

SUPERNATANT LIQUOR NEUTRALISATION WITH SEAWATER AND BAYER TAILINGS MUD VIA DEEP CONE THICKENER

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Abstract

The purpose of seawater neutralisation of supernatant pond liquor (SNL) is to precipitate heavy metal impurities to such an extent that the neutralised SNL may be discharged out to sea, thus reducing the total tailings dam inventory. Alcan Gove is actively pursuing several avenues of enhancing this process to increase the rate of processing SNL and quality of effluent for disposal.

CSIRO conducted bench tests that looked at the addition of red mud slurry to the seawater, SNL mix, and concluded that the final vanadium concentration could be significantly reduced. This led to a pilot study conducted in 2000 confirmed that the addition of red mud during the neutralisation process enhanced the precipitation of vanadium from SNL. Unfortunately, separation of precipitated material remained problematic and was considered to have resulted from design irregularities in the equipment used for the trial.

A large-scale plant trial using a Deep Cone Thickener was commissioned in early 2002 to validate the original findings and to improve separation of precipitated material from the effluent. The findings will be used to develop a continuous full-scale facility for the treatment of SNL.

Further laboratory studies have indicated that addition of alkaline earth chemicals such as calcium and magnesium hydroxides may further enhance the neutralisation process. A long-term investigation is now underway to study their efficiency, where to best introduce them into the waste disposal system and whether they would have any detrimental effect on a mud based neutralisation system.

This paper describes the progress achieved to date in all these fields of research.

1. Introduction

Alcan Gove has operated an SNL/Seawater neutralisation facility called the labyrinth since 1996. This facility operates on a simple ratio of SNL and seawater flows in an open settlement basin, with a process that efficiently removes some heavy metal species. Options to increase the processing rate of SNL are limited due to environmental restrictions and the costs of processing the precipitate generated.

Recent research by CSIRO, and confirmed by Alcan Gove in field trials, has shown that:

- Separation of the precipitate by gravity settling can be enhanced with polymer addition;
- Most heavy metal species can be efficiently extracted from the process stream with the addition of red mud slurry (more efficiently than with seawater alone); and
- Processing in a thickener facility is preferred due to the improved management of precipitate.

The aim of the recent trial was to further investigate the neutralisation chemistry by determining the minimum amount of seawater and red mud slurry required to produce an overflow that could be discharged into the environment. Minimisation of these streams would ultimately result in a more cost effective, full-scale treatment plant. The trial made use of a deep cone thickener in order to settle and thicken the precipitate-slurry.

2. Key to Acronyms

Abbreviations used throughout this document are listed below:

DW	Deep Washer (Deep Cone Thickener)
RDA	Residue Disposal Area
NOF	Neutralised Overflow
NUF	Neutralised Underflow

OF	Overflow
UF	Underflow
SW	Seawater Fresh
ESW	"Spent" seawater used in evaporation circuit
TSS	Total Suspended Solids
SNL	Supernatant liquor
DWOF	Deep Washer Overflow
DWUF	Deep Washer Underflow

3. Description of Operation

SNL, red mud slurry and seawater were mixed in a tank, in which the precipitate was formed and removal of heavy metals occurred. Approximately 10–30m³/hr of underflow was bled from a deep cone thickener, while SNL was supplied at a rate of 30m³/h. Seawater from evaporation discharge was fed at a rate of approximately 200–240m³/h. The reactants were combined in a tank and allowed to mix 15–20min.

The next step was separation of the neutralised liquor from the solids in a deep cone thickener. The neutralised slurry was then pumped via a variable speed pump into the existing feed system of the deep cone thickener. Polymer was added to the feed-well as per normal deep cone thickener operation. The overflow reported to the containment pond for security settling or the environment as required. The underflow reported to the trial stacking area, or the RDA.

4. Deep Cone Thickener Commissioning and Operation

During commissioning, time was initially spent on setting up the mud bed control and polymer addition of the trial deep cone thickener. General feed flow conditions were set to a maximum feed flow rate of 320m³/h and between 3 to 10% feed solids during this time. Three

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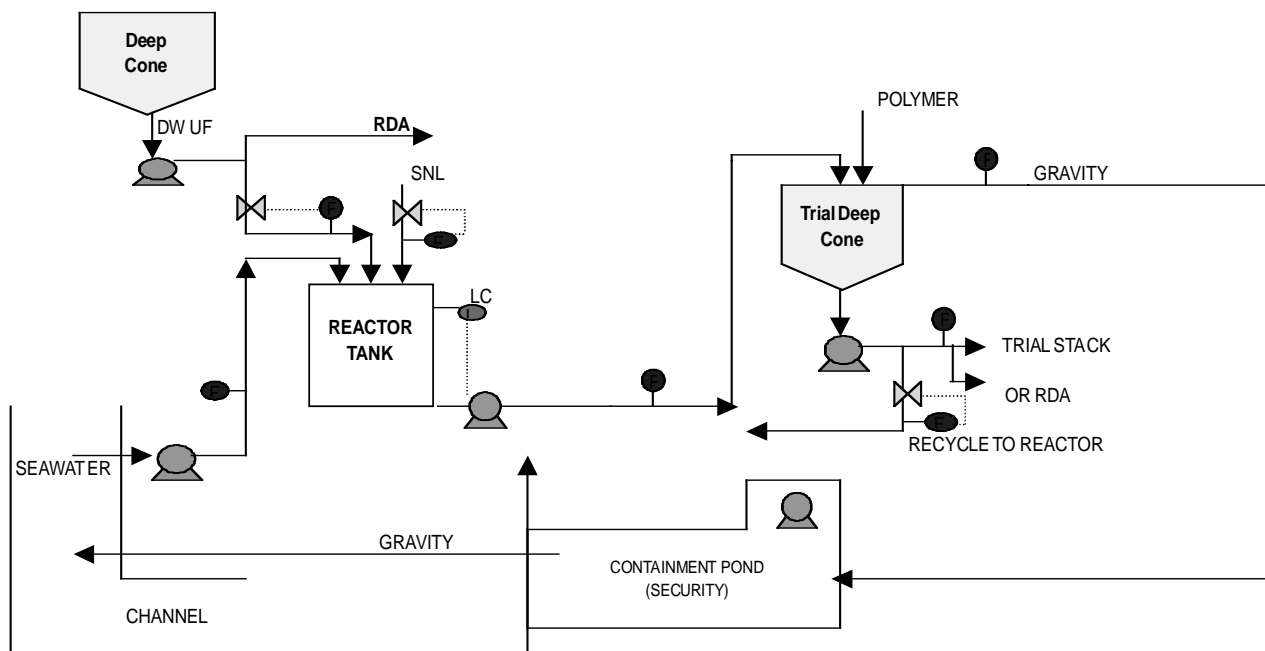


Figure 1 — Trial Layout

modes of operation of the deep cone thickener underflow pumping were tried: an auto set point of the underflow rate, auto cascade control based on mass in — mass out calculations and auto cascade control based on light mud density. It was established that the cascade control based on light mud density indication was the best performer.

An underflow recycle line of the neutralised mud was later installed in order to control to a specific feed solids concentration. This proved to be very useful in optimising the settling of the precipitate-slurry. Various conditions were investigated including using only recycle mud to settle the precipitate (i.e. no new mud). It was found that using recycle mud alone satisfactorily settled the precipitate-slurry, however metal removal was poor due to the lack of fresh deep cone thickener slurry.

4.1 Continuous Operation

The trial was normally run only during day shift to collect samples for the optimisation of the chemistry. Due to this mode of operation, the density of the underflow was limited to an average of around 29% solids and a torque of 10%. The trial was then run for an 80-hour period in order to build up a mud bed to improve the deep cone thickener underflow density. The feed rates to the deep cone thickener for the trial were low (10–20 dry t/h) compared to normal plant operation (50 t/h) and hence the density was slow to increase.

For the first 24 hours the feed rate was 3.75% feed solids at 10 t/h. The inventory build up during this time was 2 t/h and the density increased from an empty bed to 27% underflow solids. The torque increased from 10 to 24%. To speed up the process, the feed solids were increased to 10% and the SNL was turned off to maintain a reasonable overflow quality during this period. In the following 6 hours, underflow density increased to 32% solids. After 64 hours, the underflow density reached 38% solids. The trial was encouraging, however the full potential of the underflow density may not have been realised due to time constraints. It was observed that the underflow mud did compact further over time. After five days, for example, the density of the mud had compacted to 41%.

The overflow clarity was generally clear for the duration of the trial, although at the higher feed solids rate of 10% more carry over of red mud particles was observed. The overflow was less than 50g/m³ TSS (total suspended solids). The final outfall discharge median for Alcan Gove is around 60g/m³.

To ensure good overflow clarities, polymer addition was set at around 125g/t. However, limited time and flexibility meant that the addition rate was not fully optimised. Addition rates of 250 g/t or more did not seem to improve settling or overflow clarity.

4.2 Mud Stacking

Approximately 70m³ of mud at 28% solids was poured into a trial stacking area and allowed to dry. After 7 days the mud was quite dry and cracked. This is not what was expected, given the relatively low density of the mud. An additional bay was poured between 500 to 700mm deep. This is around the same depth that normal deep cone thickener mud is currently stacked at the RDA. Again the bay dried at the same rate. This is an encouraging result considering normal deep cone thickener mud takes about 30 days to dry after being repeatedly worked with heavy machinery. The accelerated drying rate suggests that the permeability of the neutralised mud is higher than normal mud and it appeared that the neutralised mud was more friable.

5. Neutralisation Chemistry

One of the key targets used by Alcan Gove for disposal of wastewater into the environment is based upon a target concentration of vanadium not exceeding 0.1g/m³. A small seawater neutralisation system (the labyrinth) that operates at 40m³/hr has been designed to lower vanadium levels in SNL to 1.0 g/m³ by addition of up to ten parts seawater. This is diluted in the main seawater discharge channel. Research into further reducing the vanadium concentration of the RDA discharge has been on going as this represents the best opportunity to increase throughput rates of a neutralisation system and decrease the significant inventory of existing wastewater. CSIRO completed a study that looked at the addition of a red mud slurry to the SNL:SW mix, and

concluded that at a reduced soda concentration the final vanadium concentration could be significantly reduced. The suggestion was that the bauxite residue solids showed an ability to scavenge vanadium at lower metal concentrations. Their observations were confirmed during a pilot trial, but as the process had not been fully optimised at that time, an additional trial (reported here) was performed.

Understanding of the chemistry of this type of neutralisation is of great importance if the process is to be further improved. The reaction between seawater and dilute sodium aluminate liquors forms a precipitate; a chalky white substance having the chemical composition $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$. Referred to as a layered, double hydroxide, this substance has a basic structure consisting of two hydroxide layers having a slight positive charge (where the aluminium ions are present) and separated by an interlayer space. Anionic compounds (in this instance, the carbonate ion) inhabit this space providing support and stability, neutralising the overall positive charge.

As vanadate (VO_4^{3-}) is the main vanadium species present at the high pH of dilute sodium aluminate, it is hypothesised that its incorporation into the interlayer space (in place of carbonate) is the principal mechanism by which vanadium is removed during the seawater neutralisation process. Even though the addition of red mud appears to assist with removal of vanadium, no definitive evidence was found that the mud solids were an instrumental factor. It is believed that the apparent improvement resulted primarily from precipitation of an additional amount of hydrotalcite, formed when the small amounts of sodium aluminate liquor present in the added mud reacts with seawater.

In addition, insoluble calcium compounds such as calcite ($CaCO_3$), whewellite (CaC_2O_4) and calcium aluminium hydroxide ($Ca_2Al(OH)_7$) or hydrocalumite will precipitate. There is evidence to suggest that some vanadium will become intercalated into hydrocalumite and possibly calcium aluminium hydroxide, but the suitability of oxalates and carbonates for vanadium removal is still open to conjecture.

The effectiveness of neutralisation can apparently be expressed in terms of the seawater volume to soda mass ratio in the feed, and the molar ratio of the magnesium in seawater to the aluminium in liquor. These are expressed as SW/ Na_2O (m^3/t) and Mg/Al (mol/mol) respectively. The results of this trial indicated that optimum vanadium

removal occurred at an Mg/Al ratio between 3 and 5, and 285 to 325 (m^3/t) Na_2O .

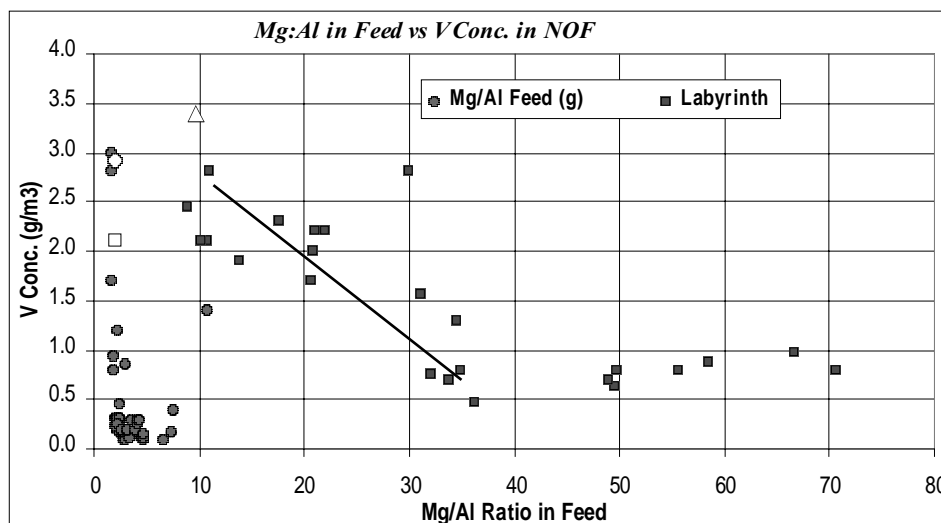
Once the Mg/Al exceeds 5 there is an excess of seawater. Whilst aluminium is used to completion, it appears that there is insufficient precipitation to remove all the vanadium. If the ratio is less than 3, precipitation of aluminium is incomplete (magnesium becomes the limiting reagent) and some vanadium will remain in solution, as the precipitate formed will already be saturated. Addition of extra seawater is therefore required to precipitate the remaining aluminium, and increase the capacity to remove the remaining vanadium. At a SW/ Na_2O of less than 285 m^3/t , the lack of seawater means that pH and alkalinity of the overflow is not effectively neutralised. At concentrations in excess of approximately 325 m^3/t , the excess of SW results in a dilution effect only.

Alcan Gove's existing seawater neutralisation facility typically utilises a Mg/Al ratio between 8 and 20 at a SW/ Na_2O ratio of 400 m^3/t . The final overflow is characterised by an excess of magnesium, complete depletion of aluminium, and a higher than desired concentration of vanadium (due to the limited formation of precipitate). Increasing the feed volume of SNL to achieve a Mg/Al ratio between 3 and 5 would result in a very low ratio of 150 m^3/t and result in high pH and alkalinity. The main reason for this is the relatively low concentration of aluminium in SNL (between 400 and 800 g/m^3), indicating that a more concentrated stream (such as deep cone thickener underflow, (DWUF) which has an aluminium concentration in the order of 5000 g/m^3) would be required for effective neutralisation.

Although deep cone thickener underflow adds extra aluminium into the process and can therefore assist with precipitate formation if the blend ratios are correct, it will also introduce additional vanadium. This leads to the suggestion that the system's efficiency could be improved if a liquor stream rich in aluminium, and without other metallic impurities was introduced. Unfortunately, such a stream is not readily available, so the use of a waste product such as deep cone thickener underflow slurry would represent the most economic option.

5.1 Addition of Deep Cone Thickener Mud and the Mg/Al Ratio

Figure 2 demonstrates the effect of Mg/Al feed ratio on vanadium concentration in the neutralised overflow. It shows that vanadium removal increases as the Mg/Al ratio



approaches the 3 to 5 range, and then falls away again as the ratio exceeds 5. Removal of vanadium is optimised (in excess of 95%) once a ratio of 3 is obtained.

A recycled stream of the neutralised underflow slurry, and no new mud was introduced into the process at ratios in excess of 8. The data indicates that the recycled stream alone does not assist with neutralisation. However, in the presence of new mud slurry, it will provide a second pass situation, where further removal of vanadium may occur whilst assisting in the settling of the precipitate-slurry.

The kinetics of the seawater neutralisation system is such that aluminium is quantitatively removed when the Mg/Al ratio reaches 3:1 (as defined by the hydrotalcite's chemical formula). This is also the point at which removal of vanadium is at its optimum, given the concentrations of the liquors examined.

Figure 2 also provides a comparison between the trial data and that obtained from the labyrinth under typical operating conditions. The dilution effect of the excess seawater at Mg/Al ratio greater than 10 is clearly visible. At this point, addition of seawater at a 40:1 ratio is required to reduce vanadium concentrations to 0.5 g/m³.

Precipitation of calcium and aluminium can result in formation of another layered double hydroxide (hydrocalumite) and follows a relationship similar to that observed for magnesium and aluminium. The cation ratio (Ca/Al) is much lower, between 0.5 and 0.8. However, hydrotalcite is the preferred form of the layered double hydroxide precipitated, as there is a much lower concentration of calcium in seawater compared to magnesium.

Laboratory experiments were conducted to confirm that these results could be duplicated in the absence of red mud. Three experiments, containing mixtures of SNL and ESW; SNL, ESW and DWUF slurry; and deep cone thickener overflow (DWO), SNL and ESW were performed. The data obtained (represented by a white, triangle, circle and square) fit well into the observed trend. Although the soda concentration of the DW liquor was underestimated (thus providing a SW:Na₂O ratio of only 250 m³/t) removal of vanadium was observed to improve significantly with the of DWO liquor in the absence of mud.

5.1.1 Vanadium Removal

The results of this trial indicate that 96–98% of vanadium present in SNL can be removed. Tighter control over the chemistry and precipitation kinetics in line with improved understanding of the changing feed conditions would assist greatly in improving the process. In response to this, Alcan Gove has been actively investigating the addition of other materials to make removal of vanadium more efficient, as a result of either precipitation of more active layered double hydroxides or through modification of the hydrotalcite crystal structure and properties.

5.1.2 Arsenic Removal

Arsenic is also readily removed by layered double hydroxide precipitation and again is optimal where a Mg/Al ratio close to 3:1 exists. The addition of red mud

appears to have very little impact on its removal, suggesting that adsorption onto the mud solids is not a favoured mechanism. Its efficient removal (>96%) with hydrotalcite precipitation most likely occurs through the same mechanism as that observed for vanadium.

5.1.3 Molybdenum Removal

No evidence could be found that suggests molybdenum is removed within the process, and any decrease in concentration is believed to be the result of seawater dilution, rather than neutralisation. The Molybdate species (eg MoO₄²⁻) are physically larger than either arsenates or vanadates making it much more difficult for them to fit into the interlayer space of a layered double hydroxide. Lack of any evidence of removal of molybdenum also suggests that absorption onto red mud solids has not occurred.

5.1.4 Aluminium Removal

At an Mg/Al ratio of less than 2, excess Al is present in the feed. Precipitation of Al is complete at Mg/Al ratios greater than 3 as precipitation of hydrotalcite is optimised.

5.1.5 Magnesium and Calcium Depletion

Magnesium and calcium are effectively depleted at ratios below 2, as they are fully consumed in the precipitation process. Additional seawater is therefore required to ensure that all of the aluminium is removed and that heavy metal removal is optimised. Once all of the aluminium has been precipitated, excess magnesium and calcium will remain in the seawater and are then free to precipitate as other species such as carbonates and oxalates.

5.2 Addition of Other Solids

Extensive laboratory tests have been performed using other common calcium and magnesium salts in an attempt to improve the neutralisation process. If suitable substances can be identified, the amount of seawater utilised in the facility could be further reduced and economic efficiency increased. The main thrust of laboratory experimentation has been directed towards finding potential candidates for field trials at a later date, if economically justified.

These tests have also allowed development of better understanding of the mechanism by which metallic species are removed from liquor during seawater neutralisation. Even though the exact mechanism of removal has yet to be fully detailed, the results thus far obtained have generally been found to be consistent with those in published literature.

5.2.1 Calcium Salts

Calcium hydroxide in the form of slaked lime (milk of lime) is available in the plant and was considered a potential candidate. When it is brought into contact with dilute sodium aluminate, a layered double hydroxide known as hydrocalumite will precipitate. This has the capacity to remove metallic species such as vanadium and arsenic in the same manner as the hydrotalcite formed during seawater neutralisation.

Table 1 — Laboratory Experiment

Test	SNL (m ³ /h)	SW (m ³ /h)	DWLiquor (m ³ /h)	Total Liquor (m ³ /h)	Feed Mg/Al (mol/mol)	SW:Na ₂ O (m ³ /t)	V Rec. %
DOF SNL ESW	14	100	8	22	2.4	246	64%
SNL ESW	14	100	0	14	10.8	458	25%
MUD SNL ESW	14	100	8	22	2.4	253	69%

Figure 3 demonstrates the effect on vanadium concentration of adding 40% milk of lime to SNL. Vanadium will only be removed once a threshold value of around 4g/l is passed, but the process then improves in efficiency quite linearly and to completion at a value around 24g/L of SNL. The threshold and final value are dependent upon concentrations of carbonate and oxalate in the SNL, both of which form calcium solids that are less soluble than hydrocalumite and need to be precipitated before the layered double hydroxide forms.

Milk of lime addition does not appear to be economically viable, but economics improve if carbonate and oxalate loads of SNL are significantly reduced. Other calcium salts (chloride, carbonate and sulphate) have been tested, but none of these were removed metallic species with the same efficiency as lime, even in the absence of dissolved carbonates and oxalates.

5.2.2 Magnesium Salts

As magnesium from seawater is required to promote the precipitation of hydrotalcite inside the neutralisation facility, a number of magnesium salts were also tested under laboratory conditions to see if they could enhance the facility's performance. Magnesium hydroxide was ineffective, hydrotalcite could not be produced under ambient conditions and none of the metals were removed.

Magnesium sulphate was found to be more useful than $Mg(OH)_2$ in that hydrotalcite was produced and arsenic removed from the liquor. Even though magnesium sulphate was used successfully to remove vanadium at levels of

100 g/m^3 from a 'synthetic' sodium aluminate solution, removal from SNL was found to be inefficient. This clearly does not fit expectations, and needs further investigation.

Although no other solids have so far been identified as suitable additives for improving the efficiency of the seawater neutralisation process, research is continuing. This includes the use of materials other than those tested as well as investigating the possibility of changing the kinetics of the system to improve the physical characteristics of the precipitate formed.

6. Seawater Minimisation

Four trials were performed to determine the effect of minimising the SW/Na_2O ratio on neutralised overflow impurities, while maintaining a constant mud to SNL ratio of approximately 1:1 by volume.

The results show that when the SW/Na_2O is between 280 and 315 m^3/t , vanadium removal greater than 90% was achieved. As rates of seawater addition below 250 m^3/t did not efficiently remove vanadium, further trials were performed only using rates that exceeded 280 m^3/t .

Figure 5 demonstrates the relationship between seawater addition and vanadium concentration in the neutralised overflow. The trend indicates that rates of seawater addition between 280 and 325 m^3/t are required to reduce final vanadium concentrations to less than 0.250 g/m^3 . Note however, that no account has been made for variables such as solids feed rates and initial concentration of other metal species.

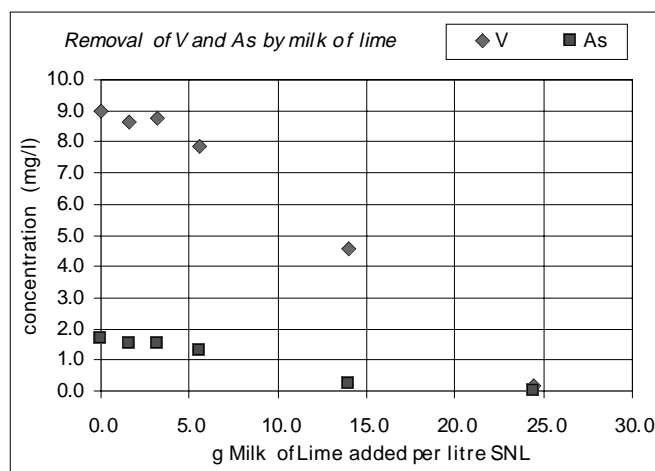


Figure 3

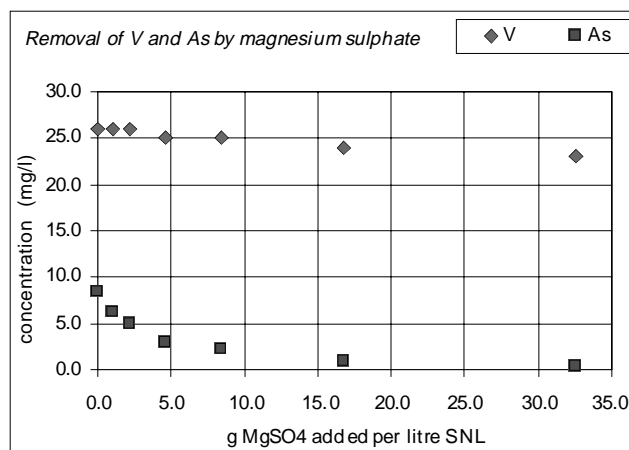


Figure 4

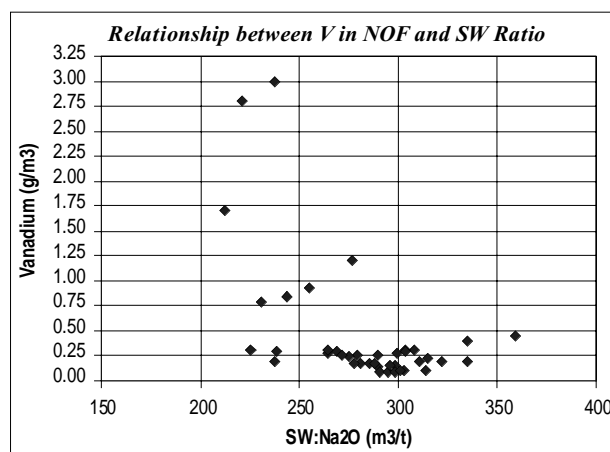


Figure 5

6.1 Excess Seawater Addition

A trial was also performed where seawater was added at a rate in excess of 1000 m³/t Na₂O. The concentration of vanadium did not decrease significantly, indicating that the most economical means of further reducing concentration of the metal species in the neutralised overflow would appear to be through post treatment dilution.

7. Repeatability of Trial Results

Due to the variable nature of the DW mud, it is difficult to exactly replicate the feed conditions over a period of several days, but the performance of five duplicate scenarios demonstrated that similar results could be achieved. The feed conditions used were approximately 5% solids, 45m³/h total feed liquor and 210m³/h seawater (or 315m³/t Na₂O). The scenarios were run over a period of eight days, with sampling performed during the middle of each.

8. Conclusions

It has been demonstrated in the field that optimum removal of vanadium and arsenic from SNL using the seawater neutralisation process can be obtained when an Mg/Al ratio of between 3 and 5 exists. In addition, a SW/Na₂O ratio between 285 and 315 is also required to

ensure extraction of around 98% of these species, however this corresponds to a high Mg/Al ratio. Findings from the field trial are supported by laboratory evidence that suggests vanadium is incorporated into the hydroxalcalite that precipitates during neutralisation.

This intimates that the addition of a more concentrated stream of sodium aluminate into the existing seawater neutralisation facility to ensure a Mg/Al ratio between 3 and 5 is required to enhance removal of vanadium from the neutralised overflow liquor.

Interpretation of the data presented here suggests that red mud serves as a source of entrained liquor containing a suitable concentration of aluminium. The mud further assists by aiding settling of the precipitate, which can be further improved if polymer addition is optimised. Approximately 3% by solids of red mud is required for effective settling of the mud-precipitate mix and production of a clear overflow slow.

One unexpected outcome was encountered in that the dewatering capability of the mud-precipitate mixture appeared better than that of red mud produced through normal operation of the plant. Further investigation is required to see if it has any practical application to mud handling operations.

Table 2 — Eight Day Trial To Test For Repeatability of Results

Date	Total SNL (m ³ /h)	176 Liquor (m ³ /h)	Total Liquor (m ³ /h)	SW Calc (m ³ /h)	% Feed Solids	Feed Mg/Al (mol/mol)	V Rec. %
25 Mar 13:00	28	16	44	200	4.75%	2.3	94.9%
26 Mar 12:30	29	16	46	195	5.72%	2.6	95.1%
27 Mar 12:30	30	16	46	213	5.29%	3.1	95.8%
28 Mar 12:30	28	16	44	216	5.42%	3.5	95.7%
2 Apr 12:30	28	16	44	218	4.94%	3.7	95.7%
Average	29	16	45	209	5.23%	3.1	95.5%

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