Contaminant removal from acidic mine pit water via in situ hydrotalcite formation

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A R T I C L E   I N F O

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A B S T R A C T

Remediation of 56 ML of acidic, contaminant-laden Baal Gammon mine pit water was undertaken using in situ hydrotalcite formation. The pit water composition was modified via the addition of MgCl₂·6H₂O to form a 2.5:1 M²⁺:M³⁺ metal ion ratio followed by the addition of NaOH to increase the pH to 10 to induce spontaneous hydrotalcite precipitation. As a result of the in situ hydrotalcite precipitation a broad spectrum of elements of environmental concern including Al, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, Ni, V and Zn were removed from solution. Significantly, an ore grade hydrotalcite precipitate containing Cu (8.0 ± 1.0%) and Zn (3.9 ± 0.5%) was produced directly from the mine pit water column allowing for potential recovery of valuable metals to offset remediation costs. The final water quality produced after in situ remediation was of a simple Na–Cl–SO₄ type.

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1. Introduction

Lime- or limestone-based neutralisation has long been the treatment of choice of acidic tailings, acid mine drainage and mine pit wastewaters (e.g. Akcil and Koldas, 2006; Hedin et al., 1994; Johnson and Hallberg, 2005; Watten et al., 2005). While this approach is often well suited to the attenuation of acidity, the use of lime has been difficult to implement at some mine sites for a number of reasons including variable quality of the lime, proximity to the end use, and the frequent presence of unreacted lime after neutralisation due to partial loss of neutralisation efficiency due to armouring (e.g. Cravotta and Trahan, 1999; Hammerstrom et al., 2003; Santomartino and Webb, 2007; Ziemkiewicz et al., 1997) giving rise to the potential for unintended, latent reactions in the sludge or tailings.

Significantly, large volumes of gypsum are often produced that require mechanical dewatering, and where necessary, transportation to final voids to allow the resumption of in-pit mining or direct access to initiate remediation or final closure activities. Thus, the management of produced lime sludge over both the short and longer term may add substantial operational costs over that of the primary neutralisation step. In addition, lime production via limestone calcination is associated with large greenhouse gas (CO₂) emissions.

Research undertaken by CSIRO over the past seven years on the neutralisation of mine pit waters or In-Situ Recovery (ISR) barren lixiviant has highlighted the possibility that the addition of reagents other than lime could provide a pathway for effective neutralisation and contaminant removal (Douglas, 2006, 2009). In particular, the formation of hydrotalcite as a repository for a suite of cations and anions has been extensively investigated (Douglas et al., 2010, 2011, 2014).

1.1. Hydrotalcite formation and composition

Hydrotalcites are a class of layered double hydroxide materials characterised by positively charged mixed metal hydroxide layers separated by interlayers containing water molecules and exchangeable anions (Cavani et al., 1991; Miyata, 1983; Shin et al., 1996; Ulibarri et al., 2001). Hydrotalcites have the general formula: M₁₋ₓ/₂⁺ Mₓ/₃⁺ (OH)₂·Aⁿ⁻ y H₂O, where M²⁺ and M³⁺ are divalent and trivalent metal ions, respectively, x denotes the proportion of the total trivalent metal ions, A⁻ is an anion of n-negative charge, and y denotes the presence of interlayer water. Typically, M²⁺:M³⁺ ratios in hydrotalcites vary from 2:1 to 3:1. A suite of other cations, including Ni, Zn, Mn, Ca, Cr and La and anions such major anions (SO₄²⁻, HCO₃⁻) or oxyanions (e.g. CrO₄²⁻, UO₂²⁻) may occupy the hydrotalcite structure (Behrens et al., 2010; Cavani et al., 1991; Miyata, 1983; Seida and Nakano, 2002; Vucelic et al., 1997). It is this inherent capacity to substitute a range of anions and cations into the hydrotalcite structure when formed in-situ that can be productively exploited to remove contaminants from mine and other wastewaters.

In addition to the potential for broad spectrum removal of contaminants as elucidated above, other specific advantages of
hydrotalcite formation include: rapid kinetics of formation, the ability to entrain particulate or colloidal material when formed in-situ, and the prospect of further stabilisation via the addition of interlayer silica which may polymerize after addition (Depege et al., 1996) or calcination to form a spinel.

1.2. Hydrotalcite formation in the context of Baal Gammon mine pit water neutralisation and contaminant removal

A common feature of acid mine wastewaters, often overlooked in analysis of potential neutralisation and contaminant removal options, is the frequent predominance of divalent (M\(^{2+}\)) and trivalent cations (M\(^{3+}\)), particularly Mg and Al, as a consequence of partial decomposition of gangue minerals (e.g. from aluminosilicate minerals) during in-pit wall rock leaching or ore processing.

Given the presence of substantial Mg and Al in the Baal Gammon mine pit water (Table 1), an opportunity existed to exploit, and in effect, work in harmony with the prevailing pit water composition. Thus M\(^{2+}\) cations (Mg + Cu + Zn), coupled with M\(^{3+}\) cations (Al + Fe) in an appropriate ratio, form the basis of hydrotalcite precipitation. With a pre-treatment M\(^{2+}\):M\(^{3+}\) ratio of ca. 0.79 this focused on the sequential addition of Mg and NaOH to the Baal Gammon mine pit lake to:

1. Modify the prevailing M\(^{2+}\):M\(^{3+}\) ratio to 2.5 which was within the known stability range of hydrotalcites.
2. Attenuate the existing acidity to facilitate the in-situ precipitation of hydrotalcites as a major secondary mineral.

2. Baal Gammon mine and pit characteristics

2.1. Baal Gammon regional and mine pit geology

The Baal Gammon mineralisation is hosted by Hodgkinson Formation sediments that have been invaded by a porphyritic sill which hosts both Cu, Ag and lesser In within a series of sulphide minerals including pyrrhotite, chalcopyrite, arsenopyrite and lesser pyrite. The Sn occurs in both with a tourmaline-cassiterite association and also in Sn sulphides such as stannites.

The Baal Gammon mine pit hosts a resource of 2.8Mt @ 1% Cu, 40 g/t Ag, 0.2% Sn and 39 g/t In. A high grade zone identified within the resource consists of 829kt @ 2.5% Cu, 96 g/t Ag, 0.4% Sn and 96 g/t In (Anon, 2013). Active mining of the Baal Gammon pit last occurred in 2012. The in-situ treatment of the acidic mine pit water was proposed to allow for a resumption of mining in early 2014.

The Baal Gammon mine pit is an irregular ovoid shape with long axes of approximately 120 m and 80 m. At 56 ML pit volume, the maximum depth is approximately nine metres in a small depression just off centre of the pit, while elsewhere, due to its mostly flat floor, the pit depth mostly varies between three and six metres.

The mine pit and its immediate catchment have an area of approximately three hectares. The immediate pit surrounds consist of rock bunds and access roads with a sand covered pad for location of pumps, and tanks used to deliver reagents and as the site for a mobile Reverse Osmosis (RO plant) used to remove residual salts remaining after in-situ remediation and prior to filtrate discharge to an adjacent creek.

Portions of the pit walls have characteristic blue malachite colour due to oxidation of the chalcopyrite mineralisation. Small groundwaters seepages and white efflorescences were also observable indicating transport of saline, possibly acidic groundwater from old workings above the pit.

3. Methods

3.1. Baal Gammon mine pit treatment

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na – Not analysed.
dissolution of each batch, the dissolved MgCl₂·6H₂O was sprayed onto the pit surface using a pontoon mounted sprinkler system which was periodically moved via attached cables to ensure an even distribution over the pit surface. In addition, large pumps located on the pit edge (pumping capacity of 11 ML/day, or approximately 20% of the pit volume) were also used concurrently to assist in circulating the pit solute to enhance mixing. After addition of the MgCl₂·6H₂O, the pit water was circulated for almost three days. Thereafter, 132 tonnes of 50% w/w NaOH was added from 1000 L Intermediate Bulk Containers (IBC) via gravity feed to an eight outlet manifold discharging approximately 3 m below pit lake surface. During this time continuous bottom to surface recirculation via multiple collection and re-injection points was maintained. An additional of 57 tonnes of 50% NaOH diluted to 1% w/w was then added to immediate subsurface via a ring shaped manifold of 100 m circumference (Supplementary Fig. 1). Continuous bottom to surface recirculation via multiple collection and re-injection points was then continued for a further five days.

3.2. Chemical analyses

3.2.1. Major and trace element analysis of Baal Gammon mine pit waters

Mine pit water samples collected pre- and post-treatment were submitted to SGS Environmental, Cairns, Queensland and/or the ChemCentre, Waterford, Western Australia. All analytical methods (e.g. pH, EC nutrient species and alkalinity) were based on American Public Health Association (APHA) (2005).

3.2.2. X-ray fluorescence (XRF) precipitate analysis – fusion

Hydrotalcite precipitate analysis using XRF for major elements (wt.% oxides): SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, SO₃, and trace elements (µg/g): Ba, Ce, Cl, Cr, Co, Cu, Ga, La, Ni, Nb, Pb, Rb, S, Sr, V, Y, Zn, and Zr using fused glass discs (Norrish and Chappell, 1977), at CSIRO Land and Water, Adelaide. Dried samples (105°C) of 1 g were accurately weighed with 4 g of 12:22 Li tetra/metaborate flux, fused at 1,050°C in a Pt/Au crucible for 20 min then poured into a 32 mm Pt/Au heated mould and cooled quickly over compressed air. The resulting glass disks were analysed on a Philips PW1480 wavelength dispersive XRF system using a dual anode Sc/Mo tube and CSIRO algorithms.

3.2.3. X-ray fluorescence (XRF) precipitate analysis – pressed powders

Samples were analysed by XRF for major elements (wt.% element): Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, S, and trace elements (µg/g): Ag, As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, I, In, La, Mo, Ni, Nb, Nd, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, and Zr using pressed powders with 4 g of each sample was accurately weighed with 1 g of Licowax binder and shaken for 30 s and pressed to 10 t with a boric acid backing. The pellets were analysed on a Spectro X-Lab 2000 energy dispersive XRF system using a Pd X-ray tube with secondary excitation targets.

3.2.4. Sediment fractionation

Bottom sediment – unfractionated, Suspended sediment – unfractionated: One gram subsamples were micronized for 10 min under ethanol, oven dried at 60°C then mixed in an agate mortar and pestle.

Bottom sediment 0.2–2 µm fraction and < 0.2 µm fraction: Both the 0.2–2 µm and < 0.2 µm fractions were separated using a sequential centrifugation steps (5000 g for up to two hours), addition of Calgon® (0.25 wt.% Na hexametaphosphate and 0.25 wt.% Na carbonate solution) as a dispersant, and decantation of the supernatant. Sonication, washing with distilled water and re-centrifugation was used to remove dissolved salts. Both fractionated samples were dried at 60°C prior to analysis.
3.2.5. X-ray diffraction (XRD) analysis

Finely powdered samples or sample fractions were lightly back pressed into stainless steel holders. The XRD patterns were recorded in steps of 0.05° 2θ with a 0.5 s count time per step with a PANalytical X’Pert Pro microprocessor-controlled diffractometer using Co Kα radiation, automatic divergence slit, graphite post-diffraction monochromator and X'Celerator fast Si strip detector.

4. Results

4.1. Pit water characteristics – physico-chemical parameters

Monitoring of the Baal Gammon pit water indicated substantial variability in a range of physico-chemical parameters as recorded by in-situ sondes in the 22 day period from 29/10/2013 to 19/11/2013. Individual parameters are shown in Fig. 2 and are discussed below:

Temperature (°C): Surface and bottom temperatures displayed a diurnal cycle. During the initial period between 29/10/2013 and 31/10/2013 and later in the period between 17/11/2013 and 19/11/2013 when in-situ mixing was not occurring a distinct temperature stratification between surface and bottom waters of ca. 1.0–1.5 °C was maintained with occasionally greater excursions due to increased surface layer heating. Once in-situ mixing of the pit occurred, however, in the period 31/10/2013 to 17/11/2013 only shorter periods of temperature stratification, (up to 1 °C) were evident in the morning and afternoon with no temperature stratification evident overnight.

Electrical conductivity (EC, µS/cm): Prior to in-situ mixing bottom EC was slightly higher than that of the surface. Upon addition of the majority of the MgCl₂·6H₂O and in-situ mixing, both surface and bottom EC increased rapidly by ca. 40% with the higher EC in the bottom maintained to a similar extent to that originally present. With continued mixing and additional minor MgCl₂·6H₂O added on 1/11/2013 small fluctuations in EC continued to occur. Thereafter, continued mixing of the pit results in increasing convergence of the surface and bottom EC. Upon the addition of NaOH commencing 3/11/2013, approximately a 10% increase in EC occurred with a similar EC maintained in the surface and bottom waters. Upon the cessation of NaOH addition on 15/11/2013 there was a notable divergence-convergence step in the bottom water EC temporally corresponding to water column temperature fluctuations.

pH: Surface and bottom water pH remained similar even during and after the addition of MgCl₂·6H₂O which had a similar pH to that of the pit waters. A substantial increase in pH occurred in both surface and bottom waters after the commencement of addition of NaOH on 3/11/2013. Slightly larger upward pH excursions in the bottom waters reflected the density-driven settling of the 50% w/w NaOH solution. Three substantial increases in both surface and bottom water pH (again initially higher in the bottom waters but equalised during subsequent mixing) commencing 12, 14 and 15/12/2013 respectively, elevated the final surface and bottom pH to approximately 10. Thereafter, there was a small near linear decline in the surface water pH by approximately 1 pH unit over the subsequent four days, while the bottom water pH displayed a similarly erratic pattern to that of temperature and EC.

Redox potential (Eh mV): After the completion of the addition of the majority of MgCl₂·6H₂O on 31/10/2013, the Eh of surface and bottom waters was similar and remained so until the commencement of the addition of NaOH on 3/11/2013. Thereafter, the Eh began to decline rapidly in both surface and bottom waters with similar excursions in Eh in bottom waters to that observed in pH. A substantial divergence on Eh occurred after the application of additional NaOH on 13/11/2013 with Eh up to 100 mV lower in the bottom waters than the surface waters with perturbations occurring with each additional application of NaOH on 12, 14 and 15/11/2013.

Turbidity (Nephelometric Turbidity Units – NTU): Turbidity was similar in both surface and bottom waters for a large portion of the treatment of the mine pit increasing from 0.1 to 20 NTU in the period 29/10/2013 to 13/11/2013. Upon the addition of NaOH on 12, 14 and 15/12/2013 respectively, large increases in bottom water turbidity occurred, likely exceeding the maximum turbidity

![Fig. 2. Time series of water quality parameters; temperature, electrical conductivity (EC), pH, redox potential (Eh), turbidity (NTU) and dissolved oxygen (percent saturation) for the period 29/10/2013 to 19/11/2013 in the Baal Gammon mine pit.](image-url)
range of the probe (1600 NTU). A decline in turbidity in the bottom waters similar to that observed in surface waters occurred in the period after the second addition of NaOH on 14/11/2013 and prior to the final addition on 15/11/2013.

Dissolved oxygen (DO, percent saturation): Dissolved oxygen remained similar in both the surface and bottom waters at between 50% and 90% saturation. The close correspondence of the DO saturation in both surface and bottom waters persisted even after the addition of MgCl₂·6H₂O and subsequent mixing of the pit. After the final addition of NaOH on 15/11/2013, however, there was an antithetic trend with a large decline in bottom water DO saturation to as low as 30% while surface water DO saturation increased from approximately 70% to 85% saturation.

4.2. Pit water characteristics – major and trace element chemistry

Pre-treatment: Prior to treatment, the Baal Gammon mine pit chemistry was highly acidic (pH 2.9, Table 1), and contained only low concentrations of most major cations and anions except for SO₄ (1247 mg/L) and F (59 mg/L). Substantial trace element enrichments were present for Al (70 mg/L), Cu (40 mg/L), Fe (59 mg/L), Mn (16 mg/L), Si (60 mg/L) and Zn (22 mg/L).

Post-treatment: After the cessation of treatment of the Baal Gammon mine pit both the major and trace element chemistry of both surface and bottom waters were substantially modified (Table 1). In terms of major elements, the Na concentration increased (34–4100 mg/L) while most other major elements were of similar concentrations except for F which was approximately halved from 59 mg/L to 33–35 mg/L. A suite of trace elements were significantly reduced in both the surface and bottom waters after treatment, many to below detection limits (As, Co, Cr, Cu, In, Mo, Ni, Pb, Sb, V and Zn). Additionally, many other trace elements were also significantly reduced after treatment including Al, Cd, In, Fe, Mn, and Si, with many reduced by at least 95%, with some exceeding 99% removal (Table 1).

Reverse osmosis: Reverse osmosis processing of the treated Baal Gammon mine pit water yielded a filtrate largely denuded of all major ions with substantial reductions in Na, SO₄ and F (Table 1). In addition, a range of trace element concentrations were further reduced.

4.3. Mineralogy of bottom and suspended sediment samples

Mineralogical analysis of bottom and suspended sediment samples collected from the Baal Gammon mine pit after hydrotalcite precipitation reveals a range of associations (Fig. 3). Within the unfractionated bottom sediment, hydrotalcite is present in addition to pre-existing quartz, illite, kaolinite and goethite that reflect the prevailing pit geology. Although some of the hydrotalcite and other mineral peaks coincide, characteristics peaks particularly at 13° ±, but also at 26.5°, and 40° and 73° ± confirm its presence. Fractionation of the bottom sediment into 0.2–2 μm and >0.2 μm fractions reveals an increasing enrichment in hydrotalcite and corresponding reduction in the abundance of quartz, illite and kaolinite and an absence of goethite. Unfractionated suspended sediment has the simplest mineralogy of all samples being dominated by hydrotalcite and lesser illite. Often broad hydrotalcite peaks may indicate a variable composition and/or degree of hydration.

4.4. Geochemical composition of hydrotalcite precipitates

Analysis of hydrotalcite precipitates from the Baal Gammon mine pit water indicates a precipitate enriched in Mg + Cu + Zn + Mn as the major divalent cations, (all expressed as MgO in Fig. 4) and Al₂O₃ commensurate with hydrotalcite chemistry/stoichiometry (Table 2). Anions present within the hydrotalcite interlayers are dominated by sulphate (13.58% as SO₄), however Si (7.19% as SiO₂) may also be present as the silicate anion or alternatively as colloidal silica or minor suspended clay minerals entrained during hydrotalcite precipitation. The majority of Na and Cl are due to halite precipitation as observed in SEM analysis. Calculated divalent (Mg + Cu + Zn + Mn) to trivalent (Al) molar ratios are 2.07 ± 0.11 in accordance with typical hydrotalcite stoichiometry of 2:1 to 4:1. Also of note is the presence of elevated mean concentrations of both Cu (8.00 ± 1.00%) and Zn (3.87 ± 0.53%).

5. Discussion

5.1. Hydrotalcite formation in the Baal Gammon mine pit context

Advantageously, the Baal Gammon pit water contained abundant Mg and Al (both 70 mg/L, Table 1) which functioned as (partial) building blocks for in-situ hydrotalcite formation (Miyata, 1983; Taylor, 1984). Based on recent research (Douglas et al., 2010, 2011), it was postulated that the formation of hydrotalcite with a suitable stoichiometry, i.e. a M²⁺:M³⁺ molar ratio of ca. 2.5, could be facilitated via addition of Mg (as MgCl₂·6H₂O). With progressive addition of Mg, the Baal Gammon mine pit water would follow a compositional trajectory defined by the solid and dashed mixing lines in Fig. 4. The addition of Mg was designed to yield a final M²⁺:M³⁺ molar ratio of 2.5 that occupied a position well within the hydrotalcite stability field. In addition, this ratio was sufficiently above that of the lower hydrotalcite M²⁺:M³⁺ compositional molar ratio of 2 to allow an operational margin for spatial or vertical variation within the pit water composition. This variation was likely due to surface or groundwater flow of a different composition or in-situ physical pit lake stratification that may have induced geochemical changes to redox-sensitive elements such as Fe.

Based on the pre-existing composition of the Baal Gammon mine pit water, in-situ formation of hydrotalcites was considered on a geochemical basis as the most viable option for the simultaneous removal and stabilisation of the broad spectrum of contaminants present. Importantly, hydrotalcites, and in particular those that contain either carbonate and/or 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 in the event that the hydrotalcite-based precipitate were exposed to additional acidity during or after disposal.

An SEM analyse of precipitates formed in situ from the Baal Gammon mine pit water document the present of extensive face-to-face layered aggregates of partially rounded hexagonal 0.2–0.5 μm hydrotalcite crystals (Fig. 5). Compositional (EDAX) analyses indicate that while the hydrotalcite is as expected enriched in Mg due to the addition of Mg (as MgCl₂·6H₂O), it is slightly less enriched than the theoretical estimate (Table 2, Fig. 4). The precipitate, however, is less enriched in Fe than the theoretical estimate. These variations may reflect in part the present of co-existing/co-precipitated illite (Fig. 3) with a general formula of K₀.₆₅Al₂.O₂[Al₉.₆₅Si₃.₃₅O₁₀](OH)₂ but with the possibility of some impurities being present: (K₂O)[Al₉.₆₅Si₃.₃₅O₁₀](OH)₂ such that the Baal Gammon mine pit water precipitate would lie on a compositional line away from the theoretical compositional estimate and towards a slightly more Al -rich position on the Mg-Al compositional line as observed (Fig. 4). The slightly lower M²⁺: M³⁺ of 2.07 ± 0.11 as determined by SEM-EDAX in the water column precipitate is also consistent with the presence of illite most prominent in the unfractinnoned bottom sediment samples (Fig. 3).

G.B. Douglas / Applied Geochemistry 51 (2014) 15–22
Alternatively, the compositional variation away from the theoretical prediction indicates some internal spatial variation in the composition of the Baal Gammon mine pit due to factors influencing pit water composition such as groundwater inputs (with a possibly different composition) as outlined above. Nonetheless, as required, the hydrotalcite precipitate formed sits well within the theoretical stability domain (Fig. 4).

5.2. Mode of hydrotalcite formation within the Baal Gammon mine pit water

The removal of a range of major and trace element cations is consistent with the solubility of metal hydroxide species which are progressively incorporated into the hydrotalcite structure. In particular there is a cascade of metal hydroxide precipitation reactions with increasing pH (Fig. 6).

Following initial NaOH addition, Al is progressively precipitated with a solubility minimum at approximately pH 6, thereafter redisolving to form the soluble aluminate (Al(OH)$_3^-$) anion with increasing pH. Analysis of temporal trends in pH and turbidity...
(Fig. 2) exemplify this process. With increasing surface and bottom pit water pH from ca. 4 to 8 commencing on 12/11/2013, there was a substantial increase in bottom water turbidity exceeding 1600 NTU corresponding to Al(OH)$_3$ formation/precipitation. Thereafter, with increasing pH the bottom water turbidity rapidly declined as re-dissolution of Al(OH)$_3$ occurred with the aluminate anion predominating at pH 8.5 to 9.0 (commencing 14/11/2013). With ongoing NaOH addition to increase surface and bottom pit water pH from 8 to 10, with the progressive formation of brucite (Mg(OH)$_2$), and the self assembly of hydrotalcite, the bottom water turbidity again increased rapidly to exceed 1600 NTU as the hydrotalcite precipitate rapidly settled into the base of the pit water column.

Similar to the precipitation/re-dissolution of Al, a range of other metals began to precipitate with a range of solubility minima predominantly between pH 8 and 10. These precipitated metal hydroxides isomorphically substituted for Mg and Al as self assembly occurred to form a multi-element hydrotalcite (Fig. 6).

Upon the final addition of NaOH to the Baal Gammon mine pit, and with this the spontaneous formation of hydrotalcite in-situ, and an increase in particle size due to aggregation and nucleation on suspended clays, rapid settling occurred. This process reflected a major divergence in turbidity manifested as a low surface pH of approximately 2–5 NTU and the sustained high turbidity in the bottom waters that exceed 1600 NTU (Fig. 2). Importantly, within three days of the completion of hydrotalcite precipitation, the clarity of the pit water had increased to approximately 7 m indicating an on-going settling and consolidation of the hydrotalcite-based precipitate. The rapid settling of hydrotalcite formed in-situ paralleled that observed in initial laboratory-based neutralisation experiments used in the experimental planning of the in-situ pit remediation.

Concomitant with the high final pH of the water column of approximately 10, absorption of atmospheric CO$_2$, primarily as a result of wind mixing of the pit surface resulted in a gradual pH decline that was not manifested in the bottom layer after cessation of active mixing of the pit water column. This relative change in the pH profile is important for two reasons. Firstly, with increasing time, the surface pH would decrease and buffer with bicarbonate (HCO$_3^-$) formation to ca. 8.5, (Table 1). Secondly, the higher pH in the bottom of the pit water column would ensure maintenance of optimal conditions for hydrotalcite formation. Nonetheless, even if the pH in the bottom of the pit declined, the hydrotalcite would remain stable, albeit with a possibly increased propensity for anion exchange as HCO$_3^-$ replaced (partial) CO$_3^{2-}$ occupation of interlayer sites. With sufficient time it could be expected that as in the upper water column, with natural mixing, or if convective overturn was induced via artificial means, the lower water column would also achieve a final pH of ca. 8.5.

5.3. Outcomes following hydrotalcite formation in the Baal Gammon mine pit

In-situ hydrotalcite precipitation to treat 56 ML of water contained within the Baal Gammon mine pit conferred major changes in water quality consistent with theoretical predictions. Following the neutralisation of the pit and the precipitation of a multi-element hydrotalcite, the chemistry of the solute assumed a predominantly Na–Cl–SO$_4$ composition impoverished in a range of trace elements (Table 1).

In the context of additional treatment by RO, of particular importance was the low post-treatment concentration of Si which was reduced by approximately 98% to 1.3 mg/L. This reduction in Si combined with the low concentrations of a suite of other elements allows for the enhanced recovery of solute via RO. Results of RO treatment (Table 1) indicate that the filtrate produced satisfied proposed water release criteria.

The presence of elevated mean concentrations of both Cu (8.00 ± 1.00%) and Zn (3.87 ± 0.53%) in the hydrotalcite precipitate is particularly significant in the context of the reprocessing to recover metal value that can offset remediation costs. Both metal concentrations are of ore grade, and given their geochemical form, a potential exists to redissolve the hydrotalcite via the addition of acid to a pH of below ca. 4 and recovery via ion-exchange from the resulting solute. This method is particularly applicable to a pump-and-treat scenario where high purity hydrotalcite, uncontaminated by mixing with pit sediments could be produced by suitable on-line addition of reagents.

The application of in-situ hydrotalcite precipitation also resulted in low residual sludge volumes (Supplementary Fig. 1). This is in contrast to large volumes of gypsum that would have been formed via lime addition that would have required dewatering in addition to a substantially larger final void volume for disposal.

6. Conclusions

The sequential addition of MgCl$_2$·6H$_2$O added according to stoichiometric requirements followed by NaOH to Baal Gammon mine pit water has been demonstrated to form a hydrotalcite-based precipitate. Importantly, the hydrotalcite-based precipitation removed a broad spectrum of trace elements of environmental concern including Al, Cd, Cr, Cu, Fe, Mn, Ni and Zn. An ore grade precipitate containing substantial Cu (8.00 ± 1.00%) and Zn (3.87 ± 0.53%) could also be produced in hydrotalcite precipitated directly from the mine pit water column.

The final water quality produced after treatment was of a simple Na–Cl–SO$_4$ type. Post-remediation in-situ monitoring of the Baal Gammon mine pit revealed a gradual decline in water column pH to ca. 9.0 with a likely eventual decline in pH to ca. 8.5. Given the substantial removal of a range of major and trace elements including the majority of foulants, RO was successfully utilised with high permeate recoveries allowing the treated solute to meet stringent water quality discharge criteria.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.09.005.

References