Hydrotalcite Formation for Contaminant Removal from Ranger Mine Process Water

G. B. Douglas · L. A. Wendling · R. Pleysier · M. G. Trefry

Abstract Process water from the Ranger Uranium Mine requires treatment to meet stringent environmental water quality criteria. The acidic water contains substantial SO_4, metals, and U. One novel treatment method under consideration is the use of Na-aluminate to both neutralise the process water and precipitate hydrotalcites. Hydrotalcites are a class of Mg–Al layered double hydroxide minerals with a typical endmember chemical composition: $Mg_6Al_2(A)(OH)_{16} \cdot n(H_2O)$, where $A = CO_3^{2-}$, SO_4^{2-}, etc. Many acidic wastewaters contain Mg and/or Al in sufficient abundance for hydrotalcite formation upon addition of alkali to achieve solution pH > 5, and Mg and/or Al to attain a Mg:Al ratio of 2 to 3:1. The utility of hydrotalcites lies in their ability to incorporate a range of cationic (Cu^{2+}, UO_2^{2+}), metalloid (AsO_4^{3-}), and (oxy)anionic contaminants (CrO_4^{2-}). The broad spectrum removal of contaminants, including U, also indicates that hydrotalcites and their derivatives could potentially be used as a containment material in nuclear waste repositories. In this study, Ranger process water derived from extraction of U from chloritic schist was treated with Na-aluminate sourced from Bayer process liquor, in combination with NaOH or $Ca(OH)_2$. Hydrotalcites formed as the primary mineral during process water neutralisation with the ability to simultaneously remove a suite of contaminants from solution.

Keywords Hydrotalcite · Uranium · Wastewater

Introduction

Ranger Uranium Mine

Ranger Mine, owned by Energy Resources of Australia Ltd (ERA), 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 ore body 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 5,000 tonnes (t) per annum of U_3O_8, which is produced using conventional sulphuric acid leach and solvent extraction techniques.

Process Water Chemistry and Current Treatment

Acidic process water from Ranger Mine contains high concentrations of SO_4, Al, Mg, and Mn in addition to residual U. Given that the mine is surrounded by Kakadu National Park, a high level of treatment is required for process water to meet stringent environmental water quality criteria prior to discharge. One concept considered for a process water treatment plant would use milk of lime [$Ca(OH)_2$] and reverse osmosis to treat 1.5 GL/year to discharge 1 GL of high purity water, with a brine balance and 85,000 t of sludge by-product, the latter requiring

G. B. Douglas (✉) · L. A. Wendling · M. G. Trefry
CSIRO Land and Water, Private Bag #5, Wembley, WA 6913, Australia
e-mail: grant.douglas@csiro.au

R. Pleysier
Parker CRC for Integrated Hydrometallurgy Solutions, CSIRO Process Science and Engineering, Waterford, Australia

M. G. Trefry
School of Earth and Environment, University of Western Australia, Crawley, WA 6009, Australia

stable long-term storage. The low pH of the process water currently stored in a tailings dam precludes this as a storage option unless re-leaching can be prevented.

Extensive characterisation of Ranger process water and sludge generated from a pilot plant using the current lime treatment, including neutralisation characteristics, mineralogy, leaching, rheology, and particle size analysis was undertaken by Pleysier et al. (2008, 2009). These studies indicated a fine, thixotropic precipitate (p80 of 16 μm) was produced as a result of lime neutralisation. X-ray diffraction (XRD), thermogravimetric, calorimetric, and X-ray fluorescence (XRF) analyses indicated gypsum (74%) as the major precipitate with lesser amounts of Mg hydroxide (17%), Mn hydroxide (5%), and other metal hydroxides. Leach analysis of lime precipitates using deionised water, sulphuric acid, and process water indicated that the sludge was generally stable, with only Mg leachable with decreasing pH.

A variety of approaches to either modify the treatment process or the sludge to obtain a more stable material for long-term storage are currently being explored by ERA. One promising treatment uses a novel precipitation via sodium aluminate using aluminate liquor from Bayer refining to form hydrotalcites. Hydrotalcite chemistry and specific advantages of the formation of hydrotalcites in the specific context of Ranger Mine wastewater treatment and the formation and characterisation of these precipitates are explored in detail below.

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 (Cavani et al. 1991; Miyata 1983; Shin et al. 1996; Ulibarri et al. 2001). 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 (Taylor 1984). 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+} as the dominanat cations, but other cations, including Ni, Zn, Mn, Ca, Cr, Zr, and La, have been observed (Behrens et al. 2010; Depege et al. 1996; Koilraj and Kannan 2010; Vucelic et al. 1997). Where substantial Fe^{2+} or Fe^{3+} is contained within the hydrotalcite, potentially unstable fougerites (green rusts)

may form (Genin et al. 2001). 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 2000, 2002). Thus, the formation of hydrotalcites is particularly well suited to application in Ranger process water treatment 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+} (Miyata 1983; Taylor 1984), which dominate the aqueous cation geochemistry by virtue of the sulphuric acid co-dissolution of chloritic schists (which host the U mineralisation, Ludwig et al. 1987) 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 concentrations of Mn^{2+}, Mn^{4+}, and N-NH_3, a reflection of the metallurgical processes used to extract the ore.

The typical $Mg^{2+}:Al^{3+}$ molar ratio in Ranger process water is $\approx 8.7:1$, however, this ratio may vary significantly and may be substantially lower ($\approx 3-4$) 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 is presented in Fig. 1.

Based on recent CSIRO research (Douglas 2004, 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;
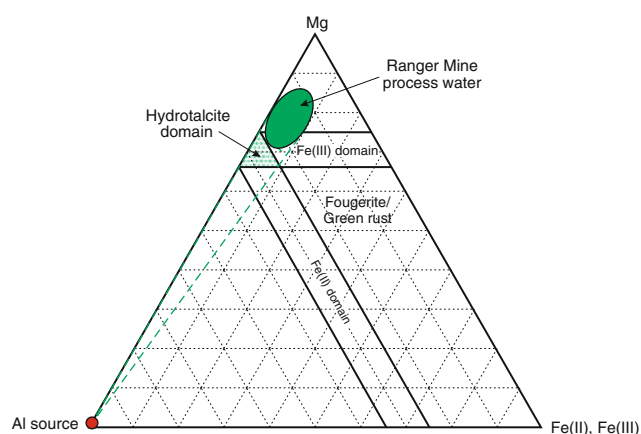
Fig. 1 Ternary Mg–Fe(II),Fe(III)-Al system showing approximate stability domain for hydrotalcites in the presence of Fe(II) and Fe(III) waters (modified after Feder et al. 2005). Approximate compositional variation of Ranger Mine process waters and mixing lines with an Al-rich source also shown

- raising of solution 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.

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:
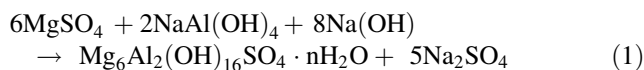
- The kinetics of hydrotalcite formation are rapid (liquid–liquid mixing) and, once formed, hydrotalcites dewater rapidly, resulting in a high-solids concentrate, as identified in this study. In contrast, lime-amended (liquid–solid mixing) precipitates frequently require more thorough mixing and mechanical dewatering, the use of flocculants, 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 a pH ≈ 11.5, while at pH ≈ 8.5, a change in the carbonate-bicarbonate equilibrium occurs 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 (Depege et al. 1996). This silicate-substituted hydrotalcite is similar in composition to the chlorite group of minerals, specifically amesite (Mg$_6$Al$_4$Si$_4$Al$_4$O$_{20}$(OH)$_{16}$), a chlorite mineral endmember. Thus, the potential exists for a substrate to be produced that is similar to that of the chlorite within the chloritic schists that 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, and the Al from the aluminate in addition to a substantial proportion of the SO$_4$ while only increasing Na (via the added aluminate). This may make treated process water more amenable to reverse osmosis polishing.

Methods

Titrations

Titration of Ranger process water was undertaken to evaluate precipitation and/or dissolution reactions over a range of pH (≈ 4 to 12) due to the addition of an alkaline titrant, specifically, aluminate + NaOH or aluminate + milk of lime (MOL). The two major reaction involved one of both of hydrotalcite formation via (1) addition of aluminate with excess NaOH contained in the Bayer process liquor to pre-existing Mg and Al in Ranger process water, or (2) gypsum precipitation via addition of lime to excess sulphate. These reactions are given below:

$$6MgSO_4 + 2NaAl(OH)_4 + 8Na(OH)$$
$$\rightarrow Mg_6Al_2(OH)_{16}SO_4 \cdot nH_2O + 5Na_2SO_4 \quad (1)$$

$$Ca(OH)_2 + SO_4^{2-} 2H^+ \rightarrow CaSO_4 \cdot 2H_2O \quad (2)$$

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 s. A program loop was used to ensure that alkali was added only up to the set pH target. Ranger process water samples were titrated with caustic (1 M NaOH), MOL (1 M 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 O$_2$ and/or CO$_2$ into the solution, as might 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. Bargar et al. 2000; Gu et al. 2003; Scheidegger et al. 1998; Thompson et al. 1999) for similar batch experiments, particularly involving U and trace elements.

Eight titration experiments were also completed (Table 1) with various M^{2+}:M^{3+} 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 XRD to determine the phases present, including hydrotalcite.

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 9,000 inductively-coupled plasma-mass spectrometer (ICP-MS) or Optima 5,300 ICP-optical emission spectrometer (ICP-OES) using standard laboratory methods (APHA 2005).

Scanning Electron Microscope Analysis

Samples of the precipitate slurries from each titration were dried overnight at 40°C below the gypsum-anhydrite

Table 1 Experimental conditions for hydrotalcite formation using NaAl(OH)$_4$ + either NaOH or Ca(OH)$_2$ to neutralise Ranger process water

Test #	M^{2+} :M^{3+}	Conditions for sampling
1	1	NaAl(OH)$_4$ + NaOH to pH 12.5
2	1.5	NaAl(OH)$_4$ + NaOH to pH 12.5
3	2	NaAl(OH)$_4$ + NaOH to pH 12.5
4	3	NaAl(OH)$_4$ + NaOH to pH 12.5
5	2	NaAl(OH)$_4$ (pH = 7.7), NaOH (pH = 12.5)
6	3	NaAl(OH)$_4$ (pH = 6.85), NaOH (pH = 12.5)
7	2	NaAl(OH)$_4$ + Ca(OH)$_2$ to pH 10.6
8	3	NaAl(OH)$_4$ + Ca(OH)$_2$ to pH 10.6

transition temperature. The dry precipitate of each sample was then thinly spread on carbon tape and sputter coated with carbon. The scanning electron microscope (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 (Allada et al. 2006) were also added to the model during the addition of NaAl(OH)$_4$ to simulate the possible formation of these minerals.

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 NaAl(OH)$_4$] substantially changes the Ranger process water solution chemistry (Table 2). The concentrations of Na and total alkalinity dramatically increase while the concentrations of Mg, Fe, and Mn decrease 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, 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

Table 2 Composition of major and selected trace elements (mg/L) 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
Na	61	10,877	2,831	124
K	129	79	107	110
Ca	543	153	461	642
Mg	6,371	2	118	250
Cl	30	13	35	43
S-SO$_4$	37,560	21,920	7,922	3,340
Fe	49	0.1	0.1	0.0
Al	812	0	0	0
Mn	2,907	0	0	1
N-NH$_3$	955	470	635	n/a
Total alkalinity	0	3,793	2,481	1,380
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

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 (Fig. 2a—aluminate + NaOH, Fig. 2b—aluminate + MOL) indicated the possible presence of hydrotalcite within a precipitate collected after hydrotalcite precipitation. A third precipitate collected after hydrotalcite precipitation and removal only contained metal salts and brucite, not hydrotalcite (Fig. 2c—aluminate + NaOH final precipitate). Third, direct EDS analysis of single particles (albeit, appearing to be amorphous precipitates) confirmed the presence of a 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 their rapid precipitation and the lack of ageing at elevated temperatures often used to produce crystalline synthetic hydrotalcites (Figs. 3, 4). 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 (Fig. 2a, b), 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 is 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 SO_4^{2-} (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 1, titrations 3, 4, 7, and 8) were prepared for compositional analysis by SEM. The metal ratios ($M^{2+}:M^{3+}$) 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.
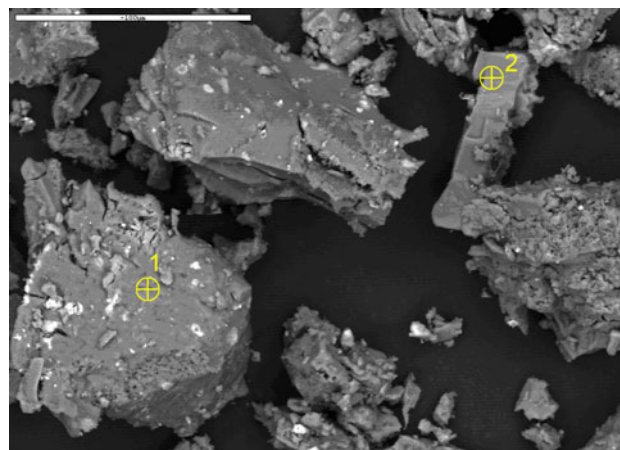
In general, Mg:Al ratios observed in individual hydrotalcite crystals by EDS were lower than those suggested by titration. In hydrotalcite crystals derived from solutions with Mg:Al ratios of 2:1, the precipitate ratio varied between 1.2 and 1.5, whilst crystals derived from solutions with Mg:Al ratios 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 (described in detail below).
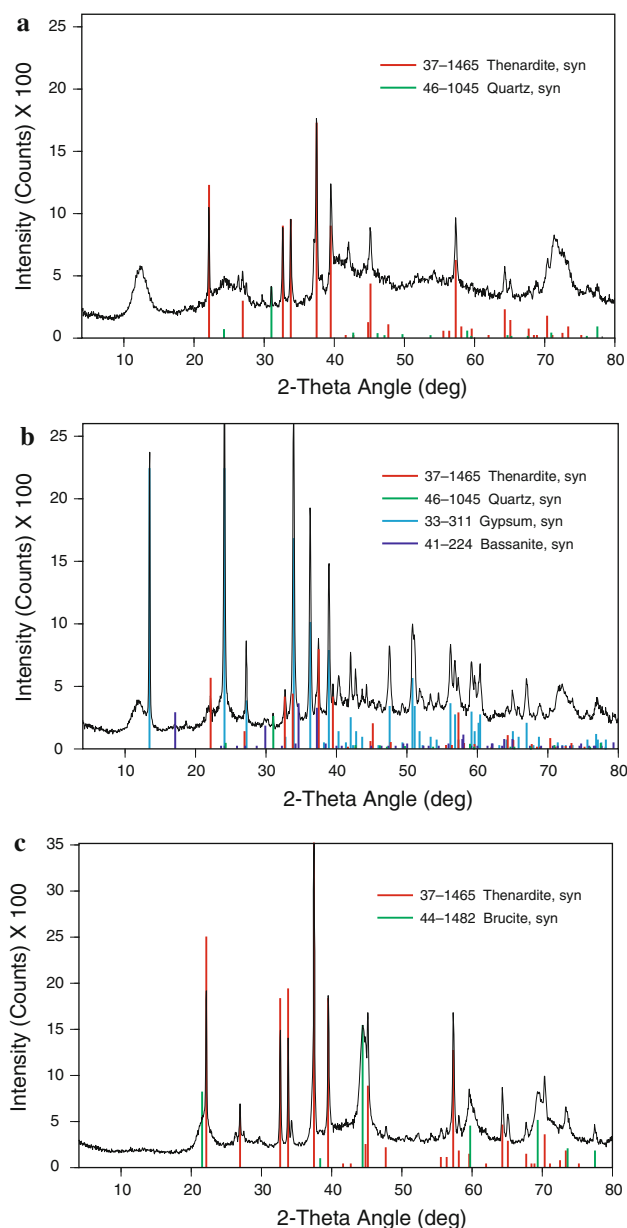
Fig. 2 **a** X-ray diffraction analysis of final precipitate of a NaAl(OH)$_4$ + NaOH titration with a final Mg:Al ratio of 3:1. Broad peaks at ≈ 12 and 24 degrees 2θ correspond to hydrotalcite. **b** X-ray diffraction analysis of final precipitate of a NaAl(OH)$_4$ + MOL titration with a final Mg:Al ratio of 3:1. Broad peaks at ≈ 12 and 24 degrees 2θ correspond to hydrotalcite. **c** 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

Fig. 3 Hydrotalcite crystal (1) and thenardite (2) precipitated from 3:1 titration with NaAl(OH)$_4$ + NaOH
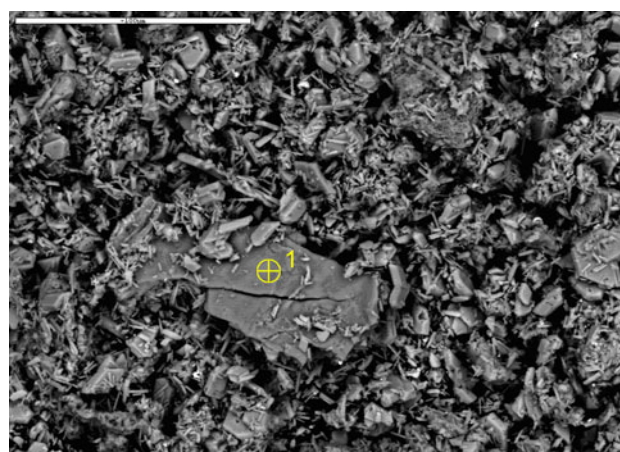
Fig. 4 Hydrotalcite crystal (1) in a mass of gypsum particles precipitated from 3:1 titration with NaAl(OH)$_4$ + Ca(OH)$_2$

Detailed SEM/EDS analysis confirmed the presence of other abundant minerals as identified in XRD analysis, such as thenardite (Na$_2$SO$_4$), occurring as solitary crystals or aggregates and fine acicular aggregates of gypsum or bassanite (CaSO$_4$·0.5H$_2$O) adhering to the amorphous hydrotalcite surface where MOL addition follows Na-aluminate. While the hydrotalcite would have consumed some of the SO$_4^{2-}$ as an interlayer ion, the reminder was consumed via precipitation with Ca 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.
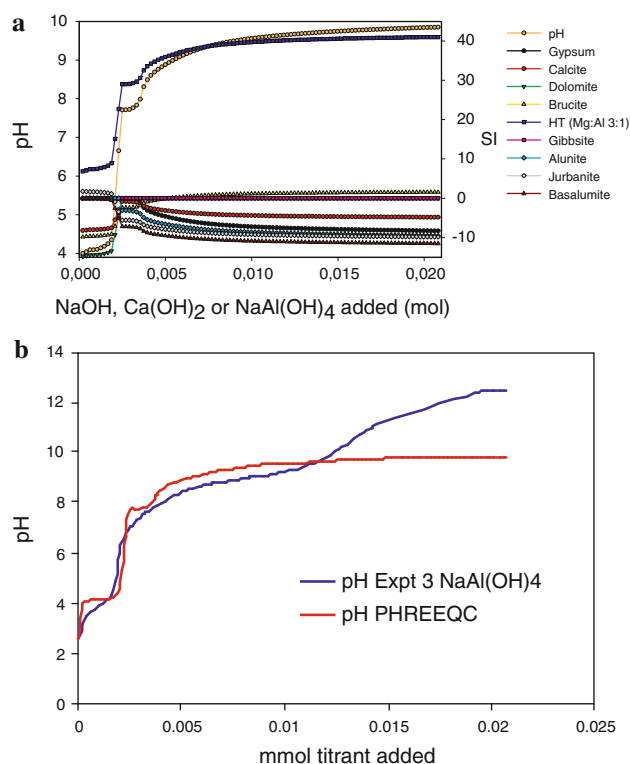
A typical precipitate by titration using a Mg:Al ratio of 3:1 with Na-aluminate and NaOH is given in Fig. 3. The hydrotalcite (1) crystal gave a Mg:Al ratio of 1.3 (via EDS). A similar image of hydrotalcite precipitated using Na-aluminate and lime is given in Fig. 4, shown within a mass of smaller gypsum particles.

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). Residual lime not modelled in this study, and perhaps present as aggregates within precipitates, may have also increased the final solution pH. Aluminate titrations produced higher pH values and more complex curves than any of the modelling data (Fig. 5a, b). 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 or intermediate mineral phases consuming Al, such as alunite and gibbsite, may also influence reaction kinetics.

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 can partition into hydrotalcite minerals during precipitation.

Conclusions

Detailed analysis of the composition and mineralogy of precipitates and analysis of residual solutions indicates that the addition of Na-aluminate, perhaps in combination with NaOH and/or MOL, to form hydrotalcites is a theoretically feasible method of treating 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 silicification 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, 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.

Fig. 5 a Experiment 3: PHREEQC model data for pH and mineral saturation (SI) after addition of $NaAl(OH)_4$ to Ranger process water (see Table 2). **b** Experiment 3: Comparison of PHREEQC model and empirical titration data after addition of $NaAl(OH)_4$ to Ranger process water (see Table 2)

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