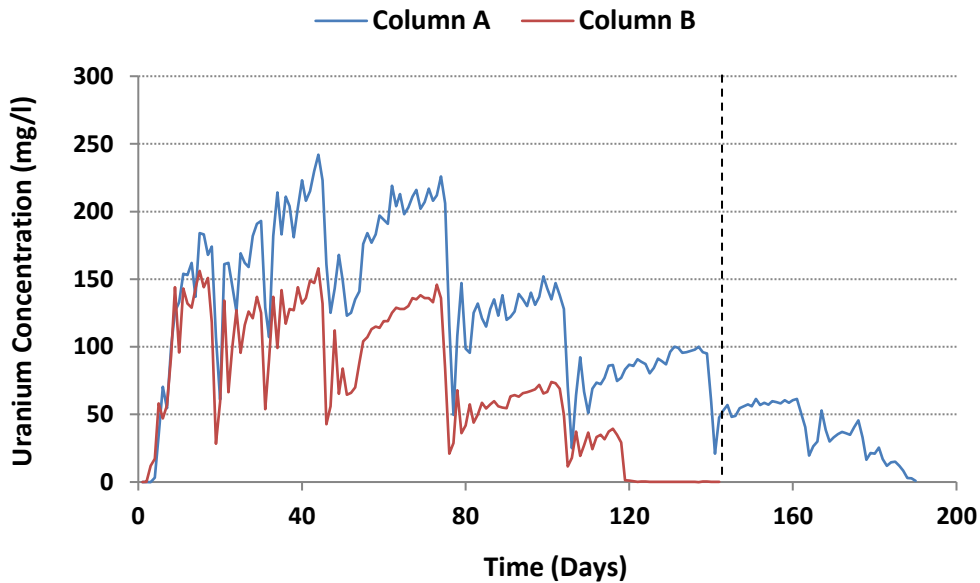


Figure 8: The variation in the uranium concentration against time. Data from PLS of Columns A and B.

The sharp and sudden decrease in uranium concentration in PLS at various times in both columns A and B (Figure 8) is due to the fact that at these days fresh solutions were added. The effect of fresh solution addition at different time periods on the leaching of uranium and vanadium is shown in Figure 9 and 10 for both column A and column B. As Figures 9 and 10 present, in all given time periods the addition of the fresh solution into the leaching process has an immediate positive effect on the uranium extraction rate on both column A with the irrigation rate of 10 (L/hr.m²) and column B with the irrigation rate of 20 (L/hr.m²) and, thereafter do not show a significant change. As shown in Figure 9 and 10 the addition of

the fresh solution is more effective during the time period of (30-44) days, (45-74) days and (75-103) days. The relatively smaller effect arising from addition of the fresh solution later in the leaching process could be attributable to a variety of issues, e.g. residual poorly leachable uranium minerals, or leach solution not accessing uranium ore, either due to its location in the agglomerated particles or hydrodynamic issues such as leach solution 'channelling'. It is worth noting that the extent of uranium recovery into PLS also appeared limited. The reason for this is not understood, but it could be affected by a solubility limit associated with uranium in solution under the operating conditions used.

The results presented in the Figure 9 and 10 indicate that based on the irrigation, the fresh solution needs to be introduced in specific time of leaching process in order to have an effective result on the valuable species extraction.

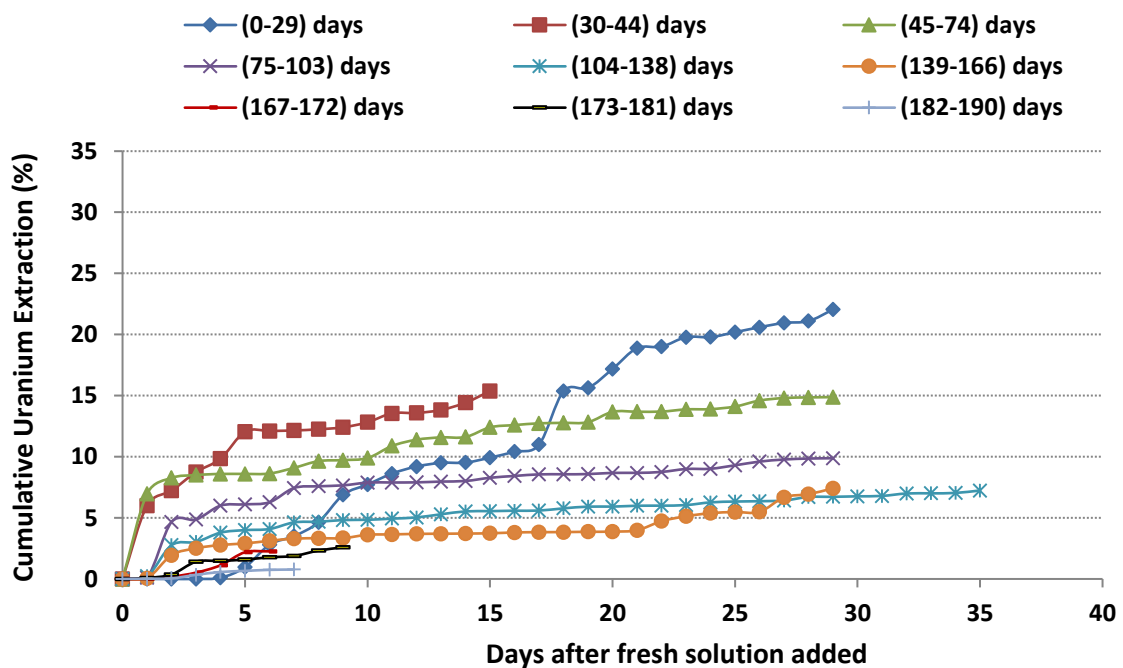


Figure 9: The effect of adding fresh solution on uranium extraction in column A with the irrigation rate of 10 (L/hr.m²).

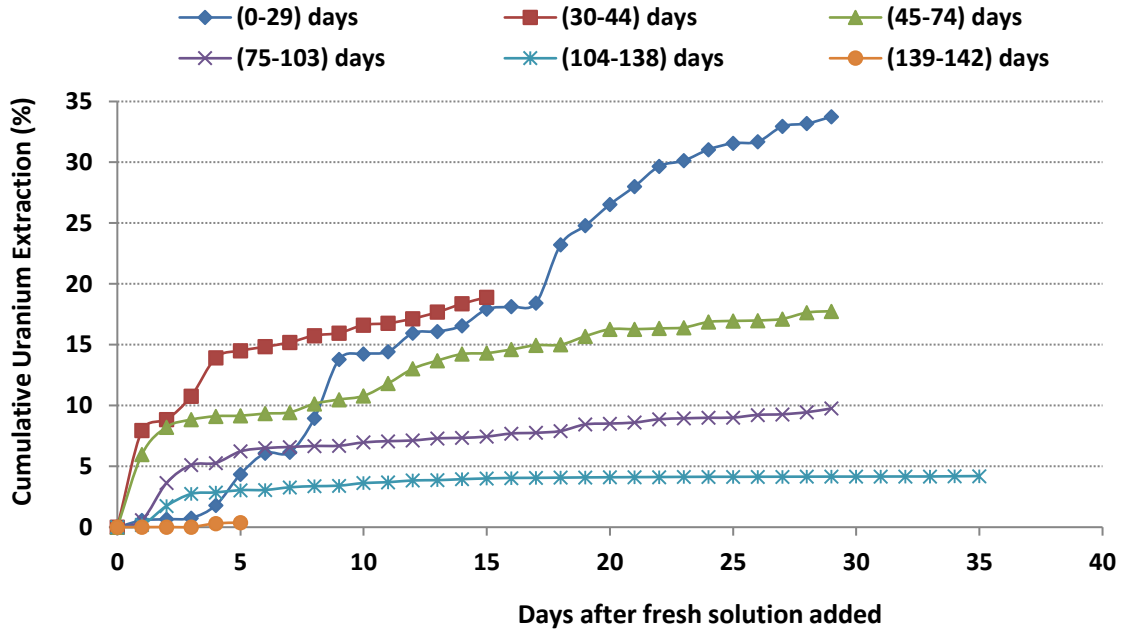


Figure 10: The effect of adding fresh solution on vanadium extraction in column B with the irrigation rate of 20 (L/hr.m²).

Comparatively, alkaline leach with carbonate and bicarbonate is much more selective for uranium than the acidic leach. Only molybdenum, if present, and vanadium in the ore could be troublesome for the uranium purification (Lunt et al., 2007; Clifford et al., 1958). Normally, molybdenum does not co-precipitate with uranium and can be removed by bleeding after uranium precipitation (du Preez, 1989). Several methods are used to remove vanadium from uranium (Lunt et al., 2007; Clifford et al., 1958). In commercial carbonate leach operations, it is common to remove vanadium by the addition of lead sulphate or ferrous sulphate to the leach solution. This forms lead or ferrous vanadate which precipitates selectively before the precipitation of uranium. When an ion exchange resin is used, vanadium could be separated from uranium by elevating the pH above 10 in the feed solution. However, uranium adsorption would be reduced significantly (Lunt, et al., 2007; Clifford et al., 1958). An SX method should have some advantages in regard to its flexibility of uranium concentration in the PLS and possible selectivity over vanadium and molybdenum. However, SX has its own problems and currently, no satisfactory SX process has been found to recover uranium from carbonate leach solutions commercially despite some meaningful investigations of such (Sole et al. 2011; Zontov, 2006; Carmen, 1986; Clifford et al. 1958).

As can be seen from reaction (1), vanadium ions would also be present in the alkali leach solution. When uranium is leached by sulfuric acid or carbonate lixiviant the vanadium is also oxidized to the 5⁺ state and co-extracted into the PLS as vanadate oxoanion together with uranium. In some cases the ratio of uranium and vanadium in the PLS can be as high as 1 to 1. Both metals are efficiently adsorbed by strong base anion resins; hence, their separation can create difficulties for production of pure uranium oxide. A predominance diagram by Pourbaix (1966) in Figure 11 shows that at the pH range of 9-11 and an Eh of

greater than zero volts, the predominant vanadium species will be HVO_4^{2-} . The oxidation state of vanadium is an important issue in the processing of uranium because the HVO_4^{2-} anion will compete with uranium loading on ion exchange resin if the vanadium concentration is above 1 gram per litre. One of the available options for the vanadium problem is reduction of the element to the 4^+ state in the PLS. In this oxidation state, vanadium will be present as a cation and will not be fixed by strong base anion exchange resins. This approach requires high accuracy as uranium must be kept in its 6^+ state. It also requires a significant expansion of the flowsheet, making it an unattractive option in practice. Guaranteed purification of uranium oxide with a lot of vanadium contamination usually results in relatively high losses of uranium (Kailasam and Rosenberg, 2012; Gorman-Lewis et al., 2008; Morss et al., 2006).

As Figure 12 shows, the concentration of vanadium in the columns A and B has almost the same trend and values with small differences after day 80. The concentration of the vanadium in the effluent of column tests was low and maximum up to 21.9 mg/l corresponding to the test performed using column A. This shows selectivity of the alkaline leach with carbonate and bicarbonate for the ore sample used in this study. As given in the Figure 13, similar to the trend in uranium extraction (Figure 7), the increase in the irrigation rate increases the vanadium extraction with maximum recovery of 49.3% was obtained in column B with the irrigation rate of 20 (L/hr.m²) compared to 25.1% recovery in column A with the irrigation rate of 10 (L/hr.m²) for the leaching period of the 142 days. Extending the leaching time in column A up to the 190 days increased the overall vanadium recovery by about 20 % and the recovery reached 44.9 %. Two times more vanadium extraction during the additional leaching time in the column A, compared to the uranium extraction (20 % vs 10 %), indicates that while after 142 days, uranium leaching process is in the slow leaching rate stage, but vanadium still is in the fast leaching rate stage (Ghorbani et al., 2013a). This is believed to be due to all fast-leaching minerals (in this study uranium bearing mineral) near the surface already being depleted, and the leach reagent has to migrate from the particle surface into the particle to recover further uranium. This results in a rim-leaching effect in larger particles (Ogbonna, 2006). Hence, if competition exists for reagents between different mineral phases (uranium and vanadium bearing mineral in this work), then this is likely to be skewed in favour of the slower-leaching mineral (vanadium bearing mineral) near the surface, rather than the faster-leaching closer to the centre (Ghorbani et al., 2011; Ogbonna, 2006).

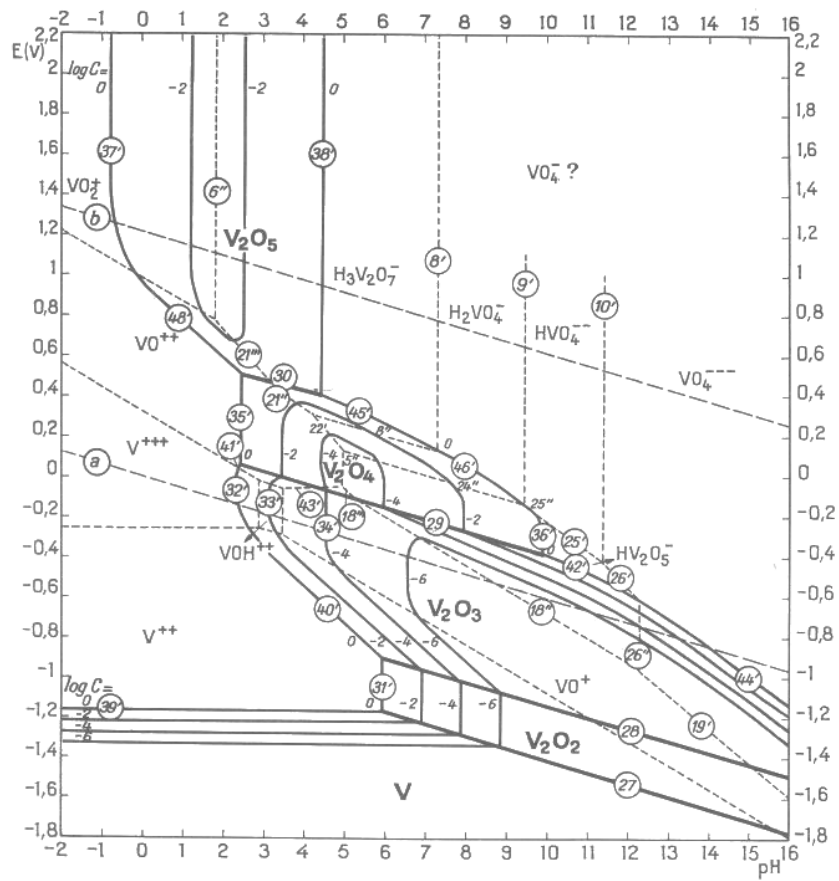


Figure 11: Potential-pH equilibrium diagram for the system vanadium-water at 25°C and with 51 g/L vanadium (Pourbaix, 1966).

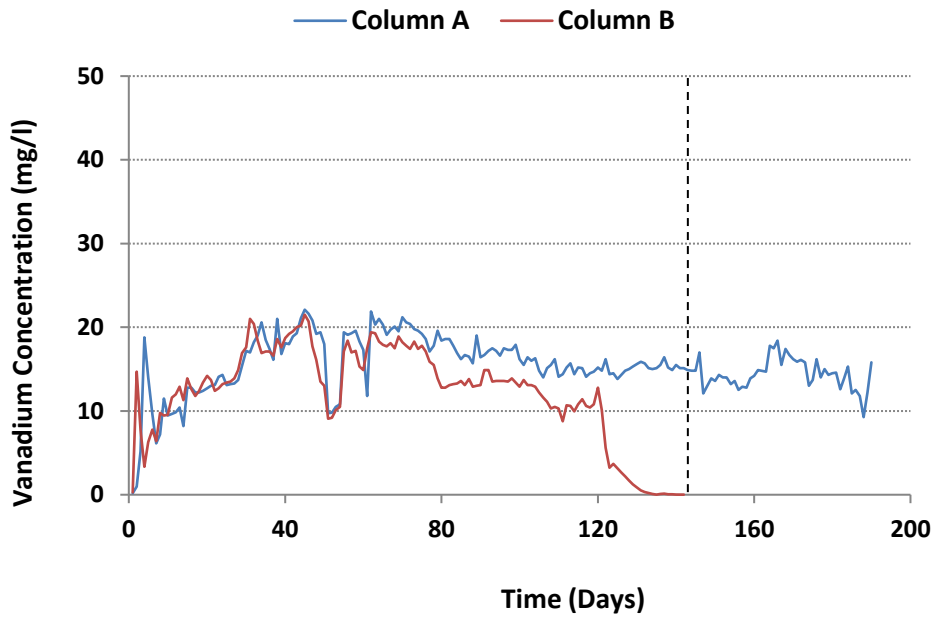


Figure 12: The variation in the vanadium concentration against time. Data from PLS of Columns A and B.

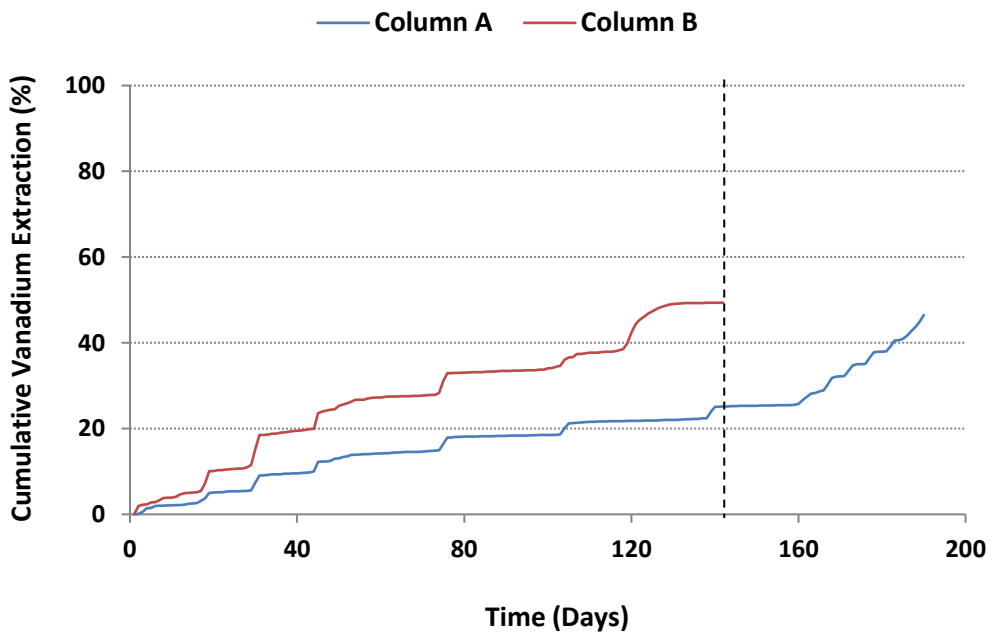


Figure 13: Cumulative vanadium extraction against time for columns A and B.

Although the solubility of Thorium (Th) in the carbonate and bicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) solutions has been reported in previous studies (Ahmed, 2014; Altmaie et al., 2005; Dhanpat et al., 1994), due to the trace and low level of the Thorium (Th) in the initial ore sample about 14 mg/dm^3 (see Table 1) and consequently in the PLS, data with regards to the dissolution of the Thorium were not reported in this study.

3.3 Effect of the clay minerals on percolation of the heap leaching

Alongside advantages of alkaline leaching, there are some limitations which include the sluggishness of the process, the suitable porosity and permeability requirement of the ore and the poor attack of the mild carbonate solutions on refractory ores. In a heap leach operation, the main problem will be swelling of some of the clays, dispersion and possibly transformation of the clays with high pH. The swelling of clay will adversely affect the solution permeability. In the sample studied in this work, the ores contain 15-16% swelling clay mineral smectite (see section 2.1 and Table 2). The clay minerals have also the ability of adsorbing positively charged metals onto their surfaces as well as absorbing metals by the interlayer substitutions. The ability of clays to adsorb onto their surfaces and absorb metals from a sodium carbonate-sodium bicarbonate leach solution is not well understood and needs further investigation.

Although both columns were fed with the same size fractions, the residue had a size distribution containing even some fines. Evaluation of the columns leach residue indicated significant changes in the PSD. The amount of the fine fraction in the PSD of the columns residue increased marginally with increase in the solution irrigation rate with $d_{80}=10$ mm in the residue of column A (10 (L/hr.m²)) and $d_{80}=8.5$ mm in the residue of column B (20 (L/hr.m²)) in compared to the feed with $d_{80}=11$ mm.

Regeneration of the fine particle fraction in the residue of the columns leach residue could be due to the active crack network growth during the leaching. Since the surface of ore particles and their inner micro pores or cracks are damaged after reacting with reagent, some fine particles would be produced. The initial crack network in the particles increases during the leaching process, which splits each single particle into two or more new ore particles and produces a particles size distribution different to the initial reactor feed (Ghorbani et al., 2013b). However, after leaching, under the coupled action of multiple factors, such as hydraulic power, gravity and chemical reactions, newly generated fine particles flow downwards through the pore space among coarse particles and deposited at local areas and an extremely small amount of fine particles are transported out of the reactor by the solution (Kodali et al., 2011; Yang et al., 2008). The most fundamentally important aspect of heap leaching is permeability of the leach and even percolation of the lixiviant solution throughout all the ore. Excessive amounts of the fines generated during the leaching process and their mobilization would result in reduced permeability as the leaching process progresses, which could have a negative effect on percolation especially over long periods of heap leaching operation. It would also prevent a uniform flow of the solution through the heaps. This leads to poor interaction between the ore and leach solution, producing inadequate metal recoveries, or the need to extend the leach time.

3.4 Assessing Model Fit

The leaching experiments data were fitted with two different approaches of first-order kinetic model. As presented in the Table 4, the tests results were evaluated with a general time dependent kinetic model

(A) and a modified kinetic model based on the ratio of the reagent consumption volume per mass of the initial valuable species (U or V). Objective functions (OF) as a statistical criterion in the form given in the Table 4, applied to non-linear regression model in this study in order to measure and minimize the difference between the measured and predicted values.

Table 4: A summary of the first-order kinetic model used in this study.

First-order kinetic equation	Parameters and the dependant variable	
$R=R_h*(1-\exp(k*D))$ where R is the recovery of the valuable species (U or V) R _h : Maximum recovery at (t=∞)	A. Time dependent R=f(t),	D=t and t: leaching time (day), k= K _t =Rate constant (1/day)
	B. Reagent volume dependent R=f(Q _v),	D=Q _v and Q _v =Reagent volume/Amount of the initial valuable species (U or V) within the ore sample (m ³ /Kg) k= K _v =Rate constant (kg/m ³)

OF =MINΣ (R_m-R_e)²
 where OF = Objective functions MIN = minimum
 R_m is the recovery values of the valuable species (U or V) obtained through column tests
 R_e is the recovery values of the valuable species (U or V) predicted through the modelling with the following boundary conditions:
 0 < R_{hm} < 1 and k_m > 0

Figure 14 shows comparison of the measured leaching data and predicted values for uranium through the general first-order kinetic model over 190 days for column A and over 142 days for column B, with the irrigation rates of 10 and 20 (L/hr.m²) respectively. As it can be seen, there is a good correlation between the trends predicted by the first order kinetic model and the cumulative uranium extraction calculated based on the column leach tests results.

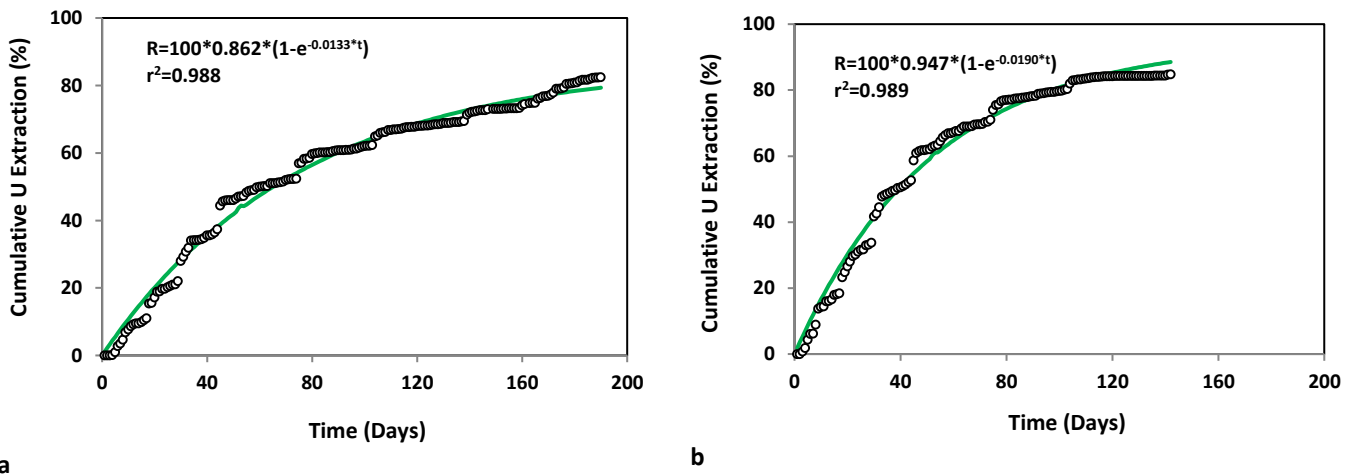
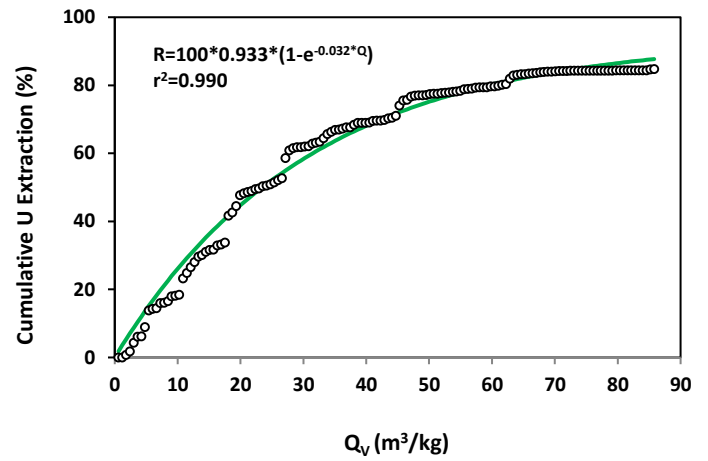
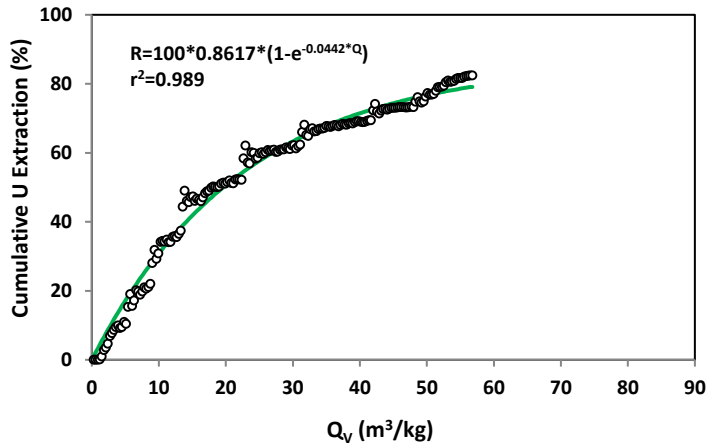


Figure 14: The comparison of the measured uranium leaching data and model predicted values over time, a. Column A (10 L/hr.m²) and b. Column B (20 L/hr.m²).

A modified first kinetic model with a new variable of Q_v as the reagent consumption per mass of the initial valuable species, instead of time variable was introduced and fitted to the experimental data. The comparison of the measured leaching data and predicted values through the revised kinetic model for columns A and B is given in the Figure 15 with a good agreement between the trends predicted by the model and the tests result for cumulative uranium extraction.

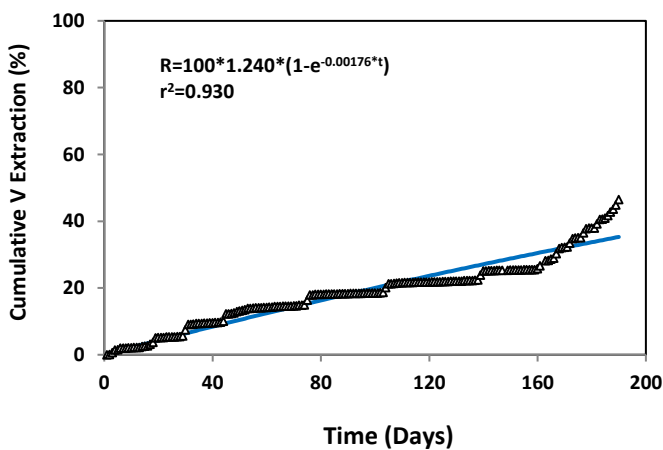


a

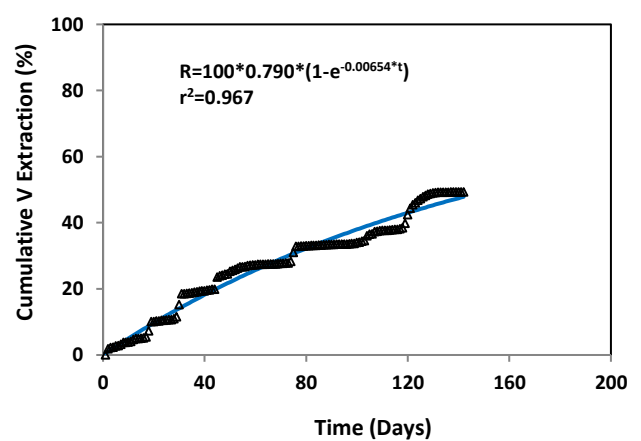
b

Figure 15: The comparison of the measured leaching data and kinetic model predicted data. The kinetic model is based on the reagent consumption per mass of the initial uranium within the ore sample for: a. Column A (10 L/hr.m²), and b. Column B (20 L/hr.m²).

As shown in the figure 16 and 17, same as uranium, the trends predicted using two different approaches of the first order kinetic model, in column A and column B were in a good agreement with the cumulative vanadium extraction data (data not presented here).

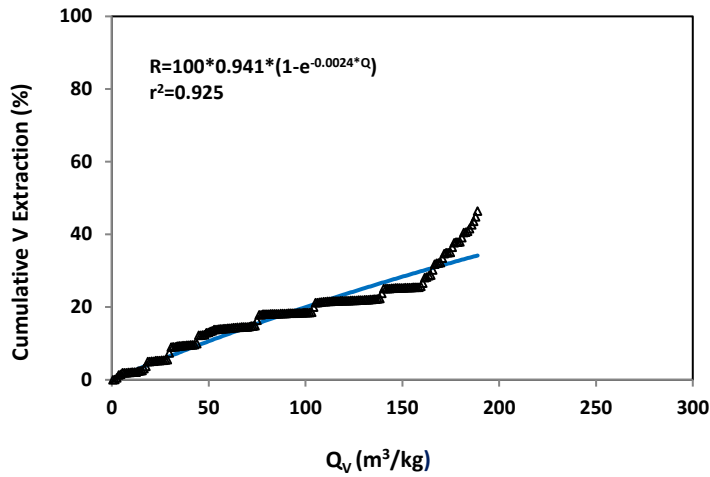


a

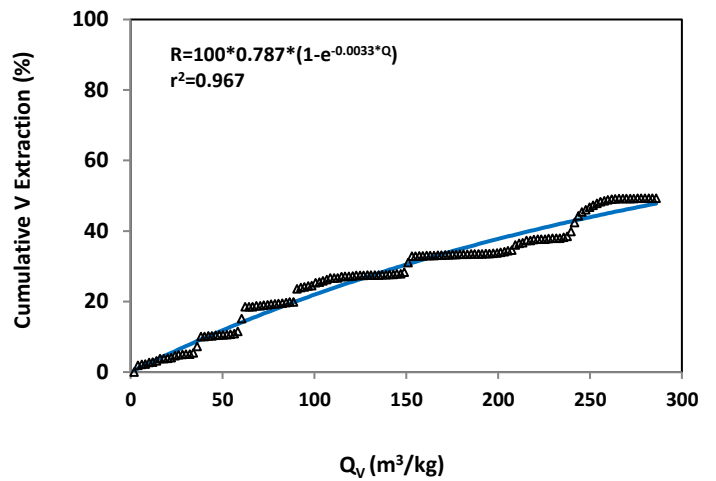


b

Figure 16: The comparison of the measured vanadium leaching data and model predicted values over time, a. Column A (10 L/hr.m²) and b. Column B (20 L/hr.m²).



a



b

Figure 17: The comparison of the measured leaching data and kinetic model predicted data. The kinetic model is based on the reagent consumption per mass of the initial vanadium within the ore sample for: a. Column A (10 L/hr.m²), and b. Column B (20 L/hr.m²).

A new leaching index of (β) is defined as the required reagent consumption per a percentage increase in the recovery of the valuable species within the ore sample with respect to different irrigation rates. As given in the Table 5, this index has been calculated for column A during the extension of leaching time from day 142, up to day 190.

The obtained result indicates that 9.7 L solution is consumed to have 1 % increase in the recovery of the column A with the irrigation rate of 10 (L / hr.m²) after day 142, while up to the day 142 the maximum solution requirement per unit of recovery was around 4 L. As it was discussed earlier it is as result of the changes in the leaching regime from fast to slow rate due to the lessening of the valuable mineral at the surface of the particle and migration of the leach solution into the ore particles. This also shows that leaching index of (β) is a techno-economical parameter which needs to be considers in decision making stage in process design to have an optimum point based on the recovery and solution consumption.

Values of the (β) vs. time are presented in the Figure 18 for the comparison of different irrigation rates in in the column A (10 L/hr.m²) and column B (20 L/hr.m²). As highlight in the Figure 18 there is no linear effect of having high irrigation rate in the column leaching. In fact there are three different stages of leaching process in the column A and B conducted with the irrigation rate of 10 (L / hr.m²) and 20 (L / hr.m²) respectively. The valuable grains are distributed and located at the surface and centre of ore particles within the large ore particles typical of the heap process and they do have different reagent consumption during the leaching process. As it discussed earlier in the section 3.2, once, the fast-leaching mineral has been depleted from the surface, leaching will continue more probably to dissolve ore values for slower-leaching minerals near the surface, rather than the faster-leaching minerals closer to the centre. The effect is exaggerated with increasing particle size (Ghorbani et al., 2011). This indicates that the variable irrigation rates during the leaching process would have techno-economic

benefits to the process. The leaching index of (β) and the kinetic model is based on the Q_v values would be a useful techno-economic factor that could be integrated into process planning models in heaps. Such a model could also incorporate losses in the leach solution due to the evaporation in the area such as arid mining regions of Australia. The leaching index of (β) could also help to select an optimum solution rates in the intermittent irrigation system in heap process.

Table 5: Summary of the values for V, maximum uranium extraction and (β) index.

Columns	Irrigation rate (L / hr.m ²)	Reagent consumption (L/day)	Leaching time (Days)	V=Total volume of the consumed leaching solution (L)	E=Uranium extraction (%)	(β) = $\left(\frac{\Delta V}{\Delta E}\right)$ (L)
A	10	2	190	Up to 142 days of leaching= 284	Up to 142 days of leaching= 72.5	$\left(\frac{(V_{C_A \text{ at day } 190} - V_{C_A \text{ at day } 142})}{(E_{C_B} - E_{C_A})}\right) = \left(\frac{380 - 284}{82.4 - 72.5}\right) = 9.7$
				Up to 190 days of leaching= 380	Up to 190 days of leaching= 82.4	
B	20	4	142	568	84.8	$\left(\frac{(V_{C_B} - V_{C_A})}{(E_{C_B} - E_{C_A})}\right) = \left(\frac{568 - 284}{84.4 - 72.5}\right) = 23.9$

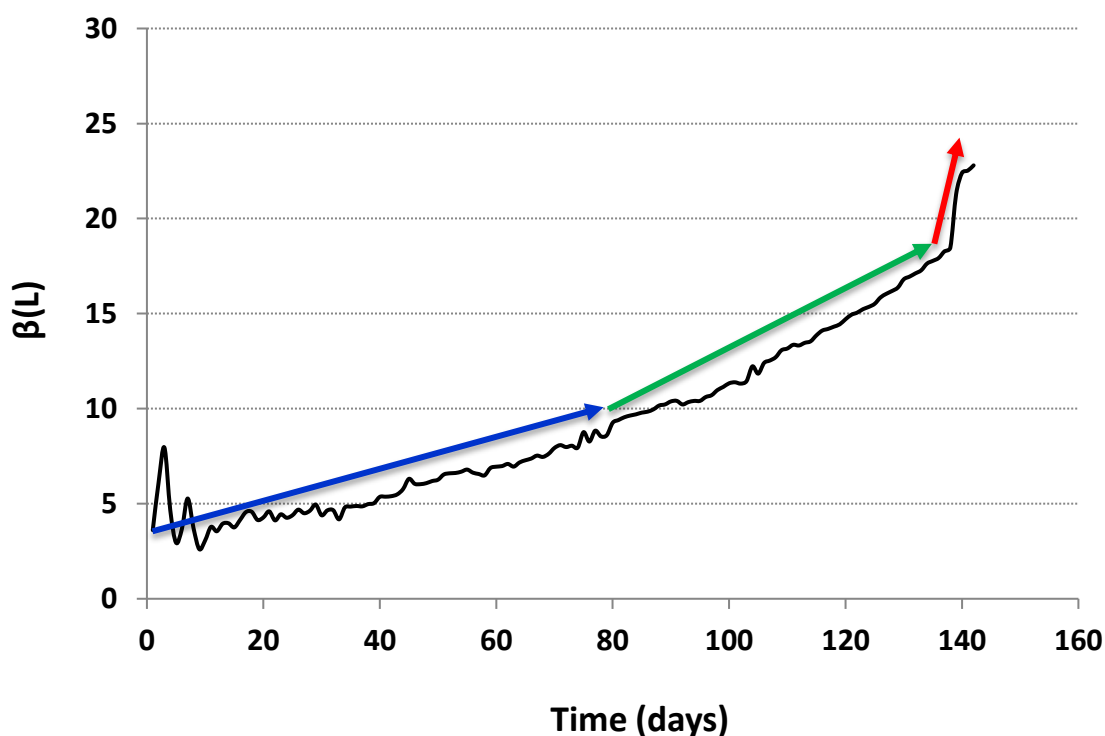


Figure 18: The changes in the (β) values vs time for the comparison of different irrigation rates in the column A (10 L/hr.m²) and column B (20 L/hr.m²).

4. Conclusion

In this study, alkaline (sodium carbonate and bicarbonate) leach data, generated from two column leach tests on a calcrete type uranium-vanadium ore from Western Australia were assessed. Leaching experiment data was fitted with a first-order kinetic model and also modeled based on the reagent consumption per mass of the initial valuable species.

The column tests were performed for 142 and 190 days using the alkali leach solution and applying irrigation rates of 10 and 20 L/(hr.m²) for Column A and column B respectively. The alkaline leach compared with acid leach dissolves less impurity into the PLS and this consequently means less problems for downstream process. The data also showed that the higher irrigation rate of 20 L/ (hr.m²) increases the uranium and vanadium extraction.

Both approaches of the first order kinetic model provide a good agreement with the column test data. Besides the simplicity and flexibility of models used, the reagent consumption based leaching kinetic model with Q_v variable and the new leaching index of (β) as techno-economic factor would benefit the process planning of uranium-vanadium heap leaching.

Due to the high amount of clays mineral present in the ore sample and their effect of the percolation, the ability to absorb metals from a sodium carbonate-sodium bicarbonate leach solution needs further investigations mostly with regard to including a proper agglomeration step as part of the alkaline heap leach process.

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