

Laboratory simulation and optimisation of stope leaching of low-grade uranium ore.

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This paper presents data from a laboratory simulation of a stope leaching process. The experimental procedure simulates underground in-situ reactors where uranium is liberated from the host rock through periodical flushing with mine or ground water. This study examines the influence of varying the leaching protocol for simulated reactors (cells) on uranium leaching. Protocol variants examined include variation of flushing frequency, flush volume, leachate recycle, nutrient solution (9 K salts) addition to cells and Fe(III) sulphate addition to cells. The data show that the time between flushes has a significant effect on the amount of uranium extracted, with experiments leached most infrequently (i.e. monthly) displaying the highest uranium recoveries (175 mg/kg in 26 weeks). This is close to the 205/kg mg U leached from cells which receive application of an acidic ferric sulphate solution (0.5g/L). The presented data highlight the sizeable improvements in uranium recovery that might be achievable by simply by varying the operating protocol for actual operational underground reactors.

Keywords: Leaching; Uranium; Column leaching.

1. Introduction

Stope leaching (Boreck et al. 1990) is essentially an underground heap leaching operation, and is considered a less costly alternative to conventional recovery methods. Ore is blasted in-situ, forming the heaps that are then leached with ground/mine water. The recovery is achieved via constant lixiviant percolation or a 'flood' leach. Stope leaching has been successfully applied for the recovery of uranium (e.g. Stanrock Uranium Mines, Elliot Lake, Canada (McGregor 1969); Agnew Lake mine in Canada (Heyman, 1980) and for the recovery of copper, lead and zinc (e.g. Avoca mine, Ireland, Burton et al. 1983). Recovery is believed to be microbiologically mediated through oxidation of sulphides minerals, in particular those that are acid forming reactions (i.e. pyrite and pyrrhotite oxidation). This paper concerns stope leaching of uranium from a urananite ore. To achieve mobilisation and recovery of uranium from the predominantly U(IV) mineral urananite, requires an oxidation step to convert U(IV) to U(VI) which is mobile in acidic (and alkaline) conditions. It is the microbially-

mediated oxidation of accessory pyrite in such ores allows the generation of an acidic ferric sulphate solution, this then acts to both oxidise U(IV) to the more mobile U(VI) and then solubilise the U(VI) in acidic solution. The role of the microbes is thought to be in recycling the oxidant (maintaining a high Fe(III)/Fe(II) ratio by re-oxidising Fe(II), utilising O₂) and concurrently forming the acidic conditions necessary to mobilise U(VI).

The current study looks at the 'flood' leaching of a urananite-bearing quartz conglomerate with accessory pyrite. The aims are to assess whether uranium can successfully be recovered from this material, and if so, what the influence of changes in leaching protocol and/or amendments make to the total uranium leached and the rate at which it is leached from the ores. The changes in protocol involved adjustments in the time (rest period between leached) or by the use of more efficient flushes (multiple floods) and by the addition of amendments, either to encourage microbial activity or by introducing an oxidant.

2. Materials and Methods

2.1 Materials Characterisation

A uranium-bearing quartz conglomerate was used in this study. Approximately 50 kg of material was received. This material was crushed through jaw and gyratory crushers. The particle size distribution (PSD) was determined using wet sieving. Samples of the bulk sample and size fractions isolated by wet sieving (milled to \approx -50 μ m 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. Uranium assay was carried out on representative subsamples which were pulverised and submitted for analysis. Samples were digested (0.1 g of the crushed sample (<100 μ m)) with 2 ml hydrogen fluoride and 6 ml aqua regia (50 ml HCl and 50 ml HNO₃) in a microwave oven-digester. Further chemical assay for a whole suite of elements (including REEs) was carried out by an external laboratory.

2.2 Leaching protocol

The proposed method of stope leaching proposed by the prospective mine operators is to blast the rock, and create a dam to allow inundation and complete flooding of the blasted heap, the exact protocol that served as the basis of the design of the laboratory reactors is as follows: The leaching stage is conducted via flooding the in-situ heap with water for a 24 hours, then draining the water (this step is referred to here as a 'flood leach'). The heap material is drained to unsaturated conditions and the rock remains in contact with the remaining interstitial water until the next flood leach (this step is referred to here as the 'rest period'). The rest period lasts for 2 weeks. Water is then introduced to begin the next flood leach and this represents the completion of one cycle. The cycling of rest periods and flood leaching for each stope heap is proposed to continue for 18 months. Uranium is recovered from the flood leach water via ion exchange.

To satisfy the aims of the study the authors designed a set of experiments that would mimic the process of cyclic flood leaching and rest periods. It was noted early on in the research that this situation is readily mimicked in so called humidity cell testing procedures which are routinely used for the assessment of ARD potential in mine wastes. Accordingly, the experiments were designed along the lines of these tests as the appropriate equipment was available in the laboratories.

Figure 1 shows an individual leaching cell arrangement. The cells are constructed from Perspex and are 100 mm in diameter. The crushed ore was riffled into representative 1 kg portions and loaded into the cells. The material sits on a filter mesh which is supported by a perforated Perspex plate. Lixiviant is introduced rapidly from the bottom of the cell from the reservoir above under gravity. The lixiviant was introduced from the bottom to prevent problems of 'air-locks' forming within the material – 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. 16 of these cells were constructed and used for the experiments. The following steps were followed:

- [1] Dry crushed ore loaded into the cell. (Valves 1 and 2 closed).
- [2] Ore flood leached with 750 ml of lixiviant by opening valve 1 (valve 2 closed)
- [3] Ore left in contact with leachant for 24 hours
- [4] Reactor drained under gravity by opening valve 2.
- [5] Ore left to react during rest period,
- [6] Steps [2] – [5] repeated for total of 18 months (note 26 weeks of data are presented here) but using 500 ml of lixiviant.

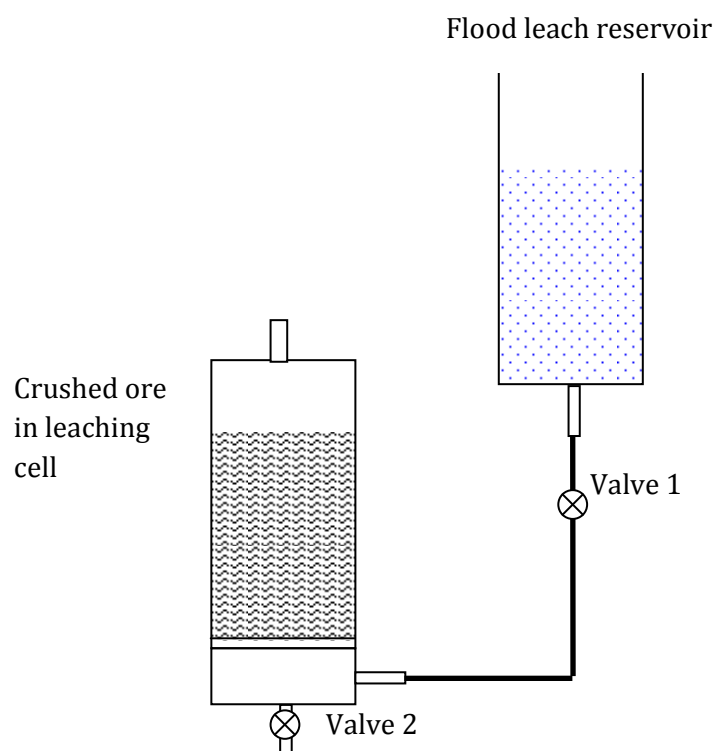


Figure 1 Schematic of leaching experiment, see text for further details

Table 1 gives the protocol variations explored in the experiments. It can be seen that variations in both the length of the rest period (1 week, 2 week, 4 week) were tested, that recycling of lixivants was tested (with and without the use of ion exchange (IX) media to remove uranium from solution), the effect of nutrient addition ('9K salts'), and the effect of oxidant addition ($\text{Fe}_2(\text{SO}_4)_3$ at 0.5 g/l) was tested. The amendments were introduced in to the cells by using the amendments as the lixiviant solution.

2.3 Chemical Analyses

Laboratory measurements of pH, redox potential (versus saturated Ag/AgCl_2) were made, (presented later after normalising to the SHE). Chemical analyses were performed on cell leachates for a suite of elements after filtration through 0.45 micron cellulose nitrate filter papers. Only results for uranium determinations are presented in this paper. All chemical analyses were performed in-house using a Perkin Elmer Optima 2100 DV ICP-OES.

Table 1 Details of leaching protocols (note: each cell has a duplicate)

Cell Name	Rest Period	Flood Leach	Notes
Control	2 weeks	1 x 500 ml tap water	
Double Flush	2 weeks	2 x 500 ml tap water	
Nutrient Addition	2 weeks	1 x 500 ml nutrient solution	<i>Nutrients '9K salts'</i>
Ferric Addition	2 weeks	1 x 500 ml $\text{Fe}_2(\text{SO}_4)_3$	<i>0.5 g/l $\text{Fe}_2(\text{SO}_4)_3$ at pH 3.5</i>
Recycle	2 weeks	1 x 500 ml recycled water	<i>Use of previous weeks leachate</i>
Recycle & IX	2 weeks	1 x 500 ml recycle water	<i>Use of previous weeks leachate passed through IX column</i>
Weekly Flush	1 week	1 x 500 ml tap water	
Monthly Flush	1 month	1 x 500 ml tap water	

3. Results

3.1. Materials Characterisation Results

The mineralogical components of the samples were determined by XRD to be quartz, with minor pyrite. After crushing the sample had a d_{50} of 4 mm and d_{20} of 1mm. The uranium content of the sample (and hence the head grade in each cell) was determined to be 696 mg/kg, the sulphur content 2.74 % and the iron content 2.88%.

3.2. Leach Data

Table 2 and Figs 2 and 3 present the cumulative uranium release data and uranium release rates respectively. Much more data has been captured during the study but for brevity here only the uranium results are discussed. Data in Table 2 show that the cells treated with ferric sulphate amendment have leached the greatest amount of uranium, and that the cells with nutrient solution addition have leached the least amount of uranium. Table 2 shows that the

cells flushed monthly have released more uranium than cells leached fortnightly and weekly in turn. Table 2 also shows that when recycling leachate to use as a lixiviant, removing uranium from the leachate with IX results in better uranium release. Fig 2 shows that uranium release rates are reasonably uniform across the 26 weeks leaching period for three different rest periods albeit at different rates. Fig 3 shows a different pattern of uranium releases for cells that have been amended with application of nutrients and oxidants. In both cases uranium release decreases from a maximum towards lower values, this is particularly noteworthy for the application of ferric sulphate.

Table 2 Total uranium extracted from experimental cells after 26 weeks experiment duration

Cell Name	Current leachate pH	Total U extracted mg/kg	% U Extracted
Control A	5.0	110	15.8
Control B	5.0	104	15.0
Double Flush A	6.7	61.8	8.9
Double Flush B	6.8	48.0	6.9
Nutrient Addition A	5.9	56.0	8.0
Nutrient Addition B	6.0	45.8	6.6
Ferric Addition A	2.7	208	29.9
Ferric Addition B	2.7	203	29.2
Recycle A	3.0	63.6	9.1
Recycle B	3.0	64.3	9.2
Recycle & IX A	3.4	115	16.5
Recycle & IX B	3.3	121	17.4
Weekly Flush A	6.4	69.7	10.0
Weekly Flush B	6.4	73.1	10.5
Monthly Flush A	3.6	187	26.9
Monthly Flush B	3.8	163	23.4

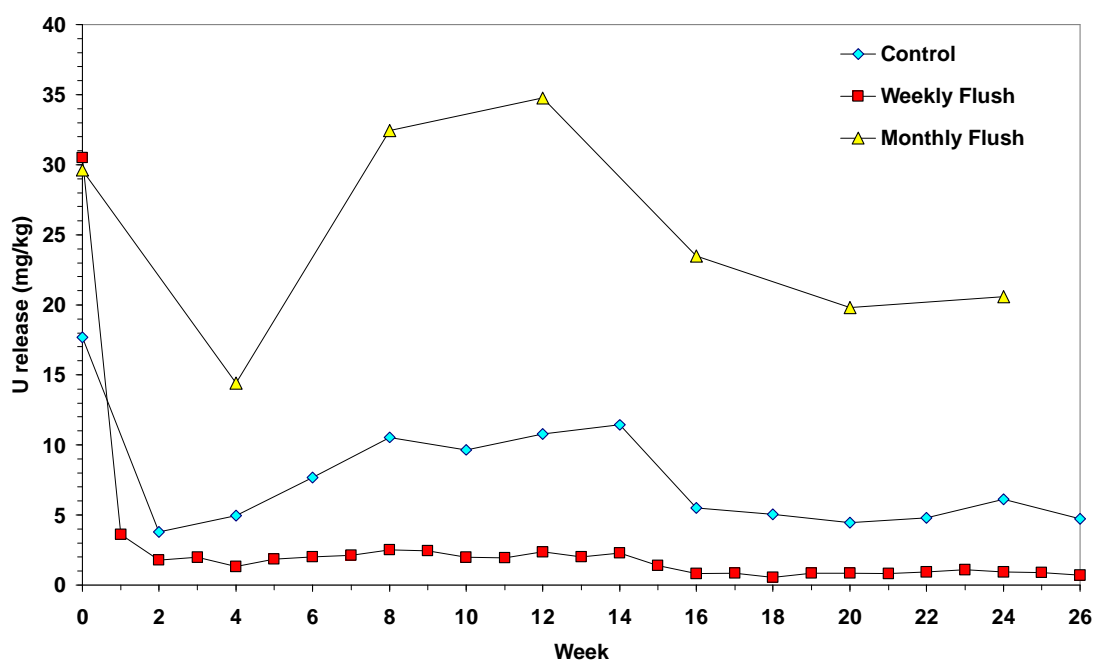


Figure 2 Averaged uranium release with time for cells with different rest periods (controls leached every 2 weeks)

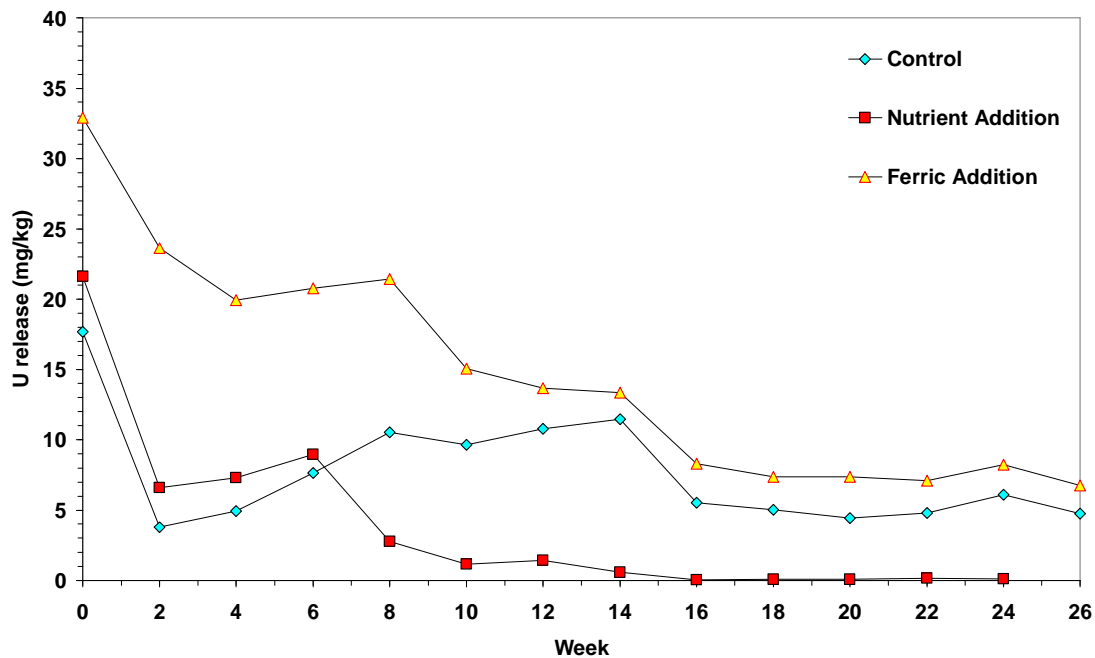


Figure 3 Averaged uranium release with time for cells with different amendments compared to control cells

4. Discussion

4.1 Ferric Sulphate Addition

The effect of addition of an acidic oxidant has clearly resulted in elevated leaching of uranium over and above the control (see Fig 3). On average the cells leached 205 mg of Uranium per kilogram (which constitutes 29.6% of the uranium available). The two mechanisms responsible are the direct solubilisation of U(VI) moiety of the urananite and/or the Fe(III)-mediated oxidation of U(IV) to U(VI) and subsequent solubilisation into the leachate. As can be seen from Fig 4 the data lie to the top-left hand side of the Eh-pH diagram, a reflection of the acidic and oxidising character of $\text{Fe}_2(\text{SO}_4)_2$ solutions. Both mechanisms are therefore plausible to explain why the uranium leached is highest from these cells. Interestingly, the shape of the uranium leach curve with time is that of a continual decline in uranium leached, suggesting that the Fe(III) mobile uranium content is close to exhaustion.

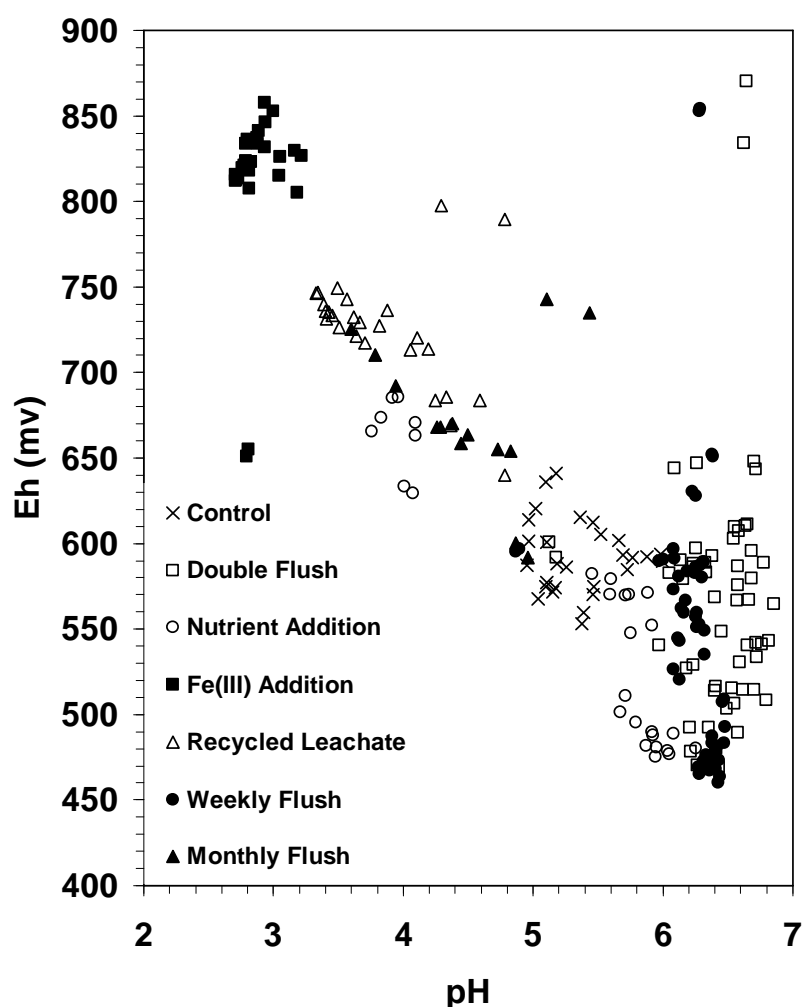


Figure 4 Eh and corresponding pH data from cell leachates (Eh versus SHE).

4.2 Variations in rest period duration and flushing

Fig 2 shows the variation in leaching of uranium in from each of the weekly, 2 weekly and monthly flushes. The cells leached a total of 71.4, 107 and 175 mg/kg of uranium respectively. This is the single most important finding of the present study. The authors suggest that the dramatic differences in uranium recovery are likely to be due to biogeochemical interactions. Fig 4 shows that the cells flushed monthly leachates have a lower pH and higher Eh than cells leached fortnightly, and these more than those leached weekly. This suggests that flooding disrupts the processes occurring in the interstitial water that are responsible for liberating the uranium. It is suggested that microenvirons of low pH and high redox potential are produced within biofilms surrounding mineral grains and/or that planktonic microbes are being flushed from the system. If the microbiological activity is allowed to continue (uninterrupted by a flood leach) then high redox conditions prevail due to rapid recycling of Fe(II) through microbiological Fe(II) oxidation. The Fe(III) produced in turn oxidising U(IV) with subsequent mobilisation of U(VI) in the resulting sulphuric acid. The indirect evidence for the contribution of Fe(II) oxidising microbes is the fact that (as shown in Fig 4) that the cell have a relatively high Eh at acidic conditions, under these acidic conditions abiotic Fe(II) oxidation is so slow (half-life of years) that it would be prohibitive for the maintenance of the elevated Eh observed.

The same mechanism has been proposed many times before for the microbial assisted leaching of uraninite-bearing rocks, but the influence of time on the leaching behaviour has not been reported elsewhere. The authors speculate that the frequent flooding has an impact on the formation of localised zones of depressed pH and elevated Eh which in turn leads to less uranium solubilised. This can also be seen in the results of cumulative leaching from the double flushed cell which has only leached an average of 54.9 mg/kg of uranium (7.9%), similarly the pH is higher and the Eh lower in these cells (see Fig 4).

It is also interesting to note that unlike the direct addition of a ferric sulphate, the microbially generated version gives a distinctly different leaching profile. Whilst the ferric sulphate amended cell displayed declining uranium releases the monthly flush seems to be on a different trend and it is anticipated that these cells will soon have released more uranium than the ferric sulphate addition. It is possible that since these cells are on 2 weekly flushes that microbial activity has not developed to the same extent.

4.3 Nutrient Addition

Given the microbiological enhancement of uranium release postulated in Section 4.2 it is perhaps surprising to find that the addition of a '9K-salt' nutrient solution did not result in greater releases of uranium. In actuality the average uranium release of the two cells was 51 mg/kg (7.5%) which was the lowest of any of the cells in the present study. Interestingly Fig 4 shows that a reasonably high Eh is noted at times for these cells but without the correspondingly higher uranium releases as seen with other cells. The explanation is

probably to do with the fact that the nutrient solution has a pH of circa pH 8 and significant buffering capacity due to some of the constituents (in particular NH_4) and therefore is likely neutralise the acidity produced by sulphide oxidation within the cells. Clearly (Fig 4) relatively oxidising conditions have developed but because the pH has been buffered, any U(VI) produced through oxidation of U(IV) is not soluble at the circumneutral pH of interstitial water within the cells (see Table 2 for cell pH data). This highlights the requirement for acidic conditions in addition to oxidising conditions for mobilisation of uranium from these types of ore.

4.4 Leachate Recycling

The recycling of leachates is a realistic simulation for actual site operations where mine water would typically be managed by recycling through the process. The effect of recycling is to decrease the uranium releases (compare 'recycle' to control in Table 2), however when the recycled leachate is passed through an ion exchange column for the targeted removal of uranium (and non-targeted removal of other constituents) then amount leached is very similar to the control. The fact that as U(VI) accumulates in the recycling leachate it curtails the further release of uranium may suggest a solubility control on the mobility of U(VI), this will be explored further with geochemical modelling of the cell leachates.

5. Conclusions

The results of this study so far are that

- The time between flushes has a significant effect on the amount of uranium extracted, with experiments leached most infrequently (i.e. monthly) displaying the highest uranium.
- Application of an acidic ferric sulphate solution leads to the greatest release of uranium over 26 weeks but the trend is for declining releases unlike the monthly leached cells without added oxidant.
- The presented data highlight the sizeable improvements in uranium recovery that might be achievable by simply by varying the operating protocol for actual operational underground reactors.
- Recycling of cell leachates has a detrimental effect on uranium recovery if the uranium (and possibly other components) are not removed by IX.
- Nutrient amendment of cells with 9K salts has detrimental effect on uranium release probably due to pH buffering.

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