

CHARACTERISATION OF RANGER MINE WATER TREATMENT SLUDGE

R.PLEYSIER¹, G. DOUGLAS², M.G. TREFRY^{2,3}, L.WENDLING², F.BENN¹,
A. GRABSCH¹ and C. KLAUBER¹

¹Parker Centre (CSIRO Minerals), Australia

²CSIRO Land and Water, Private Bag 5, Wembley WA 6913 Australia;

E-mail: grant.douglas@csiro.au

³School of Earth and Environment, University of Western Australia, Australia

ABSTRACT

Process water from ERA's Ranger Uranium Mine (Northern Territory, Australia) requires treatment to meet stringent environmental water quality criteria prior to discharge into the environment. Prior to treatment, the process water is acidic and contains high concentrations of sulfates, aluminium, magnesium and manganese in addition to residual uranium. One concept that has been considered for a process water treatment plant would use milk of lime and reverse osmosis to treat 1.5GL per annum to discharge 1GL of high purity water, with a brine balance and 85 000 tonnes of sludge by-product, the latter requiring 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.

The water treatment sludge obtained during trials was characterized via XRD, XRF, TGA and laser sizing to identify both the mineralogy and morphology of the material with the aim of understanding its properties and possible interactions with tailings and hence possible options for its secure disposal.

A variety of approaches to either modify the treatment process or the sludge to obtain a more stable material for long-term storage were explored. One promising treatment used a novel precipitation via sodium aluminate (e.g. spent aluminate liquor from Bayer process alumina refining) to form hydrotalcites, layered double hydroxide minerals of the general form $Mg_6Al_2(CO_3)(OH)_{16.n}(H_2O)$. This method utilises both the aluminium and magnesium present in the original process water and robustly allows for variations in the divalent to trivalent cation ratio from 2:1 to 3:1. Moreover, the formation of hydrotalcites in mine process water has a number of advantages over conventional treatment techniques such as rapid formation, easy dewatering, increasing stability above pH 4-5 and co-precipitation/incorporation of oxyanions other than carbonate.

1. INTRODUCTION

Energy Resources of Australia Ltd's (ERA's) Ranger Uranium Mine has been considering a water treatment plant with a capacity of 1.5 GL per annum to produce 1.0 GL of high quality water. The water treatment plant would utilise a milk of lime (MOL) solution to precipitate dissolved solids from the process water followed by reverse osmosis on the clarified stream. In addition to a high quality water stream, the plant would produce around 0.4 GL of brine solution and 85 000 tonnes of waste sludge for disposal each year. A strategy for the management and disposal of the sludge and brine has not been defined but transporting it to the tailings storage facility (TSF) is neither preferred nor sustainable.

The Australian Nuclear Science and Technology Organisation (ANSTO) trialled a continuous mini-rig for the treatment of Ranger process water and provided water treatment sludge to CSIRO for characterisation work. CSIRO determined the mineralogy and morphology of the sludge with the aim of understanding its properties and possible interaction with tailings. This paper outlines potential opportunities to modify the treatment process to obtain a material which is stable, less reactive and more suitable for long term storage.

2. EXPERIMENTAL METHODS

Samples

A small pilot plant constructed by ANSTO was used to treat Ranger process water in a series (3) of 3.66 L stirred tanks with milk of lime. The resultant slurry was thickened by settling, the solids removed and a clean water stream produced. Recycling of the thickener underflow was used to obtain sufficient solids density. Process water was treated at a rate of 138 mL/min with milk of lime (20% solids) at an addition rate equivalent to 29 g $Ca(OH)_2$ per litre of process water.

The materials produced from this pilot plant and from laboratory neutralisation tests provided the samples under investigation.

Analytical

Assays of liquor samples were conducted using ICP, ICP/MS and ISE. Characterisation of sludge was performed by XRD, XRF, and TGA at CSIRO. Identification of hydrotalcite phases were done using XRD and SEM/EDS.

Process Water Neutralisation

Laboratory neutralisation of Ranger process water was 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 seconds. A small program loop was used to ensure alkali was added only up to the set pH target.

Process water samples were titrated with caustic (1M NaOH), milk of lime (1M Ca(OH)₂) and sodium aluminate (NaAl(OH)₄), the milk of lime stirred during titrations to prevent settling.

Process water was treated with alkali to various pH values (titration inflection points) to obtain precipitates for rheology, leaching and characterisation work. Solids were collected by filtering or centrifuge and dried overnight at 105°C, and ground in a WC swing mill prior to XRF analysis.

Leaching

Samples of dried sludge from the ANSTO pilot plant were leached using DI water, dilute sulphuric acid (slurry pH =2) and Ranger process water. The leach slurries (10% solids) were bottle rolled over 24 hrs and the leach liquors assayed to determine the extent of metal re-leaching.

Rheology

Shear stress shear rate curves for the sludge were prepared using a Haake viscometer fitted with a SV2P rotor and cup. Vane rheology was also completed with a FL-100 vane controlled by Thermo-Haake RheoWin Pro software.

Sludge degradation with stirring was examined using focussed beam reflective measurements (FBRM) (Peng and Williams, 1993; Fawell et al., 1997) to establish if a change in particle size was observed with time. Measurements were performed with an M500 field unit fitted with a laboratory probe (Lasentec[®]) and the focal point of the laser set at the surface of the 12mm window. Scans (2 seconds duration) were continuously measured over the full range of chord lengths (1 to 1000 µm), split into 90 channels in a logarithmic progression.

SEM/EDS

Samples were dried overnight at 40°C. The dry precipitates were thinly spread on carbon tape and sputter coated with carbon. The SEM used was a Joel JSM-5800LV operated at 20 kV at a working distance of 12 mm. Visual analysis was used to select analytical targets, X-ray spectra obtained on selected sample crystals via energy dispersive spectrometry (EDS). Quantitative estimates of elements made from spectra using WIN-EDS software.

3. RESULTS

The proposed treatment of Ranger process water utilises lime to remove the bulk of the dissolved metals prior to reverse osmosis and disposal. A summary of the significant metals present before and after lime treatment is given in Table 1. Predicted sludge composition based on assay difference is also provided.

Table 1. Elemental analysis of process water and filtrate.

Element	Process water	Filtrate	Precipitate	Sludge composition
mg/L			Assumed	Calc %
Al	821.2	0.11	Al(OH) ₃	2.7
Ca	542.8	590.9	see SO ₄	-
Cu	21.9	0.9		-
Fe-Tot	49.4	-	Fe(OH) ₂	0.1
Mg	6371.4	7.21	Mg(OH) ₂	17.5
Mn	2907.2	-	Mn(OH) ₂	5.4
S	12520	625.8	CaSO ₄ ·2H ₂ O	73.8
Si	75	1.4	Si(OH) ₄	0.3
U	52.6	0.006		-
pH	3.06	10.72		-
Total				99.8

The process water is acidic and contains high concentrations of sulfur (sulfates) with significant amounts of aluminium, magnesium and manganese. Uranium in excess of 50 mg/L was also present.

Solution assays suggested the bulk of the sludge was composed of calcium sulfate (74%), magnesium hydroxide (17%) and manganese hydroxide (5%) with a minor amount of aluminium, iron and silicon hydroxides. Most of the added lime reports to the sludge as does all of the uranium.

Mass balance calculations indicated 86 g of sludge is produced per litre of process water which agrees well with actual figures from the ANSTO pilot rig trials (81 g/L).

Sludge Characterisation

Sludge from the pilot plant had a pH of 11.4 and retained a high moisture content (>50%) despite its solid dry appearance. The wet bulk density was 1.55 g/cc, but was significantly lower upon drying (0.55 g/cc). The specific gravity of the dried sludge was 2.57g/cc. Dried, the sludge shows a bimodal particle size distribution with a p80 of 16µm. Coarse material in the particle size distribution was predominantly insoluble sands derived from the industrial lime (Figure 1).

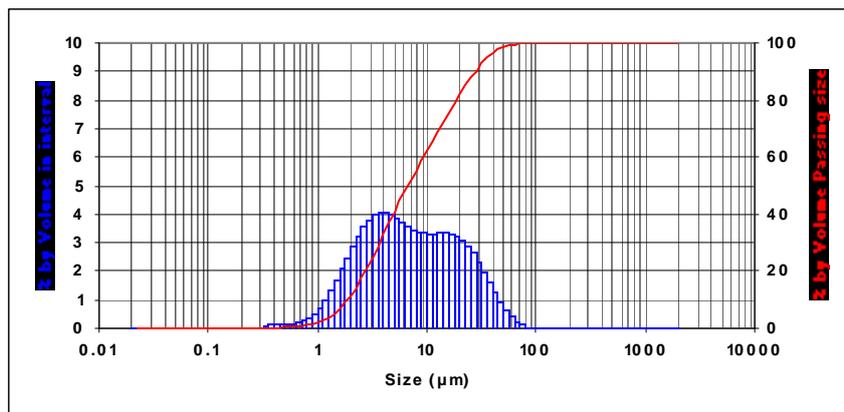


Figure 1. Size distribution of process water treatment sludge.

XRD analysis (Figure 2) of the dried sludge yielded a phase composition predominantly of bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) with two minor phases consistent with metal hydroxides and metal sulfate salts. The spectra for brucite ($\text{Mg}(\text{OH})_2$) and manganite ($\text{MnO}(\text{OH})$) were not clearly identified in this sample, possibly due to poor crystalline structure, low concentrations, or spectral patterns similar to bassanite.

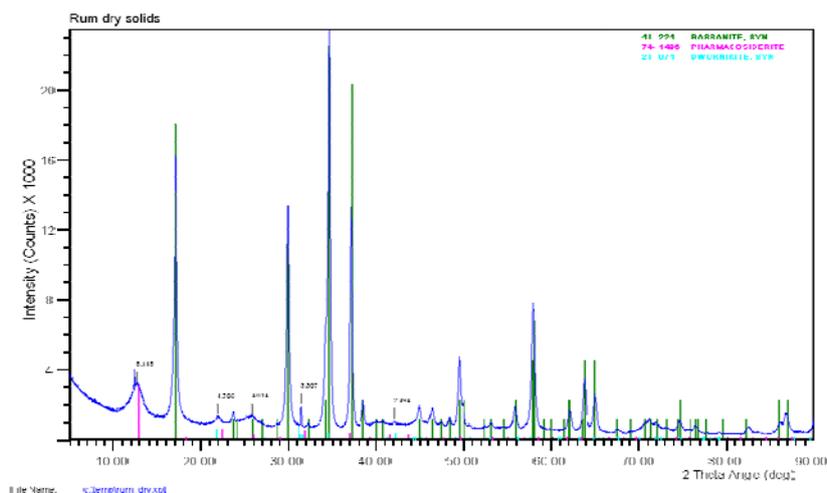


Figure 2. XRD pattern for process water treatment sludge from Ranger Uranium Mine.

A sample of the sludge was prepared as a fused bead and the major element oxide content of the sludge determined by XRF (Table 2). The composition of the original phases in the sludge was re-calculated as hydroxides except for calcium where sulfate was the known predominant phase.

Table 2. XRF analysis of process water treatment sludge.

Phase	XRF %	As	XRF % Mass	Solution % (cf Table 1)
MgO	12.94	Mg(OH) ₂	17.1	17.5
Al ₂ O ₃	2.22	Al(OH) ₃	3.1	2.7
SiO ₂	1.21	Si(OH) ₄	1.8	0.3
SO ₃	36.85	CaSO ₄ ·2H ₂ O	72.6	73.8
CaO	26.42	CaSO ₄ ·2H ₂ O	74.3	-
Mn ₃ O ₄	4.47	Mn(OH) ₂	5.1	5.4
Fe ₂ O ₃	0.264	Fe(OH) ₂	0.3	0.1
Total	85.3		100	99.8

The calculated composition from the XRF data agreed well with the solution assay data and indicated the sludge was predominantly gypsum (or bassanite) and magnesium hydroxide with minor quantity of manganese, aluminium and iron.

Thermal analysis (TG/DSC/MS) of the sludge (Figure 3) showed 4 major mass losses with temperature which can be matched with the major phases present (Table 3). Simple moisture loss was indicated up to 100°C. Decomposition of gypsum at 130°C (-1.5H₂O) gave bassanite (Dweck and Lasota, 1998) and at 170°C (-0.5 H₂O) the anhydrite (CaSO₄). Decomposition of magnesium hydroxide occurred at 350°C and residual lime at 580°C.

The mass spectrometry data (EGA/MS) confirmed mass losses were predominantly water but small amounts of CO₂ was also indicated suggesting minor carbonates may also be present.

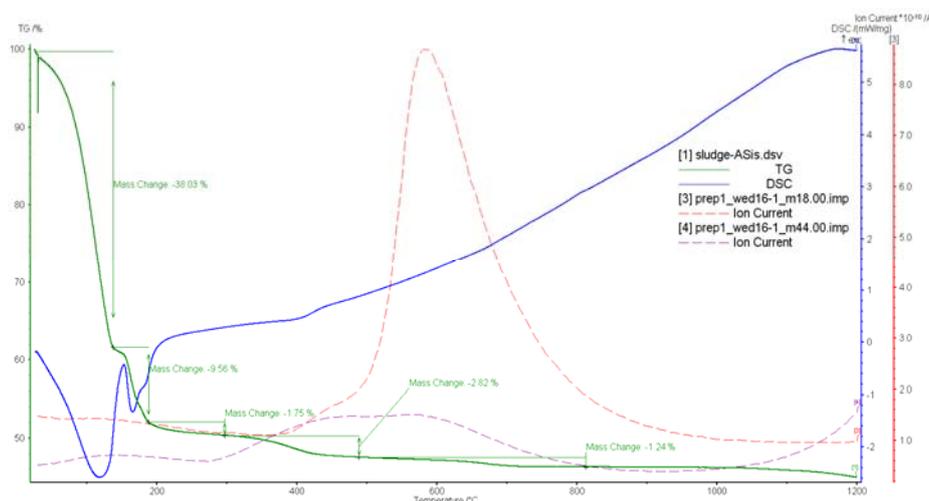


Figure 3. Thermal analysis TG/DSC/EGA-MS of process water treatment sludge.

Table 3. TGA data for process water treatment sludge.

Temp C°	Mass loss %	Possible reactions	Temp C°
0 – 130	38.03	-H ₂ O	100
130	6.4	CaSO ₄ ·2H ₂ O → CaSO ₄ · ¹ / ₂ H ₂ O + ³ / ₂ H ₂ O	130
170-200	3.16	CaSO ₄ · ¹ / ₂ H ₂ O → CaSO ₄ + ¹ / ₂ H ₂ O	170
270-390	1.75	Mn(OH) ₂ → MnO + H ₂ O	270
330-520	2.82	Mg(OH) ₂ → MgO + H ₂ O	350
520-700	1.24	Ca(OH) ₂ → CaO + H ₂ O	580

The composition of the sludge and the quantities of each mineral calculated from the mass loss data is given in Table 4. Comparative compositions from XRF and solution assays show good agreement between techniques.

Table 4. Sludge composition from thermal analysis data.

	Calculated			Actual	Comparative data		
	Sludge* composition (%)	Mass (g)	Mass Loss (%)	Actual Loss (%)	TGA (%) Dry basis	XRF (%)	Soln (%)
sample		100					
water	38	62	38	38.03			
gypsum	46	54.8	7.20	7.54	73.7	73.4	73.8
hemi	-	52.4	2.40	2.46			
Mn(OH) ₂	3	51.8	0.65	1.75	5.2	5.1	5.4
Mg(OH) ₂	10	48.5	3.3	2.82	17.1	17.1	17.5
Ca(OH) ₂	3	47.8	0.7	1.24	4.8		
Total	100						

Neutralisation Titrations

Neutralisation titrations of Ranger process water were completed in the laboratory with caustic, milk of lime and sodium aluminate. Caustic titrations were used to identify the metal hydroxide precipitates, milk of lime to produce samples indicative of the plant sludge, and the sodium aluminate to modify the resultant sludge in an attempt to improve stability. A typical neutralisation (NaOH) titration curve is given in Figure 4.

Analysis of the residual titration solutions and precipitates indicated iron, aluminium, uranium, and copper were removed from solution at low pH (buffer ~pH 4.5). Manganese and silicon were removed at pH 8 -10, and magnesium removed above pH 10.

Titration using milk of lime also precipitate gypsum, the amount dependant on the solubility product (K_{sp}) of calcium sulfate. Gypsum formation, however, does not alter the hydroxide ion concentration and as such gave similar pH neutralisation curves to the caustic titrations.

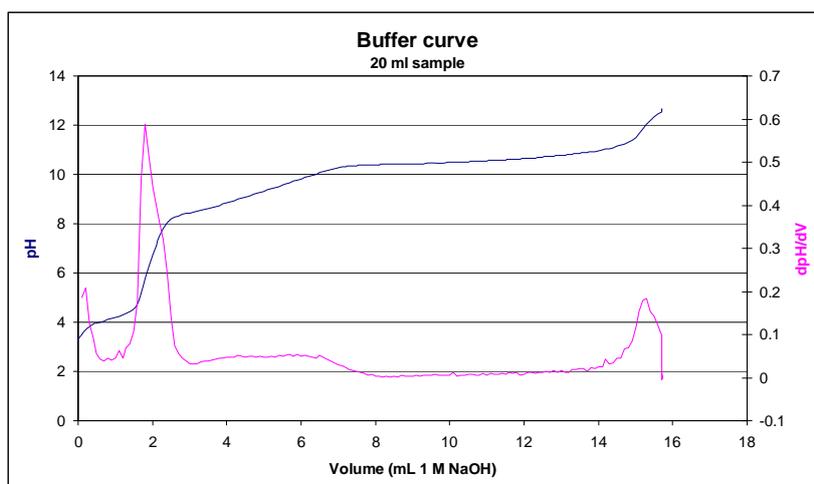


Figure 4. Typical buffer curve for Ranger process water with NaOH.

An observation in all titrations of Ranger process water was the initial removal of Mn at intermediate to high pH as a pale hydroxide precipitate, possibly manganite or pyrochroite. Upon standing, however, the precipitated Mn spontaneously transformed into a brown-black precipitate indicative of the formation of the Mn-oxide, pyrolusite.

Leaching

Dried sludge was leached using DI water, dilute sulphuric acid and Ranger process water (tailings discharge liquor) to determine the extent of metal re-leaching. The samples (10% solids) were bottle rolled over 24 hrs and the liquors assayed. The percentage of metals leached from the sludge is given in Table 5. Magnesium was the only metal to be significantly leached from the sludge, increasing at lower pH. Manganese and silicon showed some leaching in acid but neither were re solubilised in DI or Ranger process water. It was observed that sludge when added to Ranger process water was not only stable but capable of precipitating additional manganese from the process water.

Table 5. Metals re leached from Ranger process water sludge.

	pH @24hrs	Al	Ca	Cu	Fe	Mg	Mn	Si
Leached		%	%	%	%	%	%	%
DI	9.35	-	2.7	-	-	18.1	-	0.8
acid	7.04	-	2.8	-	-	82.1	5.3	10.0
PW	8.12	-	-	-	-	26.6	-	-

Rheology

Rheology measurements of fresh sludge from lime neutralisation titrations indicated the sludge was thixotropic. High initial shear stress (~900 Pa) values were obtained at low shear rates which decreased rapidly with agitation. Except for the initial thixotropic spike shear stress was generally less than 100 Pa (density <30% w/w) for shear rates up to 400 s⁻¹. Cyclic scans indicated the sludge maintained its structure in subsequent loops with the thixotropic peak observed in each cycle.

Yield stress was best represented by the Casson model which produced a value of 80 Pa at 27 % solids (w/w). The high yield stress at low percent solids indicated pumping densities in excess of 30% (w/w) would be difficult to achieve. The ANSTO pilot rig only achieved an underflow density of 27 % by recycling the underflow stream (300 %).

To determine if particle size changed with time or agitation Focussed Beam Reflective Measurements (FBRM) were made on diluted samples (7% w/w) and chord lengths measured with time for a range of stirring speeds (250-1000 rpm). The average measured initial chord length was 26 µm (at 250 rpm) which increased to 29 µm with increasing agitation speed (1000 rpm). At slow agitation speeds (250-500 rpm) chord lengths also increased with time. The small (1-10 µm) chord count decreased with both agitation speed and time. All the data suggests shear induced aggregation may be a property of this sludge.

SEM / EDS Analysis of Hydrotalcite Sludges

Precipitates were prepared from Ranger process water by titration of sodium aluminate and either caustic or milk of lime. The metal cation (M⁺² : M⁺³) ratios were prepared at 2:1 and 3:1 using procedures outlined in Douglas et al. 2009. The addition of sodium aluminate was an attempt to produce hydrotalcites in the sludge to enhance stability. Four precipitates were prepared and the phases present identified by SEM. In all 11 images were obtained from four samples with 18 EDS spectra obtained from individual crystals. Mg:Al molar ratios for each of the spectra were calculated from the EDS spectra.

In general the 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 which is common in synthetic hydrotalcites (e.g. Allada et al., 2002, Obalova and Fila, 2005), and likely in this case given the abundance of Mn in the Ranger process water.

The presence of thenardite as a precipitate in all of the titrations was confirmed by its distinctive Na-SO₄ chemistry. Similarly, gypsum/bassanite precipitates in titrations with MOL were also readily identified by their Ca-SO₄ chemistry. Mn was generally associated with Mg and Al in hydrotalcite precipitates.

A typical precipitate by titration using a Mg:Al ratio of 3:1 with a NaOH finish is given in Figure 8. The hydrotalcite (1) crystal gave a Mg:Al ratio of 1.3 (via EDS). A similar image of hydrotalcite precipitated using lime is given in Figure 9, shown within a mass of smaller gypsum particles.

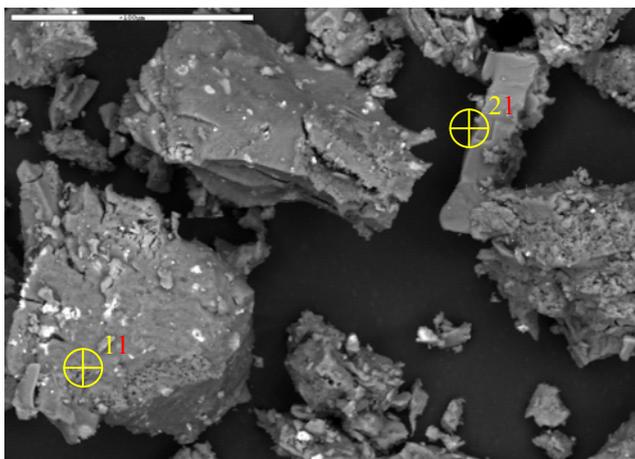


Figure 8. HT crystal (1) and thenardite (2) precipitated from 3:1 titration with NaOH.

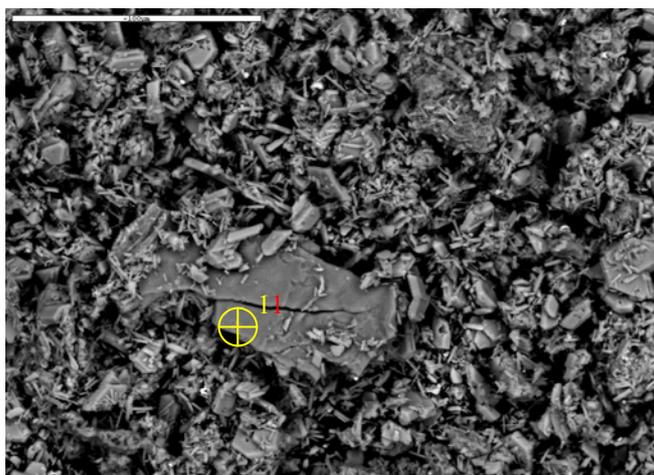


Figure 9. HT crystal (1) in a mass of gypsum particles. Precipitated from 3:1 titration with $\text{Ca}(\text{OH})_2$.

4. CONCLUSIONS

Lime neutralisation of Ranger process water produces sludge consisting predominantly of calcium sulphate (74%), magnesium hydroxide (17.5%) and manganese hydroxide (5.4%) and other minor metal hydroxides. The precipitated sludge is relatively stable within Ranger tailings water ($\text{pH} > 8$) with the exception of magnesium where significant re leaching can occur.

Rheology data indicates the sludge is thixotropic and has a high yield stress of 80 Pa at 27% solids suggesting thickening and pumping at high percent solids would be difficult.

The addition of sodium aluminate forms hydrotalcite minerals within the sludge and has potential to improve the physical characteristics and long term storage stability. Hydrotalcite formation is rapid, dewateres easily and has the ability to co-precipitate other contaminants. An assessment of these potential benefits is part of ongoing work.

Addition of aluminate to Ranger process water appears to favour the formation of 2:1 Mg:Al hydrotalcite which is predominantly amorphous and of an impure composition containing Mn and other cation substitutions. Sulphate is probably the predominant interlayer anion.

5. ACKNOWLEDGEMENTS

CSIRO wishes to acknowledge the assistance of Dr Tony Milnes, General Manager, Environmental Strategy, Energy Resources of Australia Ltd, and his staff for their support and assistance in undertaking this project.

The support of the Parker CRC for Integrated Hydrometallurgy Solutions (established and supported under the Australian Government's Cooperative Research Centres Program) is gratefully acknowledged.

6. REFERENCES

- Allada, R.K., Navrotsky, A and Boerio-Goates, J., (2002). Thermochemistry of hydrotalcite-like phases in $\text{MgO-Al}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ system: A determination of enthalpy, entropy and free energy. *American Mineralogist*, 90, 329-335.
- Albiston, L., Franklin, K.R., Lee, E. and Smeulders, J.B.A.F., (1996). Rheology and microstructure of aqueous layered double hydroxide dispersions. *J. Mater. Chem.*, 6, 871-877.

- Cavani, F., Trifiro, F and Vaccari, A., (1991). HT-type anionic clays: preparation, properties and applications. *Catalysis Today*, 11, 173-301.
- Douglas, G.B., Wendling, L.A. and Pleysier, R., (2009). Hydrotalcite Formation for Contaminant Removal from Mining Wastewaters. *International Mine Water Conference, Pretoria, South Africa*, October, 2009. (this volume)
- Dweck, J. and Lasota, E.P. (1998) Quality control of commercial plasters by thermogravimetry. *Thermochemical Acta* Volume 318 Issue 1-2 September 1998. pg 137-142
- Gu, B., Brooks, S.C., Roh, Y. and Jardine, P.M., (2003). Geochemical reactions and dynamics during titration of a contaminated groundwater with high uranium, aluminium and calcium. *Geochim. Cosmochim Acta*, 67, 2749-2761.
- Miyata, S., (1983). Anion-exchange properties of HT-like compounds. *Clays and Clay Minerals*, 31, 305-311.
- Obalova, L. and Fila, V., (2005). Kinetic analysis of N₂O decomposition over calcined hydrotalcites. *Applied Catalysis B: Environmental*, 70, 353-359.
- Parkhurst, D.L., (1995). Users guide to PHREEQC – A computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. *Wat. Res. Investigation Rpt. 95-4277, USGS*.
- Peng, S.J. and Williams, R.A. (1993), Control and optimisation of mineral flocculation and transport using on-line particle size analysis, *Minerals Eng.*, 6, 133-153.
- Seida, Y. and Nakano, Y., (2002). Removal of phosphate by layered double hydroxides containing iron. *Water Research*, 36, 1306-1312.
- Shin, H-S., Kim, M-J., Nam, S-Y. and Moon, H-C., (1996). Phosphorus removal by hydrotalcite compounds (HTLcs). *Wat. Sci. Tech.*, 34, 161-168.
- Taylor, R.M. (1984). The rapid formation of crystalline double hydroxy salts and other compounds by controlled hydrolysis. *Clay Min.*, 19, 591-603.