HYDROTALCITE FORMATION FOR CONTAMINANT REMOVAL FROM MINING WASTEWATERS

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ABSTRACT

Hydrotalcites are a class of Mg-Al layered double hydroxide minerals with the ideal 3:1 Mg:Al endmember chemical composition $Mg_6Al_2(A)(OH)_{16}.n(H_2O)$ ($A = CO_3^{2-}$, SO_4^{2-}, Cl^-, etc). Hydrotalcites may occur naturally and are a common secondary mineral formed in soils during natural attenuation of acidic, metal-laden contaminated sites. Many acidic wastewaters generated during mineral processing often contain either Mg and/or Al in sufficient abundance that the potential exists for hydrotalcite formation providing there is addition of alkali to achieve a pH >5 and Mg and/or Al to attain a Mg:Al ratio between 2:1 and 3:1. Some Fe, typically present in acidic wastewaters, may also be accommodated within the hydrotalcite structure. Advantageously, hydrotalcites form rapidly and readily dewater. The utility of hydrotalcites, which could be precipitated as part of managing mine wastewaters, lies in their ability to incorporate a wide range of cationic (Cu^{2+}, Ni^{2+}, UO_2^{2+}), metalloid (SeO_4^{2-}, AsO_4^{3-}), and (oxy)anionic contaminants (CrO_4^{2-}, MnO_4^-). Silication to form a chlorite-like phase or calcination to form a spinel-like phase may increase precipitate stability prior to disposal. CSIRO has investigated the treatment of a variety of acidic wastewaters which has resulted in the patenting of processes for both in-situ formation of hydrotalcites as a potential closure strategy for solution mining, and for the treatment of natural and acidic mining wastewaters. The broad spectrum removal of contaminants, including U which is often present as a variety of geochemical species, also lends hydrotalcites and their derivatives to use as a potential containment material in nuclear waste repositories. In this study, Ranger Mine process water, an acidic, $Mg\text{-}SO_4$ brine derived from the leaching of U ore from chloritic schist, was treated with Na-aluminate ($NaAl(OH)_4$) sourced from a commercial Bayer Process liquor, in combination with NaOH or $Ca(OH)_2$. Detailed analyses of precipitates formed during neutralisation of the process water confirm the presence of hydrotalcites as the primary mineral with the ability to simultaneously remove a suite of contaminants from solution during precipitation.

1. INTRODUCTION

Ranger Uranium Mine

Ranger Mine, owned by Energy Resources of Australia Ltd, is located approximately 250 km east of Darwin in the Northern Territory, Australia, and is surrounded by, but not part of, the World Heritage-listed Kakadu National Park. The Ranger orebody occurs predominantly as uraninite and coffinite within Proterozoic chloritic schist in an unconformity-related deposit. Ore has been mined and processed at Ranger since 1980 and the projected life of the operation currently extends to 2021. Mine production is typically around 5000 tonnes of U_3O_8 per annum produced using conventional sulfuric acid leach and solvent extraction techniques.

Hydrotalcite Chemistry

Hydrotalcites are a class of both naturally occurring and synthetically produced double layer hydroxide materials characterised by positively charged mixed metal hydroxide layers separated by interlayers that contain water molecules and a variety of exchangeable anions. Hydrotalcites are most commonly formed by the co-precipitation of divalent (e.g., Mg^{2+}, Fe^{2+}) and trivalent (e.g., Al^{3+}, Fe^{3+}) metal cations at moderate to high pH and may be represented by the general formula: $M_{(1-x)}^{2+} M_x^{3+} (OH)_2 A^{n-} y H_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively. The x value represents the proportion of the total metal ion content comprised of trivalent metal ions, A is an anion of n negative charge and y denotes variable amounts of interlayer water. Typically, M^{2+}:M^{3+} ratios in hydrotalcites vary from 2:1 to 3:1.

Hydrotalcites typically contain Mg^{2+} and Al^{3+}, but other cations, including Ni, Zn, Mn, Ca, Cr and La, have been observed. Where substantial Fe^{2+} or Fe^{3+} is contained within the hydrotalcite, potentially unstable fougerites (green rusts) may form. Hydrotalcites are well known for their capacity to remove both cationic and anionic contaminants via co-precipitation and/or ion-exchange mechanisms both during and after formation (Cavani et al., 1991; Miyata, 1983; Seida and Nakano, 2002). Thus, the formation of hydrotalcites is particularly well suited to application in Ranger process water given the diversity of cations present in addition to the domination of Mg^{2+} and Al^{3+}. A range of metals as cations (*e.g.*, Ni, Zn, Mn, Ca, Cr and La), major anions (SO_4^{2-}, HCO_3^-) or oxyanions (e.g., CrO_4^{2-}, UO_2^{2+}) may also be simultaneously co-precipitated, hence forming a polymetallic hydrotalcite with the degree of oxyanion incorporation within the interlayers strongly dependant on solution pH. This ability to simultaneously co-precipitate a suite of anionic and cationic contaminants is highly advantageous in treatment of contaminated waters.

Formation of Hydrotalcites in the Ranger Uranium Mine Context

Advantageously, the formation of hydrotalcites in Ranger process water, which forms the basis of this study, is favoured by high concentrations of both Mg^{2+} and Al^{3+} which dominate the aqueous cation geochemistry by virtue of the sulfuric acid co-dissolution of chloritic schists during ore extraction. Similarly, the anion chemistry is dominated by SO_4^{2-}. The generation of Ranger process water via the partial neutralisation of tailings slurry from *ca.* pH 2 to *ca.* pH 4 by the addition of lime as part of the current tailings treatment process ensures that considerable Ca^{2+} is also present. Also of note are the substantial Mn^{2+}, Mn^{4+} and N-NH_3 concentrations, a reflection of the metallurgical processes used to extract the ore. A typical chemistry of Ranger process water is given in Table 1.

Table 1. Composition of major and selected trace elements in Ranger process water prior to and following treatment with $NaAl(OH)_4$ + NaOH, $NaAl(OH)_4$ + $Ca(OH)_2$ or $Ca(OH)_2$ only.

Sample/ Analyte	**Ranger process water**	**$NaAl(OH)_4$ + NaOH**	**$NaAl(OH)_4$ + $Ca(OH)_2$**	**$Ca(OH)_2$ only**
	mg/L	mg/L	mg/L	mg/L
Na	61	10877	2831	124
K	129	79	107	110
Ca	543	153	461	642
Mg	6371	2	118	250
Cl	30	13	35	43
S-SO_4	37560	21920	7922	3340
Fe	49	0.1	0.1	0.0
Al	812	0	0	0
Mn	2907	0	0	1
N-NH_3	955	470	635	n/a
Tot Alk	0	3793	2481	1380
U	52.6	0.2	0.005	0.005
As	0.121	0.007	0.005	n/a
Cu	21.9	0.1	1.6	n/a
Pb	2.59	0.01	0.01	0.001
Se	0.27	0.03	0.02	0.01
Si	74.9	0.3	0.6	0.3

The typical Mg^{2+}:Al^{3+} molar ratio in Ranger process water is ~8.7:1, however, this ratio may vary significantly and may be substantially lower (~3-4) in the tailings slurry prior to lime addition. A ternary Mg-Fe(II),Fe(III)-Al system showing approximate stability domain for hydrotalcites in the presence of Fe(II) and Fe(III) waters and the approximate compositional range of Ranger Mine waters and mixing lines with an Al-rich source are presented in Figure 1.

Based on recent CSIRO research (Douglas, 2004; Douglas, 2009; Douglas et al., 2009), it was postulated that the formation of hydrotalcite with a suitable stoichiometry, *i.e.* a Mg^{2+}:Al^{3+} molar ratio of *ca.* 2:1 to 3:1, from the Mg-rich Ranger process water could be facilitated via aluminate addition from commercially-derived Bayer Process liquor. The addition of Bayer Process liquor serves three simultaneous purposes:

- reduction of the Mg^{2+}:Al^{3+} molar ratio to the desired range without significant Fe addition;
- raising of the pH (>5) sufficiently to form hydrotalcites; and,
- the provision of abundant carbonate/bicarbonate as a potential interlayer ion.

Thus, *in-situ* formation of hydrotalcites could constitute a viable option for the simultaneous removal and stabilisation of the broad spectrum of contaminants in the Ranger process water. Importantly, hydrotalcites, and in particular those that contain carbonate/bicarbonate as the predominant anion, have also been demonstrated to have a considerable capacity to neutralise a range of mineral acids via consumption of both the hydroxyl and carbonate anions contained within their structure (*e.g.,* Kameda et al., 2003). This neutralisation capacity may confer a particularly important characteristic as a mineral buffer intimately associated with the precipitate, which may also include tailings with a potential for long-term release of acidity.

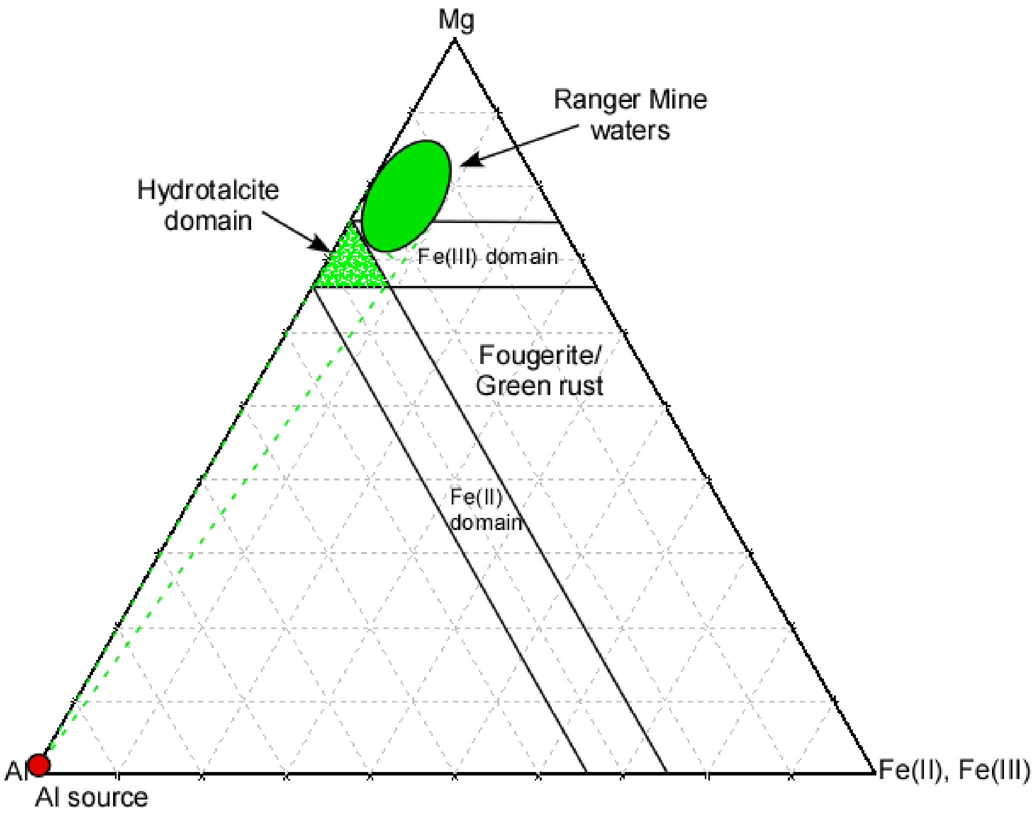

Figure 1. Ternary Mg-Fe(II),Fe(III)-Al system showing approximate stability domain for hydrotalcites in the presence of Fe(II) and Fe(III) waters. Approximate compositional variation of Ranger Mine process waters and mixing lines with an Al-rich source also shown.

There are many potential advantages of the use of Bayer Process liquor which is highly alkaline and contains Na-aluminate ($NaAl(OH)_4$) for hydrotalcite formation, in the context of treatment of Ranger process water or other types of acid mine waters elsewhere, in particular those that contain abundant Mg and/or Al. In addition to the “broad spectrum” removal of contaminants as elucidated above, specific advantages of hydrotalcites include:

- The kinetics of hydrotalcite formation are rapid (liquid-liquid mixing) and, once formed, hydrotalcites dewater rapidly, resulting in a high-solids concentrate. In contrast, lime-amended (liquid-solid mixing) precipitates frequently require more thorough mixing and mechanical de-watering or evaporation.
- During formation, *in-situ* hydrotalcite precipitation may promote entrainment or aggregation of colloidal or particulate material, thus increasing effluent clarity and solids removal.
- Hydrotalcites are stable at pH > *ca.* 5, depending on composition, and increase in stability with pH.
- Final pH can be tailored to incorporate particular anions, as carbonate is the most favoured interlayer anion up to pH ~ 11.5, while at pH ~8.5 a change in the carbonate-bicarbonate equilibrium takes place that allows for the potential incorporation of other anions.
- Hydrotalcites may also be further stabilised by the addition of interlayer silica which may polymerize after addition. This silicate-substituted hydrotalcite is similar in composition to the chlorite group of minerals, specifically amesite ($Mg_6Al_4Si_4Al_4O_{20}(OH)_{16}$), a chlorite mineral endmember. Thus, the potential exists for a substrate to be produced which is similar to that of the chlorite within the chloritic schists which host the Ranger mineralisation. If viewed in terms of its compatibility as a long-term repository, it would seem that this mineralogy may constitute an ideal solution to contaminant management.
- Hydrotalcite precipitation from Ranger process water has the potential to quantitatively remove Mg, Mn and Fe, added Al from aluminate in addition to a substantial proportion of SO_4 while only increasing Na via aluminate addition. This may make treated process water more amenable to reverse osmosis polishing.

2. METHODS

Titrations

Titration of Ranger process water was undertaken to evaluate the dynamics of precipitation and/or dissolution reactions over a range of pH conditions due to the addition of an alkaline titrant, specifically, aluminate + NaOH or aluminate + Milk of Lime (MOL). Commercial aluminate liquor generated from the Bayer Process was used. Titrations were performed using a Metrohm Dosimat 776 and a DT50 data logger to record pH values with alkali additions. Conditions varied with samples and reagents but titrations were generally performed on 20 mL aliquots at a rate of 0.1 mL every 10 seconds. A program loop was used to ensure alkali was added only up to the set pH target. Ranger process water samples were titrated with caustic (1M NaOH), MOL (1M $Ca(OH)_2$) and Na-aluminate (NaAl(OH)4). The MOL was constantly stirred to prevent settling.

All titrations were conducted in contact with the atmosphere to simulate the dissolution of ambient O2 and/or CO2 into the solution as might be expected to occur during a minesite-scale neutralization of the Ranger process water. Previous laboratory studies indicate that substantial equilibration times (typically days to months) over a range of pH are required (e.g., Scheidegger et al., 1998; Thompson et al., 1999; Bargar et al., 2000; Gu et al., 2003) for similar batch experiments, particularly involving U and trace elements.

Eight titration experiments were also completed (Table 2) with various M2+:M3+ ratios and alkali additions. Sampling of precipitates was carried out at final pH with the exception of Tests 5 and 6. In these tests, precipitates formed at lower pH were removed prior to final alkali addition. Precipitates recovered were analysed by X-ray diffraction (XRD) to determine the phases present, including hydrotalcite.

Table 2. Experimental conditions for hydrotalcite formation

Test #	$M^{2+}:M^{3+}$	Conditions for sampling
1	1	$NaAlO_2$ + NaOH to pH 12.5
2	1.5	$NaAlO_2$ + NaOH to pH 12.5
3	2	$NaAlO_2$ + NaOH to pH 12.5
4	3	$NaAlO_2$ + NaOH to pH 12.5
5	2	$NaAlO_2$ (pH=7.7), NaOH (pH=12.5)
6	3	$NaAlO_2$ (pH =6.85), NaOH (pH=12.5)
7	2	$NaAlO_2$ + $Ca(OH)_2$ to pH 10.6
8	3	$NaAlO_2$ + $Ca(OH)_2$ to pH 10.6

Sample Analysis

Ranger process water and supernatant solutions after alkali (NaOH, $Ca(OH)_2$ and/or $NaAl(OH)_4$) addition and precipitation reactions were analysed on a Perkin Elmer Elan 9000 inductively-coupled plasma-mass spectrometer (ICP-MS) or Optima 5300 ICP-optical emission spectrometer (ICP-OES) using standard laboratory methods (APHA, 2005).

Scanning Electron Microscope (SEM) Analysis

Samples of the precipitate slurries from each titration were dried overnight at 40°C. The dry precipitate of each sample was then thinly spread on carbon tape and sputter coated with carbon. The SEM used in this study was a Joel JSM-5800LV and was operated at 20 kV at a working distance of 12 mm. After visual analysis to select analytical targets, X-ray spectra were obtained on selected sample crystals via energy dispersive spectrometry (EDS). Locations of individual spectra were marked on images. Quantitative estimates of elements were made from spectra using WIN-EDS software. From the EDS output, Mg:Al mol ratios for each of the spectra were calculated.

Geochemical Modelling Using PHREEQC

To investigate the neutralization of Ranger process water using different sources of alkalinity, geochemical modelling was undertaken using PHREEQC for Windows V1.5.10 (Parkhurst, 1995). The primary aim of the modelling process was to fit a modelled pH curve to the observed data. Mineral phases were added to better fit the model to the actual titration curves. Thermodynamic data for hydrotalcite mineral phases were also added to the model during the addition of $NaAl(OH)_4$ to simulate the possible formation of these minerals.

3. RESULTS AND DISCUSSION

Influence of Alkali Addition on Ranger Process Water Solution Chemistry

Mineral precipitation brought about by the addition of alkali (NaOH, $Ca(OH)_2$ and/or Na-aluminate - $NaAl(OH)_4$) or $Ca(OH)_2$ confers substantial changes on the Ranger process water solution chemistry (Table 1). The most substantial changes occur in the form of large increases in Na and total alkalinity and reductions in Mg, Fe and Mn in both the aluminate + NaOH or aluminate + MOL additions. Reductions also occur in SO_4-S, particularly in the aluminate + MOL additions, due to the formation of gypsum where an increase in residual supernatant Ca also occurs. For the majority of other major and trace elements, there are similar reductions in residual supernatant solution concentrations irrespective of aluminate + NaOH or aluminate + MOL addition.

SEM and XRD Characterisation of Precipitates

Three separate approaches were used to characterise and/or identify the minerals, in particular investigation of the presence of hydrotalcite in precipitates produced by the titration of Na-aluminate into Ranger process water. First, on a purely thermodynamic basis, PHREEQC modelling (Parkhurst, 1995) indicated that it was possible that hydrotalcite was theoretically stable within the precipitates from Ranger process water via the addition of aluminate or MOL (Pleysier et al., 2008). Second, XRD analysis of the undifferentiated precipitates (Figure 2a – aluminate + NaOH, 2b aluminate + MOL, 2) indicated the possible presence of hydrotalcite within a precipitate collected after theoretical hydrotalcite precipitation only contained metal salts and brucite, but not hydrotalcite (2c – aluminate + NaOH final precipitate). Third, direct EDS analysis of single crystals (albeit appearing to be amorphous precipitates) confirmed the presence of an Mg-Al rich phase with a molar ratio consistent with hydrotalcite formation.

In contrast to synthetic hydrotalcites which often have a platy, hexagonal appearance, the precipitates formed from the titration of Na-aluminate into Ranger process water were predominantly amorphous, most likely reflecting the rapid precipitation and lack of ageing at elevated temperatures often used to produce crystalline synthetic hydrotalcites. In addition, the complex solution chemistry from which the hydrotalcites were derived, and the probable substitution of a variety of other ions, as suggested by the broad XRD peak at ~12 and 24 degrees, 2ϴ (Figures 2a, 2b), and the association of Mn with the hydrotalcite precipitates, may effectively prevent the formation of more crystalline phases with more sharply defined peaks. Substitution by Mn is common in synthetic hydrotalcites (e.g., Allada et al., 2002; Obalova and Fila, 2005), and likely here given the abundance of Mn in the Ranger process water. Although Mn-precipitates were also noted as a discrete phase forming late in the titration at high pH, the partial incorporation of Mn into hydrotalcite is a reasonable scenario for the fate of at least part of the Mn in the original solution. In addition to the incorporation of Mn and a range of trace elements into the hydroxyl structural layers within the hydrotalcite, there may also be a diversity of interlayer ions. Given the preponderance of sulphate (ca. 38,000 mg/L) in Ranger process water, it is likely that this is the major interlayer ion; however, other ions such as silicate may also be present.

Precipitates from four of the titrations (Table 2, titrations 3, 4, 7 and 8) were prepared for compositional analysis by SEM. The metal ratios (M2+:M3+) were 2:1 and 3:1 using both NaOH and MOL. In all, 11 images were obtained from the four samples with 18 EDS spectra obtained from individual crystals. The Mg:Al molar ratios for each of the spectra were calculated from the EDS spectra. Images of SEM analysis of precipitates are given in Pleysier et al. (2009).

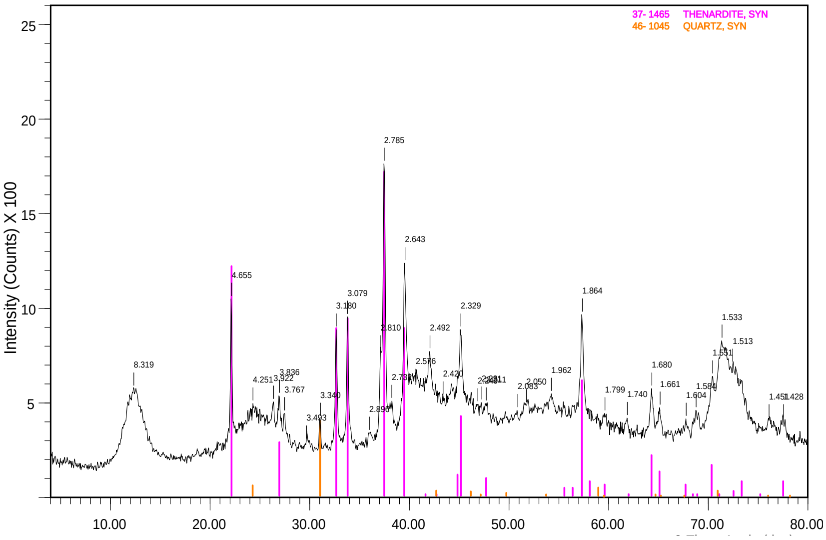

Figure 2a. X-ray diffraction analysis of final precipitate of a $NaAl(OH)_4$ + NaOH titration with a final Mg:Al ratio of 3:1. Broad peaks at ~12 and 24 degrees 2ϴ correspond to hydrotalcite.

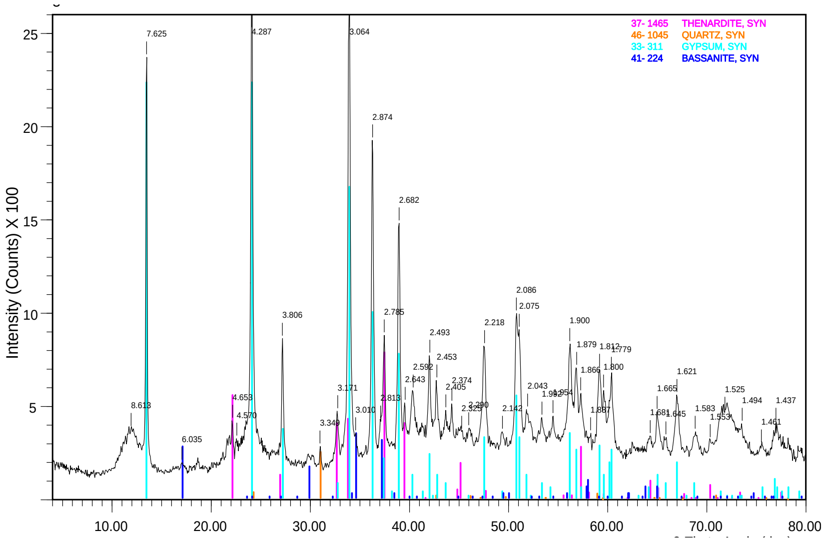

Figure 2b. X-ray diffraction analysis of final precipitate of a $NaAl(OH)_4$ + MOL titration with a final Mg:Al ratio of 3:1. Broad peaks at ~12 and 24 degrees 2ϴ correspond to hydrotalcite.

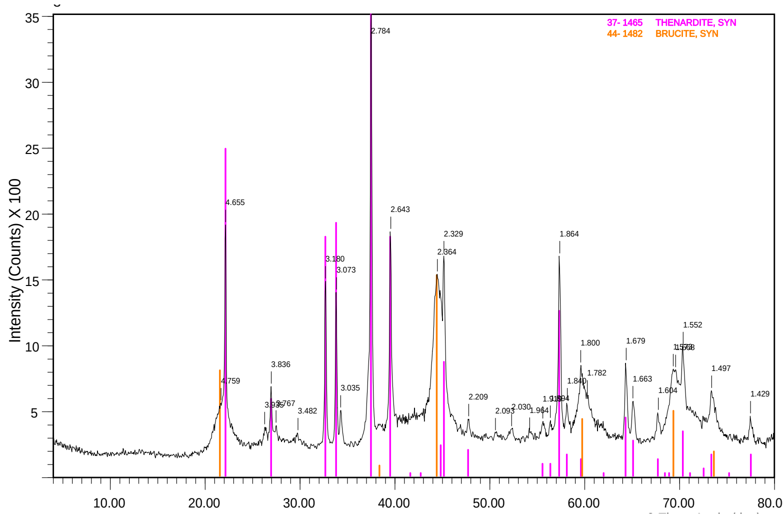

Figure 2c. X-ray diffraction analysis of final precipitate of a $NaAl(OH)_4$ + NaOH titration with a final Mg:Al ratio of 2:1. Lower pH precipitate removed prior to collection.

In general, Mg:Al ratios observed in individual hydrotalcite crystals by EDS were lower than those suggested by titration. In hydrotalcite crystals derived from solutions with Mg:Al ratios of 2:1 the precipitate ratio varied between 1.2 and 1.5, whilst crystals derived from solutions with Mg:Al ratios of 3:1 the precipitate ratio varied between 1.7 and 2.0. The lower Mg may be due to Mn-substitution as outlined above. The formation of other transient, non-hydrotalcite phases such as alunite or other phases that consume Mg or Al such as brucite, dolomite, or $Al(OH)_3$ as identified by PHREEQC modelling of the Ranger process water titrations may also have occurred (see later).

Detailed SEM/EDS analysis confirmed the presence of other abundant minerals as identified in XRD analysis, such as thenardite (Na_2SO_4), occurring as solitary crystals or aggregates and fine acicular aggregates of gypsum or bassanite ($CaSO_4.0.5H_2O$) adhering to the amorphous hydrotalcite surface where MOL addition follows aluminate. While the hydrotalcite would have consumed some of the sulphate as an interlayer ion, the reminder was consumed via precipitation with calcium from the MOL. The presence of thenardite is likely due to its precipitation during drying in preparation for SEM analysis. As postulated above, SEM/EDS analyses indicated that Mn was generally associated with the hydrotalcite precipitates.

Geochemical Modelling of Aluminate Addition

Modelling for alkali additions simulated the titration data well at low pH but generally produced lower equilibrium pH values at higher pH. Variation between actual and modelled solution pH may reflect non-equilibrium conditions due to differences in reaction kinetics, a condition noted by Gu et al. (2003). Aluminate titrations produced higher pH values and more complex curves than any of the modelling data (Figures 3a, 3b). In many cases inflection points in the Na-aluminate titration curves occur at similar locations to those in the modelled outcomes, however, differences in reaction kinetics may offset the actual point at which the reaction occurs or result in a different slope in the pH versus titrant addition curves.

In addition, the formation of transient mineral phases consuming Al, such as alunite and gibbsite, may also influence reaction kinetics.

Furthermore, the composition of the precipitating mineral phase may also be important as it has been previously noted that a diversity of cations, anions and oxyanions may partition into hydrotalcite minerals during precipitation.

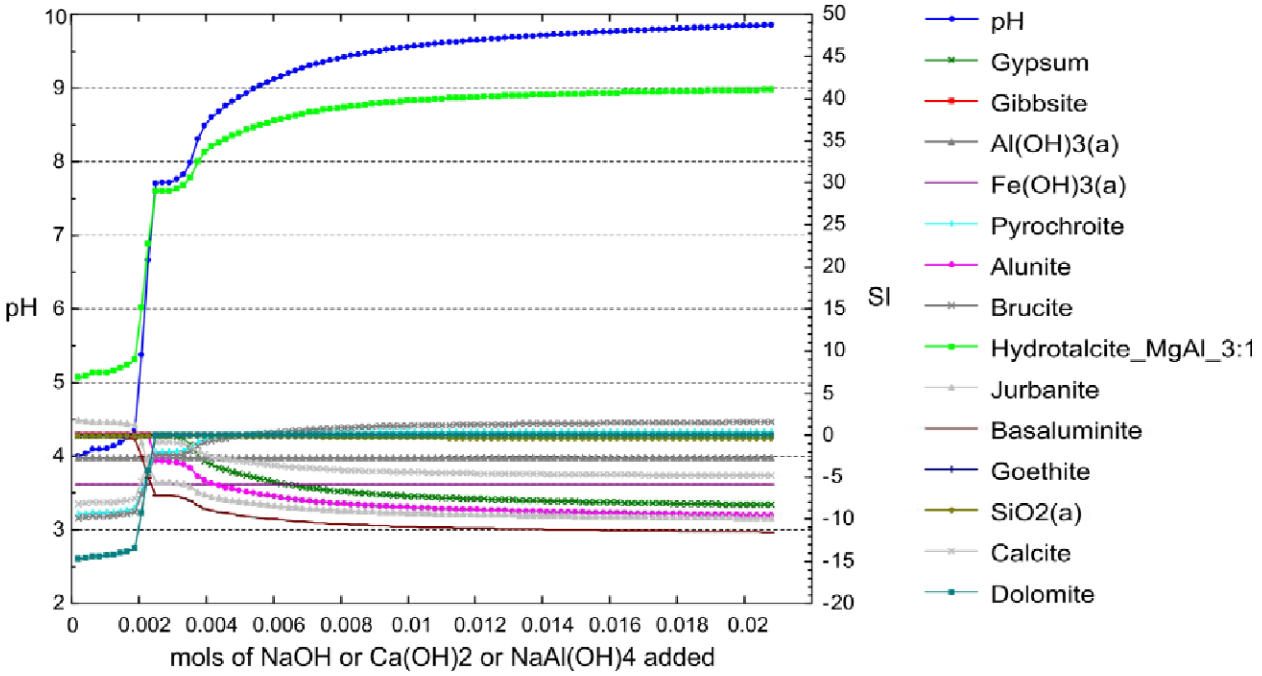

Figure 3a. Experiment 3: PHREEQC model data for pH and mineral saturation (SI) after addition of $NaAl(OH)_4$ to Ranger process water (see Table 1

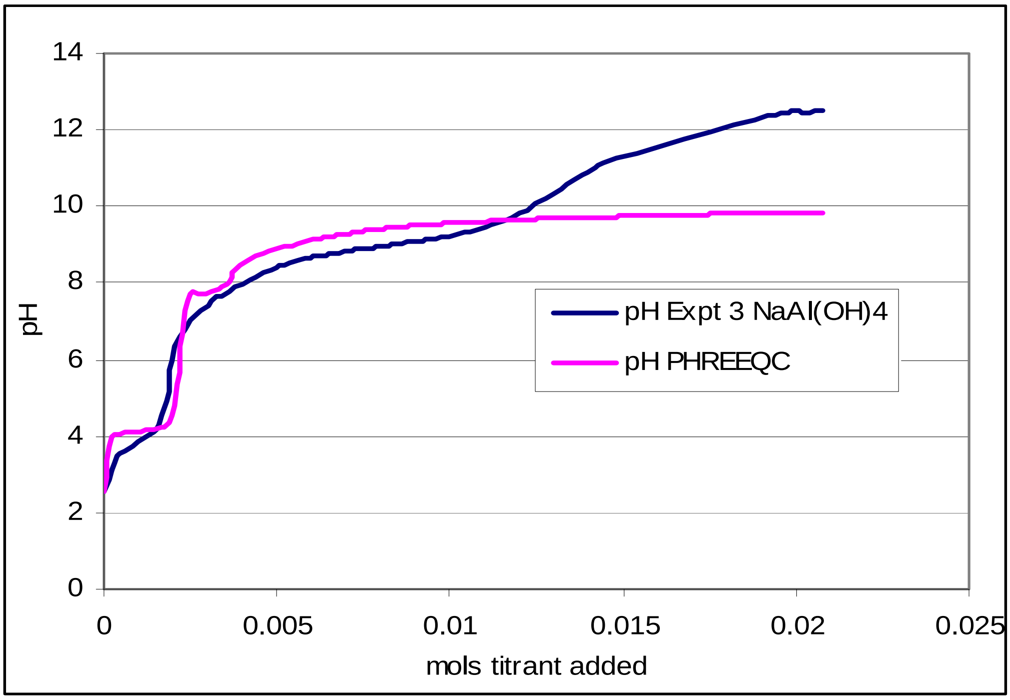

Figure 3b. Experiment 3: Comparison of PHREEQC model and empirical titration data after addition of $NaAl(OH)_4$ to Ranger process water (see Table 1)

4. CONCLUSIONS

Detailed analysis of the composition and mineralogy of precipitates and analysis of residual solutions indicates that the addition of aluminate, perhaps in combination with NaOH and/or MOL, to form hydrotalcites is a theoretically feasible method of treatment of Ranger process water. In addition to the simultaneous “broad spectrum” removal of a range of cationic, anionic and oxyanion contaminants, the rapidity of hydrotalcite precipitation, and the final mineralogy which may be amenable to further stabilisation via silication or calcination to a spinel-like mineralogy, confer a range of potential benefits over the existing treatment process using MOL addition. Acid mine waters or groundwaters from other mining or processing operations similarly enriched in Mg and/or Al and low in Fe may also potentially be treated via the formation of hydrotalcites (Douglas, 2004; Douglas, 2009) with the concomitant removal of a suite of other contaminants present in a variety of species.

If hydrotalcites were to be considered as a part of the treatment for Ranger process water, a source of low-cost aluminate and alkalinity is required. Similarly, at other mine sites, either aluminate (where Mg is in excess) or calcined magnesia (where Al is in excess) could be used as a source of Al or Mg and alkalinity.

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