

Application of Hydrotalcites for Remediation of Beverley In-Situ Recovery Uranium Mine Barren Lixiviant

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ABSTRACT: An assessment of hydrotalcite formation as a method to neutralise acidity and remove trace elements was undertaken using barren lixiviant from Heathgate Resources' Beverley In-Situ Recovery (ISR) uranium mine in South Australia. Batch-scale studies have demonstrated proof of concept in terms of the neutralisation of acidity and concomitant removal of a range of trace elements from the barren lixiviant using either MgO or MgO and sodium aluminate (NaAlO₂). Hydrotalcite was the predominant mineral formed during the neutralisation of the barren lixiviant, hosting a wide range of contaminants including substantial uranium (~1% U) and rare earth elements (~2% REE). High U and REE recovery (~99%) from barren lixiviant after hydrotalcite precipitation indicates a potential to both remediate barren lixiviant prior to aquifer re-injection and to offset remediation costs. Alternatively, hydrotalcite precipitates formed during barren lixiviant neutralisation may be further stabilised via calcination, silicification or a combination thereof. Both methods facilitate the formation of minerals potentially amenable for inclusion in a long-term waste repository at the cessation of ISR mining. Formation of a residual Na-SO₄ brine during lixiviant neutralisation creates the option to use electrolysis to generate H₂SO₄ and NaOH, for use in mining activities and to also further offset lixiviant remediation costs. Importantly, the major and trace element composition of the neutralised barren lixiviant produced via hydrotalcite precipitation is similar to that of existing groundwater allowing for direct mine water disposal. In the Beverley context, the hydrotalcite-based remediation technique is considered a potential additional groundwater treatment, should it be required, for the future closure of its Beverley North operations. Whilst the ionic composition of Beverley's barren lixiviant would mean easier application of this technology there, there is potential to apply it to other uranium mines with suitable addition of reagents. Hence, this hydrotalcite-based remediation technology, after scale-up and performance validation, allows for the prospect of a fully integrated ISR mining, processing and lixiviant remediation strategy consistent with stringent environmental management and mine closure standards.

KEYWORDS: hydrotalcite, Beverley, uranium, lixiviant

I. INTRODUCTION

1. Beverley Uranium Mine

The Beverley *in situ* recovery (ISR) uranium mine in South Australia, owned and operated by Heathgate Resources Pty Ltd (Heathgate), is the only operational ISR uranium mine in Australia. The Beverley deposit is located ~550 km north of Adelaide (Fig. 1). Uranium mineralisation was first discovered in 1969. In 1990, Heathgate acquired the 21,000 t deposit and commenced ISR mining in 2000.

Mineralisation is hosted within a series of palaeochannels ~100-140 m below the surface within unconsolidated Beverley sands, silts and clays of the Tertiary (Miocene) Namba Formation. Ore primarily occurs as coffinite and uraninite associated with organic-rich layers of the palaeochannel sediments. Other element enrichments include Th, Zn, Mo, V and As [1-3]. Palaeochannel groundwater salinity varies from 3,000-15,000 mg/L with aquifer waters of an Na-HCO₃-Cl-SO₄ type (Table 1).

2. Uranium Extraction and Recovery

Aquifer pH is reduced from ~7.0-8.0 to 1.5-2.5 using H₂SO₄, with H₂O₂ used as an oxidant to assist in U solubilisation. Uranium within pregnant lixiviant is pumped to the surface and recovered. Post U extraction, the lixiviant is refortified and re-injected to assist in further ore extraction. After cessation of mining within a mineralised aquifer, under current arrangements barren lixiviant remains in the mined-out aquifer to undergo natural attenuation. Typical lixiviant compositions are given in Table 1.

3. Hydrotalcite formation

Hydrotalcites (HT) are a class of naturally-occurring and synthetic materials characterised by positively charged mixed metal hydroxide layers separated by interlayers containing water molecules and exchangeable anions [4-6]. Hydrotalcites form via co-precipitation of divalent and trivalent metal cation solutions at moderate to high pH with

the general formula: $M_{(1-x)}^{2+}M_x^{3+}(\text{OH})_2A^{n-} \cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively [7], x is the proportion of trivalent metal ion, y is interlayer water and A^{n-} the anion. In Beverley barren lixiviant, Mg^{2+} , Al^{3+} , and SO_4^{2-} predominate giving the formula: $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{SO}_4 \cdot n\text{H}_2\text{O}$.



Fig. 1. Location of Beverley *in situ* recovery (ISR) U mine, SA.

Hydrotalcites typically contain Mg^{2+} and Al^{3+} , in the molar ratio of 2:1 to 3:1, but other cations including Ni, Zn, and La may occur [8, 9] via co-precipitation and ion-exchange both during and after formation [4, 10-12]. Simultaneous removal of a suite of inorganic contaminants (to form a polymetallic HT) is highly advantageous in treatment of contaminated waters.

Addition of Mg and/or Al and an alkalinity source are required to optimise conditions for HT formation in barren lixiviant [13]. Alkalinity, Mg and Al may be obtained from a variety of sources including sodium aluminate (NaAlO_2), other Al salts, Bayer liquor from alumina refining, sodium hydroxide (NaOH) and calcined magnesia (MgO). Formation of HT in the specific context of Beverley ISR barren lixiviant may also have other advantages, including:

- broad spectrum contaminant (common within U mineralisation) removal;
- rapid formation and dewatering, resulting in a high solids concentration in addition to flocculation of colloidal/material from suspension;
- formation of stable HT precipitates above a pH of *ca.* 4-5 with stability increasing with pH;
- removal of Mg^{2+} and substantial SO_4^{2-} while only adding Na^+ ; and
- generation of neutralised solute (mostly Na-SO_4) amenable to RO/electrodialysis of a concentrated solution producing H_2SO_4 and NaOH for use in lixiviant production/barren lixiviant neutralisation, respectively.

Advantageously, the formation of HT in Beverley ISR Mine barren lixiviant is favoured by high Mg concentrations in the aquifer augmented by Mg and Al liberated during ISR (Table

1). With a Mg:Al mol ratio of ~ 1.6 , Beverley ISR barren lixiviant is potentially suitable for HT formation after addition of further Mg and Al (to increase the mass of HT precipitated) and a source of alkalinity. Importantly, low Fe mitigates formation of unstable green rusts [14].

It was postulated that the formation of HT of suitable stoichiometry, ($\text{Mg}^{2+}:\text{Al}^{3+}$ molar ratio of $\sim 2:1$ to $3:1$), from the Mg, Al-rich Beverley barren lixiviant could be facilitated via $\text{MgO} + \text{NaAlO}_2$ addition. The addition of these reagents serves two simultaneous purposes: adjustment of the Mg:Al molar ratio to a desired range without Fe addition, and as a source of alkalinity to increase pH to induce the formation of HT as a sink for a suite of contaminants including U.

Table 1. Typical groundwater and average extraction and injection lixiviant compositions (mg/L) from Beverley ISR U mine (Heathgate data) neutralised lixiviant (Lix + MgO + NaAlO_2) and post-Beverley aquifer sediment column (this study).

Analyte	Ground water	Lix Inj	Lix Extrac	Barren Lix	Lix+MgO+ NaAlO ₂	Post-Column
pH	7.3	2.1	2.3	1.7	6.9	7.3
EC	831	1324	1199	2470	1900	1980
Al	0.22	36.7	36.9	200	0.094	0.011
As	0.002	0.04	0.05	<0.05	<0.05	0.026
Ba	53	37	39	0.035	0.065	0.055
Ca	370	546	547	638	705	657
Cd	0.2	41	42	0.16	0.078	0.014
Cl	1988	1895	1975	3700	4220	4580
Co	0.11	4.06	4.18	6.7	1.7	0.7
Cr	0.02	0.03	0.58	0.18	0.003	0.002
Cu	0.03	0.12	0.03	0.47	0.005	0.008
Fe	0.74	26.1	25.9	79	0.013	<0.005
HCO ₃	n/a	<1	<1	<1	67	165
K	42	59	59	117	109	121
La	n/a	n/a	n/a	0.79	0.13	0.001
Mg	198	303	303	454	1570	1580
Mn	0.19	0.52	0.55	14	11	9.9
Na	1188	1423	1427	1710	2300	2680
Ni	0.004	1.99	2.04	3.7	1.2	0.4
Pb	0.04	0.1	0.15	0.16	<0.0005	<0.0020
S	508	1378	1303	2300	2500	2600
Sc	n/a	n/a	n/a	0.53	<0.0025	<0.0025
Se	0.001	0.26	0.25	<0.05	0.06	0.09
Si	48	125	126	300	37	42
Th	n/a	n/a	n/a	1.1	0.0051	0.0024
Ti	n/a	n/a	n/a	0.028	<0.002	<0.002
U	0.41	15	211	19	1.3	0.7
V	0.001	0.76	0.78	0.9	<0.005	<0.005
Zn	0.29	0.17	0.25	4.2	0.44	3

II. METHODS

1. Beverley ISR Mine Batch Neutralisation Experiments

A 2 L sample of barren lixiviant was rapidly stirred in an acid-washed flask. Both MgO and NaAlO_2 were rapidly added as dry powders. A precipitate formed immediately and was stirred for ~ 0.5 hours. The resultant suspension was

covered and aged at 50°C in an oven for 7 days, separated, washed with deionised water, and oven-dried at 50°C. Part of the neutralised supernatant was passed through a 1 m long column containing unmineralised Beverley aquifer sands. A precipitate sub-sample was ground in a mortar and pestle and calcined in a Pt crucible at 650°C for 30 min and re-weighed for mass loss. Dried and calcined precipitate mineralogy was analysed using X-ray diffraction (XRD) and major and trace elements using X-ray fluorescence (XRF). Supernatant solutions were analysed for major and trace elements via ICP-MS/OES using standard methods.

Scanning electron microscopy (SEM) of HT was performed on a Zeiss 1555 VP-FESEM equipped with an energy dispersive spectrometer (EDS). For imaging, dried samples were placed onto Al stubs and Au-coated. An In Lens detector used a 30 µm aperture, accelerating voltage of 3 kV, and 4 mm working distance. For microprobe analysis dried samples were placed onto a glass slide and coated with carbon. EDS spectra from single points were used to determine elemental composition. Microprobe analysis was performed with a 120 µm aperture, 20 kV accelerating voltage and 16mm working distance. Element maps were generated after 35 to 70 scans. Semi quantitative analyses on these samples were performed at 15kV, 120 µm aperture and 16mm working distance. Cu was used to calibrate gain zero, and appropriate standards were used. Count rates were approximately 14,000 cps and deadtime 30%.

III RESULTS AND DISCUSSION

1. Beverley ISR Mine Batch Neutralisation Experiments

Relative to the initial barren lixiviant pH of 1.7, MgO + NaAlO₂ addition resulted in a final pH of 6.9 (Table 1). with a concomitant reduction of dissolved Al concentrations (200 to <0.1 mg/L). Considerable Mg (454 to 1,570 mg/L) was present as MgO was added in excess of stoichiometric requirements. Reductions in lixiviant major and trace elements concentrations included Al, Ca, Cd, Co, Fe, La, Ni, Th, and U from (19 to 1.3 mg/L). Most trace element concentrations were further reduced, and pH increased to 7.3 after passage of neutralised solute through a column of unmineralised Beverley aquifer sediments (Table 1). The resultant solute chemistry is similar to the original groundwater + Mg-Na-SO₄ (Table 1).

Geochemical modelling (PHREEQC, [15]) indicated after addition of MgO + NaAlO₂, HT at pH 6.9 was ~10²³ times oversaturated with respect to the solution. Mineralogical (XRD) analysis confirmed HT as the principal mineral.

The major and trace element composition of the HT precipitate formed from the addition of MgO + NaAlO₂ to Beverley ISR mine barren lixiviant and after calcination at 650°C is dominated by MgO and Al₂O₃ that collectively constitute ~45% and 59%, respectively (Table 2). The 30% mass increase is consistent with the conversion of HT to spinel (confirmed by mineralogical analysis). Sulphate, (as SO₃) was the major solution anion, and hence predominant

HT interlayer anion constituting ~10% in the HT and 14% after calcination to spinel.

Dissolved U from the barren lixiviant (19 mg/L) was concentrated within the HT (7,162 µg/g, 0.85% eU₃O₈) and calcined HT (9,778 µg/g, or 1.15% eU₃O₈), comparable to primary ore grade (Table 2). Rare earth elements (REE) were also concentrated; the sum of REE (La+Ce+Nd+Sm+Yb) was 5,867 and 8,233 µg/g, respectively, in the HT and calcined HT. Estimated total REE concentrations based on interpolation were 9,000 and 12,500 µg/g, respectively. Notable was the enrichment of heavy REE over light REE. Heavy REE such as Yb and Y, a surrogate mid-HREE, had concentrations 4,731 and 6,403 µg/g in the HT and calcined HT (spinel), respectively. Scandium, frequently found in association with REE, also had elevated concentrations of 290 and 405 µg/g, respectively.

In addition to U and REE, many trace elements (Co, Ni, Zn) exceeded 1,000 µg/g in both the HT and the calcined derivative, with other elements (Cu, Cr, Th) exceeding 100 µg/g. Given the enrichments of U, Th and trace elements, it is likely that U-Th series radionuclides were also concentrated within the HT.

Table 2. Major element oxide (%) and trace element (µg/g) geochemistry of Beverley ISR mine barren lixiviant (lix) precipitates.

Element/oxide	Lix + MgO + NaAlO ₂	Calcined Lix + MgO + NaAlO ₂
SiO ₂	7.45	9.91
TiO ₂	<0.002	0.01
Al ₂ O ₃	25.8	34.14
Fe ₂ O ₃	3.86	4.99
MnO	0.19	0.26
MgO	18.79	24.77
CaO	1.36	2.03
Na ₂ O	1.31	1.71
K ₂ O	0.06	0.09
SO ₃	10.16	13.91
As	22	29
Ce	1896	2708
Co	2432	3125
Cr	96	116
Cu	179	218
La	317	448
Mo	18	24
Nd	2068	2894
Ni	1175	1527
Pb	51	14
Sc	290	405
Se	10	9
Sm	946	1308
Th	431	569
U	7162	9778
V	470	647
Y	4731	6403
Yb	640	875
Zn	1859	1717

Analysis by SEM revealed flat, hexagonal crystals arranged as edge-to-edge aggregates within botryoidal masses (Fig. 2). Element mapping revealed similar distributions of Mg-Al with an Mg:Al molar ratio of ~1. While lower than that of HT, abundant Si (~7%) and a Si:Al molar ratio of ~1 suggests co-precipitation of an amorphous phase with other cation substitution also decreasing the Mg:Al ratio.

Element mapping of U (~1%) indicated that it was present in a diffuse distribution within HT rather than as a discrete secondary uraniferous precipitate. This suggests a uniform distribution of U (in addition to other elements) within the HT.

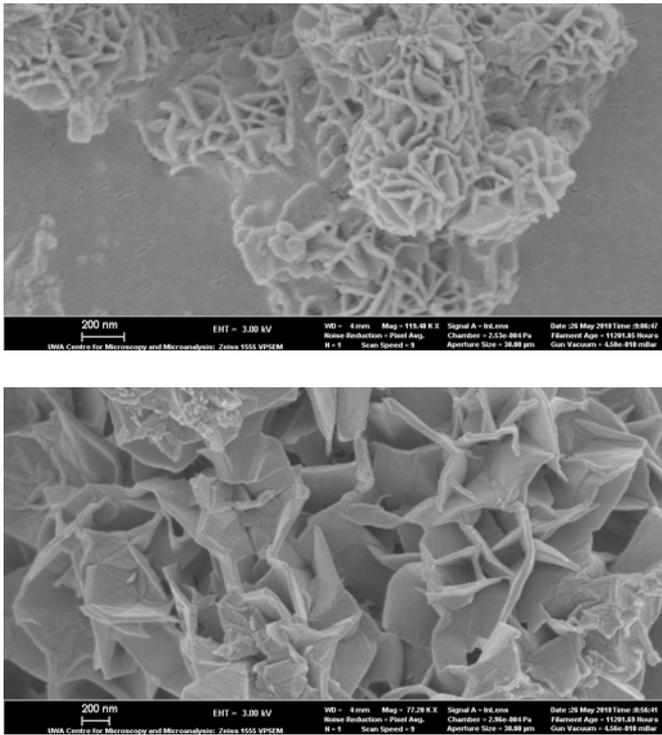
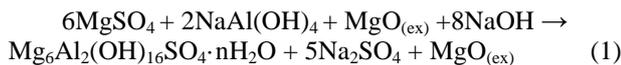


Fig. 2. Hydrotalcite (HT) botryoids and detail of face to edge and edge to edge HT aggregates. Scale bars are 200 nm.

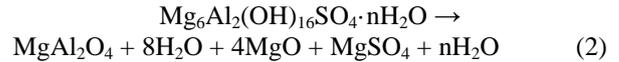
Batch experiment results have demonstrated that a range of major and trace elements are removed during HT precipitation and confirms aspects of the patents of Douglas [16, 17], that the combined addition of MgO + NaAlO₂ act concurrently as a pH neutralising agent and as building blocks for HT formation. A HT precipitation reaction, reflecting the barren lixiviant composition is:



where MgO_(ex) reflects excess MgO added as a Mg source and neutralising agent. Post-neutralisation solutes were predominantly Na-SO₄ reflecting the presence of SO₄ from the acidic barren lixiviant and Na derived from NaAlO₂ addition.

Calcination resulted in the dehydration and re-crystallisation of HT to spinel (MgAl₂O₄). Conversion to spinel occurs by

the following reaction where the Mg not utilised in the spinel is converted to MgSO₄ or MgO:



Calcination of HT resulted in a mass loss of ~30% due to dehydration. The MgO formed during the calcination is present in a 4:1 mol ratio, constituting a large buffering capacity in the event of low pH conditions. Alternatively, HT addition of silica as an interlayer anion results in a chlorite-like composition that could potentially be used as a “natural” repository. Formation of an Na₂SO₄-rich solution after precipitation also enables the possible use of electrolysis to produce H₂SO₄ for lixiviant generation, and NaOH for neutralisation.

IV. CONCLUSIONS

Batch-scale studies have demonstrated proof of concept for the neutralisation of acidity and removal of contaminants from Beverley ISR mine barren lixiviant using MgO + NaAlO₂. Hydrotalcite formed during neutralisation hosts a range of contaminants, notably ~1% U and ~2% REE indicating a potential to both remediate barren lixiviant prior to aquifer re-injection and to offset remediation costs. Importantly, the ionic composition of the neutralised barren lixiviant is similar to existing groundwater allowing for direct disposal. Hydrotalcite formed during neutralisation may be further stabilised via calcination and/or silicification producing minerals potentially amenable for inclusion in a long-term waste repository.

In the Beverley context, the HT-based remediation technology is considered a potential groundwater treatment, if required, for the future closure of its Beverley North operations. Whilst Beverley’s ionic composition would mean easier application of this technology there, potential exists to apply it to other mines. This remediation technology, after scale-up and performance validation, allows for the prospect of a fully integrated ISR mining, processing and lixiviant remediation strategy consistent with stringent environmental and mine closure standards.

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VI. NOMENCLATURE

Lixiviant: a solute used to extract the desired metal from an ore or orebody.

In-Situ Recovery (ISR): method of uranium mining utilising lixiviant pumped into an aquifer to dissolve uranium minerals. This lixiviant is pumped back to the surface where the

uranium is extracted.

Botryoid: spherical mineral aggregates similar in appearance to a bunch of grapes.

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