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SILICA SCALE MITIGATION FOR HIGH RECOVERY REVERSE OSMOSIS OF GROUNDWATER FOR A MINING PROCESS

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Abstract:

The feasibility of silica removal in RO treatment of groundwater from a Western Australian mining and processing operation to prevent scaling and enhance water recovery was investigated. This study has shown that it is possible to decrease the silica concentration in RO concentrate to levels that would allow an overall water recovery of 90% to 95% using 10 g/L of regenerable activated alumina adsorbent. Regeneration of the adsorbent using 2% NaOH was found to be effective for at least three regeneration cycles. A preliminary costing of the high water recovery RO process using silica removal by adsorption indicated product water (permeate) costs of $5.6/kL and savings due to a reduction in brine volume from the current 40% of feed volume to 5-10% of feed volume. It also allows better utilization of a scarce groundwater resource, allowing the production of up to 1.6 times more low salt water from a given volume of groundwater. These results warrant larger scale investigation of silica removal and adsorbent regeneration for high recovery RO processing for mining operations, and application of silica removal to RO treatment of other silica laden waters such as coal seam gas produced water.

Keywords: Silica, reverse osmosis, groundwater, scaling, high-recovery RO.

1. **Introduction**

The quality and quantity of process water used in mining and mineral processing operations often have a major impact on the efficiency of the process. In many remote mining operations in arid regions, the only source of water is groundwater, and there is often a need to demineralize this by reverse osmosis (RO) for process stages such as steam generation.

The presence of ionic components such as calcium, magnesium, carbonate, sulfate, phosphate and silicate, and components such as soluble silica (silicic acid), in the feed water of an RO process can limit the achievable water recovery by forming insoluble scale that hinders membrane filtration. While it is possible to mitigate scale formation in RO processes by ionic components by removing them using ion exchange resins [1] or accelerated seeded precipitation [2, 3], the mitigation of silica scale remains a challenge which requires more research [4].

Silica scale mitigation in RO processes is a challenge because it is difficult to accurately predict scale formation as the threshold limits of silica scale formation are influenced by a large number of parameters [5]. Although it is possible to estimate silica scaling potential of a test water based on the pure water solubility limits [6], the scaling potential of the water can be expected to be higher than this prediction if even small quantities of trivalent metal ions are present [7] or if the ionic strength is high [8], and lower than this prediction under conditions where the polymerization reactions responsible for the formation of amorphous silica are slow, e.g., at low pH [8].

Silica scale mitigation is also a challenge because silica removal can lead to waste products that pose engineering challenges for their management. It is possible, for example, to precipitate silica in the presence of metal ions such as Fe(III) and Al(III) [9], but the resulting precipitate is gel-like and difficult to dewater [10]. It is also possible to adsorb the silica onto metal oxides such as alumina, goethite and hematite [11, 12, 13]. If these are colloidal, however, this too can lead to sludge management problems. In this paper, silica removal by adsorption onto activated alumina is studied.

Activated alumina was chosen due to its effectiveness as an adsorbent for silica [11,14] and the tendency of the adsorbed silica to form a soft, gel-like, layer around the adsorbent [15], thus potentially facilitating adsorbent regeneration. In contrast, silica adsorption has been found to form hard, glass like, layers around iron oxide adsorbents [16]. The removal of silica by various concentrations of activated alumina, at different pH values and at different temperatures was studied. The feasibility of regeneration of the activated alumina with caustic rinsing was also investigated.

2. <u>Experimental</u>

2.1 Materials

The test water used in these experiments was the RO concentrate that had been derived from the 60% RO water recovery of a Western Australian groundwater. Only one batch of test water was used in all experiments, and the water was collected and transported without acidification or preservation. The test water was sampled for complete analysis on receipt and stored at ambient indoor conditions (~20°C) until needed (~ 2 weeks). All experiments were performed within a one month period and no changes in water quality were detected during this period. The activated alumina used in these experiments (Rio Tinto Alcan, nominal specific surface area: 250-270 m^2/g, d_{50}<15 µm) was used as supplied.

2.2 Chemical Analyses

Initial chemical characterization of the RO concentrate (ROC) test brine was performed by a commercial analytical laboratory. Subsequent silica, calcium and magnesium analyses were performed by Inductively Coupled Plasma spectroscopy. The pH measurements were performed using a Hach pH meter with gel filled double junction reference electrode and built-in temperature sensor.

2.3 Scaling Potential

The RO scaling potential was estimated for 90% water recovery of the ROC using ROSA8 Dow Filmtec Software. The maximum silica concentration above which the silica precipitates in the ROC was determined experimentally using a flat sheet Sterlitech Sepa CF RO module, operated with full recycle of the concentrate such that the water recovery increased with time during the experiment, similar to the procedure of Jawor 2009 [17] and Zach-Maor 2008 [18]. The concentrate reservoir and its content were maintained at 20°C by immersion in a constant temperature chilled water bath. The membranes were wet before being loaded into the flat sheet module by immersion in deionised water overnight. Samples of the concentrate were taken, filtered, and analysed for silica, calcium and magnesium by ICP. The operating conditions for the flat sheet RO experiments are shown in Table 1. The clean water flux of the membranes was measured over a 20 minute period immediately prior to the RO concentrate scaling experiment. The average clean water flux for the different membranes was found to be 25.3 ± 7.1 L/m^2/h.

Table 1: Operating conditions used in scaling study (0.635 mm shim, 1.2 mm feed spacer

Parameter	Value/type
Membrane type	SW30-ULE
Membrane area (m^2)	0.014
Concentrate flow (L/min)	2.0
Temperature (°C)	20
Approximate initial permeate flow (L/min)	0.005
Approximate initial flux (L/m2/h)	21
Cross flow velocity (m/s)	0.28
Applied pressure (kPa)	2,500

2.4 Silica removal

2.4.1   Optimization of adsorption conditions

All experiments were performed using 100 mL of RO concentrate in stirred beakers. An IKA RCT Basic (IKAMAG) magnetic stirrer with integrated temperature control was used. Experiments investigated the effect of pH with activated alumina at a dose of 2 g/L, and with 15 minute contact time. The effect of contact time was investigated at 20°C and 45°C and at 2 g/L and 10 g/L, at native pH (8.6). The effect of temperature was investigated at native pH, 2 g/L adsorbent dose, at 20°C, 35°C and 45°C. The test solution was sampled and filtered through 0.45 micron cellulose acetate syringe filter, and acidified with 3 drops of concentrated nitric acid prior to ICP analysis.

2.4.2   Activated Alumina Regeneration
2.4.2.1 Loading of silica onto adsorbent

The activated alumina was recycled through several adsorption steps before regeneration to better utilise the capacity of the activated alumina. Such processing would also be used industrially to minimise the activated alumina and adsorbent regeneration requirements for the process.

Unused alumina was loaded with silica from the ROC by recycling each batch of alumina through a series of adsorption steps, so that the adsorption capacity of the alumina could be approached. Loading was performed in a series of batch 100 mL adsorption steps at the set adsorbent concentration of 10 g/L, at 25 °C, and with 60 minute contact time. In between each batch adsorption step, the liquor was filtered through 0.45 micron cellulose acetate filter and analysed for silica by ICP to determine the extent of loading. Loading was ceased when the residual silica concentration was approximately 80% of the untreated ROC concentration, i.e. after 5 loading steps.

Loading of regenerated alumina were performed under the same conditions as the loading of unused alumina, using 5 silica loading steps.

The cumulative quantity of silica loaded onto the adsorbent (L_x) was calculated form the quantity of silica on the adsorbent from the previous loading cycle (L_{x-1}), the before and after adsorption concentration (CB and CA), the volume of test solution (V), and the quantity of adsorbent used (M), as shown in Equation 1.

$$L_x = L_{x-1} + \frac{(CB-CA).V}{M}$$

[1]

2.4.2.2 Adsorbent Regeneration

The loaded adsorbent was filtered through 0.45 micron cellulose acetate filter and then dispersed in approx. 100 mL of 2% NaOH solution to give an adsorbent concentration of 10 g/L (assuming no losses during loading stages), and stirred for 30 minutes. The alumina suspension resulting from this step (Step 1) in the regeneration was filtered through a 0.45 micron cellulose acetate membrane filter. A 15 mL sample of the filtrate was acidified with concentrated nitric acid and analysed for silicon, aluminium, calcium and magnesium by ICP to determine how much silica has been removed, how much of the alumina adsorbent had dissolved and if any calcium and magnesium had been adsorbed and released during regeneration. The removed adsorbent was redispersed in 100 mL of fresh 2% NaOH and the process repeated 8 times, giving a total of 9 regeneration steps. The alumina remaining at the end of the 9th step was lightly rinsed with 5 mL of deionised water and the loading/ regeneration cycle was repeated two times. A diagrammatic representation of one loading/regeneration cycle is shown in Figure 1.

The cumulative quantity of silica desorbed during regeneration (D_x) as a percentage of the silica present on the adsorbent after step 5 in the loading cycle (L_5, Equation 1) was calculated (as SiO2) from the silicon concentration in the regenerant solution (C_{Si}), the volume of regenerant used (V), the weight of adsorbent (M), and the atomic/molecular weight of Si and SiO_2 (28 and 60 respectively) as shown in Equation 2.

$$D_x = D_{x-1} + \left(\frac{C_{Si} \cdot \left(\frac{60}{28}\right) \cdot V}{\frac{L_5}{M}} \right) \cdot 100 \qquad [2]$$

The cumulative quantity of adsorbent lost by dissolution during regeneration (AL_x) as a percentage of the added alumina (M) was calculated from the aluminium loss in the previous regeneration step (AL_{x-1}), the concentration in the regenerant solution (C_{Al}), the volume of regenerant (V), and the atomic/molecular weight of Al and Al_2O_3 (27 and 102 respectively) as shown in Equation 3.

$$AL_x = AL_{x-1} + \left(\frac{C_{Al} \cdot \left(\frac{102}{27}\right) \cdot V}{M} \right) \cdot 100 \qquad [3]$$
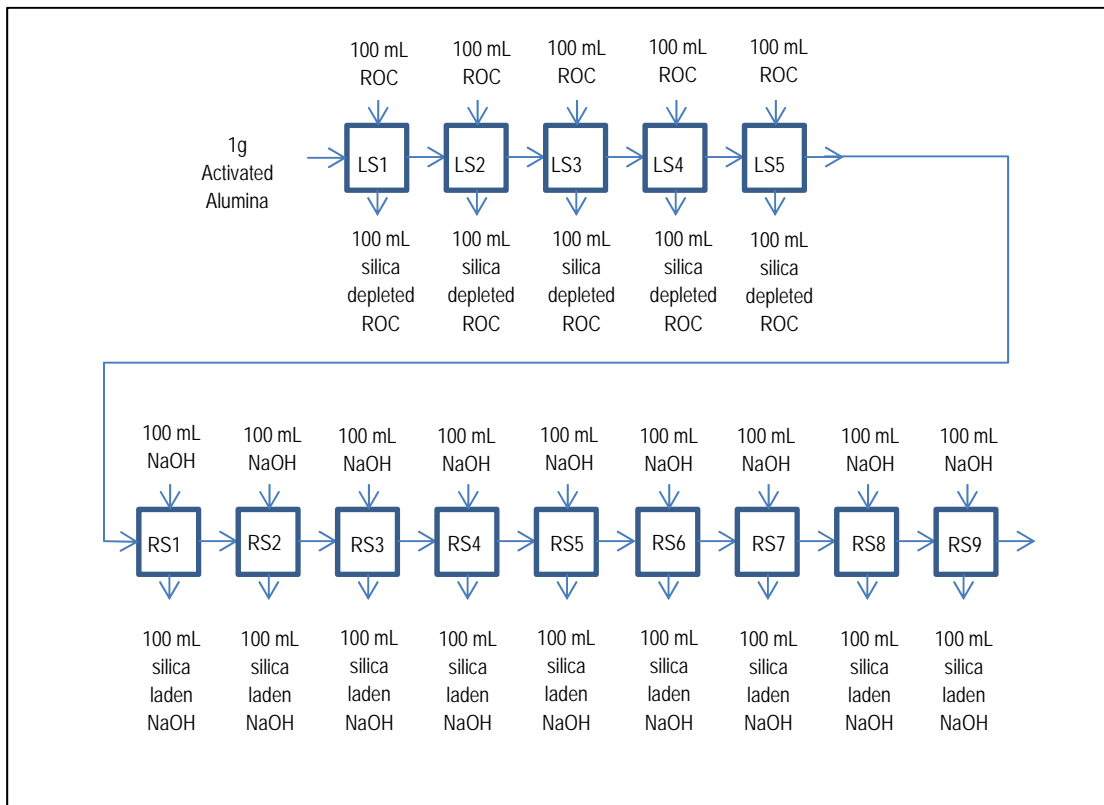

Figure 1: Summary of one loading-regeneration cycle showing 5 loading steps (LS) and nine regeneration steps (RS), using RO concentrate (ROC) and 2% NaOH regenerant.

3. Results and Discussion

3.1 Characterization of Minara Resources RO concentrate

The composition of the RO concentrate (ROC) generated at the mining site for an RO water recovery of 60% is shown in Table 2.

Table 2: Chemical analysis of RO Concentrate, as performed by a commercial NATA, Australia, accredited laboratory.

Parameter	Units	Value
pH	pH units	8.6
Reactive P (HL) - Phosphorus, reactive as P	mg P / L	0.06
TKN/TP (HL) - Total Kjeldahl Nitrogen as N	mg N / L	0.3
TOC - Total Organic Carbon	mg/L	17
TDS at 180°C - Total Dissolved Solids	mg/L	5800
Fluoride - Fluoride, as F	mg/L	2.0
Chloride - Chloride, as Cl	mg/L	2900
SO4 DA - Sulphate, as SO4	mg/L	810
Sulphide - Sulphide, total	mg/L	<0.1
Alkalinity - Bicarbonate Alkalinity as CaCO3	mg CaCO3 / L	460
Alkalinity - Carbonate Alkalinity as CaCO3	mg CaCO3 / L	54
Alkalinity - Hydroxide Alkalinity as CaCO3	mg CaCO3 / L	<2
Alkalinity - Total Alkalinity as CaCO3	mg CaCO3 / L	510
TCN - Total Nitrogen as N (Calc)	mg/L	42
NH3 as N (DA) - Ammonia, as N	mg N / L	<0.1
React. Silica - Silica, reactive as SiO2	mg/L	160
MS Total Metals - Aluminium	mg/L	0.7
MS Total Metals - Barium	mg/L	0.10
MS Total Metals - Boron	mg/L	3.0
MS Total Metals - Cobalt	mg/L	<0.01
MS Total Metals - Copper	mg/L	<0.01
MS Total Metals - Iron	mg/L	<0.2
MS Total Metals - Lead	mg/L	<0.01
MS Total Metals - Manganese	mg/L	<0.01
MS Total Metals - Nickel	mg/L	<0.01
MS Total Metals - Strontium	mg/L	3.0
MS Total Metals - Zinc	mg/L	<0.01
OES Scan - Calcium	mg/L	280
OES Scan - Magnesium	mg/L	230
OES Scan - Potassium	mg/L	73
OES Scan - Sodium	mg/L	1300
OES Scan - Acid soluble Si, as SiO2	mg/L	160

It can be seen from Table 2 that the main cationic constituents of the brine were Na, Ca and Mg. The main anionic constituents were Cl, SO_4 and CO_3. The silica content of the brine was 160 mg/L and this was totally in the reactive (non-polymeric) form as both the reactive silica and acid soluble silica concentrations were the same.

3.2 . Scaling potential of ROC

The scaling potential of the test brine (Feed) and a 90% water recovery RO concentrate with respect to calcium carbonate, calcium sulfate and silica, as predicted by the Dow Filmtec Rosa 8.0 modelling software, is summarised in Table 3.

Table 3: ROSA8 Dow Filmtec Software Scaling Information with respect to the major potential scale constituents of the test water at the native pH of 8.6 and 90% water recovery.

LSI		$CaSO_4$ Saturation (%)		Silica Saturation (%)	
Feed	**Concentrate**	**Feed**	**Concentrate**	**Feed**	**Concentrate**
1.8	4.8	16	250	81	445

It can be seen in Table 3 that the test brine (ROC) had a high potential for $CaCO_3$ scale formation, as indicated by the high positive values of the Langelier Saturation Index (LSI). The potential for $CaSO_4$ scale formation was also high. The use of lower pH and antiscalants is recommended for RO treatment of this water. The $CaSO_4$ saturation is slightly above the conservative upper limit of 230 - 400% of saturation recommended by membrane manufacturers [19], indicating that calcium removal may also be needed if higher water recoveries than 90% are required. The software also predicts that a 90% water recovery will give rise to silica scale formation. This assessment, however, is based on the silica solubility in pure water and does not take into account kinetic factors that can give rise to different solubility behaviours in complex solutions [8, 20].

The silica, calcium and magnesium concentrations in the samples taken during the flat sheet RO scaling tests are shown in Figure 2. The silica concentration (Figure 2a) shows that the silica concentration remained at approximately 170 mg/L, indicating that the silica had precipitated to its solubility limit. Comparison of this figure with the starting silica concentration of 160 mg/L reveals that the initial RO concentrate was close to this silica solubility limit before the start of the experiment. The calcium concentrations (Figure 2b) do not significantly deviate from the calculated no-precipitation line, suggesting that calcium did not precipitate. This is in contrast to the ROSA modelling which is based on equilibrium solubility data alone, which showed an LSI of 4.8 for the

concentrate, which is conducive for precipitation [21]. This may be attributable to the large quantities of magnesium present, which can act as a powerful inhibitor of calcium carbonate precipitation [22]. The magnesium concentration (Figure 2c) also does not deviate from the no-precipitation line at water recoveries less than 80%. For magnesium, however, there seems to be a downward deviation at water recoveries greater than approximately 82%, suggesting that the magnesium may be involved with the silica precipitation at water recoveries higher than approximately 82%. The ROSA modelling did not indicate that the magnesium concentration was conducive to magnesium hydroxide scale formation (results not shown).
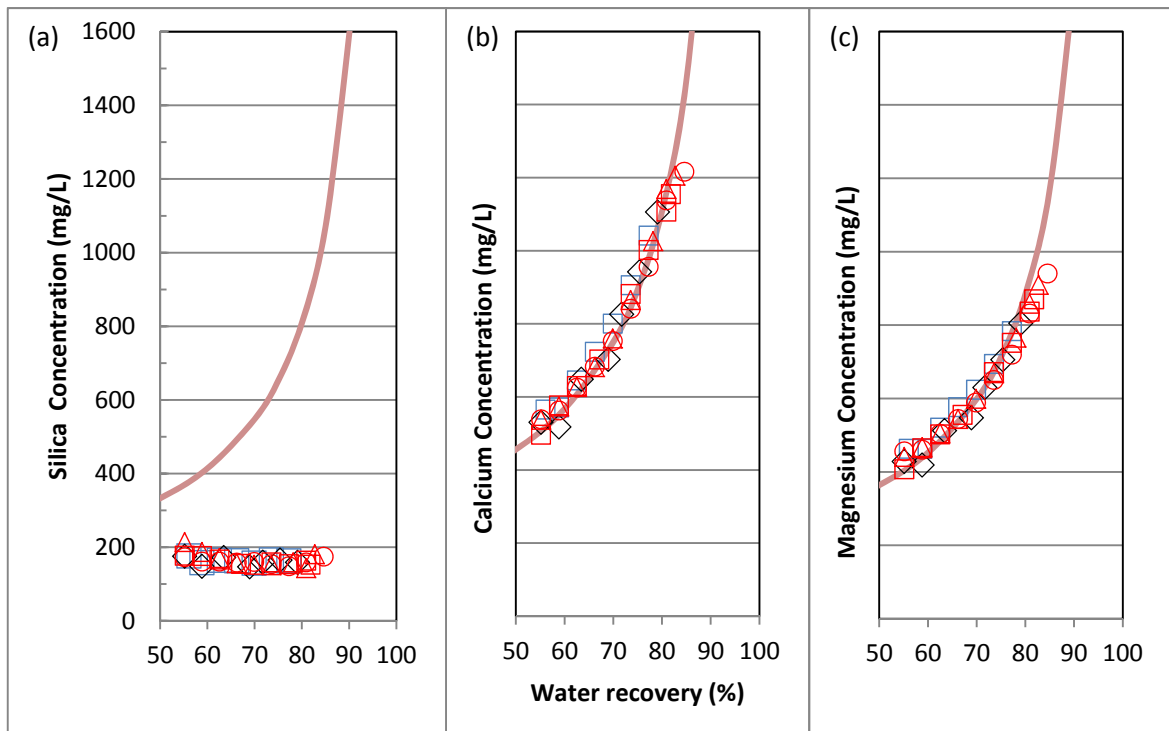

Figure 2: Silica, calcium and magnesium concentration as a function of water recovery, solid line represents the expected concentration in the absence of scale formation, different symbols are the results obtained on replicate experiments.

The approximately 170 mg/L silica solubility limit indicated in Figure 2a allows estimation of the target initial silica concentrations required to achieve different water recoveries in the RO treatment of ROC, as shown in Figure 3. It can be seen from Figure 3 that if, for example, a 40 mg/L residual silica concentration could be achieved, this would allow a 78% water recovery in the second stage treatment of ROC before reaching 170 mg/L silica, equating to an overall water recovery of 92%, i.e., 60% (the water recovery achieved in the production of the ROC test water) + 78% of the remaining 40%.
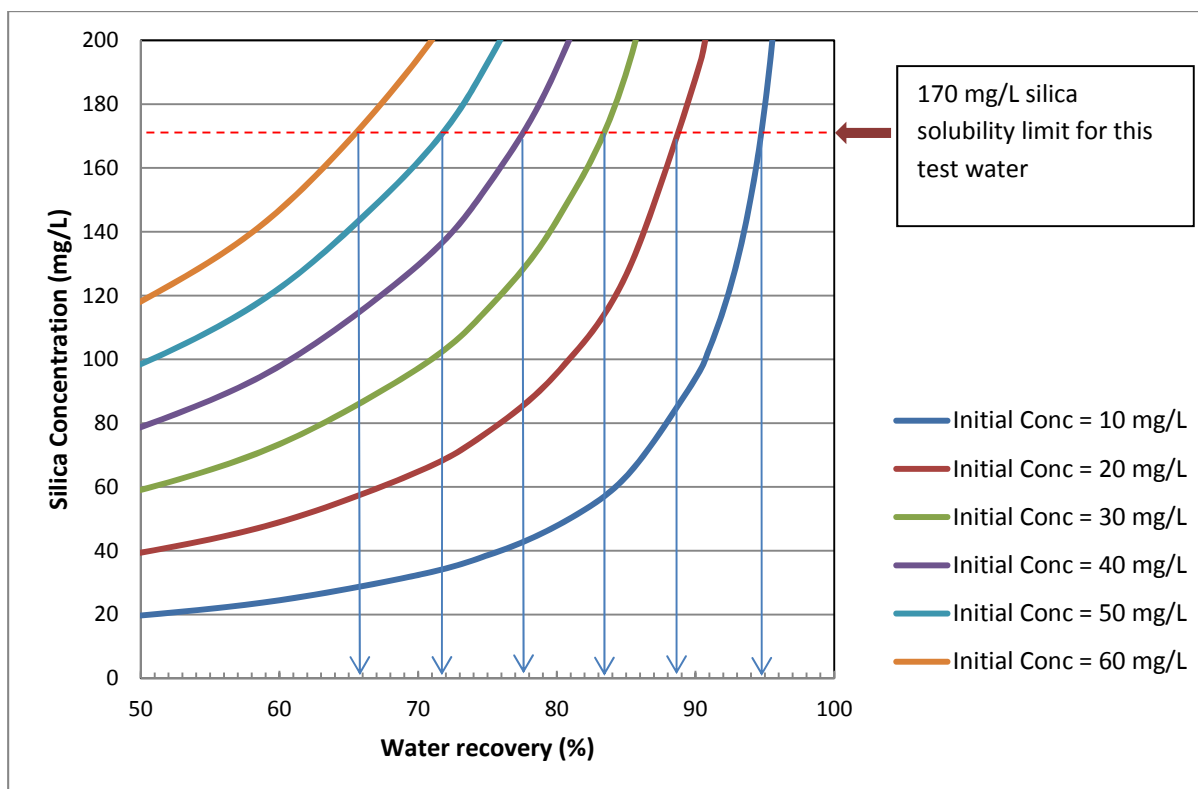
Figure 3: Prediction of target silica concentrations to achieve different water recoveries in the second RO stage (after silica removal). The lines represent the expected silica concentration in the absence of scale formation.

Although these scaling studies illustrate the difficulty involved in prediction of scaling conditions, it is noteworthy that the conditions of the batch mode flat sheet experiments with concentrate recirculation used in the current study are different to those prevailing in conventional industrial scale spiral wound continuous RO process where the concentrate enters and leaves the membrane system in a much shorter time. Slow precipitation of brine constituents may not lead to scaling in the continuous process because the brine may have left the membrane system by the time the precipitation takes place. In the recirculation mode experiments, however, where typically 10 to 12 hours were required for the desired water recovery to be achieved, scale formation from slowly precipitating constituents is more likely. The batch mode recirculation mode experiments are, therefore, potentially more vulnerable to scale formation from slow precipitation than continuous mode experiments and provide a more conservative estimation of scaling propensity. Clearly, these batch-made recirculation mode studies are not a substitute for on-site scaling studies at the proposed design conditions.

3.3 <u>Silica removal by adsorption</u>

3.3.1 Introduction

In order to achieve a system water recovery of 90% or above, a minimum of 75% water recovery must be achievable on the remaining concentrate from the primary RO process. As can be seen in Figure 3, the target silica concentration for the feed water to the second RO stage required to achieve these water recoveries for the ROC is approximately 45 mg/L.

3.3.2 Effect of pH

The precipitation behaviour of silica is not as well understood as that of other scale forming chemicals such as calcium carbonate or calcium sulfate [14]. In the absence of multivalent metal ions it is believed to involve the polymerization of silicic acid ($Si(OH)_4$) to form amorphous silica [23]. In the presence of multivalent metal ions, however, the formation of metal silicates is possible at pH values close to the pKa of silicic acid (9.8) [23]. The ROC used in these experiments contained sufficient quantities of calcium, magnesium and aluminium for silicate scale formation to occur at alkaline pH values [7]. The presence of calcium and magnesium have also been found to accelerate polymerization of silicic acid at acidic pH values, but the mechanism for this is not clearly understood [9]. This effect was found to be particularly pronounced at low silica concentrations (~100 mg/L).

The effect of pH on the concentration of soluble silica, calcium and magnesium, after contact with activated alumina for 15 minutes at ambient temperature is compared to the silica, calcium and magnesium concentration in the absence of adsorbent in Figure 4. It can be seen that in the absence of adsorbents, the silica concentration decreases at pH values higher than the native pH of the ROC (8.6). The calcium and magnesium concentration data indicates that the large decrease in silica concentration that occurs between pH 8.6 and pH 9.6 in the absence of adsorbent does not involve large decreases in calcium or magnesium concentrations, suggesting the silica concentration decreases is due to polymerization of the silicic acid to form insoluble polymeric silica in this pH range. As the pH is increased past the first pKa of silicic acid (9.8 at 25°C), the silica, calcium and magnesium concentrations all decrease considerably, suggesting the formation of calcium and/or magnesium silicates due to the increasing concentration of silicate ion, and/or the formation of calcium carbonate and magnesium hydroxide at these higher pH values.

Comparison of the data in the presence and in the absence of activated alumina reveals that the maximum decreases in silica concentration over what is achieved in the absence of adsorbent occurred at the native solution pH of 8.6. The calcium concentration decrease of 34 mg/L (0.85 mM)

observed at this pH suggests the formation of calcium silicate. The silica concentration decrease of 44 mg/L (0.46 mM) suggests that at least some of the calcium precipitation does not involve silica. The observed adsorption maximum is in agreement with the results of Bouguerra et al (2007) [11] which showed a maximum adsorption of silica onto activated alumina at approximately pH 8. These authors performed a regression analysis of the equilibrium data and found that the data fitted both Langmuir and Freundlich adsorption isotherms, suggesting that the adsorption process involves monolayer sorption onto a surface with a finite number of identical sites. They hypothesised that silica adsorbs as the silicate anion which increases in concentration as the pH is increased towards and past the pKa of silicic acid, and the decrease in adsorption at pH values higher than approximately 8 was due to electrostatic repulsion between adsorbent and adsorbate resulting from the generation of negative surface sites on the activated alumina at these pH values. Similarly, Bond et al (2007) [14] argued that the decrease in adsorption at high pH was due to competition for anion adsorption sites by hydroxyl ions.

3.3.3 Effect of adsorbent dose, temperatures and contact time

The effect of activated alumina adsorbent dose at various temperatures is shown in Figure 5a. It can be seen that at 2 g/L, an increase in temperature from 20°C to 45°C has very little effect on silica removal. These results are consistent with the results of Matson et al (1981) [24] who found that an increase in temperature up to 50°C did not significantly increase silica adsorption onto activated alumina at a dose of 2 g/L. It can, however, be seen that the use of a higher temperature (45°C) with a higher alumina doses (10 g/L) with a long contact time (60 minutes), is advantageous, allowing the achievement of silica concentration well below the target value of approximately 45 mg/L or the use of shorter contact time. The use of elevated temperatures is an attractive option for mining operations where the process produces large quantities of waste heat that can be used to elevate the temperature of the RO concentrate. This would, however, require the location of the silica removal process near the source of waste heat (e.g. near the sulphuric acid leach autoclaves in the mining process).

The effect of extension of the contact time to one hour at various temperatures and adsorbent doses is shown in Figure 5b. It can be seen that extension of the contact time to one hour makes little difference at low adsorbent dose, indicating that the alumina adsorbent surface is saturated with silica at low adsorbent dose. Surface saturation at low adsorbent dose is confirmed by the high adsorbent dose data which shows considerable further removal of silica. It can also be seen that the target silica concentration for 90% water recovery (45 mg/L) can be achieved at high dose and low temperature with a one hour contact time, but that higher temperatures and adsorbent doses are

required if shorter contact times are to be used. If higher water recoveries are required, the use of high adsorbent dose (10 g/L) and high temperatures (45°C) and contact time are needed, giving a silica concentration of approximately 15 mg/L and a water recovery of 96% (90% in the second RO stage, see Figure 3).
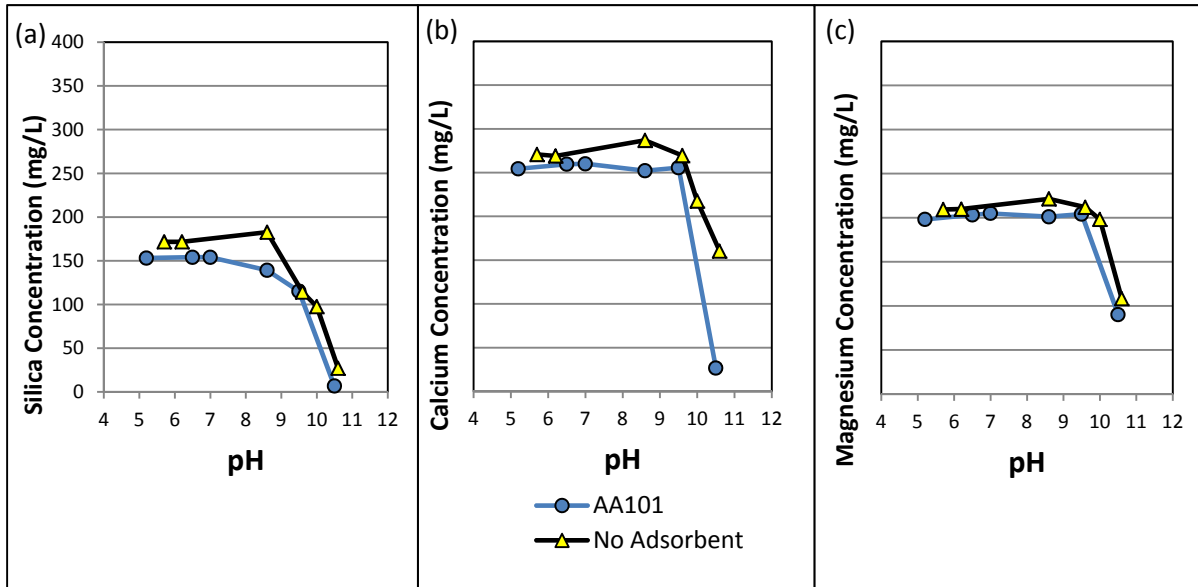

Figure 4: Residual silica, calcium and magnesium concentration after 15 min contact time with various adsorbents at various pH vales, 2 g/L adsorbent dose, ambient temperature.
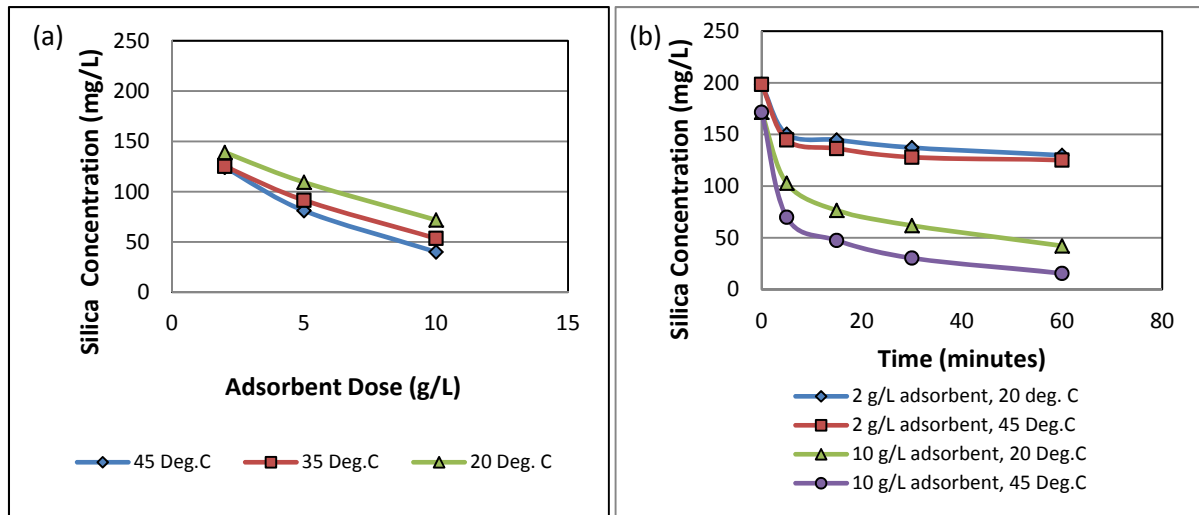

Figure5: Residual silica concentration at pH 8.6, Left: after 15 min contact time with 2 g/L AA101 adsorbent at various temperatures, Right: at contact times up to one hour, at various temperatures and AA101 adsorbent doses.

3.3.4 Regeneration of activated alumina adsorbent

The kinetics of silica adsorption on activated alumina is such that high concentrations of activated alumina (approx. 10g/L) were required to treat the RO concentrate water in a reasonable time (eg. 30-60 minutes). The use of high concentrations of activated alumina, however, results in low utilisation of the adsorption capacity of the activated alumina, so the activated alumina was recycled through several adsorption steps to better utilise the capacity of the activated alumina. Such processing would also be used industrially to improve the kinetics of adsorption and to minimise the activated alumina and adsorbent regeneration requirements for the process.

The silica loaded during five consecutive additions and removal by filtration of 100 mL of RO concentrate to 1.0 g of AA101 at ambient temperature (18°C) with 60 minute contact time, for the virgin adsorbent (First Loading), once regenerated adsorbent (Second Loading) and twice regenerated AA101 adsorbent (Third Loading) are shown in Figure 6a. This figure also includes a second order polynomial fit trend line to allow estimation of the adsorption capacity of the alumina before and after the regeneration cycles. The quantity of silica that came off the loaded adsorbent during the regeneration steps is shown in Figure 6b. The quantity of aluminium lost from the adsorbent during the regeneration is shown in Figure 6c. The release of silica, aluminium, calcium and magnesium during regeneration is shown in Figures 7a to 7d respectively. It can be seen from Figure 6a that the loading capacity of the alumina was approximately 50 mg SiO2/g alumina, and that this increased to approximately 60 mg SiO_2/g alumina after regeneration. Figure 5b shows that approximately 90% removal of adsorbed silica was achieved in the first regeneration, and that this was achieved after 4 regeneration steps. The second and third regenerations, however, were found to require more regeneration steps. The quantity of alumina lost during each regeneration (Figure 6c) was found to be greatest during the first regeneration (~30%) and decreased dramatically in the second and third regenerations (to ~2%).

These results are consistent with dissolution of small alumina particles in the first regeneration and the formation of an adsorption layer during the second and third adsorption stages that is less soluble than the silica loaded, non-regenerated, alumina in the 2%NaOH regenerant. Such an adsorption layer may, for example, be the result of reaction of silicate ions with aluminium ions liberated from the alumina at alkaline conditions (Figure 7b) to form an aluminosilicate. This aluminosilicate layer may initially be a better adsorbent than virgin alumina [25], and this may explain the slightly better adsorbent performance during the second loading (Figure 6a), the lower silica desorption (Figure 6b) and lower adsorbent loss during the second regeneration (Figure 6c). This effect is, however, likely to eventually lead to poorer adsorption due to a decrease in the specific surface area of the activated alumina substrate, possibly resulting from blocking of the pore

network by the adsorbed aluminosilicate. This may explain the slightly poorer adsorption performance in the third loading than in the second loading (Figure 6a). Further research on a larger scale would be required to optimise the regeneration process and determine the lifetime of the adsorbent.
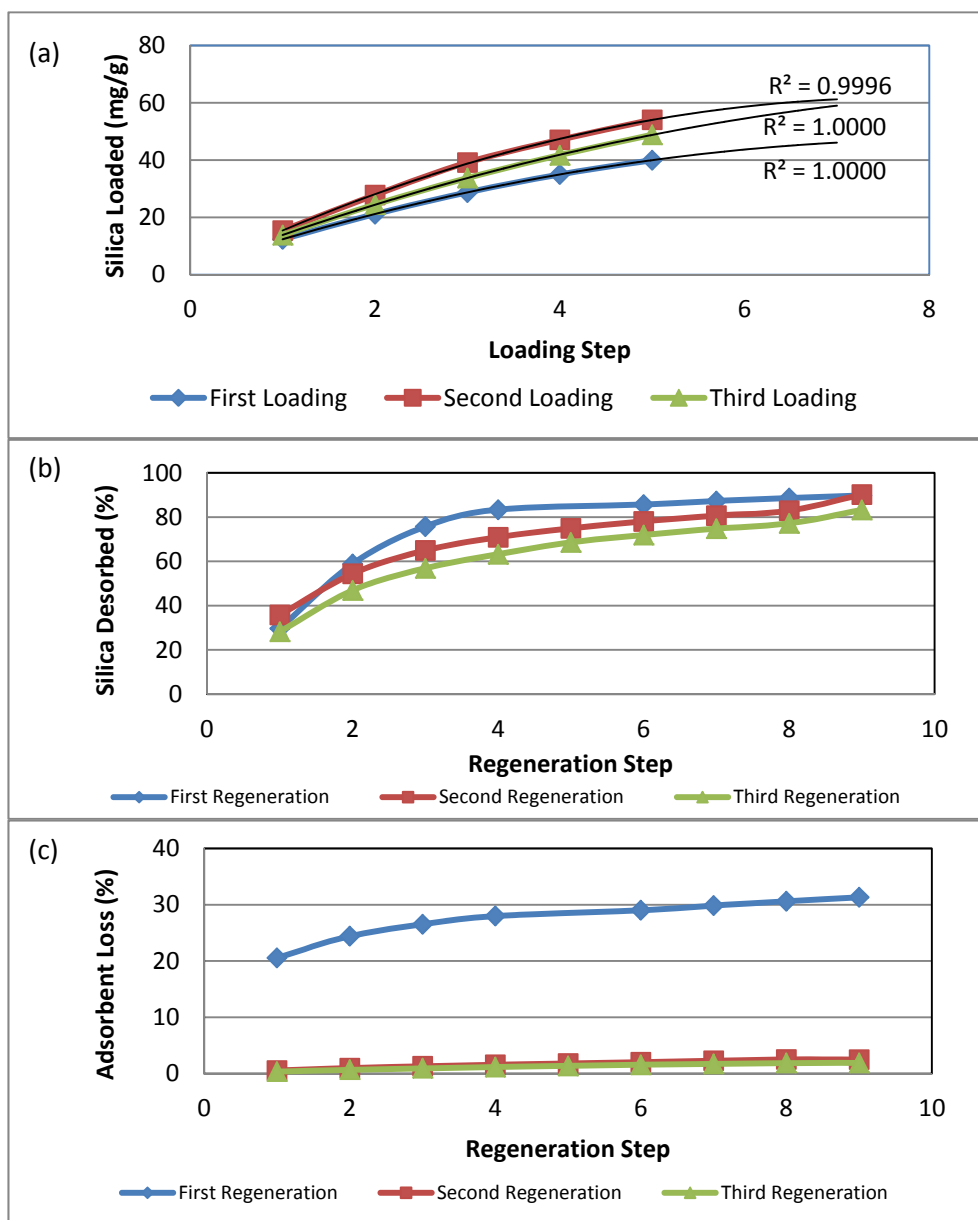

Figure 6: The quantity of silica loaded during loading cycles (a), quantity of silica desorbed during regeneration cycles (b), quantity of alumina lost (as Al_2O_3) during regeneration (c)

An interesting feature of the analysis of the 2% NaOH solution during the various regeneration steps and regeneration stages (Figure 7), is the presence of measurable quantities of calcium and magnesium in the regenerant (Figures 7c and 7d respectively).
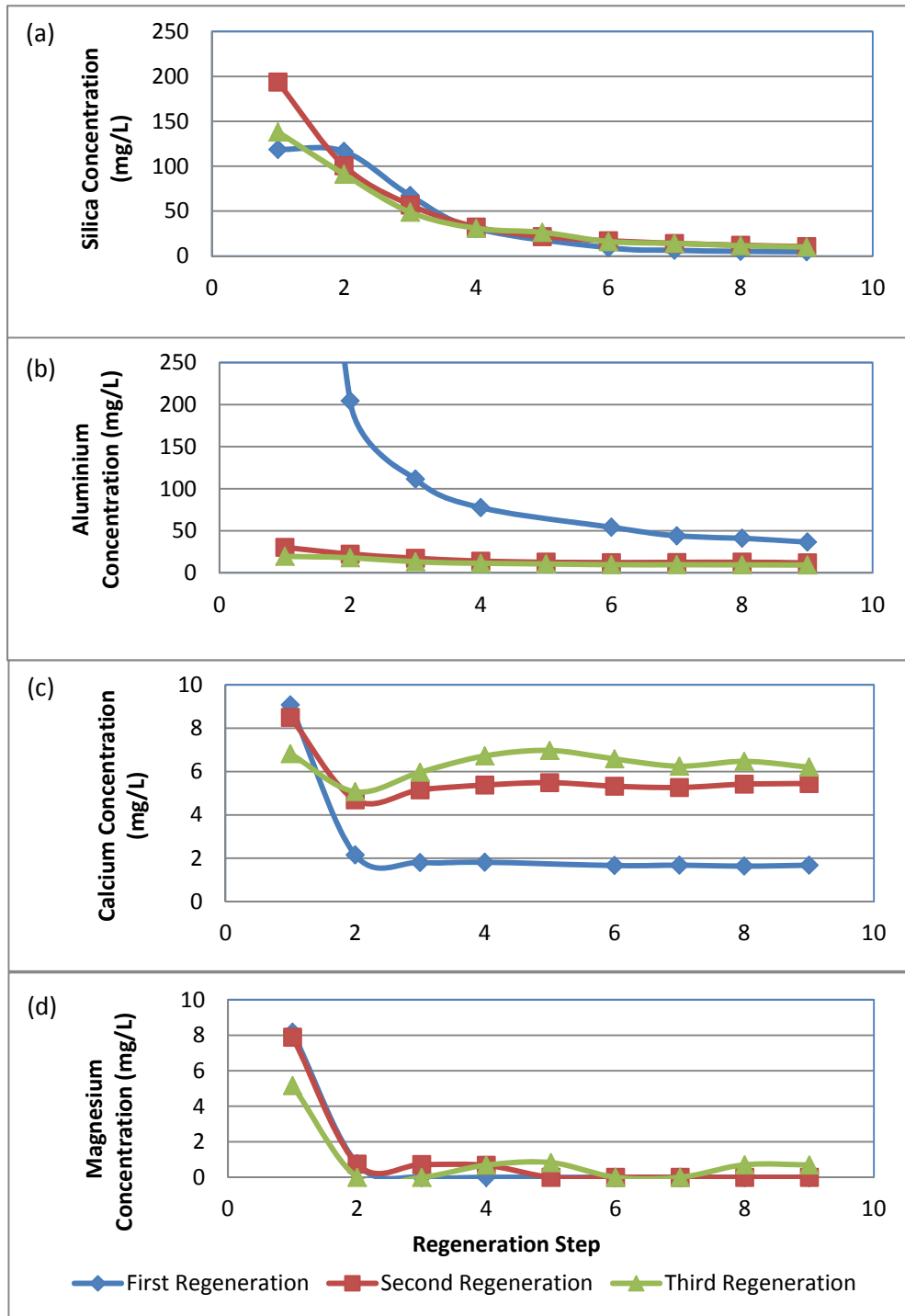
Figure 7: Measured levels of silica (a), aluminium (b), calcium (c) and magnesium (d) in the 2% NaOH regenerant solution during regeneration.

The quantity of magnesium released during regeneration (Figure 7d) was larger in the first step and decreased to nearly zero during subsequent steps for all three regeneration stages. This indicates that magnesium was being adsorbed along with the silica during loading, and that it was being

adsorbed to the same extent and in a similar manner onto the virgin and regenerated alumina surfaces. It also suggests that this adsorbed magnesium species is not evenly distributed throughout the adsorbed silica layer, but is predominantly on the outer surface of the adsorbed layer since it was easily removed in only one regeneration step. This behaviour is different to that observed for calcium (Figure 7c). The quantity of calcium released during the first step of the three regeneration stages was approximately the same for all three regeneration stages, and decreased markedly for the second and subsequent steps during the first regeneration, as was the case for magnesium. This pattern is, however, not seen in the second and third regeneration, where the calcium level remains approximately the same for all the regeneration steps. This calcium desorption pattern suggests that the adsorption of calcium is similar to that of magnesium during the first loading stage, but that calcium is more evenly distributed throughout the silica adsorption layer than magnesium in the second and third loading stages. This, in turn, suggests that at least some of the silica adsorbs as a low solubility calcium silicate and/or calcium aluminium silicate during the second and third loading stages. These findings and tentative explanations highlight the complexity of the chemical interactions involved in the current system, the feedwater specificity of the outcome of adsorption processes, and the need for a better understanding of chemistry involved in order to gain better control over the process.

4. Preliminary Costing

The three RO concentrate treatment options considered for preliminary costing were those that resulted in silica concentration below the target concentration for 90% system water recovery (45 mg/L, 75% water recovery in the SWRO second stage):

- Option 1: The silica is removed by high pH precipitation in the absence of adsorbent, with precipitate removal using a clarifier, the overflow being neutralised with acid before processing through a continuous SWRO plant.
- Option 2: The silica is adsorbed onto the alumina at native pH of the ROC, at ambient temperature, with no pH adjustment before processing through a continuous SWRO plant. The adsorbent is regenerated using 2% NaOH.
- Option 3: As for Option 2, but at an elevated temperature (45°C), using waste heat from processing plant

A diagrammatic representation of the process flows is shown in Figure 8. The designs are based on a total permeate flow of 500 m^3/hr. The assumptions used for the OPEX estimates are shown in Table 4. The estimated capital expenditure (CAPEX) and operating expenditure (OPEX) are summarized in Table 5.
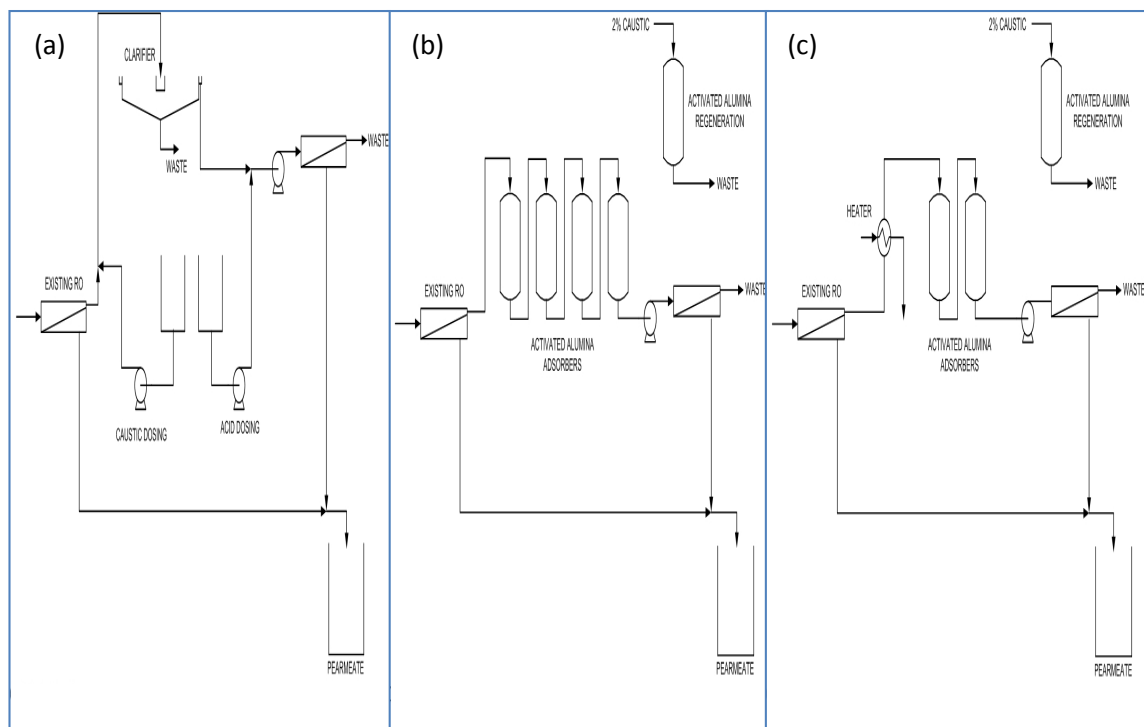
Figure 8: Block Flow Diagrams of costed treatment options, Option 1(a), Option2 (b), Option 3 (c).

High pH precipitation: This option has a significantly higher cost ($4M). It is included here, however, for comparison with the adsorption options. The major equipment considered in this preliminary costing for this option are a caustic dosing system including pH controller, a clarifier, a sulphuric acid dosing system including pH controller to neutralise clarifier overflow prior to membrane plant, and modifications to current piping systems. This option will have one effluent stream which is the underflow from clarifier containing 22 kg/hr silica. Volume is estimated to be 200 l/hr. This would be

directed to the tailings storage facility. The chemical usage will mainly be caustic and sulphuric acid. Caustic is used to raise pH in order to precipitate silica. Sulphuric acid is used after the silica has been removed in order to neutralise the caustic prior to the SWRO plant. Estimated requirements are 50% caustic solution at 300 l/hr and 98% concentrated sulphuric acid at 150 L/hr. The chemical usage is estimated to be $25,000 per day which equates to $2/kL of total system permeate (500 m3/hr).

Table 4: Assumed parameters settings for preliminary operating cost estimates

Parameter	Value	Comments
System water recovery (%)	90	75% water recovery in second RO stage
Adsorption Capacity (mg SiO_2/g AA)	50	See Figure 6(a)
Volume of concentrate to be treated (kL/hr)	222	Concentrate produced at 60% water recovery at 500 m3/hr permeate production
Required silica concentration decrease (mg/L)	115	Initial 160 mg/L to be reduced to 45 mg/L by adsorption
Adsorbent loss on 1st regeneration (%)	30	See Figure 6(c)
Adsorbent loss on subsequent regenerations (%)	2	See Figure 6(c)
Average adsorbent loss over 10 regeneration cycles (%)	6	Average over first 10 regeneration cycles
50% Caustic : AA requirement (L : kg)	18	Using 5 regeneration steps (see Figure 6)
Number of days between regenerations	5	Based on adsorption capacity and size of adsorption vessels
Number of times regenerant is reused	10	Estimated
Cost of adsorbent ($/kg)	1.2	Estimated
50% NaOH solution ($/L)	3	Estimated
98% H_2SO_4 ($/L)	1	Estimated

Activated alumina adsorption at ambient temperature: This option has a significantly lower capital cost ($2.7M) than alkaline precipitation (Option 1). The concentrate from the existing membrane plant is passed through a fixed bed of activated alumina. The silica is adsorbed onto the alumina reducing the concentration to a level where an SWRO plant can achieve 75% recovery, and therefore an overall 90% recovery. Once the activated alumina is fully loaded the silica can be washed off using a 2% caustic solution. This will regenerate the alumina so it can be re-used. Some alumina will also be dissolved by the regeneration solution (average 6%, see Table 4) and will require replacement. The major equipment required for this option are activated alumina adsorption vessels, surge tanks for feed to and product water from adsorption vessels, automated regeneration system using in-line caustic dosing, and modifications to current piping systems. There is one effluent stream – the spent regenerant stream containing redissolved silica and some alumina. The volume is estimated to be 23 m^3/hr containing 2% caustic, 900 ppm silica and 620 ppm alumina. This stream would be discharged to the current mine tailings storage facility. It is anticipated that there will be several adsorption vessels in series and that it will be around 5 days between regenerations when water production is at full capacity. Effluent production will occur during regeneration. Effluent will be less when water production is lower. The major chemical use will be 22 m^3/day of 50% caustic solution, and 740

kg/day of activated alumina at a total cost of $67,000 per day, equating to 5.6 $/kL of total system permeate.

Activated alumina adsorption at 45°C: This option is very similar to Option 3, but the adsorption takes place at 45 °C. A heat source is required to elevate the temperature of the feed stream prior to the first adsorption vessel. Ideally, the low silica exit stream would then be used to provide some of the heat to the feed stream via heat exchangers, so that a dedicated cooling medium is not required in order to reduce the feed temperature to the RO plant. Subject to the final location of the adsorption stage, the required heat may be available as waste heat from current steam generation processes. For clarity, heating and cooling stages are not shown in Figure 8. The estimated capital cost are lower than for Option 2 due to the smaller number of adsorption vessels ($2.2 M). The chemical costs are expected to be the same as for Option 2 (5.6 $/kL of total system permeate).

Table 5: Preliminary Cost estimates of 90% water recovery RO operation involving silica removal

Option	CAPEX ($M)	OPEX ($/kL of permeate)
1: High pH silica precipitation and removal using sedimentation.	4.0	2.0
2: Silica removal using activated alumina adsorbent at ambient temperature	2.7	5.6
3: Silica removal using activated alumina adsorbent at 45 °C	2.2	5.6

5. Conclusions

It was shown that it is possible to decrease the silica concentration in RO concentrate to levels that would allow an overall water recovery of 90% or above using high concentrations (10 g/L) of activated alumina adsorbent. Regeneration of the adsorbent using 2% NaOH as regenerant is effective for at least three regeneration cycles. Analysis of the 2% NaOH regenerant solution after use gave evidence that suggests that the alumina surface chemistry is modified by the regeneration process. The regenerated alumina was found to be less soluble and have a higher adsorption capacity than the un-regenerated alumina. The liberation of adsorbed silica from the regenerated alumina was also lower than for the un-regenerated alumina. These changes in surface chemistry were tentatively attributed to the formation of aluminium silicate on the alumina surface during

regeneration. Regeneration was also found to release considerable quantities of calcium, suggesting the possibility of the formation of calcium silicate and/or calcium aluminium silicate on the adsorbent surface. These findings highlight the complexity of the chemical interactions involved in silica removal by adsorption, the feedwater specificity of the outcome of adsorption processes, and the need for a better understanding of chemistry involved in order to gain better control over the process.

Preliminary costing of the high recovery RO process with an added silica removal stage indicates that this added stage leads to high product water costs ($5.6/kL), and is likely to significantly decreases the brine management costs due to the reduction of the brine volume from the current 40% to 5% of the feed volume. It also allows greater mineral production in situations where groundwater availability is a limiting factor. These results warrant larger scale investigation of silica removal using adsorption column, and adsorbent regeneration.

Acknowledgements

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