

# Application of alkaline coal seam gas waters to remediate AMD from historical sulfide ore mining operation

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**Abstract** Treatment of acid and metalliferous mine waters remains a major global environmental issue. Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>-rich brine concentrate produced by reverse osmosis treatment of co-produced water from coal seam gas extraction at Narrabri, Australia, has proven effective at neutralising and removing major and trace elements. pH-dependent removal of metals between this neutralant and the more conventional Ca(OH)<sub>2</sub>, NaOH and CaCO<sub>3</sub> is similar. Laboratory experiments on the brine and a pilot field application of an analogue dilute Na<sub>2</sub>CO<sub>3</sub> solution as neutralant are described in this paper. Whereas removal of Fe and Al is via precipitation of oxyhydroxides, removal of other trace metals appears largely controlled by adsorption on the Fe/Al-oxyhydroxides, though co-precipitation may also be a contributory factor.

**Key words** Acid and metalliferous drainage, solid precipitation, trace metal adsorption

## Introduction

Production of gas from non-conventional sources such as coal seams and shale has exhibited exponential growth in the last two decades (Day 2009). It is typically necessary for CSG operations to extract large volumes of co-produced water to facilitate gas production. The concentration and composition of salt in solution varies with geological characteristics of the basin from within which the gas is produced. The salinity of co-produced water typically exceeds concentrations that allow it to be used without treatment. Most commonly, reverse osmosis (RO) is used to reclaim water for on- or off-site beneficial uses. The salt concentration in the reject stream from RO treatment is a function of the recovery achieved in the RO processing. Concentrated brines can be further treated using thermal processing technologies to ultimately produce crystallised salts. Industry is continuing to examine commercial uses for such salt products as opposed to disposal in regulated landfill sites which is relatively high cost.

The relatively high concentrations of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions in co-produced water extracted in the Narrabri area renders them potentially beneficial in neutralising various acidic materials, including remediation of acid and metalliferous drainage (AMD) at a range of operational and legacy resource extraction sites (Commonwealth of Australia 2016; INAP 2009). This study compares the performance of Na carbonate-rich brine with more conventional neutralants in neutralising the acidity and removing metals from AMD.

## Materials

Co-produced water from the CSG operations at Narrabri, Australia, have variable salinities over the project area, with TDS up to 20,000 mg/L of which the bulk is derived from  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{NaCl}$ . This water also contains low concentrations of silica,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  compared with brines from other CSG operations. The high (bi)carbonate content and low levels of hydrocarbons and toxic metals makes the water an ideal candidate for this study. Co-produced water received directly from CSG wells was collected from a storage tank in the water gathering system that forms part of the Narrabri CSG operations. Salt was produced by evaporating the water to dryness at  $150^\circ\text{C}$ . A portion of this salt was further heated to  $200^\circ\text{C}$  to determine if subjecting the salt to higher temperatures affected the bicarbonate/carbonate content of the salt product due to decomposition of bicarbonate when heated. *Siroquant*<sup>TM</sup> XRD analysis indicated the salt produced in the drying oven at  $150^\circ\text{C}$  contained 89% natrite ( $\text{Na}_2\text{CO}_3$ ) and 11% halite ( $\text{NaCl}$ ) with minimal nahcolite ( $\text{NaHCO}_3$ ). Further heating to  $200^\circ\text{C}$  did not change the mineral composition substantially.

The acidic mine water sample was collected from the main adit of the abandoned Sunny Corner Ag-Pb-Zn-(As-Cu) volcanogenic massive sulphide deposit near Lithgow, NSW. It has a pH around 2.8 and EC of 2.84 mS/cm. Bulk water samples were collected and sealed in plastic containers with no headspace. Subsamples of the water were centrifuged and acidified with nitric acid in the laboratory and analysed for chemical composition by ICP-OES/MS (Table 1).

Neutralisation experiments were conducted on the Sunny Corner mine water using the Narrabri brine salt and three common neutralising agents –  $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . A 106g/L solution of the Narrabri salt (90g/L  $\text{CaCO}_3$  alkalinity equivalent) and a 1M  $\text{NaOH}$  solution (50g/L  $\text{CaCO}_3$  alkalinity equivalent) were prepared. As  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  have very limited solubility, the experimental work was conducted by direct addition of the solid salts to the acidic mine waters.

**Table 1.** Composition of mine water from Sunny Corner and Narrabri co-production water (as received). Concentrations in mg/L, EC in mS/cm.

	pH	EC	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Zn	Si	SO <sub>4</sub>	Cl
Sunny Corner	2.57	2.84	57.4	21.6	3.7	173	0.6	47.8	4.2	4.8	298	21.4	1750	3.6
Narrabri co-produced water	8.3	18.14	0.04	11.5	<0.1	0.24	46.9	7.2	<0.1	5660	<0.1	9.8	5.1	1210

## Methods

### pH controlled precipitation tests

The Narrabri brine salt and  $\text{NaOH}$  solutions, and the  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  powders were used to titrate the AMD samples from Sunny Corner from its original pH value of ~2.8 to

an end point where additional neutralant did not substantially alter solution pH. For each run, a series of 50mL Falcon tubes was filled with 40mL of the mine water and measured volumes of salt solution or masses of solid neutralant added to yield the necessary range of final pH values. After addition of the neutralant, the tubes were sealed and placed on a rotary mixer for 10 minutes, centrifuged, the final pH value measured and the clear supernatant transferred (without further filtration) to 15mL Falcon tubes containing a drop of conc. nitric acid to stabilise the metals in solution prior to ICP-OES/MS multi-element analysis.

### Desorption tests

To investigate the reversibility of metal uptake by the Fe/Al-oxyhydroxide/hydroxysulfate precipitates generated in the above tests, a 1L sample of the mine water was rapidly raised to pH 10 using 1M NaOH, accompanied by vigorous sample agitation. This caused rapid formation of orange gelatinous precipitates (as observed in the previous test at neutral to high pH values). After 15 minutes, the suspension was centrifuged and the compacted pellet was washed with deionised water and centrifuged again. This procedure was repeated twice more. The precipitate was resuspended in deionised water, the density determined gravimetrically, and stabilised at pH 10 for 1 hour. The suspension was then titrated with nitric acid back down to pH 2.5 in 0.5 pH increments (with 10 minutes residence at each pH value) and sub-samples extracted, quickly centrifuged and the supernatant solutions decanted for ICP analysis of metals. After the last samples were collected at pH 2.5, the remaining suspensions were titrated to below pH 1 where the majority of suspended solids were dissolved.

### Field trial at Sunny Corner

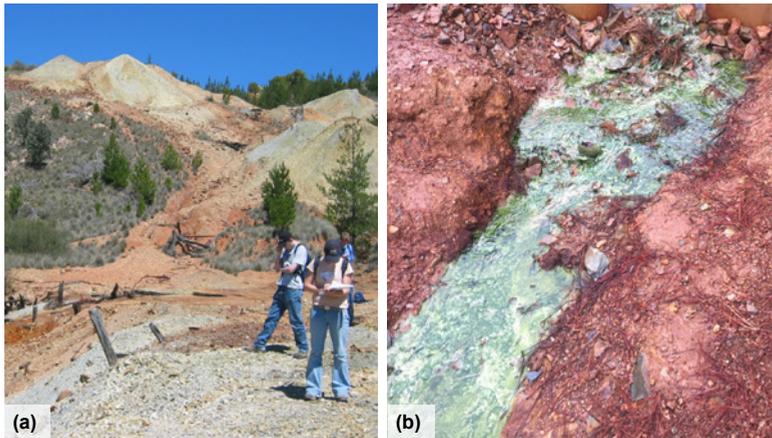
A preliminary field trial of the effect of addition of a small slug of concentrated  $\text{Na}_2\text{CO}_3$  solution (an analogue of the Narrabri brine composition) was conducted in the drainage exiting the main adit at the abandoned Sunny Corner mine (Fig. 1). Three sampling stations were set up along the stream at intervals of ~50m. At time zero, the slug was added into the acidic mine water stream near the adit. Water samples were collected at each station as soon as the stream pH started to rise and thereafter at intervals of 30-60 seconds until the pH returned to pre-slug (normal) values. Each sample was collected in duplicate with 50mL Falcon tubes and no headspace. The pH and EC values were also recorded with sampling time. The bulk of the stream water containing the slug was also collected (~20L) for subsequent laboratory work.

The samples were centrifuged immediately after transportation back to the analytical laboratory of UNSW. The clean supernatants were transferred into 15mL Falcon tubes containing a drop of conc. nitric acid to stabilise the metal content for ICP analysis.

## Results and Discussion

### Metal precipitation

The general pH dependence of removal of metals was similar for all of the neutralants (within the comparable pH range). The Narrabri salt (predominantly  $\text{Na}_2\text{CO}_3$ ) and both hydroxides ( $\text{Ca}(\text{OH})_2$  and NaOH) were able to increase the pH of the mine water to >12 (Fig. 2).



**Figure 1.** (a) Sulfidic waste dumps at the abandoned Sunny Corner Ag-Pb-Zn mine and (b) pH 2.8 AMD waters exiting main adit with green algae mats.

The inflection points indicate the formation of amphoteric Fe/Al-oxyhydroxides or hydroxysulfates.  $\text{CaCO}_3$  only managed to raise the pH of the acidic mine water to a maximum  $\sim 6.5$  which is consistent with the findings of previously published work (Ouakibi et al. 2013; Maree et al. 2013; Lakovleva et al. 2015).

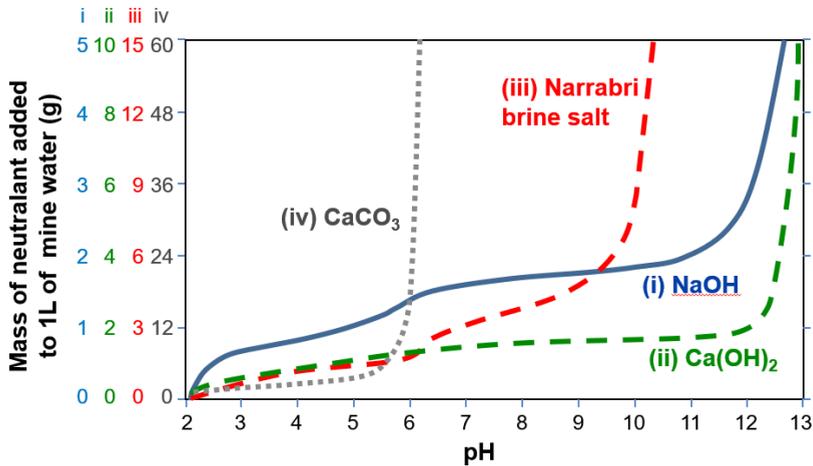
The addition of the Narrabri salt, NaOH and  $\text{Ca}(\text{OH})_2$  increased the electrical conductivity of the treated mine water significantly from pre-treated level of  $\sim 2.7$  mS/cm to 10.3, 13.2 and 7.9 mS/cm respectively. In contrast,  $\text{CaCO}_3$  only increased EC to 3.0 mS/cm. The increase in EC is linked to the relative increase in Na and Ca, compared with precipitation of metals as the neutralants are added.

The removal of sulfate in the samples by sodium bearing salts was limited and likely due to formation of small amounts of schwertmannite. Calcium bearing neutralants are more effective to remove sulfate from water as precipitate of gypsum.

In the neutralisation experiments performed on Sunny Corner water in the lab, Fe normally precipitated mainly as ferric hydroxide species (indicated by the orange colour). However, a dark teal colour Fe(II) hydroxide species (possibly a combination of Fe(II) and Fe(III)) was observed to initially precipitate in the field trial after the analogue of the Narrabri brine was added into the acidic mine water stream. The colour soon changed to orange as Fe quickly oxidised from ferrous to ferric forms at the higher pH (Morgan and Lahav, 2007). The observation was basically in agreement with Chapman et al. (1982) that 36% of the total dissolved Fe is present as  $\text{Fe}^{2+}$  in the pH 2.9 water collected from the main adit at Sunny Corner.

The removal of selected ions from the bench-top experiments are plotted as a function of pH in Fig. 3, along with the ion removal profiles predicted by MINTEQ (precipitation only) and various published profiles of metal adsorption onto Fe-oxyhydroxides (Gerth 1983; Dz-

ombak and Morell 1986; Swedlund and Webster 2001; Appelo et al. 2002; Webster et al. 2004; Gustafsson et al. 2011). The close correspondence of the experimental results to the adsorption lines indicates that removal of the metal ions in the mine water is dominated by adsorption to the Fe/Al-oxyhydroxides rather than simple precipitation of metal hydroxides or carbonates.



**Figure 2.** Relationship between pH and amount of neutralant added to 1L of Sunny Corner AMD water.

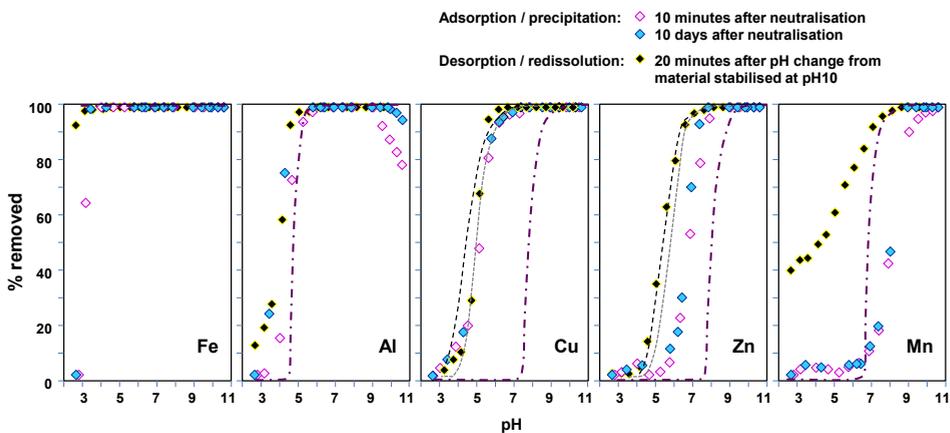
### Desorption of Metals

As the pH of the precipitate-bearing solutions was progressively dropped from 10 to 3, most metals desorbed from the Fe/Al-oxyhydroxide or otherwise re-dissolved with the relationship to pH largely corresponding to the original adsorption/precipitation trends (Fig. 3). Both the ease of dissolution and lack of correlation with Fe dissolution suggest that the removal of most of the transition metals is not controlled by co-precipitation. This is despite the speed at which the Fe-oxyhydroxides initially precipitated and the capacity of such metals to substitute into Fe-oxyhydroxides (Davranche and Bollinger 2000; Buekers et al. 2008). Unlike Fe, Mn starts to gradually dissolve at ~pH 8, but just under 50% of total Mn remains in the solid phase at pH 2. This could be the result of co-precipitation with Fe-oxyhydroxide (Bafghi et al. 2008) and/or formation of MnO<sub>2</sub> or Mn-bearing oxyhydroxides at the higher pH value attained in the initial forward titration.

### Field Trial

Due to the relatively lower concentration of the Na<sub>2</sub>CO<sub>3</sub> slug used in the field trial, the maximum pH of the treated stream water was pH 8, which was measured at the sampling station closest to where the small amount of Na<sub>2</sub>CO<sub>3</sub> was added. Nevertheless, the field trial results are generally in agreement with the observations from the laboratory experiments.

Whereas the experiments conducted in the laboratory showed that Fe quickly precipitated out as the pH rose from 2 to 4, the field trial data shows a much gentler declining slope of dissolved Fe, in both rising and falling pH environments. This could be caused by the “smeared concentration” due to hydrodynamic dispersion. It is also likely that the discrepancy resulted from oxidation of ferrous to ferric Fe (over a timespan of ~20 minutes) and subsequent precipitation of Fe/Al-oxyhydroxides (Fig. 4). Two samples collected at the first sampling site in the first run of the trial give higher dissolved Fe concentrations compared to other samples in the similar pH range. This can be explained by a portion of the more soluble ferrous Fe in the samples having insufficient time to oxidise and precipitate as Fe (III) oxyhydroxides and therefore remained in the water. The desorption trends for Al and Cu are similar in shape and do not match the respective initial removal patterns in the pH range of 3 and 5. This may indicate differences in the rate of sorption and desorption.



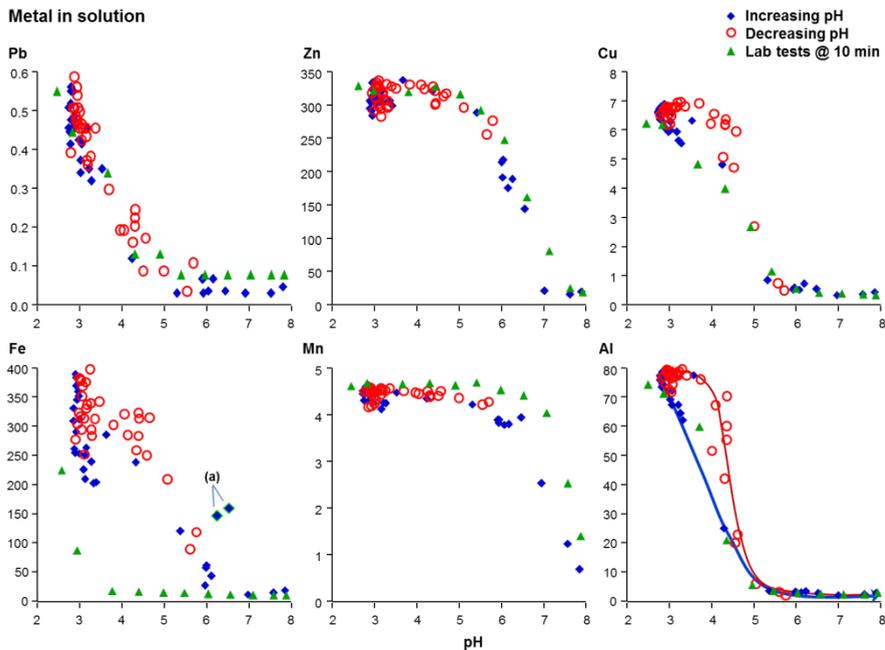
**Figure 3.** pH-dependent removal of selected metals after 10 minutes and 10 days using Narrabri brine compared with desorption of metals from initially produced 15 minutes Fe-oxyhydroxide precipitates as the pH is progressively adjusted back to 2.8. Dashed lines show adsorption of Cu and Zn onto synthetic schwertmannite (.....) and ferrihydrite (.-.-.-) at elevated  $\text{SO}_4^{2-}$  concentrations from Swedlund et al. (2009) and Webster et al. (1998), and MINTEQ modelled proportion of metals in solution due to precipitation (.-.-.-).

## Conclusion

$\text{Na}_2\text{CO}_3$ -rich Narrabri brine (or derived salt) shows similar performance to NaOH and  $\text{Ca}(\text{OH})_2$  for acid neutralisation and metals removal. The absence of Ca in the neutralant limits its capability to remove sulfates, and may present issues with regards to hardness and sodium adsorption ratio (SAR) in the neutralised stream. On a mass basis it is also necessary to use a greater mass of salt when compared with  $\text{Ca}(\text{OH})_2$  for equivalent neutralising capacity.

For most metals (apart from Mn), pH 7.5 is the optimum for removal from Sunny Corner AMD waters. This will be factored into subsequent economic and environmental cost/benefits modelling of various processing options for the Narrabri co-produced water and

comparison with other conventional neutralants (as alternatives or in combination with the Narrabri material). Owing to the identified issues such as non-removal of sulfate and increased transport mass compared with  $\text{Ca}(\text{OH})_2$  in particular, when utilising salt derived from Narrabri brines in isolation, further investigation are being undertaken into combining salt derived from Narrabri brine with  $\text{Ca}(\text{OH})_2$ . This is expected to yield a neutralised product with more favourable environmental properties (such as salinity, SAR and hardness) while reducing the cost of acidic waste neutralisation due to the reduction of costs associated with commercially produced  $\text{Ca}(\text{OH})_2$ .



**Figure 4.** Metal concentrations (mg/L) in the Sunny Corner stream water collected from three sampling stations after the addition of Narrabri salt analogue. Laboratory experimental results (10 minutes reaction time) are provided for comparison.

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