

Process water treatment at the Ranger uranium mine, Northern Australia

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Abstract The conceptual development and piloting of an innovative water treatment system for process water produced by a uranium mine mill is described. The process incorporates lime/CO₂ softening (Stage 1), reverse osmosis (Stage 2) and biopolishing (Stage 3) to produce water of quality suitable for release to the receiving environment. Comprehensive performance data are presented for each stage. The unique features of the proposed process are:

- recycling of the lime/CO₂ softening sludge to the uranium mill as a neutralant,
- the use of power station off-gas for carbonation,
- the use of residual ammonia as the pH buffer in carbonation; and
- the recovery and recycling of ammonia from the RO reject stream.

Keywords Ammonium biopolishing; lime softening; mine process water treatment; radionuclide removal; residue recycle; reverse osmosis

Introduction

Energy Resources of Australia Ltd (ERA), a subsidiary of Rio Tinto, operates the Ranger uranium mine. The mine has been producing since 1981 and is located in the Ranger Project Area approximately 250 km east of Darwin in a tropical monsoonal climate zone. Since the Project Area has been progressively surrounded by, but remains separate from, the World Heritage listed Kakadu National Park, protection of the environment is a key operational concern.

Uranium is extracted from the ore using conventional sulfuric acid leaching and solvent extraction. The leach residue consisting of gangue minerals is an acidic 55 wt% solids slurry which is neutralised with lime and currently deposited into a mined-out pit. The decant supernatant (process water) from the settled slurry is recycled to the milling process. Prior to 1996 the residue was placed in a purpose-built containment dam. This dam is still part of the process water circuit with the available surface area being used for evaporation.

Following a series of five well above-average wet seasons a surplus of water has been captured in the process water circuit. Apart from evaporation there is no mechanism available to reduce the volume of contained water. In dry years the circuit is a net loser of water – but in wet years there are strong positive gains. Surplus water in the pit reduces available storage capacity and compromises the consolidation rate of deposited residues. Good consolidation is the key to not only maximising the storage capacity of the pit but in the long run is critical to minimising the cost of capping the deposited residues.

There is thus the need to implement a more effective process water management system that maximises available storage in the pit, facilitates efficient use of milling consumables

and enables expeditious capping and rehabilitation of the pit once it has been filled. The long range objective is to remove approximately 9,500 ML of water from the process circuit over the next 10 years using technically and operationally sound processes that are both practicable and supported by the Company's key stakeholders. The shorter-term objective is to bring the system into balance by 2003. This will require the removal of an additional 900 ML/y of water over and above current evaporation.

One of the options being considered is to treat the process water to a standard such that the product will be suitable for release with no measurable detrimental impact on the receiving environment. This paper describes the development of the water treatment process through laboratory testwork, bench scale tests under batch and continuous conditions, and finally to on-site pilot testing in a purpose built plant.

Development of conceptual process

The composition of the process water (Table 1) indicates the scope of the technical challenge for a water purification process. There are a number of solute species, some occurring at high concentrations, and with different chemistries.

Ion exchange was eliminated from initial consideration since it would not be economically viable given the high total dissolved solids concentration. The concentrations of calcium, sulfate and manganese in the process water ruled out direct reverse osmosis treatment owing to the low water recovery rates from such saline water and the potential for scaling *via* precipitation of calcium sulfate and formation of Mn oxides.

Initial considerations focussed on identifying a primary treatment process that would remove a substantial proportion of the more troublesome major ion components. Lime treatment was a potential contender since it is well known that most metal ions (including Mn) are removed from solution if sufficient lime is added to raise the pH to 10–11 (Eckenfelder, 1980). Small scale laboratory batch testing showed that the majority of the Mg, U, Mn and a considerable proportion of the sulfate could be removed by the addition of lime to pH 11.

Since addition of lime was already an established part of the uranium milling process there was no technical impediment to its use in the water treatment process. However, first pass economic analysis showed that it would be cost prohibitive to use additional lime for this purpose. The resolution to this initial impasse was provided by the critical insight that the sludge produced from water treatment could in fact be used to replace the majority of the lime that would otherwise be used directly for residue neutralisation. Thus the waste from water treatment could be entirely recycled as neutralant for the mill residue stream. The effective operating cost for lime addition for water treatment with sludge recycle was estimated to be one-third of that for the case where the residue was not re-used.

The first stage of the conceptual process was therefore proposed to be lime addition to raise the pH sufficiently to precipitate the dissolved metals as their hydroxides and a large proportion of the sulfate as gypsum. However, a consequence of treatment with lime is an

Table 1 Major ion composition of Ranger process water

Parameter	Value
pH	4.5–5.5
EC $\mu\text{S/cm}$	18,000
Ca^{2+} mg/L	468
Mg^{2+} mg/L	2,920
Mn^{2+} mg/L	1,520
NH_4^+ (as NH_3) mg/L	826
SO_4^{2-} mg/L	16,800
^{226}Ra Bq/L	12.6

increase in calcium concentration in the treated water and supersaturation with gypsum. Most of this calcium must subsequently be removed to allow the application of a membrane polishing process such as reverse osmosis (RO). One of the most common and robust processes to remove calcium involves carbonation by addition of sodium carbonate or injection of carbon dioxide gas to precipitate calcium carbonate.

As the Ranger mine is located at a remote site it has its own diesel-fuelled power station (25 MW capacity). The opportunity therefore exists to source the required CO₂ from the power station off-gas. Initial testwork showed that suitably scrubbed stack off-gas functioned just as well as cylinder gas in precipitating calcium carbonate from the primary lime-treated water. Thus another waste stream could be used for water treatment. In addition, the calcium carbonate product could be recycled to residue neutralisation contributing to a further reduction in net operating costs for water treatment.

Initial batch testwork indicated that lime treatment plus CO₂ carbonation had the potential to remove most of the major and minor cations and sulfate from solution, with the product water containing only the ammonia and residual sulfate. At this point the removal of ammonia became the primary focus. Initial technical and costing analysis focussed on gas stripping technology. However, the starting concentration of 700–800 mg/L meant that very large and energy intensive gas stripping infrastructure would be required. Moreover, the concentration of sulfate in the product stream would still be an issue. Thus attention shifted back to RO treatment which would remove both ammonium and sulfate ions. Reverse osmosis was considered to be the most applicable technology given the maturity of the process and the experience of potential supplier companies in the Australian market.

The concentration of ammonium in the RO reject stream would be five to 10-fold higher than in the input. This increase in concentration meant that ammonia recovery processes would be much more economically attractive. Ammonia is used in the uranium production process, and full recovery and recycle of ammonium hydroxide solution from water treatment would meet a significant proportion of the annual site needs of this process chemical.

Performance projections of RO treatment using an industry software package indicated that ammonium ion (at 10–15 mg/L) would be the only solute likely to require further polishing prior to discharge of the water to the receiving environment. Ammonium at this concentration is readily amenable to wetland treatment so it was proposed that biopolishing would be the final treatment step.

A schematic flowchart of the conceptual treatment process that evolved from the process of technical, economic and environmental analysis described above is shown in Figure 1. It should be noted that a filtration step is located prior to reverse osmosis. It is standard industry practice to use microfiltration (and ultrafiltration) to provide maximum protection to the much more costly reverse osmosis membranes.

The potential for the build-up of salts in the pit supernatant as a consequence of sludge recycle is being addressed in the context of overall management of the process water circuit. This aspect will be specifically addressed elsewhere.

Bench scale testwork

Background

It was recognised that considerable testwork at the bench pilot scale would be required to establish optimum physicochemical conditions, test viability under batch and continuous flow conditions, and provide design criteria for large scale pilot testwork. The critical factors to be investigated were:

- effect of pH on performance (lime treatment, carbonation, and RO);
- rates of reaction and effect of residence time (lime treatment, carbonation); and
- solids/liquids separation.

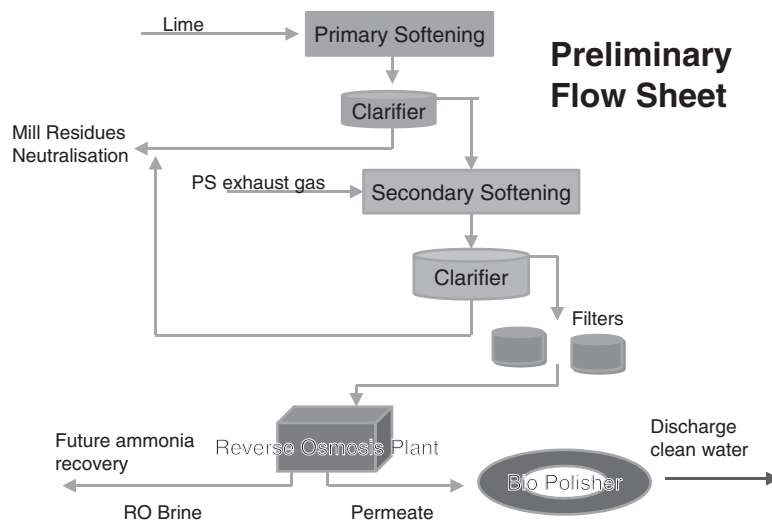


Figure 1 Conceptual flowchart for process water treatment

Summary of work program

Final bench scale testwork for the lime treatment step employed a three-tank sludge recycle/conditioning lime softening circuit operated at pH 10.8, 35°C and with a total residence time of 1 h. A major concern was the effectiveness, under continuous operating conditions, of solids/liquids separation following the primary lime treatment and secondary carbonation steps. As the settling rates and settled density of crystallite particles are of fundamental importance, considerable effort was spent in investigating and optimising residence time, the application of sludge recycle and addition of flocculant.

Bench test results

The removal of Mg and Mn, solids settling characteristics and thickener underflow density were specifically investigated in the lime treatment stage. Addition of lime was found to almost completely remove Mg and Mn at pH 11, and there were no advantages to be gained by operating at a higher pH. The solids produced when operating in sludge recycle mode required a feedwell dilution of at least 1:1 and use of a weakly anionic flocculant to achieve acceptable settling rates.

A three tank carbonation circuit operated at 35°C was found to give best results with a residence time of 1.5 h. Carbon dioxide alone, carbon dioxide plus sodium hydroxide to trim pH and sodium carbonate as a substitute for CO₂ were investigated to check all aspects of reaction stoichiometry and process performance. Residual calcium was readily removed from the lime-treated water to levels as low as 35 mg/L. It was found that the optimum pH for calcium removal was around 8.5. The composition of water from lime treatment/carbonation was judged to be suitable, following adjustment of pH to 6 with sulfuric acid, for feed to reverse osmosis.

Water from the carbonation step was filtered through 5 µm and 1 µm in-line filters in series (to simulate microfiltration pretreatment) prior to RO. A small RO unit was used at a maximum operating pressure of 1.4 Mpa and flow rate of 60 L/h. With the exception of ammonium ion, the water was found to meet quality targets. Total gross alpha and beta activities were less than 10 mBq/L which is well below the most stringent of water quality guidelines. The concentration of ²²⁶Ra was found to be 5 mBq/L consistent with the low gross alpha value.

Conclusions

The results from the bench scale pilot work confirmed the technical viability of the components of the conceptual process flow chart and showed that it could produce water of quality suitable for final biopolishing. Ammonium was the only species in the RO permeate identified as requiring additional polishing.

Pilot plant testwork

Overview

The optimum pH and residence time parameters from the bench scale work were applied to the design of a pilot plant (components constructed in Melbourne and Perth) assembled and tested on the Ranger site. Schematics of the lime treatment/carbonation and microfiltration/RO sections are provided in Figures 2 and 3, respectively.

The lime treatment/carbonation section was designed to treat 1 m³/h of process water. However, owing to limits imposed by minimum available industrial sizes of RO units the capacity of the microfiltration/RO section was 2 m³/h. Consequently the system had to be run in campaign mode with an intermediate holding tank being used to accumulate sufficient product water from lime treatment/carbonation to permit 12 h operation of RO. As the RO was operating for only 12 h per day on the first pass, the opportunity was taken to test both one-pass and two-pass RO.

Chemical and physical analysis methods

The concentrations of a considerable range of solute species were measured at many points within the process train. The decreasing concentrations of many analytes through the process also meant that methods with lower detection limits had to be used for later stages. A combination of Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES), ICP Mass Spectrometry (ICPMS) and solution X-ray Fluorescence (XRF) spectrometry was used to track the concentrations of major cations and trace metals. A full quantitative ICPMS scan was done to profile the process water so that the concentrations of all potentially relevant elements could be tracked through the process. Ammonia was determined colorimetrically using the indo-phenol blue method and the concentration of ²²⁶Ra was

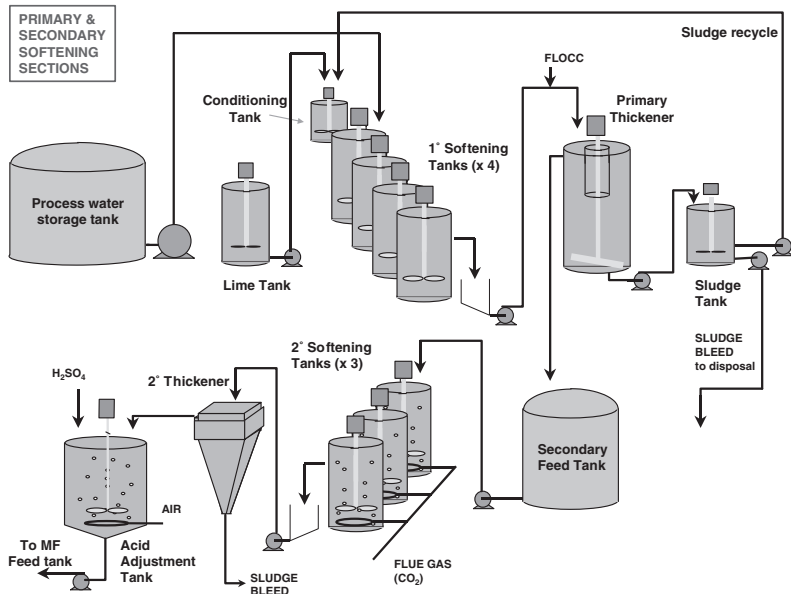


Figure 2 Schematic of lime addition and carbonation components of the pilot plant

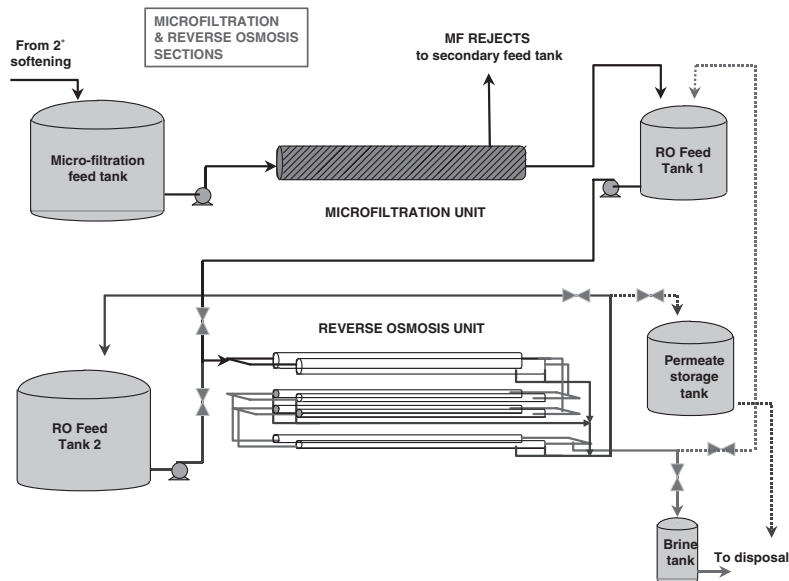


Figure 3 Schematic of microfiltration and reverse osmosis components of pilot plant

measured using the technique of radon emanation/gamma counting. Standard methods were used to measure sludge settling rates and to evaluate the effects of different types of flocculants.

Results and discussion

The first campaign of water treatment was carried out during September and October 2001, with the pilot plant operating on a 24 h continuous regime. This provided the opportunity for optimising the pH of the process stages, and for a thorough investigation and optimisation of the performance of the thickeners and the solids recycle ratios in the lime treatment and carbonation stages. The need for pH control by the addition of NaOH in the carbonation stage and the effectiveness of sodium carbonate compared with carbon dioxide gas were also evaluated. The carbonation stage was initially run using CO₂ gas from cylinders to remove power station gas as a variable in the system. The final runs were done using flue gas that had undergone a minimum of cleaning through a condensate trap.

In conventional carbonation, sodium hydroxide must be added to counter the acidity of the CO₂ gas and prevent the formation of the highly soluble calcium bicarbonate that occurs below pH 8. The feed water contains about 700 mg/L of ammonium ion, which is fully deprotonated during lime treatment. During the subsequent addition of CO₂ this free ammonia is progressively protonated to ammonium ion as the calcite is precipitated, thus buffering the pH. Theoretically, about 600 mg/L of ammonium is required as a pH buffer during precipitation of calcium from saturated gypsum solution. The pilot plant testwork showed that calcium precipitation was effectively complete with the pH decreasing from 10.8 to 8.5 with no requirement for addition of sodium hydroxide. The actual cost saving from not having to add sodium hydroxide is about AUD\$1.20 per tonne of water treated. Since ammonia must be in the protonated ammonium form for maximum rejection by reverse osmosis, a double benefit is realised by having ammonia as the proton acceptor in the carbonation stage.

The concentration data for the key major and trace elements measured at each stage of the optimised treatment process are presented in Table 2. Essentially all of the rare earth elements present in the process water were removed in the first stage (yttrium, Y, is provided as an example in Table 2).

Table 2 Performance of pilot water treatment plant

Element:	Units	Process water	Post lime addition	Post carbonation	RO Pass 1 permeate	RO Pass 2 permeate	Retention pond 1
Major species							
Ca	Mg/L	468	626	30	0.8	0.1	3.1
Mg	Mg/L	2,920	56	81	0.4	<0.1	25.4
Mn	Mg/L	1,520	0.016	2.4	0.013	0.010	0.011
SO ₄	Mg/L	16,800	1930	2490	10.6	0.4	74.2
NH ₃	Mg/L	826	721	755	13.6	1.7	<0.05
Trace elements							
Al	µg/L	12,550	41	39	13	12	25
Br	µg/L	425	201	195	<10	<10	53
Cd	µg/L	20.5	0.4	0.4	0.2	<0.2	<0.2
Co	µg/L	1,410	2.3	2.1	<0.1	<0.1	<0.1
Cu	µg/L	4,070	34	41	13.1	3.0	0.8
Ni	µg/L	2,790	31	12.9	3.4	0.2	1.9
Pb	µg/L	3,670	43	34	35	23	0.3
U	µg/L	6,660	7.98	11.9	0.40	0.39	21.4
Y	µg/L	9,250	<0.1	1.9	<0.1	<0.1	<0.1
Zn	µg/L	2,930	13	21	10	<5	<5
Radionuclides							
²²⁶ Ra	Bq/L	12.6	7.40	0.65	0.01	n/a	0.05

The average concentration data in Retention Pond 1 (RP1) for the 2000/2001 wet season at the Ranger mine have been included for comparison in Table 2. This is the most relevant set of data to use for first pass performance assessment since water from RP1 is allowed by the regulatory authorities (with agreement from other stakeholder groups) to be freely discharged off the lease. It can be seen that for most of the major cations and trace metals, and the key radionuclide ²²⁶Ra, that single stage RO is sufficient to remove residuals from the primary treatment stage to levels comparable to or much less than those in RP1 water.

Copper (Cu), lead (Pb), and zinc (Zn) are the exceptions to the excellent performance data for the metals since measurable levels were detected even after two stages of RO treatment. What is especially surprising is that the concentration of Pb did not fall substantially between the RO treatment stages. It is probable that the measured levels of Cu, Pb, and Zn are as a result of contamination from brass (Cu, Zn) and PVC (Pb) components used in the construction of the RO unit. Lead may also have been present as an impurity in the acid used to preserve the filtered samples prior to analysis. The issues of contamination from system components and sample preservation will be investigated in more detail during the second pilot campaign in December 2001.

Apart from the specific issues with Cu, Pb and Zn identified above, and the already anticipated higher levels of ammonium in the RO permeate, it appears that single stage RO treatment should produce water of a quality that will be readily amenable to final biological polishing (wetland treatment).

In summary the pilot plant results were consistent with the bench scale work and, in addition, showed:

- that pH 10.3 was the optimum pH for lime treatment
- much higher solids density than anticipated was achieved in the primary clarifier (lime treatment) so additional dewatering of solids was not required;
- the need for good pH control in the carbonation step, and addition of flocculant to ensure maximum removal of solids prior to microfiltration;
- supplemental addition of sodium hydroxide was not required for the carbonation step;
- essentially no difference in performance between bottled gas and power station exhaust gas in the carbonation stage; and

- the need for the pH of the RO feedwater to be 7 to achieve the best removal of ammonia (as ammonium ion).

Biopolishing of RO permeate

Wetland treatment has been used successfully at large operational scale over the past five years at the Ranger mine for the treatment of non-process water containing low levels of Mn, U and nitrate. Although published wetland performance data indicate that wetlands should be readily capable of treating water containing 10–20 mg/L of ammonium, it was decided to run a full scale test in the existing constructed wetland (Kadlec and Knight, 1996). The results showed that although good initial removal was obtained, the performance was not sustainable. It was suspected that the lack of performance may have been due to an imbalance in the N/P ratio in the wetland. This proposition was confirmed by the results of *ex situ* microcosm trials which showed that the addition of trace levels of P dramatically stimulated ammonium removal via nitrification/de-nitrification (Earth Water Life Sciences, unpublished data).

A wetland system (biopolisher) for the treatment of RO permeate was constructed in November 2001 to allow sufficient time for maturation prior to being needed towards the end of 2002. It is anticipated that the leading cells of this system will be supplemented with rock phosphate to provide sustained low level release of this critical nutrient.

Conclusions

The results from bench and large scale pilot plant testwork have confirmed the technical viability of the proposed flowsheet for treatment of process water at the Ranger Uranium Mine. The recycle of treatment sludge to mill residue neutralisation, the use of power station off-gas for carbonation and the function of the ammonia/ammonium couple as a buffer in carbonation will result in environmental benefit and substantial operational cost savings relative to conventional implementations of the proposed technologies.

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