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Uranium extraction from a low-grade, stockpiled, non-sulfidic ore: Impact of added iron and the native microbial consortia

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ABSTRACT

The biogeochemistry of the acid leaching of a non-sulfidic, weathered uranium ore from Ranger Mine (Australia) in relation to varied iron concentrations and Fe(III)/Fe(II) ratios was examined in this work. Controlled column studies which simulate a heap-leaching process, showed rapid uranium leaching during the initial stages of operation. This was thought to be a product of both the enhanced mobility of U(VI) in the stockpiled ore, possible aided by enhanced ion exchange with Fe(III) under higher Fe(III)/Fe(II) ratios. Indeed, it was observed that any elevated Fe(II) which was originally present in the leaching solution irreversibly hampered maximal uranium recovery when compared to Fe(III)-rich leaching counterparts (~10% in U recovery). Importantly though, the mine-derived native microbial community, once established, was able to oxidise the continuous supply of Fe(II). In doing so, the microbial consortium was able to restore chemical conditions amenable to enhanced uranium recovery. The Fe-oxidising bacteria (FeOB) did not correspond to mesophilic bacteria typically found in sulfidic ores. Furthermore, the planktic and benthic communities were vastly different from each other. Collectively, this research provides key insights into the biogeochemical processes that are important to maximising uranium resource recovery from heap leaching activities.

1. Introduction

The mining of primary ore bodies frequently produces large amounts of low-grade rock material that is stockpiled in on-site facilities with uranium no exception. For example, it has been estimated that at the Ranger Uranium Mine facilities (Northern Territory, Australia) the low-grade material, incapable of being processed by the current extraction circuit as a result of its low U-content, still contains up to 20,000 t of U_3O_8. Depending on the prevailing market price for uranium this might constitute a profitable future venture. Similarly, many deposits that contain vast amounts of low-grade uranium resources, such as the Turamdih mine in India (Abhilash et al., 2011), face a similar situation. However, in order for mineral extraction from low-grade ore to be cost-effective, there needs to be minimal capital investment and minor ongoing running expenses, characteristics which bioleaching tend to exhibit.

Chemical leaching of uranium is frequently performed under either acid or alkaline conditions depending on the host rock mineralogy. If the alkalinity of the host rock is too high, the use of an acid leaching process (an economically preferred option) becomes prohibitive due to the high costs associated with neutralisation. Additionally, the acid leaching process requires the use of an oxidant (commonly ferric iron) to oxidise the uranium usually present as U(IV), e.g. uraninite (UO_{2+x}), to its mobile U(VI) moiety. Uraninite, and to a greater extent, coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) and brannerite (UTi_2O_6), require strong oxidising conditions to achieve acceptable uranium extraction (Charalambous et al., 2014).

When ferric iron is used as the primary oxidant and reacts with U(IV) minerals, the accumulated ferrous iron can have a detrimental effect on further uranium extraction (Ram et al., 2011). This is avoided by adding a secondary, strong oxidising agent such as hydrogen peroxide or manganese dioxide, which are considered one of the major costs associated with this process (Muñoz et al., 1995). As such, only when the ferrous iron is re-oxidised (or recycled), can the full economic benefit of the leaching process be realised (Ring, 1980). Indeed, the balance between Fe(III) and Fe(II) and associated maintenance of the redox potential (E_h), is critical to the oxidation and dissolution of U(IV) (Ram et al., 2011).

Despite being designed for the chemical leaching of ore, the acidic leaching process unintentionally creates a suitable environment where acidophilic microorganisms can proliferate. In the case of uranium ore bodies with a substantial content of pyrite or other iron sulfides,

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this was widely exploited during the early days of uranium mining (Harrison et al., 1966; MacGregor, 1968; Miller et al., 1963). Iron- and sulfur-oxidising bacteria such as *Leptospirillum* spp. and *Acidithiobacillus* spp., constitute a cheap way to recycle Fe(II) to Fe(III) and act as a source of acidity (Rawlings, 2005). Microbial consortia, dominated by acidophilic, iron-oxidising autotrophic prokaryotes are regarded as a robust alternative to pure cultures as a way of assisting mineral leaching (Rawlings and Johnson, 2007). However, in conditions where uranium ore is not associated with sulfide minerals, such as the Ranger Mine in this study, little is known about the functioning and composition of the microbial community that may naturally develop and its efficacy with regard to metal extraction. Although studies on microbially-supported uranium extraction have been performed on low-sulfide ores, they have focused on the use of model bioleaching organisms (Abhilash et al., 2010; Abhilash and Pandey, 2013a, 2013b, 2013c).

In this study, an experimental column system is used to emulate the heap leaching process but on a much smaller and controlled scale in order to evaluate the leaching biogeochemistry of a non-sulfidic ore. An indigenous, active microbial community was prepared by concentrating biomass derived from the uranium extraction process from the Ranger Uranium Mine, to assess the microbial impact on uranium extraction from the low-grade ore. Furthermore, two separate leachants were prepared differing only in their Fe(III)/Fe(II) ratios and, as a consequence, their initial E_h, as a way of investigating the uranium recovery under differing extraction scenarios. The objectives of this study were to evaluate the leachability of a highly weathered uranium ore and characterise the native microbial community in a lab-scale leaching system.

2. Material and methods

2.1. Uranium ore and agglomeration

The ore used in the experiments was a mixed, weathered, low-grade composite obtained from the Ranger Uranium Mine (Northern Territory, Australia). The major minerals present in the composite were magnesium chlorite and quartz (>60%), followed by muscovite and gypsum. Uranium was present as a minor component (0.042%), and was originally mined in the form of uraninite and brannerite (Sinclair et al., 2006). Rock pieces larger than 1 cm^3 were manually removed.

Ore was agglomerated by adding mine-derived raffinate as has been described previously (Vázquez-Campos et al., 2014), and sulfuric acid (98%) in a ratio of 14:1 and mixed in a clean, HDPE bucket fixed within a cement mixer. The agglomerated ore, with a size range from 5 to 30 mm, was then allowed to cure for 72 h in the sealed HDPE bucket before assembling the columns. These processes, albeit on a smaller scale, can be considered to approximate a typical heap-leaching preparation scenario. Additionally, the HDPE bucket was acid-washed and wiped repeatedly with 70% (*w*/*w*) ethanol prior to operation.

2.2. Column design and setup

Columns were constructed with PVC pipe (50 mm internal diameter) and closed at both ends with PVC caps. The bottom of the pipes contained a single outlet for leachate outflow through a Masterflex® P/S High Performance Tygon® lab R-3603 (06409-24, Cole-Parmer) tube glued with 'Plumbers Mate' Type N PVC-U Pipe Cement (Bostik). The top caps contained five holes: four evenly spaced inlets for leachant drip release and one aeration hole. Leachant solution was supplied using four independent channels per column, supplied by an ISMATEC® IPC-N 24 ISM939D peristaltic pump (Cole-Parmer). Three layers of fibreglass mesh (2 mm mesh) were placed at the base of the column followed by a 60 g cushion of acid-washed silica sand, a second layer of fibreglass mesh and 650 g of agglomerated ore, leaving 5–10 cm of headspace at the top of the column (Fig. S1). All column components were acid-washed prior operation and/or thoroughly cleaned with 70% (*w*/*w*) ethanol.

All columns were placed in a custom-built poly(methyl methacrylate) water bath with temperature controlled using a TU1 Analogue Heater Circulator (Thermoline Scientific) (Fig. S1).

2.3. Operational parameters

Experiments were performed over a period of 30 days at a fixed temperature of 30 °C, with a flow rate of 70 μL/min (equating to 2.73 mL/kg·h) with no recirculation through the columns. Again, flow rates through the ore were chosen to represent those found in typical heap-leaching operations. Columns were monitored daily to ensure flow rates were consistent and blockages did not occur (Fig. S2).

2.4. Leachant composition

Synthetic mine water was formulated to mimic diluted mine waters, which are commonly used in heap-leaching operations. The composition was based on the synthetic raffinate previously described by Vázquez-Campos et al., (2014) and modified to include silicon. Two different leachants were used. The first solution, henceforth referred to as Fe(III)-rich, was most similar to the source raffinate with composition as follows: 18.75 mM $Al_2(SO_4)_3$, 4.55 mM $CaSO_4$, 0.25 mM $Ca(NO_3)_2$, 0.425 mM $CaCl_2$, 0.4 mM $CuSO_4$, 20.93 mM $NH_4Fe(SO_4)_2$, 2.075 mM $(NH_4)_2Fe(SO_4)_2$, 0.5 mM $FeSO_4$, 205 mM $MgSO_4$, 13.5 mM $MnSO_4$, 1.625 mM Na_2SiO_3, 1.5 mM KH_2PO_4, 0.05 mM $ZnSO_4$ and adjusted to pH 1.65 ± 0.06 with H_2SO_4. This solution can be considered a good approximation of the leachant that would be used in a typical heap-leaching scenario. The second solution, referred to as Fe(II)-rich, only differed from the first solution in that it contained 12.75 mM $NH_4Fe(SO_4)_2$ and 4.1 mM $(NH_4)_2Fe(SO_4)_2$. This leaching solution was examined in order to assess the implications of a continual source of Fe(II), present as a result of Fe(III)-induced U(IV) oxidation, that required re-oxidation.

2.5. Inocula preparation

Column inocula were obtained by incubating 100 mL of each leachant with a raffinate cell concentrate (20 mL in 1 mL) at 30 °C and 150 rpm for 30 days. Samples of the initial mine-derived raffinate and prepared inocula were retained for microbial community analysis. Cultures were filtered through Millex®-GV 0.45 μm PDVF syringe filters (Millipore) to remove excess fungal biomass. Immediately prior to column operation, 20 mL of inocula were added to the top of each column with a serological pipette to ensure an even distribution.

2.6. Sample collection

Leachate samples (~10 mL per column) were collected periodically to measure pH, E_h, and dissolved concentrations of Fe(II), Fe(III), Al, Ca, Cu, K, Mg, Mn, P, S, Si and U. Sample collection was achieved by placing a clean, empty vial at the exit point of each column with samples collected every 24 h. Samples were filtered with Millex®-GV 0.45 μm PDVF syringe filters (Millipore) prior to elemental analysis. Additional samples of leachate for DNA extraction (40–50 mL) were frozen after collection (every 10 days) and stored at −20 °C until further processing, as described below.

At the end of the experiment, the pump was shut down and the columns were allowed to drain. The leached solid material (ripios) was gently pushed from the columns such that contamination and mixing of different layers was avoided (Fig. S3). Ripios samples were collected at three different heights (i.e. top, middle and bottom) of the columns. Sampling points were defined in 2 cm bands at the indicated heights (Fig. S3). Samples were frozen and subsequently freeze-dried, and stored at −80 °C until the DNA extraction was performed.