Impact of beneficiated seawater on red mud neutralization

Mark Mullett[1], D. Johnstone[2], Callan Gault[1], and S. Couperthwaite[2]
1.Hatch Pty Ltd, Perth, Western Australia, Australia
2. School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, Queensland, Australia
Corresponding author: mmullett@hatch.com.au

Abstract

The neutralisation of Bayer liquor with seawater triggers precipitation of stable alkaline products. This precipitation causes a reduction in solution pH and dissolved metal concentrations in the effluent, which is suitable for discharge into marine environments. Magnesium and calcium are the key reagents in the neutralisation process. Enhancing the concentration of these reagents in seawater could potentially improve the volume efficiency of the neutralisation process as well as the kinetics associated with precipitation of the neutralisation products. This investigation compared alternative sources of seawater where the magnesium and calcium were both beneficiated using water filtration technology: nanofiltration and reverse osmosis. The investigations indicated that solutions with beneficiated magnesium and calcium increase the productivity potential of the neutralisation process with minimal implications on the composition and stability of precipitates formed. The application of the beneficiated sources also enhances the associated environmental benefits. The study also compared potential capital and energy savings associated with the use of beneficiated calcium and magnesium on downstream neutralisation processes by looking at a range of possible flow sheet options.

Keywords: Seawater neutralisation; nanofiltration; reverse osmosis; hydrotalcite; calcite.

1. Introduction

Bauxite residue produced by the Bayer process is a complex alkaline tailings containing many different metal oxides, oxyhydroxides and trace metals. The alkalinity of the residue exists in both solid and solution as [1]:

- Entrained liquor (sodium hydroxide, sodium aluminate and sodium carbonate)
- Calcium compounds, such as hydrocalumite, tri-calcium aluminate and lime
- Sodalite.

McChonchie *et al,* [2] described a red mud neutralisation procedure that uses magnesium and calcium from seawater, or enriched sources of magnesium and calcium such as seawater brines, as the most cost-effective neutralisation procedure for red mud at the time. The neutralisation involves the precipitation of predominantly hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) and calcium carbonate ($CaCO_3$) [3, 4] as a result of mixing magnesium and calcium salts with alkaline Bayer liquor entrained within red mud. Large volumes of seawater are required (15 to 20 times the volume of red mud) to achieve the required neutralisation and the environmental standards necessary for discharge back to marine environments [5].

The cost of alumina production is generally increasing and one aspect of this is the mining of lower grade bauxite ore for processing. It is therefore necessary to find opportunities to reduce capital and operating costs to offset this trend. Taylor *et al* [6] explored the option of beneficiating the calcium and magnesium using nanofiltration. The goal was to reduce the volume of seawater required for the neutralisation reaction and to improve the reagent

efficiency of the precipitation reactions. These reductions in reagent flows could translate into increased productivity with reduced infrastructure and energy costs. Some high level cost analyses were also performed.

The solutions used in this assessment were unaltered seawater and two beneficiated seawater brines produced using reverse osmosis (SWRO) and nanofiltration (NF) membranes. In basic terms, RO rejects 99.5 to 99.8 % of all salts at relatively neutral pH. The degree of concentration of salts in seawater is primarily controlled by the osmotic pressure of the solution and as a result the volume recovery of the filtered permeate ranges between 40 and 50 %. For a plant that achieves a 50 % volume recovery, the net concentration factor for all salts is approximately double. NF has a slightly different rejection mechanism, which largely relies on the charge density of the membrane polymer and dissolved species. In general, at near neutral pH, multivalent ions, such as Mg and Ca, achieve a 98.5 – 99.5 % rejection whereas monovalent ions, such as Na and Cl, achieve minimal to no rejection. The deportment of these monovalent ions is largely dependant on the overall solution charge balance between the permeate and concentrate streams. A significant advantage of using NF over RO, in addition to the higher concentration factors for Mg^{2+} and Ca^{2+}, is the considerably lower Na^{+} and Cl^{-} concentrations relative to the enhanced Mg^{2+} and Ca^{2+} concentrations. This could have significant benefits when considering re-use options for red mud (Taylor *et* al, 2011, Couperthwaite *et al*, 2014).

This study has expanded on the work completed by McConchie *et al* [2] and Taylor *et* al [6] by comparing the neutralisation efficiency of different membrane filtered seawaters and completing cost estimate comparisons for different flow sheet options. The cost analyses were conducted to assess whether the capital associated with a purpose built membrane plant could be offset by reductions in downstream pumping, piping, tailings storage and other neutralisation capital. The laboratory tests for this study were completed using unaltered seawater, seawater beneficiated by a NF membrane (70 % volume recovery) and SWRO (50 % volume recovery). The concentration factor for both Mg^{2+} and Ca^{2+} in these beneficiated seawaters is approximately triple and double respectively. The cost analyses for the NF plant option were based on a volume recovery of 75 % and a Mg^{2+} and Ca^{2+} concentration factor of 4, a recovery achieved by the investigators in additional tests. The cost analyses for the RO plant option were based on a volume recovery of 40%, which is a standard recovery for SWRO plants. This provides a concentration factor of 1.7.

2. Experimental

2.1 Materials

Bayer liquor used in this study was created from a saturated evaporated liquid (SEL) with a Al_2O_3 concentration of 96 g/L. Solutions similar to those used in previous studies were prepared by the dilution of SEL with known amounts of ultrapure water, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) as required to simulate the decant liquor from red mud discharge (Couperthwaite et al. 2013).

Seawater (SW) was collected from Perth (Western Australia) at a depth of 4 m. The SW was pre-filtered using 5 μm cartridge filters before membrane filtration. A portion of this seawater was then processed by NF and SWRO filtration to provide the beneficiated test solutions. Another portion was spiked with known amounts of AR grade magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$).

NF seawater was prepared using a 101.6 mm (4”) diameter spiral wound DK membrane from GE Power and Water at a constant pressure of 2500 kPa and flux of 30 L/m^{2}h

(LMH). Magnesium and calcium were concentrated in the reject stream until a volume recovery of 70 % was reached. The volume recovery was conservatively limited to 70 % to prevent the precipitation of gypsum as calcium approached supersaturation levels.

RO brine was prepared by processing seawater using a 4" diameter spiral wound CSM 40-40-SHM seawater membrane. The pressure was increased gradually to maintain a flux of 20 LMH. A maximum recovery of 50 % was reached at 6000 kPa. The volume recovery in this case was limited by osmotic pressure.

The solution characteristics of all feed sources are shown in Table 1.

Table 1. Seawater compositions using ICP-OES.

Seawater source	Concentration (mg/L)			Concentration factor (rounded)	
	Na^+	Mg^{2+}	Ca^{2+}	Ca^{2+} / Mg^{2+}	Na^+
SW	12532	1425	468	Nil	Nil
RO*	23940	2788	981	2	2
RO**	20045	2290	745	1.6	1.6
NF*	14520	4450	1427	3	1
NF**	14640	5586	1834	4	1

* Solution used in laboratory tests
** Solution used in capital estimates

2.2 Experimental procedure

The following solutions were used in the assessment:

- Seawater (SW)
- Membrane filtered seawater (SWRO and NF) with beneficiated Mg^{2+} and Ca^{2+}
- SW solutions spiked with Mg^{2+}, Ca^{2+}
- SW into which Mg^{2+} and Ca^{2+} were added in proportionally increasing concentrations

Each seawater source was titrated with Bayer liquor until a pH of 9.25 was reached. The pH and conductivity of the neutralised solution was logged following each addition of seawater source, which was stirred on a bench top stirrer at 500 rpm. After the target pH of 9.25 was reached, the solution was centrifuged for 5 minutes at 2500 rpm using a Centurion Scientific C2 series centrifuge, after which the supernatant was retained for further analysis. The solid portion was then washed in 400 mL of H_2O and stirred using an IKA overhead impellor stirrer (35 mm) at 500 rpm for 15 minutes. The washed supernatant was again centrifuged at 2500 rpm for 5 minutes, at which point the solution was discarded and the solid portion left in an oven at 80 °C overnight to dry.

X-ray diffraction (XRD) patterns were collected using a Philips X'pert wide angle X-ray diffractometer, operating in step scan mode, with Co Kα radiation (1.7903 Å). Patterns were collected in the range 5 to 90° 2θ with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as Vaseline thin films on silica wafers, which were then placed onto aluminium sample holders.

Solutions were diluted 1 in 100 in ~ 2 % HNO_3, while approximately 0.05 g of dried precipitate was digested in 50 mL of HNO_3/HCl for 1 hour at 90°C prior to analysis using an inductively coupled plasma – optical emission spectroscopy (ICP-OES) analysis using a Hamilton Diluter. Solutions were analysed using a VISTA-MPX CCD simultaneous ICP-OES instrument using an integration time of 0.15 seconds with 3 replications, with the following wavelengths: Al (396.153), Mg (285.213), Ca (317.933), and Na (589.592). A certified standard from Australian Chemical Reagents (ACR) containing 1000 mg/L of aluminium, calcium, magnesium, and sodium was diluted to form a multi-level calibration curve using a Hamilton Diluter.

2.3 Engineering and cost estimation

There are a number of scenarios that can be considered when comparing the cost benefits of using beneficiated seawater. These include:

- Standard SW neutralisation (SWN) circuit with zero brine beneficiation
- Utilise the brine from existing SWRO capital already installed to provide potable water to the site or for municipal purposes
- New SWRO plant, dedicated to producing brine with desalinated potable water as a value added by-product of the beneficiation process
- New NF plant dedicated to provide the beneficiated seawater
- New NF plant with the saline NF permeate reporting to a SWRO plant to allow desalination of the softened feed water to provide municipal or plant supplies

The cost analysis was conducted to determine if the advantages of using membrane filtered SW could offset or reduce the initial neutralisation plant costs. For a fixed flow of seawater required for the standard seawater neutralisation process for a given circuit (Q), the concentration factors for Mg^{2+} and Ca^{2+} (Table 1) determine the volume of the beneficiated streams required to achieve the same stoichiometry. The flow in the RO brine is 0.6 Q, and for NF it is 0.25 Q. The cost analysis was based on an Australian refinery case study and is represented in AUD. The scenarios compared were:

- Standard SWN circuit with zero brine beneficiation
- New purpose built NF plant added to SWN circuit
- New purpose built SWRO added to SWN circuit
- Brine sourced from a pre-installed SWRO plant (existing capital)

Figure 1 defines the battery limits for the cost estimates within the SWN circuit. The green areas refer to the scope additions including the membrane plants, the red areas include the areas where the implementation of the membrane plants results in scope reductions, and the grey areas denote regions where the cost estimates are unaltered.

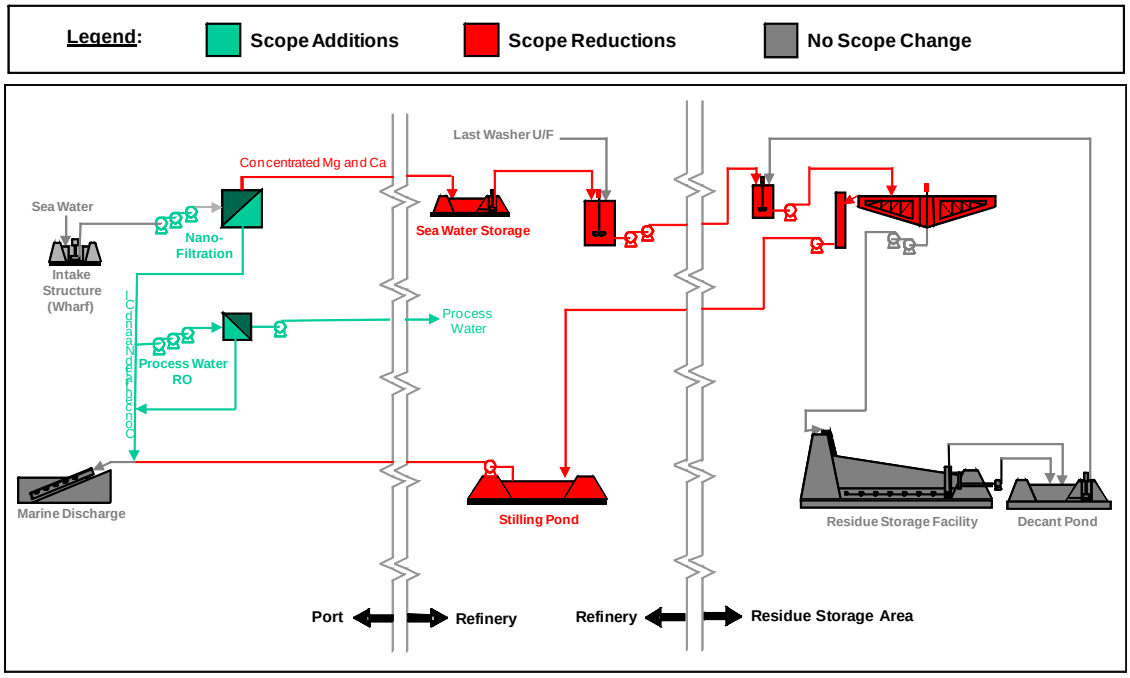

Figure 1. Scope delineation for cost estimate.

3. Results and Discussion

3.1 SWN laboratory tests

The seawater sources were titrated against simulated Bayer red mud decant solution. The test solutions and the precipitates formed during the tests were characterised using XRD and ICP-OES to determine if each seawater source produced the same mineralogy.

XRD determined that precipitates formed during SWRO and NF neutralisation showed very similar mineralogy consisting of hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), calcite ($CaCO_3$ – rhombohedral), aragonite ($CaCO_3$ – orthorhombic), thenardite (Na_2SO_4) and halite (NaCl). This indicated that the SWRO and NF sources produced the same mineralogy as SW.

Table 2 shows the concentration profile of the initial solutions, the solutions following neutralisation (pH 9.25) and the precipitates formed. Significant reductions in the volumes required to reach neutralisation were achieved using both SWRO and NF beneficiated seawater, and these reductions were relative to the stoichiometric increases in the Mg^{2+} and Ca^{2+} concentrations [7, 8]. SWRO effectively doubled the concentration of Mg^{2+}, Ca^{2+}, Na^{+} and Cl^{-} in seawater, while NF treatment increased the concentration of Mg^{2+} and Ca^{2+} by approximately three times with relatively no change in the Na^{+} and Cl^{-} content (Table 2). The results indicate that the neutralisation efficiency is related to the concentration of both Mg^{2+} and Ca^{2+} in the feed solution, resulting in a greater reagent efficiency that improves the extent of the reaction. The concentration of Mg^{2+} had the greatest impact on neutralisation efficiency followed by Ca^{2+}, while the concentration of other species did not exert a significant impact.

Table 2. Concentration profile of test solutions.

Solutions	Concentration			
	Mg	Al	Ca	Na
Initial seawater and Bayer liquor (mg/L)				
Seawater	1425	-	468	12532
RO seawater	2788	-	981	23940
NF seawater	4450	-	1427	14520
Bayer liquor (6 g/L Al_2O_3)	-	3041	1.73	27534
Neutralized solutions (mg/L)				
Seawater	366	14	183	13945
RO seawater	398	17	237	22943
NF seawater	818	7	347	15543
Precipitates (mg/kg)				
Seawater	1640	360	360	512
RO Seawater	1534	342	355	662
NF Seawater	1595	345	373	493

In all cases the neutralisation of simulated Bayer liquor to pH 9.25 resulted in > 99 % removal of aluminium from solution (Table 2). The removal is attributed to the formation of hydrotalcite and aluminium hydroxide. NF seawater was the most efficient in removing Al^{3+} from solution with 99.7 % removal. The improvement in volume efficiency is also due to the formation of hydrotalcite. The increased concentration of Mg^{2+} ions from the beneficiated SW, when titrated against Al^{3+}, OH^- and CO_3^{2-} in Bayer liquor, provided suitable conditions for hydrotalcite precipitation [9]. This confirmed that magnesium is the primary driving force behind pH neutralisation and indicated that beneficiated SW would be an effective strategy to lower the volumes required by current SWN processes. Increasing the concentration of Ca^{2+} had a reduced impact on the volume efficiency of the neutralisation process, with only slight increases in efficiency in the initial reaction stages. Calcium removes alkalinity primarily through the precipitation of calcium carbonate species, a combination of both species in solution has been shown to be the most effective approach for neutralising Bayer liquor.

3.3 Engineering and cost estimation

The pre-treatment of SW using membrane plants will add additional upstream capital to a flow sheet when compared to a standard SWN circuit, however the analysis was conducted to determine if the capital is off set by the associated reduction in the sizing of the downstream capital, which includes pumping, piping, reaction vessels, thickeners and clarifiers. The offset would also be a function of the distance from the seawater source to the refinery and hence the associated pumping and piping costs. The cost estimate for the downstream capital was therefore based on increments of 1 km up to 10 km piping length.

For greenfield refineries, any capital savings could be built into the engineering phase through reduced sizing of downstream residue infrastructure and footprint, as well as reduced power associated with pumping costs. Brownfield plants may be able to utilise existing SWN infrastructure to facilitate increased throughput following an upgrade, by using a membrane plant to maintain the SWN design flows with higher Mg^{2+} and Ca^{2+} concentrations provided. An ideal scenario for significant capital cost reductions is where an existing SWRO plant is located within the vicinity of the alumina refinery and is able to provide the brine. The two industries could operate synergistically by sharing in the capital

investment and the alumina refinery receiving the desalination plant's brine discharge stream.

The basis of design for the NF and SWRO plants are shown in Table 3. The estimates produced were for equipment and other direct capital costs. All costs are based on Australian material and construction costs. The membrane plant (Table 4) and downstream capital (Table 5) cost estimates are +/- 30 % based on industry pricing factors and internal data current at the time of the analysis. The NF plant equipment cost is greater than the SWRO because the requirement to reach a 75 % volume recovery requires additional plant capital (second filtration stage). This is somewhat offset by the higher flux rates achieved and the lower pumping costs required by the NF plant.

Table 3. SWRO and NF basis of design.

Parameters	**Units**	**RO**	**NF**
Seawater Feed Rate	MLD	96	96
Seawater Feed Rate	m^3/h	4 000	4 000
Concentrate Flow Rate	MLD	58	24
Concentrate Flow Rate	m^3/h	**2 400**	**1 000**
Permeate Flow Rate	MLD	38	72
Permeate Flow Rate	m^3/h	1 600	3 000
SWN Flow reduction	%	**40**	**75**
Mg/Ca concentration increase	%	167	400
DAF	Y/N	Y	Y
Media Filters	Y/N	Y	Y
Cartridge filters	Y/N	Y	Y
Product Quality	Text	Potable	Brine
System Availability	%	98	98
Energy Requirements	MW	5.2	6.3
Energy Recovery	%	45	0
Intake Structure	Y/N	Y	Y
Intake Chemical Treatment	Y/N	Y	Y
Sea Water Pumps	Y/N	Y	Y
Brine discharge structure	Y/N	Y	Y
Primary/Preliminary Chemical Pre-treatment	Y/N	Y	Y
Number of Stages	No.	1	3
Number of Passes	No.	1	1
Membrane Type	Text	SWRO	NF270
Concentrate	Text	Super Duplex	Super Duplex
Permeate	Text	316L SS	316L SS
Clean in Place system	Y/N	Y	Y
Process & Control Instrumentation	Y/N	Y	Y

Table 4. SWRO and NF cost estimates.

Direct Costs (Equipment & Installation)	SWRO Total	NF Total
Technical Building & Civil Works	$9 036 720.00	$9 036 720.00
Desalination Plant (Single stage)	$39 159120.00	$50 906 856.00
Seawater pumps	$1 807 344.00	$1 807 344.00
Intake	$6 024 480.00	$6 024 480.00
Brine	$4 217 136.00	$4 217 136.00
Total (Direct Costs)	**$60 244 800**	**$71 992 536**

Table 5. Downstream SWN capital as a function of distance from seawater source.

Distance from seawater source (m)	Base case SWN	RO beneficiation	NF Beneficiation
1000	$26 326 594	$20 497 715	$14 262 237
2000	$30 591 311	$24 085 650	$16 729 334
3000	$35 825 552	$27 665 833	$19 480 709
4000	$40 411 416	$31 261 420	$22 170 578
5000	$45 579 021	$34 844 224	$25 340 027
6000	$50 247 507	$39 537 967	$29 040 317
7000	$53 390 391	$43 901 811	$31 905 407
8000	$57 869 488	$47 740 924	$34 766 643
9000	$62 341 694	$51 575 819	$37 624 879
10000	$68 165 511	$56 510 893	$41 071 962

Table 6 shows the costs associated with each case when all direct capital cost items are combined. It demonstrates that significant savings are associated with the reduction of reagent flows pumped following beneficiation, particularly as a function of distance. The value of these savings, however, is less than the cost of providing a purpose built membrane plant. When all direct capital costs (including costs associated with the membrane plant and seawater intake/outfall) are combined for the various process options, the savings are not able to offset the membrane plant capital.

Table 6. Total capital as a function of distance from seawater source.

Distance from seawater source (m)	Base case SWN	RO beneficiation	NF Beneficiation
1000	$36 326 594	$80 742 515	$86 254 773
2000	$40 591 311	$84 330 450	$88 721 870
3000	$45 825 552	$87 910 633	$91 473 245
4000	$50 411 416	$91 506 220	$94 163 114
5000	$55 579 021	$95 089 024	$97 332 563
6000	$60 247 507	$99 782 767	$101 032 853
7000	$63 390 391	$104 146 611	$103 897 943
8000	$67 869 488	$107 985 724	$106 759 179
9000	$72 341 694	$111 820 619	$109 617 415
10000	$78 165 511	$116 755 693	$113 064 498

The capital costs are also represented in Figure 2, where they are compared to the costs of receiving and pumping brine from a pre-existing SWRO plant that has been installed for nearby municipal use or is part of other capital allocations to supply potable water to the refinery and associated support infrastructure. The following can be drawn from Figure 2:

- The installation of purpose built membrane plants will not offset the capital associated with reduced sizing in downstream SWN equipment and facilities.
- At a pumping distance of 7 km the volume reduction associated with the NF plant (75 %) creates greater savings compared to SWRO (40 %) despite the higher equipment costs.
- Brine is sourced from a pre-existing SWRO plant ~ 5.5 km from the refinery, has the same capital outlay as a Base Case SWN ~ 1 km from the coast.
- There may be a business case for a refinery to increase its red mud neutralisation capacity during an upgrade by installing a membrane plant to beneficiate seawater rather than upgrade much of the existing plant neutralisation infrastructure

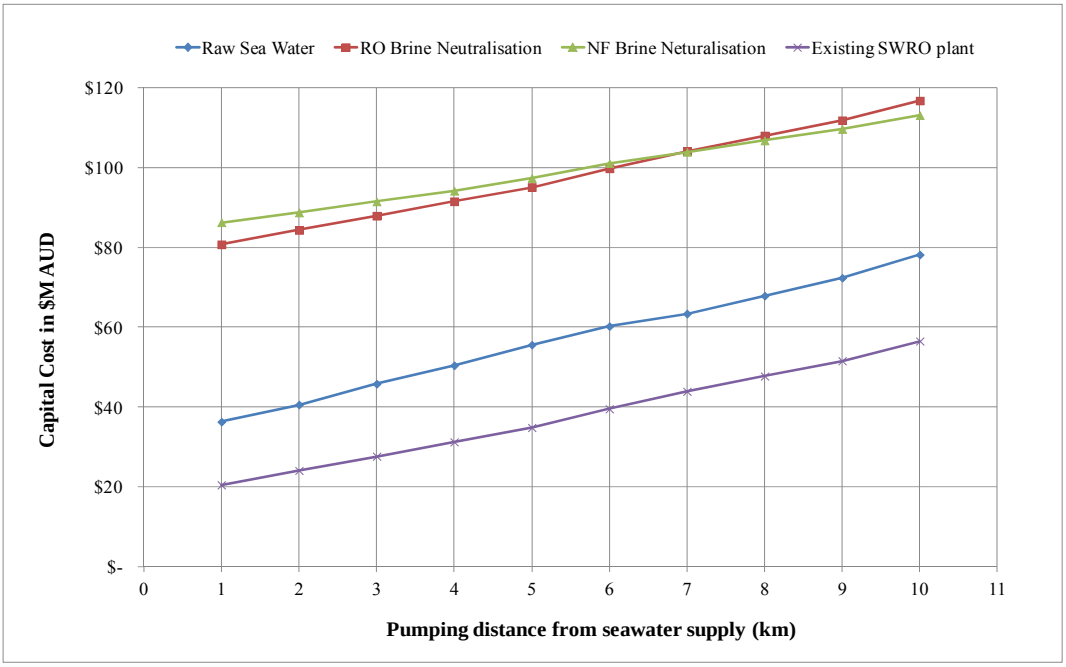

Figure 2. Total capital as a function of distance from seawater source.

4 Conclusions

- The beneficiation of SW using both RO and NF creates significant reductions in the volumes required to reach neutralisation of red mud decant liquor. These reductions were relative to the stoichiometric increases in the Mg^{2+} and Ca^{2+} concentrations.
- In all test cases the neutralisation of Bayer liquor to pH 9.25 resulted in >99 % removal of aluminium from solution with NF brine being the most efficient, removing 99.7 % aluminium.
- Significant savings in the downstream SWN capital are associated with the reduction in the volume of reagent pumping following beneficiation, particularly as a function of distance, however the savings are not able to offset the capital associated with providing purpose built membrane plants.
- If SW brine is sourced from a pre-existing SWRO plant, significant savings in downstream capital can be achieved, providing the pumping distances are not excessive.

- There may be a business case for a refinery to increase its red mud neutralisation capacity during an upgrade by installing a membrane plant to beneficiate seawater rather than upgrade much of the existing plant neutralisation infrastructure.

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