

Application of a Coal Seam Gas Waste Product as part of the Rehabilitation Program for a Copper Heap Leach Operation ©

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Abstract

There are few examples of successful collaboration between the mining industry and other industries in Australia, particularly where waste products have been used as part of mine rehabilitation activities to lower the risk of potential impacts to the environment. It is therefore important to highlight examples of where such successful collaboration is occurring.

From a near zero base, Australia has seen a massive growth in production of coal seam gas (CSG) since 1995 (Roarty, 2011). CSG production, requires the extraction of significant volumes of groundwater. The chemistry of the extracted water is a function of the geology in the region from which the water is extracted. The extracted water (produced water) is typically treated using RO to produce a treated water stream that can be used beneficially. The RO treatment process also produces a highly saline waste stream that can be further processed with thermal treatment processes to produce a highly saline stream and a dry salt material respectively. Managing the disposal or beneficially use of the salt product(s) ultimately produced, has been the subject of ongoing investigation. Over the past few years, a CSG producer has commissioned studies to investigate the potential for reusing the alkaline by-product in the mining industry to facilitate the remediation of acidic mine waste materials and acid and metalliferous drainage (AMD).

Preliminary studies have demonstrated the potential for the alkaline salt product to be successfully used in these activities. Further studies are now underway to look at the use of the alkaline salt by-product as part of rehabilitation plans for a copper heap leach facility. These studies involve both laboratory and field scale neutralisation trials, to harness the alkalinity from bicarbonate and carbonate species present in the produced water stream, to neutralise the acidity in the heap leach materials and immobilise dissolved metal species through precipitation.

The objective of the laboratory and field scale neutralisation trials is to reduce the risk of ongoing poor-quality seepage from the heap leach materials following the application of a soil cover system as part of rehabilitation activities. It is expected that the successful application of the alkaline CSG waste product at this mine site will lead to a positive outcome not only for the industry stakeholders and regulators, but for the environment.

Keywords: ICARD | IMWA | MWD 2018, Waste, Rehabilitation, AMD, Heap Leach, Collaboration

Introduction

AMD is an important environmental issue for the mining and mineral processing industries with reactive mine wastes generating acidic leachate, which can contain elevated concentrations of dissolved metals, metalloids and salts (INAP, 2009; COA, 2016). Neutralisation of AMD and precipitation of metals using alkaline reagents such as hydrated lime $(Ca(OH)_2)$ remains the most widely used primary treatment process. The resulting neutralised waters can generally be recycled or may require secondary treatment (eg. reverse osmosis (RO)) prior to discharge to the environment. RO is expensive and can be subject to fouling through use of hydrated



lime in the primary treatment step due to formation of insoluble gypsum $(CaSO_4)$. Additionally, the mining of limestone and subsequent processing required to produce lime is not without environmental impacts as carbon dioxide (CO_2) is produced in the decomposition of limestone to produce lime and the combustion of fossil fuels used to facilitate the decomposition of limestone.

Coal seam gas (CSG) production in Australia has seen exponential growth in recent years and requires the extraction of large volumes of co-produced water, which commonly has high concentrations of dissolved salts dominated by Na⁺, HCO₃ and Cl⁻ (Davies et al., 2015). The co-produced water generally requires RO treatment to reduce the salt concentration and reclaim water for beneficial re-use. The RO treatment process also results in a much smaller volume of highly concentrated brine being produced which contains substantial alkalinity from bicarbonate and carbonate species. A dry alkaline salt can also be produced from the RO brine using evaporation and/or heating, which can contain a high concentration of sodium carbonate [Na₂CO₂]. The produced alkaline salt is typically transferred, and disposed of, to landfill and the overall process has substantial economic penalties, due to the energy required to generate the dry salt as well as transport and landfill costs.

Sodium carbonate offers some technical advantages over Ca-based neutralants, due to its high solubility with carbonate ions yielding high acid neutralising potential, and metal precipitation per unit mass. Also, unlike Ca-based salts, sodium carbonate will not exacerbate fouling of RO membranes by gypsum (CaSO₄). Carbonate-rich brines and salts generated from the CSG industry are an alternative source of sodium carbonate neutralant material, with the advantage that the waste output of one resource extraction industry has the potential to be converted into a valuable input for another industry.

Over the past few years, an Australian CSG producer has commissioned several studies to investigate the potential for reuse of an alkaline brine/salt by-product in the mining industry for the remediation of acidic mine waste materials and AMD (Chen et al., 2017; Cohen et al., 2017). These studies have

demonstrated the potential for the alkaline brine/salt by-product to be successfully used in these activities.

This paper provides the findings from the first phase (laboratory scale neutralisation trials) of a study into at the planned use of the CSG alkaline brine/salt by-product as part of rehabilitation plans for a copper heap leach facility in NSW, Australia.

Methods

Heap Leach Samples

The methodology used to obtain representative samples of heap leach materials was undertaken in accordance with recognised industry guidelines. Existing technical guidelines for the geochemical assessment of mine waste materials in Australia (COA, 2016) were utilised as a framework for the sampling program. The sampling strategy was based on:

- An existing knowledge of the geochemistry of the heap leach materials of the site and potential for any significant environmental or health impacts;
- Size of operation and material volume;
- Sample representation requirements; and
- Level of confidence in predictive ability and cost

Site personnel collected 20 x 40 kg samples of heap leach materials and transferred the samples to ALS Brisbane laboratory (ALS) for static geochemical characterisation testing. The 20 samples represented composite High Sulfur (10 samples) and Low Sulfur (10 samples) heap leach materials taken from the three heap leach pads at the site. The sulfur content of the heap leach material varies due to the differing ore types that were progressively mined for placement on the heap leach pads over the project life. The samples were obtained using an excavator digging down to approximately 5 m depth and the operator collecting an approximate 40 kg sample by dragging the excavator bucket up the side of the hole. An approximate 2 kg sub-sample was collected and analysed for total sulfur using hand-held X-Ray Fluorescence (XRF) equipment during drilling to guide the field sampling program and indicate whether the samples were High Sulfur (HS) or Low Sulfur (LS). The XRF analyses were subsequently



verified using a 2-acid digest to quantify the concentration of sulfur, major cations and metals and metalloids in each of the 2 kg sub-samples.

The 20 heap leach samples provided good lateral coverage of the 3 existing heap leach pads at the site and provided a reasonable statistical representation of the heap leach materials. The 20 heap leach samples were composited into four HS samples and four LS samples at ALS; each composite sample was approximately 75 kg; sub-samples of these eight composite samples taken and subjected to static geochemical characterisation and particle size distribution (PSD) tests at ALS.

Brine Sample

A 1,000L bulk sample of liquid brine from the CSG producer RO water treatment plant was obtained and a 20L sub-sample dried at 150°C and characterised as a dry salt at ALS. The bulk liquid brine sample was then used in dynamic neutralisation tests for the heap leach materials.

Neutralisation Tests

Following receipt and interpretation of the static geochemical characterisation results, six dynamic neutralisation tests were set up at the RGS in-house laboratory in Brisbane using the two bulk composite HS and LS heap leach samples from the site and the bulk liquid brine sample from the RO plant at Leewood.

The dynamic neutralisation tests involved six individual 60L open-top cone-bottom plastic tanks, each used to contain approximately 75 kg of heap leach material. The open-top vessels allowed heap leach materials and liquid brine to be easily added to the tank and the cone-bottom and stand also facilitated periodic leachate collection. The six tanks comprised:

- Test 1: Control test for LS heap leach material – ie no brine added – Test 1
- Test 2: Control test for HS heap leach material – ie no brine added – Test 2
- Test 3: Immersion in concentrated liquid brine LS heap leach material Test 3
- Test 4: Immersion in concentrated liquid brine HS heap leach material Test 4
- Test 5: Sprinkled with diluted liquid brine HS heap leach material – Test 5
- Test 6: Sprinkled with diluted liquid brine HS heap leach material – Test 6

The leachate data presented in this paper for the dynamic neutralisation tests covers the period November 2017 to March 2018. The tests were operated under various controlled conditions and leaching cycles, and leachate was tested for pH, conductivity, acidity, alkalinity, major cations and anions, and soluble metals/metalloids.

Results

Heap Leach Samples

The LS and HS composite samples are dominated by fine gravel and coarse sand. The results of the static geochemical tests on the composite HS and LS heap leach samples are provided in Table 1. The samples have low pH values, elevated conductivity and appreciable titratable actual acidity (TAA). Compared to the HS sample, the LS sample has very little inherent sulfide sulfur (as measured by Scr) remaining and therefore has little capacity to generate additional acidity through sulfide oxidation.

Multi-element results for the LS and HS heap leach samples show that some metal/ metalloid concentrations are enriched compared to median values in un-mineralised soils (eg. As, Cd and Cu) (Bowen 1979). The enrichment of some metals/metalloids in the heap leach materials is expected, given that

Table 1 Static geochemical characterisation results for heap leach materials.

Sample	рН	EC (µS/cm)	TAA (mol H+/t)	S (%)	Scr (%)	MPA	ANC	NAPP	Classification
HS Comp.	3.3	4,800	139	4.45	2.950	90.3	<0.5	90.3	Acid Forming
LS Comp.	3.5	3,290	121	0.83	0.125	3.8	<0.5	3.8	Acid Forming

Notes: EC = Electrical Conductivity; TAA = Titratable Actual Acidity; Scr = Chromium Reducible Sulfur. MPA = Maximum Potential Acidity; ANC = Acid Neutralising Capacity and NAPP = Net Acid Producing Potential in kg H_3SO_4/t



these materials were obtained from a mineralised ore body and are being heap leached under acidic conditions to obtain copper.

Brine Sample

The brine sample from the RO treatment plant was tested at ALS Brisbane and had a pH of 9.3, EC of 76,000 μ S/cm, carbonate alkalinity of 27,700 mg/L (as CaCO₃) and bicarbonate alkalinity of 45,800 mg/L for a total alkalinity of 73,500 mg/L.

Table 2 provides the major ion composition of the brine from the RO water treatment plant as provided by the CSG producer.

The combined carbonate and bicarbonate content of the salt contained in the brine is between 53.3 % and 65.0 %. When the carbonate and bicarbonate salts contained in the brine react with acid (H^+) they form water and carbon dioxide gas according to the neutralisation reactions.

Carbonate neutralisation reaction; $CO_{3}^{2-}(aq} + 2H^{+}(aq) \Rightarrow H_{2}O_{(l)} + CO_{2(g)}$

Bicarbonate neutralisation reaction; $HCO_{3}^{-}{}_{(aq)} + H^{+}{}_{(aq)} \Leftrightarrow H_{2}O_{(l)} + CO_{2(g)}$

The sodium, potassium and chloride ions (approximately 35 % to 46.7 % of the salts in the brine) that do not take part in the neutralisation reactions remain and have the potential to increase the salinity of a neutralised acidic material. However, at the copper heap leach site, groundwater is naturally highly saline and additional salt from brine neutralisation would not materially impact upon this level of salinity. Additional work is planned in future to verify that the potential impact of the proposed remediation activity and rehabilitation program, interms of salinity, is negligible.

Trace element analysis results for the brine sample indicate that the concentration

Table 2 Major ion composition in brine.

Species	Minimum Mass (%)	Maximum Mass (%)		
Sodium	32.7	35.5		
Bicarbonate	39.8	44.8		
Carbonate	13.5	20.2		
Chloride	5.7	6.7		
Potassium	0.2	0.4		

of most of dissolved trace metals/metalloids is below the applied trigger values for moderately disturbed freshwater ecosystems (95 % species protection level). The exceptions are the concentrations of boron (5.6 mg/L) and fluoride (46.7 mg/L), which are elevated compared to the applied livestock drinking water guideline values for these elements (5 mg/L and 2 mg/L, respectively) (ANZECC & ARMCANZ, 2000).

Neutralisation Tests

Neutralisation tests were undertaken for LS and HS heap leach samples contained in six tanks subjected to different leachate compositions (deionised water and/or alkaline brine) and addition methods as detailed in previously in this paper. The pH results for the six samples over a period of four months is provided in Fig. 1. The results demonstrate that the brine has the potential to neutralise the titratable acidity in the heap leach materials but slow (sprinkled) addition of diluted brine provided a slower and more sustainable increase in pH than total immersion in concentrated brine. It is expected that addition of diluted brine to heap leach materials through a similar sprinkler system to that currently used at the site is the most practical and efficient method of adding alkalinity to the system. There is also the opportunity to physically disturb (turnover) the heap leach materials, where required, and to recycle collected leachate with excess alkalinity to promote efficient contact and neutralisation.

The quality of the leachate collected from the HS control sample (Test 2) is presented in Table 3 alongside the quality of leachate collected from the HS sample (Test 6) sprinkled with diluted brine (three-fold dilution to obtain sufficient leachate for analysis). The results show that addition of alkaline brine to the HS heap leach material has the potential to increase the pH and alkalinity of leachate, and reduce the concentration of acidity and several parameters/analytes in leachate (eg. Al, Cd, Co, Cu, F, Mn, Ni, and Zn), in some cases by several orders of magnitude. On the other hand, the concentration of some parameters (eg. EC, K, Na, Cl, Br, As, B, Mo and Se) have the potential to increase, to some extent, in leachate from heap leach materials neutralised with brine. It should be noted





Figure 1 pH results for heap leach neutralisation tests.

that the CSG producer has the potential to remove some of these species from the final byproduct by incorporation of additional treatment steps in water processing, should this be required. Additionally, a lower final end pH would also reduce the quantity of alkaline salt that needs to be added, which would in turn reduce the salinity in the treated neutralised material. Future work is proposed to optimise the dosing rate for both high sulfur and low sulfur ores found in the heap leach material taking into consideration the competing objectives of reducing dissolved metal concentrations, reducing the potential for re-acidification and minimising salinity in the treated neutralised material.

	Test 2	Test 6		Test 2	Test 6
Parameter	Concentration (mg/L)		Parameter	Concentration (mg/L)	
pH (pH units)	3.06	9.41	Barium	<0.005	<0.005
EC (µS/cm)	15,840	47,550	Cadmium	2.3	0.0028
Acidity	21,800	<1	Cobalt	39	0.016
Alkalinity	<1	13,100	Chromium	0.33	<0.005
Calcium	136	4	Copper	320	0.596
Potassium	<1	71	Iron	734	<0.05
Magnesium	2,810	150	Mercury	<0.0005	<0.0005
Sodium	2	15,300	Manganese	99	0.36
Chloride	488	3,050	Molybdenum	<0.005	0.13
Fluoride	25	8.6	Nickel	12.5	<0.005
Sulfate	20,100	14,200	Lead	< 0.005	<0.005
Bromide	<0.5	8.3	Strontium	0.036	<0.005
Aluminium	2300.00	0.22	Silicon	7.40	1.5
Arsenic	0.02	0.109	Selenium	0.1	1.19
Boron	<0.05	0.790	Vanadium	<0.05	<0.05
Beryllium	0.07	<0.005	Zinc	234	0.033

Table 3 Leachate quality obtained from brine neutralisation Test 2 and Test 6



Conclusions

Laboratory scale neutralisation trials have been completed which demonstrate the potential to harness the alkalinity from bicarbonate and carbonate species in a CSG waste product, to neutralise the acidity in the heap leach materials from a copper heap leach operation and immobilise dissolved metal species through precipitation. Initial results from the study indicate that brine neutralisation has the potential to reduce the risk of ongoing poor-quality seepage from the heap leach materials following the application of a soil cover system as part of rehabilitation activities. However, there will be an increase in salinity and potentially in the concentration of some oxyanions in seepage under alkaline conditions

The laboratory-scale trials are continuing, and the sustainability of the water quality improvement is currently being investigated, by continuing the leaching of brine-neutralised HS materials with deionised water (with and without addition of agricultural limestone). It is planned that the findings of the laboratoryscale trials be used to inform the design of field scale trials planned to be constructed within the next 12 months. It is expected that the successful application of the alkaline CSG waste product at this mine site will lead to a positive outcome not only for the industry stakeholders and regulators, but for the environment.

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