The use of regeneration profiles as a tool to optimise the performance of demineralisation water treatment plants

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Abstract

Demineralised water is used as make-up water to compensate for losses in the condensate-boiler feed-water stream at power stations and other steam raising plants. Demineralisation plants are designed to produce pure water that contains virtually no impurities. Ion exchange is invariably used for demineralisation. Effective regeneration of exhausted resin is an important aspect to ensure optimal performance of the ion exchange process. Regeneration profiles were used in this investigation to determine the effectiveness of regeneration and to optimise the regeneration process.

Keywords: demineralisation, regeneration profiles, optimised regeneration

Introduction

The make-up water for modern high-pressure fossil-fuelled boilers has to be of extremely high quality with virtually complete removal of salts and gases. Impure water may cause failure of a turbine or boiler that will result in large financial losses amounting to millions of Rand per day. The make-up water quality depends on the design and unit operations incorporated in a treatment system. A number of processes may be used in the pretreatment of raw water, but invariably the final stage is an ion-exchange demineralisation process (Modern Power Station Practice, 1992; Drew, 1994). This article focuses on the use of regeneration profiles to optimise ion-exchange regeneration and to increase run lengths, thereby reducing water production costs.

Boiler make-up quality

Boiler make-up water is the product water from a demineralisation plant that is fed into the boiler drum to compensate for water losses. The quality of the boiler make-up water determines the boiler operating efficiency (Harfst, 1993). The Eskom chemistry standard for make-up water for drum boilers operating at 17 MPa and above is listed in Table 1.

Ion-exchange process

Ion exchange is a process whereby pretreated water is stripped from unwanted cations and anions to give a product water of specific quality. Ion exchange comprises the reversible exchange of ions between a solid (resin) and a liquid in which there is no substantial change in the structure of the solid. At the start of a service cycle the predominant ionic form of the resins is either the hydrogen (cation) or hydroxyl (anion) form. The hydrogen and hydroxyl ions are exchanged respectively for unwanted cations and anions in the feed water. Exhausted resins are regenerated with a highly concentrated regenerant solution, restoring the resin bed to the ionic form that is again useful to the process (Frederick, 1996).

Demineralisation consists of the following steps:

Cation exchange
The cation exchanger contains two types of cation resins, namely strong-acid exchange resins (SAC) and weak-acid exchange resins (WAC). The SAC can split neutral salts, i.e. remove non-carbonate hardness, while WAC can only remove carbonate hardness from the water. On exhaustion the resins are restored to the original state by regenerating the WAC downwards with a 0.8 to 1.5% H_2SO_4 solution, while the SAC is regenerated upwards with a 5% H_2SO_4 solution.

Degasification
The raw water entering the cation exchangers contains alkalinity (bicarbonate and carbonate ions) that decomposes into carbon dioxide (CO_2) and water. Forced draft degasifiers are used to remove the CO_2 to reduce the load on the anion exchanger (Meyers, 1996).

TABLE 1
Recommended water quality limits for boiler make-up water

Parameter	Units	Limit
Turbidity	(NTU)	0.2
Specific conductivity(25ºC)	(µS/cm)	0.1
Sodium (as Na^+)	(µg/kg)	2
Silica (as SiO_2)	(µg/kg)	10
Chloride (as Cl^-)	(µg/kg)	2
Sulphate (as SO_4^{2-})	(µg/kg)	2
TOC (as C)	(µg/kg)	300
Source: Eskom, 2001		

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TABLE 2 Regeneration procedure applied at Matla Power Station					
Cation unit			Anion unit		
Step	Step description	Duration (min)	Step	Step description	Duration (min)
01	Backwash top	8	01(a)	Backwash weak base	8
02	Settle	2	02(a)	Drain weak base	15
03	Forced settle	4	01(b)	Drain strong base	15
04	Establish flows	3	02(b)	Pre-injection strong base	
05(a)	0.5/2.0% acid injection - top and bottom	80	03(a)	4% NaOH injection strong base	50
05(b)	0.8/3.0% acid injection - top and bottom	20	03(b)	NaOH injection strong and weak base	30
06	Rinse top and bottom	80	04	Slow rinse/pump flush	75
07	Downward rinse	30	05	Fast rinse strong and weak base	45
08	Backwash top	3	06	Drain weak base	15
				Refill strong base	14
			07	Refill weak base	10
			08	Fast rinse weak base	20
Source: Foster Wheeler Delta Cochrane, 1978					

Anion exchange

The weak-base exchange resins (WBA) and strong-base exchange resins (SBA) are held in two separate exchangers. The strong-base and weak-base anion exchangers are regenerated in the upward and downward direction with 4% NaOH at 49°C respectively. The weak-base anion exchanger is regenerated with used regenerant from the strong-base unit.

Mixed bed exchanger

The mixed bed exchanger is filled with SAC and SBA resins that "polish" the effluent of the strong-base anion exchanger. The SAC and SBA are regenerated with 6% H_2SO_4 and 4% NaOH at 49°C respectively.

Optimisation of regeneration

The regeneration process can be optimised by analysing concentration profiles of the different ions and substances in the regenerant streams. A regeneration profile is a valuable tool to assess the efficiency and efficacy of the different regeneration steps and the run length of the demineraliser. It is a graphical representation produced by analysing samples taken during regeneration at various time intervals. Regeneration profiles are useful as a tool to answer questions such as:

* Are the backwash steps long enough to remove all colloids?
* Are the correct acid and caustic strengths used in the injection phases?
* Are the rinse times in line with design values?
* What is the condition of the ion-exchange resins in use?

To develop a regeneration profile the following has to be done:

* Ion-exchange resin samples evaluated before and after regeneration.

* Effluent samples taken and analysed at various points in the process at different time intervals during regeneration.
* Analysis results plotted to determine trends.

Cation and anion resin regeneration can be profiled separately, plotting the various parameters analysed as a function of time.

Study objectives

The efficiency of regeneration is generally evaluated in terms of the restoration of the exchange capacity of the resins. This routine procedure does not give any specific information about the efficiency of the individual regeneration steps and inefficiencies may therefore go undetected. The purpose of this study was to evaluate the use of regeneration profiles as a tool to optimise the regeneration process.

Regeneration studies

Background information

The investigations were carried out at the demineralisation plant of the Eskom Matla Power Station. The plant consists of three parallel treatment trains, each producing a maximum flow of 220 m³/h with a total hydraulic capacity of 660 m³/h. The regeneration procedure applied at Matla Power Station is illustrated in Table 2 and includes a description of process steps and the time required for each step. The mixed bed regeneration is excluded from the table because the profile was only done on the cation and anion resin regeneration.

Methodology

The following procedure was followed in creating regeneration profiles:

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TABLE 3
Chemical analysis on the various regeneration processes

Cation regeneration	Anion regeneration
Acid strength on the top and bottom acid injection (expressed in percentage)	Caustic strength on injection steps (expressed in percentage)
Acid strength on the effluent (expressed in percentage)	Caustic strength on the effluent (expressed in percentage)
Turbidity (expressed as NTU)	Turbidity (expressed as NTU)
Electric cond.(expressed in mS/cm) at 25°C	Electric cond.(expressed in mS/cm) at 25°C
Total hardness (expressed as mg/l $CaCO_3$)	Sulphate (expressed as SO_4^{2-})
Calcium hardness (expressed as mg/l $CaCO_3$)	Chloride (expressed as Cl^-)
Magnesium hardness (expressed as mg/l $CaCO_3$)	Silica (expressed as SiO_2)
Sodium (expressed as Na^+)	Colour (indications for organics) (expressed as percentage) – own technique
Potassium (expressed as K^+)	

- The demineralisation process is operated to maximum capacity. In this case the maximum capacity was determined by run-length and was set at 12 000 m³. The run-length was based on conductivity and a safety margin was allowed.
- Water samples for the regeneration profiles were taken at exhaustion of the demineralisation run.
- Samples were taken at predetermined time intervals to carry out analysis on the different parameters. The time intervals varied from 1 to 2 min at the beginning of each regeneration step to 5 min later in the process.
- Chemical analysis was done according to *Standard Methods*, 1995.
- The analysis results were plotted as individual graphs.
- Regeneration profiles were analysed to identify possible shortcomings in the regeneration processes.
- Regeneration procedures were then adjusted to eliminate shortcomings.

The analyses done to determine the profiles are given in Table 3.

After making changes to the regeneration processes to eliminate shortcomings, a second profile was compiled to assess improvements to the regeneration processes. Based on the findings from the first regeneration run, the following changes were introduced to optimise the process steps. The reasons for the changes are discussed in the section on results and discussion.

TABLE 4
Chemical analysis of demineraliser effluent before regeneration of both

Parameter	Units	Cation inlet 2 July 2002	Cation inlet 24 July 2002
Calcium hardness	mg/l	14	14
Magnesium hardness	mg/l	21	24
Total hardness	mg/l	35	38
Sodium	mg/l	7.4	8.7
Potassium	mg/l	2	2.7
Chloride	mg/l	10	10.2
Silica	µg/l	350	410
Sulphate	mg/l	7.6	7.5

The cation resin regeneration changes are:

For the 1st acid injection step:
- The acid strength of 0.5% top injection/2.0% bottom injection was changed to 0.7% top injection/2.0% bottom injection.
- The injection time was decreased from 80 to 70 min.

For the 2nd acid injection step:
- The acid strength of 0.8% top injection/3.0% bottom injection was changed to 0.7% top injection/4.0% bottom injection.
- The injection time was increased from 20 to 30 min.

Downward rinse: The rinsing time was increased from 30 to 35 min.

The anion resin regeneration changes are:

On the 4% caustic injection to the strong base step:
- The strong base resin caustic injection time was increased from 50 to 60 min.
- From the 40th to the 50th min in the injection step additional samples were taken every 2 min for silica analysis.

On the weak base caustic injection step:
- The injection time was increased from 30 to 40 min.

Results

Demineralisation plant chemical analysis

Table 4 shows the analyses of the inlet to the cation exchanger before the first regeneration run (2 July 2002) and before the second regeneration run incorporating changes to optimise the process (24 July 2002).

Only cation and anion regeneration profiles were determined for the most important process steps. Steps 1, 2, and 3 of the cation regeneration and Steps 1(a), 2(a), and 1(b) of the anion regeneration were omitted (refer to Table 2). The profiles started with the H_2SO_4 injection for the cation and NaOH injection for the anion because the major changes take place during these steps. The cation and anion regeneration profiles done on 02 July 2002, are given in Figs. 1 to 3 and those done on 24 July 2002 are given in Figs. 4 to 6. Table 3 gives the analysis results. The species loaded onto the resins during the service runs and removed during the regenerations are given in Table 5.

Discussion

Cation regeneration

Table 6 shows the top and bottom acid injection strength during the two cation regeneration runs.

For the **1st regeneration** the top acid remained at 0.5% throughout the 1st and 2nd injection steps. It was supposed to remain at 0.5% for the 1st 80 min and then increased to 0.8% for the last 20 min injection step according to prescribed procedures. The bottom acid remained at 2.5% for the entire 100 min but was supposed to increase from 2% (1st injection, 80 min) to 3% (2nd injection, 20 min).

For the **2nd regeneration** the top acid remained at 0.6% for the entire 100 min. It was supposed to remain at 0.7% for the duration of the two injection steps. The bottom acid had an average strength of 2.6% during the 1st injection step of 70 min, but should have been 2%. For the 2nd injection step of 30 min the average strength was 3.1%, which should have been 4%. For optimisation purposes the top acid strength was changed from 0.5% (1st injection) and 0.8% (2nd injection) to 0.7% for the entire 100 min injection time. The bottom acid strength was changed from 2% (1st injection) and 3% (2nd injection) to 2% (1st injection) and 4% (2nd injection). The time for the 1st injection was decreased from 80 to 70 min and increased for the 2nd injection from 20 to 30 min for a total of 100 min injection time.

The reason for these changes was to remove as many of the hardness salts exchanged by the WAC resin as quickly as possible before the rinse steps. The acid strength increases had to be done manually during the 2nd regeneration by either turning up the acid dosing pump stroke or reducing the dilution water flow. The existing system could not ensure automatic control of increased acid concentration. This caused the acid strengths to fluctuate. In both regenerations the effluent acid strengths started to increase in the 55th min of the injection steps, indicating that most of the regeneration process was completed. This, however, was only true for calcium and magnesium.

Calcium, magnesium, and total hardness removal

Table 5 shows that more calcium and magnesium ions were loaded on to the resin during the 2nd service run and also that more ions were removed during regeneration. This can be ascribed to the higher average top acid strength for the 2nd regeneration of 0.6%, against 0.5% for the 1st regeneration. Figures 1 and 4 show that the top acid injection strength for both regenerations was never obtained and was, on average, lower than anticipated. This had the effect of insufficient removal of calcium and mgnesium ions. The dotted line on the total hardness graphs illustrates an assumption of what the removal would have been if the top acid strengths were correct.

Sodium and potassium removal

The SAC resin removes sodium and potassium ions. From Table 5 it can be seen that the removal percentage for sodium virtually remained the same for both regenerations at about 90%. However, there was a marked difference in the case of potassium. During the second regeneration 92.6% was removed compared to 88.4% during the 1st regeneration. Although the SAC resin has greater preference for sodium ions than for potassium ions, the preference for sodium release during the service run before potassium could clearly be seen on the two individual graphs. Unlike calcium and magnesium the bulk of the sodium and potassium ions was not removed during the acid injection phases but rather during the "Rinse Top and Bottom" step. The reason for this was that the bottom acid strength was never controlled at the specification values (see Table 6). The 2nd injection bottom acid strength for both regenerations on average was lower than what was expected, that is 2.5% against 3% (1st regeneration) and 3.1% against 4% (2nd regeneration).

Conductivity removal

In order to reduce the conductivity of the effluent, the time for the downward rinse step was increased from 30 (1st regeneration) to 35 min (2nd regeneration). During the first regeneration the conductivity was 1 950 µS/cm after 30 min, whereas during the second

regeneration after 35 min it was 1 550 μS/cm. In both cases it should have been below 200 μS/cm. From the above it is obvious that more tests are needed to determine the correct rinse times.

Anion regeneration

The anion regeneration is done on the weak base and strong base resins in two separate vessels. Results are therefore discussed separately (Table 7).

First regeneration: Figs. 2 and 3 (2 July 2002)

The NaOH strength for the strong base regeneration average met the specification of 4.0%, whereas the NaOH strength for the weak base regeneration was lower than the specified value of 4.0%. Referring to Figs. 1(b) and 1(c) it was evident that the injection times were too short because a large amount of ions were removed during the rinse steps instead of during the NaOH injection step.

Second regeneration: Figs. 5 and 6 (24 July 2002)

The injection times for the strong base regeneration steps were increased from 50 to 60 min (1st injection) and 30 to 40 min (2nd injection). For the weak base regeneration the injection time was increased from 30 to 40 min. The reason for this decision was to remove the majority of the ions during the injection phase.

Chloride removal

Table 5 shows that more chloride ions were loaded on to the anion resins during the 1st service run than on to the 2nd. Also, more chloride was removed from the resin during the 1st regeneration although the injection times were increased by a total of 20 min. Table 8 shows that when comparing the two regenerations, the SBA resin removed more chlorides during the 1st regeneration than the 2nd. The opposite happened with the WBA resin, more chlorides were removed during the 2nd regeneration.

This shows that the 2nd weak base regeneration benefited more from the 10 min increase in injection time than the strong base with reference to % removal vs. loading. This confirms the theory that chlorides are predominantly exchanged by the weak base resins.
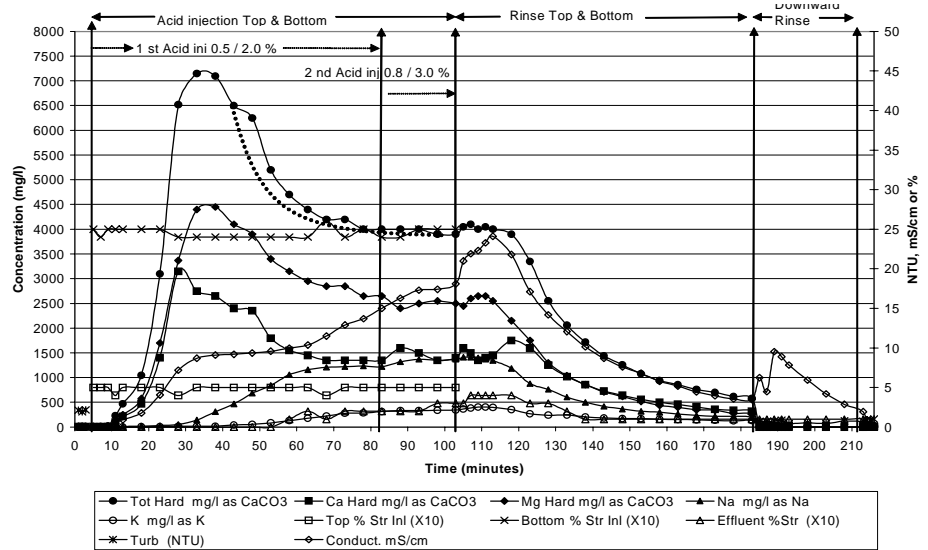

Figure 1
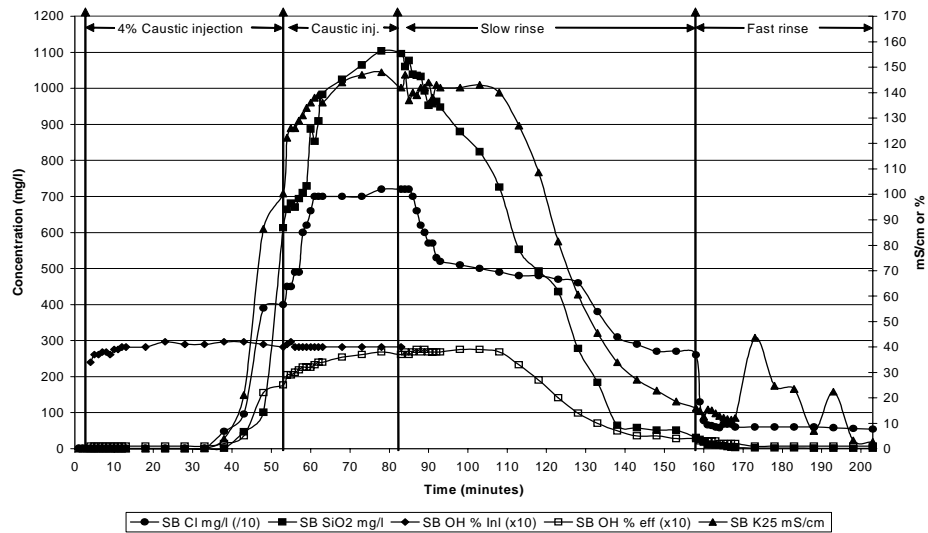*CATION 1 REGEN PROFILE - Major steps only - 2 July 2002*

Figure 2
ANION 1 REGEN PROFILE - Strong Base - Major steps only - 2 July
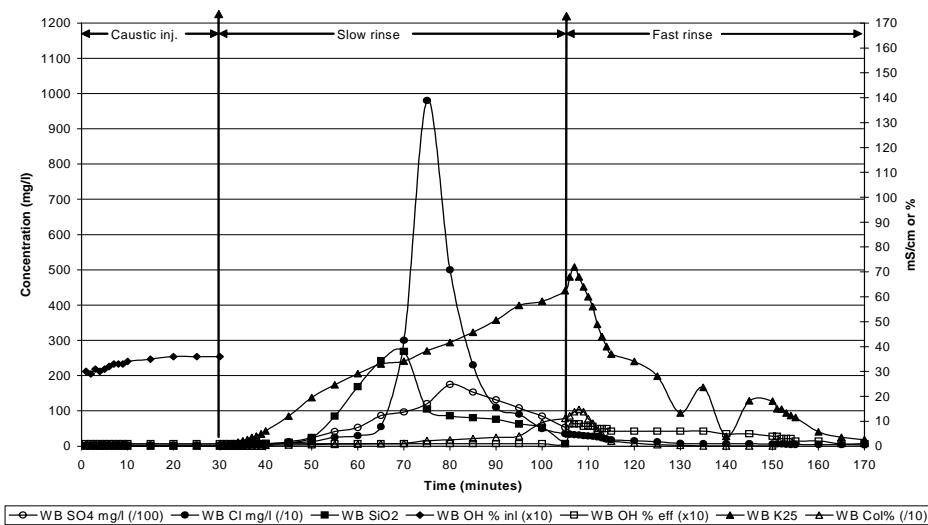

Figure 3
ANION 1 REGEN PROFILE - Weak Base - Major steps only - 2 July 2002
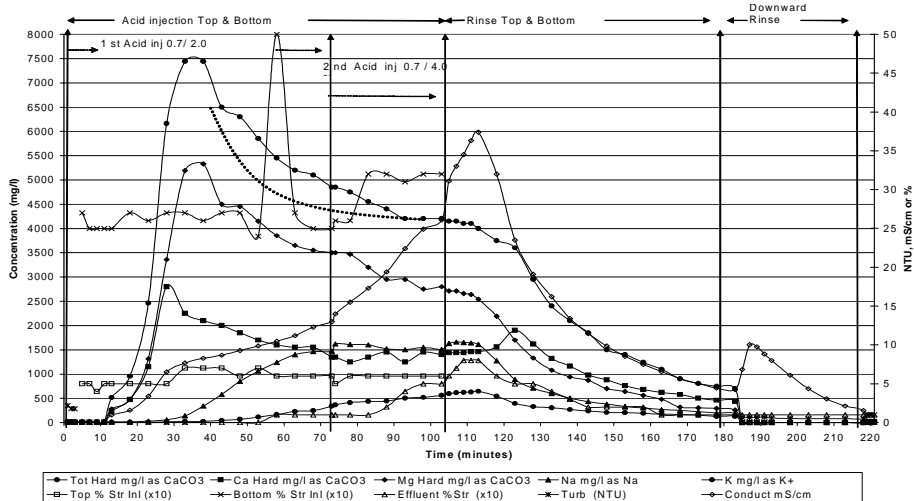
Figure 4
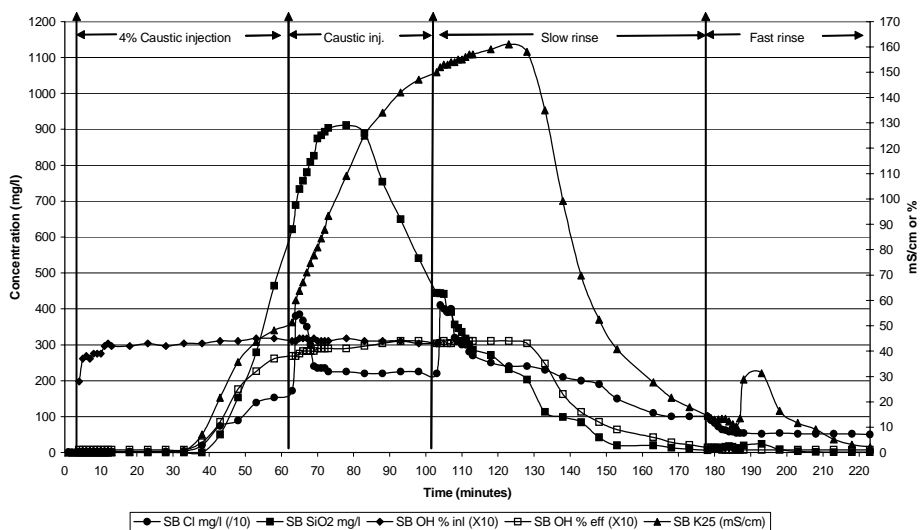CATION 1 REGEN PROFILE - Major steps only - 24 July 2002

Figure 5
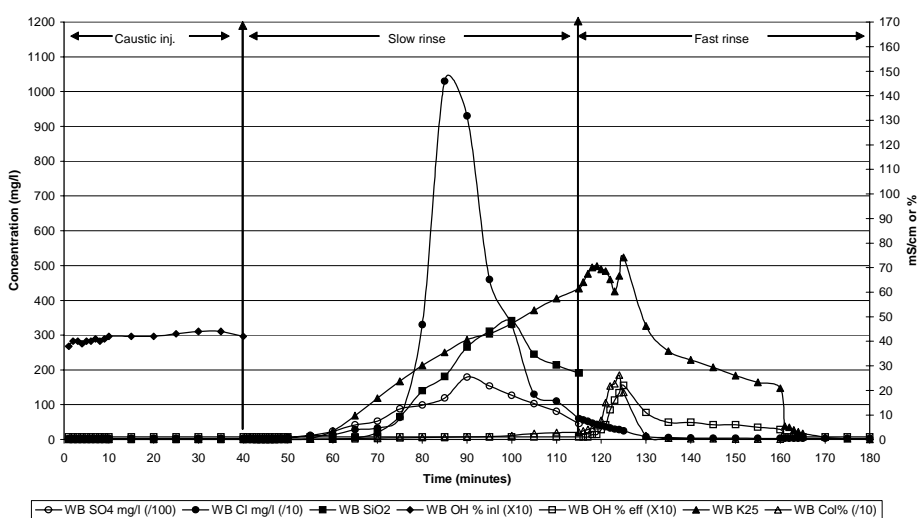ANION 1 REGEN PROFILE - Strong Base Major steps only - 24 July 2002

Figure 6
ANION 1 REGEN PROFILE - Weak Base Major steps only - 24 July 2002

Silica removal

Table 5 shows that more silica was removed than was loaded on the resin. When comparing Figs. 2 and 3 and Figs. 5 and 6 it appears that more silica was loaded from the strong base onto the weak base than was removed by the weak base during the rinse steps. When comparing loaded figures with removal figures, as indicated in Table 5, it is evident that the analysis could not be correct. Silica was determined colorimetrically on a spectrophotometer at wavelength 810 nm. The following may be reasons why the analysis failed to give the correct concentrations:

- The sample was too alkaline in the case of the strong base regeneration and inadequate neutralisation was done. In the case of the weak base regeneration the sample was not as alkaline as in the case of the strong base.
- The dilution factor was too large, causing a significant error in the calculated values.
- Precipitation of silica before analysis could have taken place.

Silica determinations in high alkaline solutions should be further investigated for future regeneration profile compilation.

Sulphate removal

Table 5 indicates that more sulphates were removed during the 2nd regeneration. This can be ascribed to the longer injection times during the 2nd regeneration.

Colour

During the regeneration process a change in colour of the weak base effluent was evident. This colour change from clear to a dark toffee colour occurred during the initial stages of the fast rinse step due to the release of organic material from the ion-exchange resins.

To determine organic material of high concentrations, is very complex and difficult. Methods like Oxygen Absorbed (4 h method) and Total Organic Carbon (TOC) is available but in this case it was impractical to use it, because of the high concentrations encountered. It was decided to use the colour method to distinguish between different concentrations. The absorption taken up

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TABLE 6
Top and bottom acid injection strengths during cation regeneration

	1st Regeneration			2nd Regeneration		
	Top Acid %	Bottom Acid %	Time Min	Top Acid %	Bottom Acid %	Time Min
1st Injection	0.5	2.5	80	0.6	2.6	70
Specification	0.5	2.0	80	0.7	2.0	70
2nd Injection	0.5	2.5	20	0.6	3.1	30
Specification	0.8	2.0	20	0.7	4.0	30

TABLE 7
NaOH injection strengths during 1st and 2nd regenerations

	1st Regeneration		2nd Regeneration	
	NaOH %	Time Min	NaOH %	Time Min
Injection to strong base only	3.4-4.2	50	2.8-4.5	60
Specification	4.0	50	4.0	60
Injection to strong base and weak base*				
Specification	4.04.0	3030	4.44.0	4040
Injection to strong base and weak base**	2.9-3.6	30	3.8-4.4	40
Specification	4.0	30	4.0	40

by each sample was measured on a spectrophotometer at wavelength 425 nm. A graph, absorbance on the y-axis against percentage on the x-axis, was drawn up. Absorbance of 1.0 was taken as 100% and a straight line graph was obtained. The concentration of each sample was read from the graph. In cases where the sample had a colour greater than the absorbance of 1.0 the sample was diluted. More organic material was removed by the WBA resins during the 2nd regeneration than during the 1st. This increase was most probably due to the longer injection times during the 2nd regeneration (refer Table 5).

Conductivity
The conductivity appeared very erratic during the fast rinse step (Figs. 2 and 5). This was due to changes in flow direction through the weak base resin.

Recommendations

The research indicated a number of changes that could be made to the plant and process to improve the overall regeneration process and/or to obtain longer run lengths. These are:

Cation regeneration

Modify the existing top and bottom acid injection step
To control the acid strengths an automated system should be installed. During the project it was proved that manual acid operations were risky and control was poor. This can result in calcium sulphate precipitation on the cation resins. It is also recommended that demineralised water instead of filtered water be used as dilution water for both top and bottom acid injections.

TABLE 8
Chloride removal by strong and weak base resins during the two regenerations

	Total chloride removal	Strong base chloride removal	Weak base chloride removal
First regeneration	103.19 kg	85.83 kg	17.36 kg
Second regeneration	94.86 kg	71.31 kg	23.55 kg

Increase acid injection strengths
For the 2nd regeneration the acid strengths for both top and bottom injections were adjusted from 0.5%/2.0% (1st injection) and 0.8%/3.0% (2nd injection) to 0.7%/2.0% and 0.7/4.0% (see Table 6) respectively. It is recommended that the adjusted acid strengths be used since it is evident from Table 5 that more species were removed during the 2nd regeneration.

Decrease the time for the 1st acid injection and increase it for the 2nd
It is recommended that the time for the 1st acid injection be reduced from 80 to 70 min and the time for the 2nd acid injection be increased from 20 to 30 min. The total injection time should remain at 100 min. The aim of this change is to remove more species from the resins during the regeneration step and not allowing this to happen in the rinse steps.

Anion regeneration

Increase the strong base NaOH injection time in both injection steps

It is recommended that the injection time be increased from 50 to 60 min for the strong base regeneration, and from 30 to 40 min for the strong base/weak base parallel injection. The total injection time for the strong base was increased from 80 to 100 min. The reason for this change was to remove as much silica and chloride as possible during the injection steps and not during the rinse steps.

Conclusions

Conclusions that can be made from the study of the regeneration profiles are that longer injection times for both the cation and anion regenerations are needed for better removal of most of the species. The study indicated that a large portion of species removal is obtained from the rinse steps.

Regeneration profiles are the 'fingerprints' of the demineralisation process. By analysing the fingerprints, inefficiencies can be eliminated and unnecessary costs and time delays can be avoided. The studies showed that regeneration profiles can be used effectively to identify plant and process problems and therefore to optimise the process.

It is recommended that regeneration profiles be done on an annual basis on all demineralisation trains. As experience grows it might not be necessary to analyse for the full extent of the regeneration process and for all parameters.

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