FEASIBILITY STUDY OF IN-HOUSE TREATMENT OF WASTEWATER FROM A NITROUS OXIDE PRODUCTION PLANT

by

Jabulane Attwell Ntuli

A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering.

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DECLARATION

I declare that this research report is my own unaided work. It is being submitted in partial fulfilment of the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

…Jabulane Ntuli………
Signature

17 October 2014……..
Date

ABSTRACT

A feasibility study into the use of ion exchange technology for in-house treatment of wastewater from a nitrous oxide (N_2O) production plant was carried out at the AFROX Northern Operations GOC in Gauteng.

The N_2O plant at GOC produces large quantities of acidic wastewater effluent on a daily basis. Municipal by-laws require the company to either treat this wastewater effluent before discharging it into the municipal sewer or to use a suitable wastewater removal company to remove the effluent and discharge it at an approved wastewater disposal site.

The objectives of this study were three-fold:

- to propose the best approach technologically, for treating N_2O wastewater produced by GOC such that it reaches regulatory requirements for discharge into the municipal sewer system;
- to determine whether the proposed treatment method may produce reclaimed water that may have alternative beneficial uses (for example, in boilers or coolers); and
- to carry out a cost-benefit analysis that compares the financial feasibility of the proposed in-house treatment method over the existing practice of outsourcing wastewater removal and disposal.

The study makes suggestions as to a suitable technique for wastewater treatment and reuse in the N_2O production plant. Although the actual implementation of the findings will depend on AFROX, adoption of these findings will ensure that AFROX Northern Operations GOC goes beyond reactive compliance with environmental regulations and takes a step towards sustainable water usage – with benefits for both the company and the environment.

Results from the laboratory bench-scale tests indicated that weak base anion (WBA) resins (Lewatit MP 68) with a theoretical capacity of 1.3 eq/L were suitable for treatment of the high strength and high nitrate concentration wastewater however their limited operating capacity impacted their effectiveness in recovering large amounts of the treated wastewater. The test further indicated that for ion exchange technology to be used successfully to treat the high strength wastewater, a high capacity special resin, LEWATIT A356 with theoretical capacity of 3.4 eq/L and operating capacity of 1.92 eq/L ought to be employed.

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α^{i}	binary separation factor
eq/L	equivalent per liter
$[H^{+}]$	concentration of hydrogen ions
HNO_3	nitric acid
K_B^A	Coefficient for either cation
$KMNO_4$	potassium permanganate
mg/L	milligrams per liter
NaCl	sodium chloride
NaOH	caustic soda
$NaHSO_3$	sodium hydrogen sulphite
$NH_{3\ (g)}$	ammonia gas
NH_4NO_3	liquid ammonium nitrate
N_2O	nitrous oxide gas
NO_x	nitrogen oxides
pH	- log $[H^{+}]$
SO_4^{2-}	sulphates
K_{ij}	Apparent equilibrium constant or selectivity

LIST OF JARGON AND ABBREVIATIONS

AFROX

African Oxygen

Dumping

The elevation of nitrates in the effluent water, such that the nitrate levels in the effluent are greater than the nitrate levels in the influent water.

GOC

Gas Operation Centre

LAN

Liquid ammonium nitrate

ppm

Parts per million, mass fraction unit; 1 ppm is 1 gram solute per million grams of solution.

Quaternary ammonium

Term describing a specific group that imparts strongly basic exchange ability to some anion exchange resins.

Regenerant

Chemical used to convert an ion exchange resin to the desired ionic form for re-use.

Rejection

Salt separation performance characteristic for reverse osmosis membranes.

RO

Reverse osmosis membranes; membranes that reject most particles and many low molar mass species such as salt ions.

Selectivity

Difference in attraction of one ion over another to an ion exchange resin.

Slow rinse

Portion of the rinse that follows the regenerant solution and is passed through the ion exchange material at the same flow rate as the regenerant.

Strong base anion resin

Resins employed in chloride anion dealkalizers and deionization systems.

TDS

Total dissolved solids.

ZAR

South African Rand

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

African Oxygen Limited (AFROX) is a gases and welding business with operations throughout sub-Saharan African and is part of the LINDE Group. Northern Operations Gas Operating Centre (GOC) is part of the Northern Region of AFROX in Gauteng, South Africa. GOC manufactures two main gases on site, namely nitrous oxide (N_2O) and acetylene, and bottles a number of other gases on site. Approximately 5000 to 6000 cylinders are filled per day, making GOC the largest gas operation centre in the LINDE Group.

The N_2O plant at GOC produces large quantities of N_2O wastewater (acidic in nature) on a daily basis. Municipal by-laws require the company to either treat its wastewater effluent before discharging it into the municipal sewer or find a suitable wastewater removal company to remove and discharge the effluent at an approved wastewater disposal site.

Previously, the wastewater was treated in-house but the treated effluent was not compliant with municipal by-laws. As a result, the removal of effluent and disposal was outsourced to an approved waste disposal company. Financially, this option proved to be costly, and the feasibility of in-house wastewater treatment is once again being considered.

The primary aim of this study is to determine the technical and financial feasibility of in-house treatment of wastewater produced by the N_2O plant at AFROX Northern Operations GOC in Gauteng.

The objectives of this study are three-fold:

- to propose the best technological approach for treating N_2O wastewater produced by GOC to within the regulatory requirements for discharge into the municipal sewer system;
- to determine whether the proposed treatment method may produce reclaimed water that may have alternate beneficial uses (for example in boilers or coolers); and
- to carry out a cost-benefit analysis that compares the financial feasibility of the proposed in-house treatment method over the existing practice of outsourcing wastewater removal and disposal.

Due to the large quantities of wastewater being produced by the N_2O plant at GOC, it is hypothesised that in-house treatment of effluent may result in significant cost savings in terms of effluent collection and disposal. In addition, reclamation of treated effluent may save a significant amount of money for the N_2O production plant in terms of water consumption costs.

The study only suggests a suitable technique for wastewater treatment and reuse in the N_2O production plant. Actual implementation of the findings will depend on the response of AFROX. However, adoption of these findings will ensure that AFROX Northern Operations GOC will go beyond reactive compliance with environmental regulations and take a step towards sustainable water usage – with benefits for both the company and the environment.

This report is structured as follows:

Chapter 1 introduces the research problem, and outlines the aim, objectives and rationale of this study.

Chapter 2 describes the N_2O production process, and identifies the wastewater streams that are produced throughout the process. The chemical loading in the wastewater streams is explained, and the main chemical species of concern are identified. Chapter 2 also states the legal water quality requirements of treated effluent.

Chapter 3 details the methodology followed in this study. It explains the process followed to determine the most feasible method for wastewater treatment. It then goes on to describe the bench-scale testing of the preferred technology; the design of the wastewater treatment plant; and the economic benefits analysis of the preferred treatment option.

The choice of technology is based on the findings from a literature review summarised in Chapter 4. A literature review of wastewater treatment methods: biological, chemical and physical, is undertaken and used to contrast the suitability of the methods against each other. Of the three alternatives, physical methods are selected as most suitable; and three advanced wastewater treatment technologies – electrodialysis (ED), ion exchange (IX), and reverse osmosis (RO) – are further considered as potential technologies for in-house wastewater treatment.

Chapter 5 compares and contrast(s) the three advanced wastewater treatment technologies and select the most feasible technology that will be employed in the study.

Chapter 6 expands on the principles of the preferred technology, ion exchange.

Chapter 7 presents and analyses the results of the bench scale testing of the most feasible technology.

Using the results of previous chapters, Chapter 8 presents a preliminary design of the proposed wastewater treatment facility. Chapter 8 also presents a cost-benefit analysis, the financial feasibility, and sustainability benefits of the preferred in-house wastewater treatment method over the existing practice of outsourcing wastewater removal and disposal**.**

Chapter 9 summarises the findings and recommendations of this research project.

CHAPTER 2: PRODUCTION PROCESS OF N_2O GAS

In this chapter an overview of the industrial process used by AFROX GOC to produce N_2O is given. The waste streams generated by the process are highlighted, and the need for an improved effluent treatment programme is discussed.

2.1 CHEMISTRY OF N_2O PRODUCTION

The industrial process for the production of N_2O is based on the thermal decomposition of liquid ammonium nitrate (LAN) at temperatures that are slightly higher than its melting point of 170ºC. Pure ammonium nitrate is a white odourless salt and has a chemical formula NH_4NO_3 and a molecular weight of 80 g/mole (Shah & Roberts, 1969: 172).

Thermal decomposition of LAN is a complex process that has the potential to follow a multitude of routes if it is not carefully controlled. Pure N_2O is produced by carefully heating LAN solution of a concentration strength varying from 80 – 95% at temperatures of approximately 250^0C – 255^0C. The heat is best regulated by gas firing otherwise explosions might occur. If the temperature is too high, the decomposition will yield N_2, NH_3 and the poisonous NO. Decomposition of LAN occurs under acidic conditions in the presence of small amounts of chlorides; this decomposition is accentuated by the presence of stainless steel (Solomon & Barclay, 1965: 24).

The main desired reaction from the production process is:

$$NH_4NO_3(l) \rightarrow N_2O(g) + 2H_2O(l) \quad \text{Equation 2.1}$$

The reaction is exothermic and generates 59 kJ/mol at approximately 250 ºC. The reaction is a first order reaction with an estimated energy of activation of 150 – 200 kJ/mol at standard conditions (273 K, 1013 mbar) (EIGA, 2007: 9).

In addition to the first order reaction, and the evaporation of water, the following chemical side reactions leading to the decomposition of LAN with the formation of HNO_3 and NH_3, and, to a lesser extent, N_2 and nitrogen oxides (the reactions are endothermic) occur:

$$NH_4NO_3 \leftrightarrow NH_3(g) + HNO_3(g) \quad \text{Equation 2.2}$$

$$\Delta H \approx +159.9 \text{ kJ/mole} \quad @250^{\circ}C$$

$$12HNO_3 + 16NH_3 \rightarrow 30H_2O + 3O_2 + 14N_2 \quad \text{Equation 2.3}$$

$$12NH_4NO_3 \rightarrow 23H_2O + N_2O_3 + 2HNO_3 + N_2O_4 + 9N_2 \quad \text{Equation 2.4}$$

$$\Delta H \approx 69.75 \text{ kJ/mole}$$

The by-products of side reactions (Equation 2.2 and Equation 2.3) greatly influence the quality of N_2O, as they lead to the formation of significant amounts of the toxic nitrogen oxides (NO_x) (EIGA, 2007: 9). The concentrations of these impurities therefore need to be monitored and controlled.

2.2 OVERVIEW OF THE INDUSTRIAL PROCESS

A schematic of the industrial process used by AFROX GOC to produce N_2O is shown in Figure 2.1.

LAN is stored in a melter – a transfer vessel in which the temperature is maintained between 125ºC and 130ºC to prevent the crystallisation of LAN. To prevent re-crystallisation of the LAN during the transfer of LAN from the transfer vessel to the reactor, the pipe connection between the melter and the reactor must be heated. The hot LAN is injected into the reactor where it undergoes thermal decomposition into N2O and water vapour.

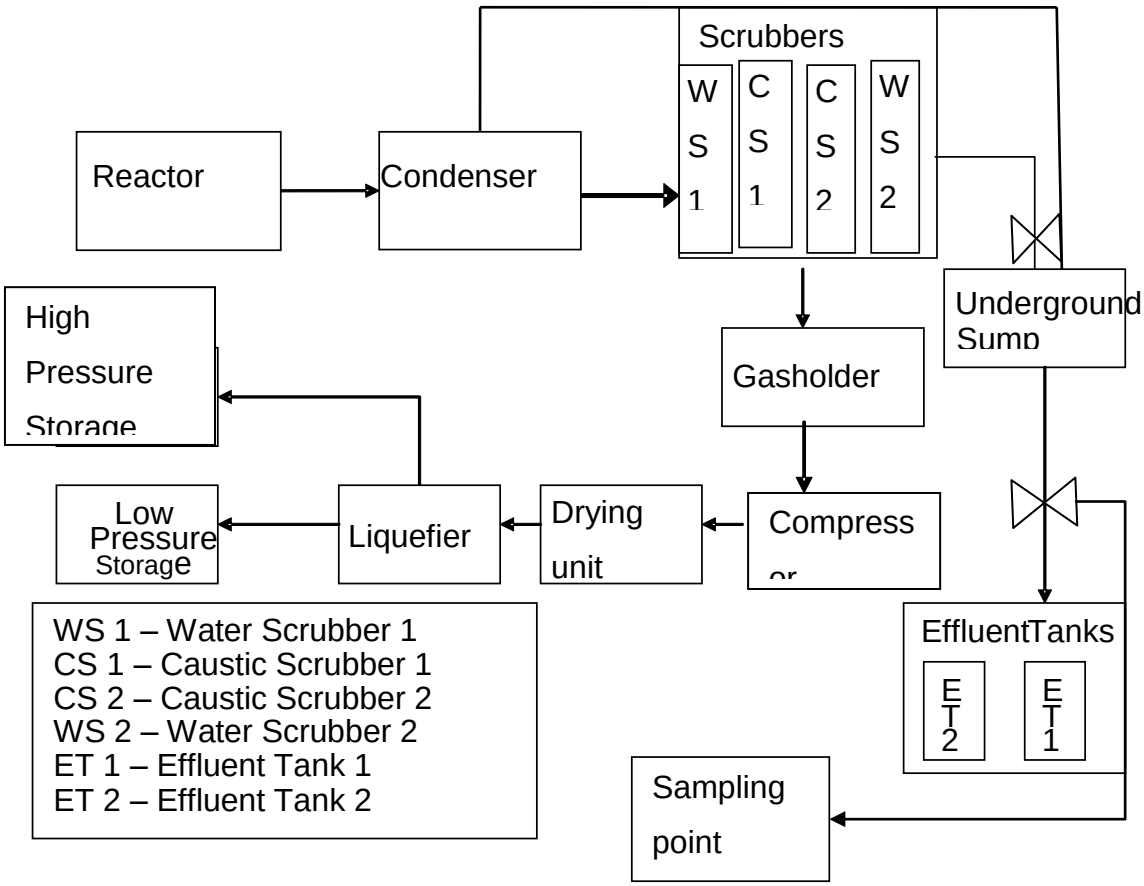

Figure 2-1 Schematic view of the production process (derived EIGA, 2007: 11), indicating sampling sites.

After-cooler (condenser)

The purpose of the condenser is to reduce the temperature of the gas that passes through it and remove the impurities from the gas (it acts as a water scrubber). The produced gas passes through the condenser at an operating pressure ranging between 26 – 34 kPa and the temperature of the water in the condenser (chiller) is ±12.5 ^{0}C.

Series of scrubbers

The purpose of gas scrubbing is to transfer pollutants from a gas phase into a liquid phase for removal (i.e. water scrubber or caustic scrubber). The absorption may be accelerated by reacting dissolved gas chemically with components of the liquid phase. The reagents used in the scrubbing liquor are consumed and must be replaced (Degremont, 1991: 1330).

The gas stream passes through a number of chemical purification steps using towers. Impurities (e.g. NO_x, HNO_3, NH_3) are washed out in a sequence of absorption towers (water scrubbers) employing water, a mixture of $KMnO_4$ and NaOH, H_2SO_4 and water.

Gasholder

The purified N_2O is accumulated in the gasholder and it also acts as compensator for variations in production (its capacity is approximately 8 m^3/h).

Compressor

N_2O is compressed to liquefaction pressure.

Drying Unit

N_2O is dried to remove water (the gas is passed through two adsorbers arranged in parallel and filled with alumina, silica-gel or molecular sieve).

Liquefier

N_2O is liquefied with cooling water or non-flammable refrigerant. The product is then stored and is ready for filling cylinders or for bulk transport.

Underground sump and effluent tanks

The wastewater sump contains two diaphragm pumps, which are activated by a high level switch and can transfer sump contents to the above ground effluent tank. These pumps are controlled by a low-level trip switch in the sump. The pumps distribute an equal amount of wastewater from the sump to the two wastewater tanks situated outside the N_2O plant. A breakdown in one of the pumps results in varying chemical composition of effluent contained in the two wastewater storage tanks.

2.3 DESCRIPTION OF GENERATED WASTEWATER

There are four streams of wastewater produced in the N_2O plant described above in Figure 2-1~~Figure 2-1~~.

Diluted LAN

This type of effluent is primarily made up of spill-over from the LAN bulk storage tank although it is also used to drain the contents of the reactor. The water contains up to 3% of the dissolved NH_3 and un-reacted NH_4NO_3 (its concentration can be significantly higher if the reactor contents has been discharged by flushing the lines during the maintenance or cleaning of the reactor or during prestart-up following a plant shutdown)

Caustic permanganate scrubber liquor

The spent scrubber liquor generated in both Caustic Scrubber 1 and Caustic Scrubber 2 respectively is composed of a solution of diluted caustic soda ($NaOH$) and $KMnO_4$. The caustic permanganate scrubber is used to remove traces of nitric oxide from the N_2O.The spent liquor is generated when the scrubber is recharged, after which it is discharged into the sump inside the plant. The scrubber is recharged at a frequency of 48 hours at normal plant operations. The caustic permanganate scrubber solution is made up of 18.5 kg NaOH and 1.7 kg $KMnO_4$ in 180L of water. The final strength of the solution is as follows: Caustic Soda = 10%; Permanganate = 1.1% (AFROX, 2005: 8). As per operational procedures (NTO-03-08: Operating the purification system and NTO-03-16: Monitoring products and processes onsite, the concentration of the caustic permanganate scrubber solution is measured at the beginning of every shift. The results are used to verify that the scrubber concentration is accurate and to inform the decision to be made by operators in taking corrective action in the event of a deviation in concentration (AFROX, 2007: 13). The two caustic scrubber towers generate a combined volume of 360L spent caustic permanganate scrubber liquor that is discharged into the sump at a frequency of about 48 hours at normal operations.

Process water scrubber

A portion of process water which does not require treatment is discharged into to the sewer. This effluent is produced from the two water scrubbers that are arranged in series with the caustic permanganate scrubbers. The water scrubbers are labelled Water Scrubber 1 and Water Scrubber 2, and the two caustic scrubbers are placed between them (see Figure 2-1~~Figure 2-1~~). These scrubbers are used to remove any ammonia or ammonium nitrate carry-over in the produced N_2O, and are recharged at an eight-hour frequency (i.e. three times a day). The volumetric capacity of the two water

scrubbers is 150L each. Therefore, at full capacity, a total of 300L of the spent water scrubber is discharged into the sump after every eight hours of operation. The total volume of water scrubber effluent discharged in a 24-hour operation of the plant into the sump is 900L (i.e. 27000 L/month).

Effluent overflowing from the after-cooler (condenser)

The effluent generated from the condenser is acidic – its pH is similar to that of the effluent produced in the first water scrubber. The produced gas is cooled and the water vapour is condensed in a counter-current water cooled condenser.

Whenever LAN is injected into the reactor, the after-cooler discharges the effluent into the wastewater sump. The condensed water contains ammonium nitrate, ammonia and nitric acid and can be reused. The condensate overflows from the condenser and discharges into the sump. The condensate mixes with the scrubber liquor and is pumped into the same wastewater storage tank.

Chemical by-products found in the wastewater

Ammonia (NH_3) and nitric acid (HNO3) are found in the generated wastewater from the N2O production process. These by-products originate from the normal competition reaction in the N2O production. They can be detected by their distinctive smell or by conducting an online testing using a dragger test tube (AFROX, 2007:6). In compliance to Good Manufacturing Practice (GMP) standards (EIGA, 2003: 26), the N2O gas produced must be free of acids or alkalis and any NH3 gas should be below the detection limit (i.e. detection limit of 0.001 mg/L when measured with a dragger test tube). The water scrubbers eliminate these by-products. Figure 2-1 summarises the removal of NO_x impurities from the produced N_2O and the limitation of this removal step.

Table 2-1 Nitrous Oxide (NO/NO_2) removal table.

Origin	'Over oxidation' of NH_3 gas in NO_x
Elimination	$NaOH + KMnO_4$ scrubbing
Limitation	Keep reaction temperature low (below 252^0 C)

The process produces industrial wastewater of which the chemical composition poses greater challenges to municipal sewer facilities due to high concentration of highly soluble NO_3^- . The wastewater produced from the thermal decomposition of LAN is corrosive, contains high levels of NO_3^- and may only be discharged into the municipal sewer once the organisation has ensured that the wastewater meets the local municipality wastewater discharge by-laws.

The N_2O production process at AFROX GOC (as depicted in Figure 2-1) utilises potable municipal water, which is later discharged as process wastewater consisting of a mixture of process by-products and feedstock chemicals.

The release of effluent containing a high concentration of NO_3^- into the environment can cause eutrophication in rivers, deterioration of water quality and potential for human health problems (nitrates and nitrites have a potential to form N-nitrous compounds, which are carcinogenic) (Metcalf & Eddy, 2003:62).

2.4 Drivers for an improved effluent treatment programme

There is an ongoing need for AFROX GOC to comply with the Ekurhuleni Metropolitan Municipality wastewater discharge by-laws. Proactive compliance with regulatory requirements will reduce fines, notices of improvements, breaches of local by-laws and complaints by the municipality and other stakeholders.

Currently the organisation complies by outsourcing wastewater treatment to a waste management company that collects the waste and discharges it into an authorised waste disposal facility. The option has cost implications with regards to service charges and product stewardship requirements.

Product stewardship requirements compel the organisation to monitor and ensure that the authorised waste management contractor disposes the wastewater responsibly in line with legal requirements. This is achieved through periodic audits of the contractor's processes and systems.

The authorised contractor's wastewater collection services are inconsistent and unreliable as wastewater is not collected as scheduled. This poses a risk to the production process as the plant might have to be shut down due to lack of storage for the generated excess wastewater. The plant start-ups are costly as they consume more fuel (in the form of gas) and it takes a long time before the plant can get back on line and operate optimally.

By investigating the feasibility of in-house wastewater treatment, the organisation stands to save on the costs of outsourcing the effluent discharge, as well as on the hidden costs associated with unreliable service. In terms of additional labour costs, the process can be managed internally by the existing N_2O plant operators once it is up and running.

In addition to reducing compliance costs, AFROX GOC also stands to benefit from a more proactive sustainable approach to wastewater treatment. In-house wastewater treatment, together with the integration of industrial ecology principles into the existing production process, can lead to costs savings as well as improved corporate image.

Generated effluent can be reduced by reusing treated wastewater in the plant. The only waste generated will be in the form of concentrated regenerant waste (ammonium nitrate). The produced regenerant waste can be resold to the ammonium nitrate manufacturers as a feed to their production processes. It can also be sold to the fertiliser manufacturing industries for use in manufacturing of nitrate based fertilisers thus ensuring

a zero discharge practice. Potable water usage savings will also be realised in the plant due to the reuse of treated wastewater.

What remains is to investigate whether the potential savings associated with the in-house wastewater treatment outweigh the costs of implementing the system. This is the focus of the feasibility study.

2.5 LEGAL REQUIREMENTS

Ekurhuleni Metropolitan municipality water and wastewater by-laws and tariffs (Ekurhuleni Metropolitan Municipality, 2007: 17) need to be adhered to by all companies located within the municipal boundaries.

Table 2-2 compares the chemical analysis results of wastewater samples that were sampled from the two effluent tanks with the Ekurhuleni Metropolitan Municipality wastewater discharge limits (Ekurhuleni Metropolitan Municipality, 2007: 18). The analytical results indicate that the concentration of the generated wastewater (especially pH, conductivity, sodium, nitrates, orthophosphates and ammonium nitrogen) exceeds the municipality's wastewater discharge limits; and thus cannot be discharged into the municipal sewer without being treated. To comply with the wastewater discharge limits, the organisation has the following three options:

- to contract out the wastewater discharge to a waste disposal company;
- to treat the wastewater to the discharge standard of the municipality and discharge into the municipality sewer; or
- to treat the wastewater and reuse the treated water in the N_2O production process.

Table 2-2 Municipal wastewater discharge: Concentration limits (Ekurhuleni Metropolitan Municipality, 2007: 18).

Element	Acceptable range	Effluent Tank 1	Effluent Tank 2
pH at 25°C	6.00 - 10.0	1.2	7.9
Conductivity @ 25°C	< 500 µS/cm	35800 µS/cm	34900 µS/cm
Caustic alkalinity (expressed as $CaCO_3$)	< 2000 mg/l	Below detection	100 mg/l
Sulphates (expressed as (SO_4^{2-})	< 1800 mg/l	< 0.1 mg/l	< 0.1 mg/l
Chloride (expressed as Cl^-)	< 500 mg/l	Below detection	710 mg/l
Sodium (Na^+)	< 500 mg/l	700 mg/l	900 mg/l
Nitrates (NO_3^-)	<15 mg/l	10090.0 mg/l	10000.0 mg/l
Orthophosphates as P	< 50 mg/l	500 mg/l	100 mg/l
Ammonium Nitrogen as N	< 200 mg/l	5057 mg/l	4592 mg/l

2.6 COST OF OUTSOURCING

Table 2-3 summarises the cost of outsourcing wastewater treatment by using an authorised contractor to dispose of the generated wastewater. The N_2O plant produces 30 000 litres of wastewater per week, which is an average of 4286 litres per day. Annually the AFROX GOC spends about R1,872,000 in disposing wastewater through outsourcing. This cost does not include the cost of potable water that is used in the production of N_2O as the organisation does not have a water meter to measure the amount of water that the plant uses in the process.

Table 2-3 Nitrous oxide plant effluent collection costs (AFROX records).

	Daily	Weekly	Monthly	Annually
Effluent produced (L)	4,286	30,000	120,000	1,440,000
Effluent collection cost (per 1000L of wastewater) (ZAR/m^3)	1,300			
Total collection cost (ZAR)	5,850	39,000	156,000	1,872,000

CHAPTER 3: METHODOLOGY

The main aim of this research was to identify the most appropriate in-house wastewater treatment method for AFROX GOC N_2O plant; and to determine the technical and financial feasibility of implementing this in-house wastewater treatment method.

Table 3-1 gives an overview of the methodology that was followed in conducting the study. Where necessary, the steps are further explained below.

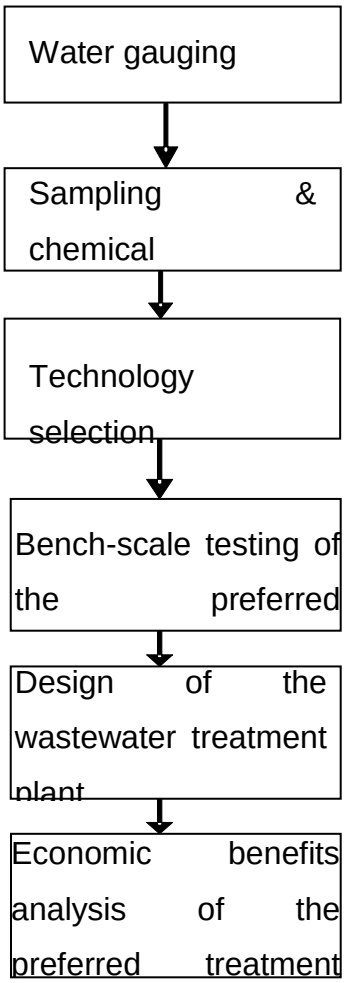

Figure 3-1 Process flow-chart of the research methodology.

3.1 WATER GAUGING

In order to determine the most appropriate in-house wastewater treatment method, information on the quantity and strength of wastewater coming from the plant was required.

Water gauging was carried out in order to establish the flow rates of the various effluent streams contributing to the wastewater exiting the plant, as well to establish an understanding of the strength of the wastewater and the temporal variability thereof.

This data was used to identify the location of the key sources of pollution in the production process, and to inform the timing and positioning of sampling. Knowing the location of key contributors to pollution assists in developing new plant designs that will minimise waste and improve the efficiency of proposed wastewater treatment processes. Timing and positioning of sampling is important because the strength of pollution varies over time. Wastewater plant design needs to cater for the worst case scenario, and hence representative water quality data needed to be used as design parameters. In addition, if resin ion exchange methods were chosen to treat the wastewater, then the pH of the wastewater would be an important contributor to the efficiency of the treatment process.

An instrumental profile of the pH and flow rate at pre-existing sampling sites indicated in Figure 3-3 was carried out in order to determine the above information. Even though full water quality data is required, pH was used as an indicator of the strength of wastewater. The pH of the wastewater was monitored because the concentration of species of most chemical constituents is dependent on the hydrogen ion concentration of the solution. Wastewater that has an extreme concentration of hydrogen ions is difficult to treat using biological methods. The pre-existing sampling

points had sampling taps which were used to decant the sample into a clean glass beaker for measuring.

The pH and flow rates were measured daily at the same time over a period of ten days by the plant operators. This was done to ensure that the wastewater gauging was reflective of the changing wastewater stream. The pH was measured using a Metrohm 704 pH meter. The pH meter was calibrated with pre-packaged pH 4 and pH 7 mercury free buffer solutions obtained from Merck Chemicals to ensure accuracy of the pH meter. The pH meter was stored in a 3 mol/L potassium chloride (KCl) electrolyte solution which was prepared in line with the manufacturer's guidelines (Metrohm AG, 2007: 2) to prevent the diaphragm from drying out.

The flow rates were determined by reading the N_2O plant operation manual for wastewater generation trends and scrubber recharging trends (AFROX, 2004: 12). These flow rates were confirmed by visual observation of the plant in operation.

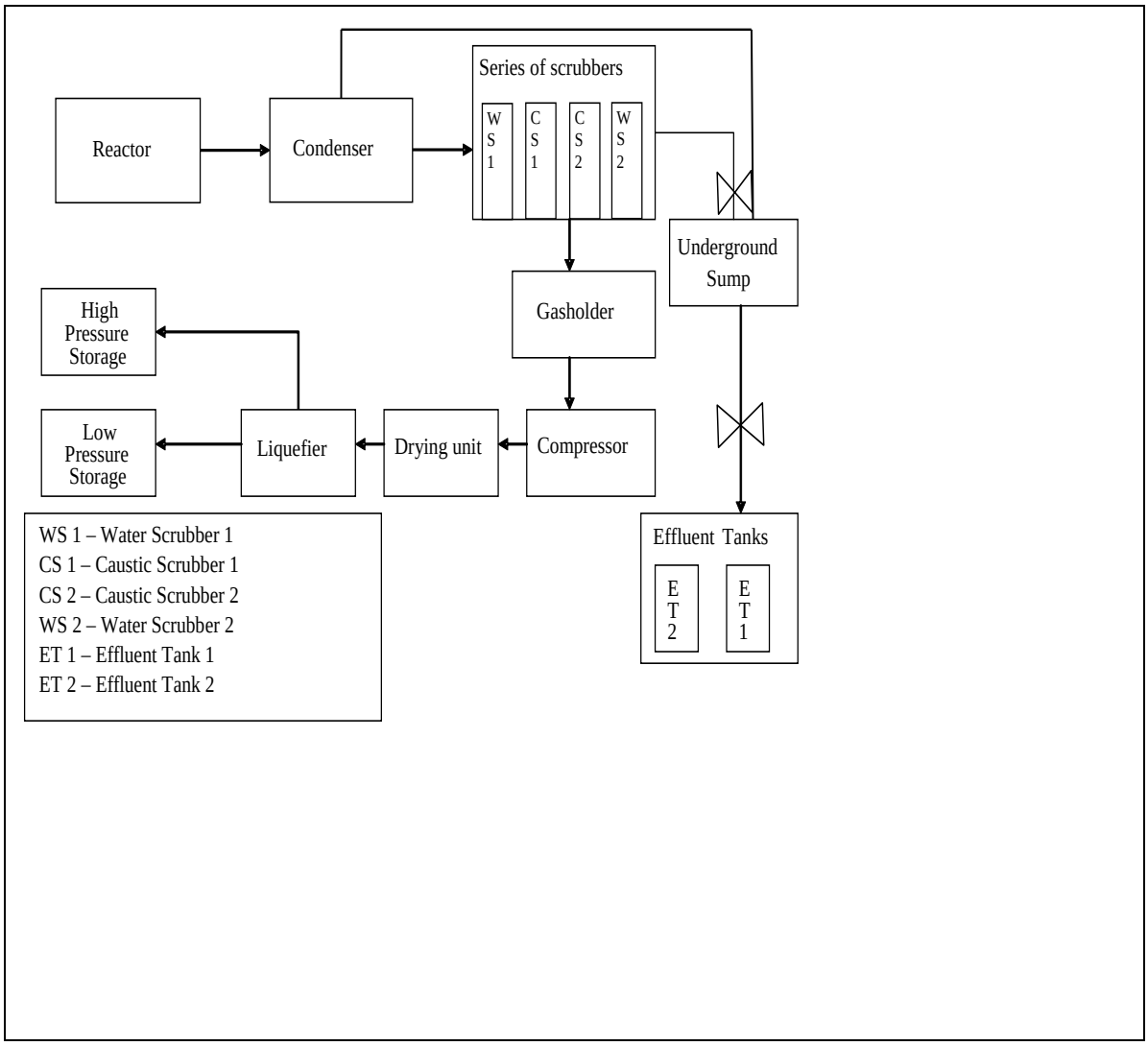

Figure 3-2 Schematic view of the production process (derived from EIGA, 2007:11).

3.2 SAMPLING AND CHEMICAL LABORATORY ANALYSIS

The time variability of pH is shown in Figure 3-3 below. The figure depicts the pH profile of wastewater streams during normal operation of the production plant (measured over 10 consecutive days without a gap).
The identified pH trend is important in determining how the various effluent streams in the N_2O production process contribute to the final pH of the effluent collected in the wastewater collection tanks. The final pH of the effluent is important to determine if a chosen wastewater treatment method will be able to process the effluent as it is or if a pretreatment step is required prior to proceeding with the chosen treatment method.

Effluent Tanks 1 & 2 were identified as the sampling locations that give the most representative sample to be used to determine the final pH of the effluent. The pH readings that are indicated in Figure 3-3 highlight the importance of a properly maintained production plant for the consistent and reliable production of representative effluent. The final pH of the effluent in both effluent tanks 1 & 2 (ET 1 & ET 2) must not vary significantly as the effluent is supposed to be equally distributed by the pump used to drain the sump.

Sampling was conducted in line with *method 1060: Collection and preservation of samples* as documented in (Clesceri et al, 1998: 1- 27).

The collected samples were sent to an independent South African National Accreditation System (SANAS) accredited laboratory for chemical analysis. The samples analysis suite that the laboratory was requested to conduct included cations (Ca^{2+}, Na^{+}, Mn^{2+} and K^{+}) and anions (NO_3^-, $\left(SO_4^{2-}\right)$, $Cl-$ and $\left(PO_4^{3-}\right)$. The samples were analysed in line with American Standard Testing method (ASTM) approved procedures, ASTM:

D4327 Standard test method for anions in water by chemically suppressed Ion Chromatography (Clesceri et al, 1998: 1- 27).

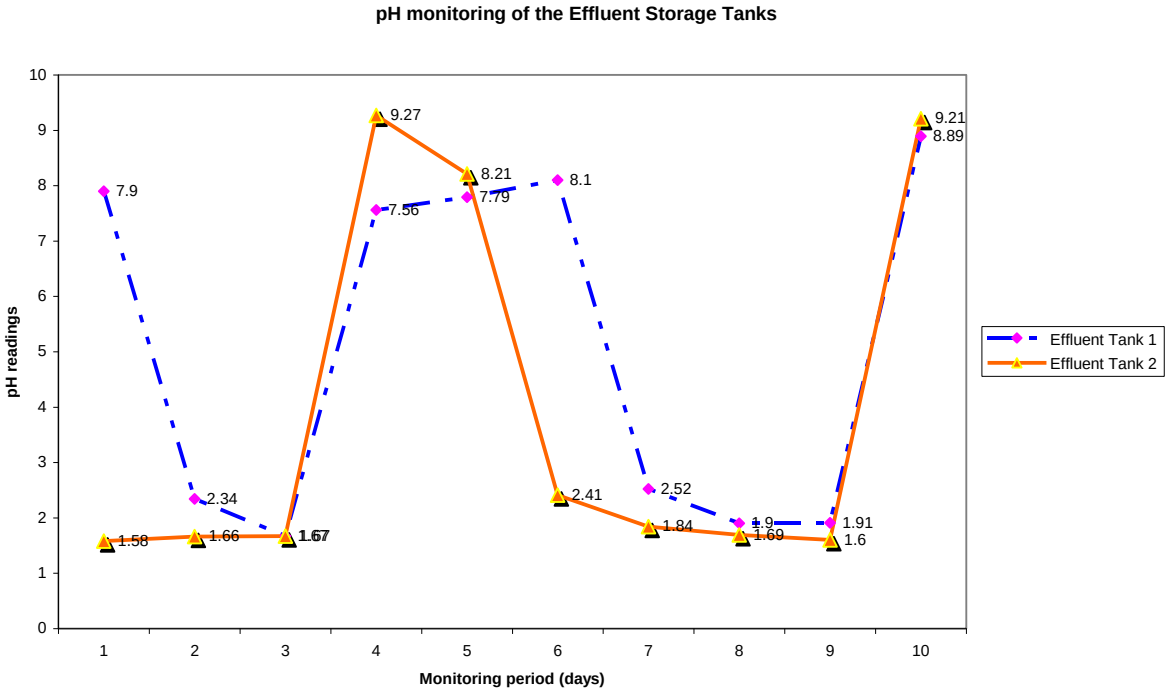

Figure 3-3 pH monitoring of the N2O plant effluent stream.

3.3 TECHNOLOGY SELECTION

A literature review of existing wastewater treatment methods was conducted. The literature review started by reviewing different water treatment methods, i.e. physical, chemical and biological. The methods were contrasted against one another in view of their abilities to deal with the characteristics displayed by the wastewater to be treated. The preferred technology was selected based on the following design parameters: the characteristics of the wastewater, quality required for the treated water, availability of resources locally, and local economy.

Characterisation of wastewater was conducted further under the following headings: wastewater quality, wastewater flow, wastewater volume, and pattern of flow. Quality considerations involved determining the intended usage of the treated wastewater. The local economy was assessed for the availability of resources that are critical for the selection of the preferred technology; for example, surge-free electricity supply, or uninterruptible power supply system and availability of chemicals where required.

3.4 BENCH-SCALE TESTING

Based on the literature review and outcomes of the gauging and sampling activities, the most feasible wastewater treatment option was determined to be ion exchange. Laboratory experiments to determine the effectiveness of this technique in treating the wastewater, and its technical feasibility were carried out.

The laboratory equipment must be arranged such that it simulated the proposed wastewater treatment technology. The test results are used to help determine proper pilot plant protocols. Shake flask tests were used to determine the optimum bed volume of resin required (amount of resins required to pack the column in which the treated water will flow through).

Ion exchange (both cation and anion) bench-scale tests were carried out to; confirm the bed volume, characterise the breakthrough, evaluate the regeneration efficiency and identify the conditions for pilot testing and large scale implementation. The flask test results were also used in determining the equilibrium adsorption capacity of the resins that would be used in the bench-scale test. This equilibrium capacity was important in determining the capacity of the resins in contact with the background ionic content. The operating capacity was determined from a breakthrough curve, and gave the plant sizing, taking into account factors such as pH, kinetics and concentration.

The bench-scale test results were used in the sizing of the equipment that would be used in the design of the wastewater treatment plant and also used to determine the operating parameters of the wastewater treatment plant. The gathered information will be used in the design phase of the ion exchange wastewater treatment plant. Plant sizing and operating parameters data will be used in determining financial feasibility of the wastewater treatment plant.

3.4.1 Isotherm shake flask tests

Prior to commencing with the bench-scale test, an adsorption isotherm test was conducted using the WBA type resin (Lewatit MP 68). The objective of the test was to determine the effectiveness of the selected resin to remove the target pollutant (nitrate ions) from the type of wastewater being treated and to determine the adsorption capacity of the selected resin. The resulting data was interpreted by constructing an adsorption. The test does not necessarily define the final process conditions however it offers valuable insight about ability of the selected resins to solve the problem (Dow, 1997: 1).

Five Erlenmeyer flasks each filled with 100ml samples of the wastewater solution were dosed with different quantities of weak base anion (WBA)

resin (i.e. 0.5g, 1.0g, 2.5g, 5g, 10g respectively) in granular form (see Appendix H: Product information Lewatit Monoplus MP 68). The pH and conductivity of the solutions in the flasks were measured and recorded at the start of the experiment. The solutions were then placed in a mechanical shaker and shaken for approximately 24 hours at a constant temperature (room temperature (25°C)) until the contents of all the flasks had reached equilibrium. After the 24 hours the test was stopped, the final pH and conductivity of the solutions were measured. The resins were separated from the solution by filtration and the concentration of the nitrate in the solution was determined in line with operating manual method 14542: Determination of nitrates using a Merck SQ-118 photometer spectrophotometer (see Appendix N). The collected data was used to develop isotherm curves (see Figure 7-2) that showed the relationship between the concentration of the adsorbate in solution after equilibrium has been reached and the quantity of adsorbate adsorbed per unit mass of adsorbent.

3.4.2 Resin Ion exchange column test

In order to test the initial bed volume determined above, bench-scale testing was carried out in the laboratory. Glass columns with sintered bottoms were used to carry out the tests; both columns were packed with cation and anion resins respectively.

The objective of the bench scale test was to determine the technical feasibility of the selected candidate technology. The two sintered glass columns were clamped onto a stand. Each sintered glass column was loaded with 1Bed Volume (1BV equivalent 50ml) of resins, (i.e. strong acid cation (SAC) (Lewatit S108) and weak base anion (WBA) (Lewatit mono plus 68) resins respectively. 5BV (equivalent to 250 ml) of sample (wastewater) was passed down through the packed bed of resins in the column (at approximately 1BV (50 ml) per hour or ‘equivalent of 0.0139 ml per second).

The 250ml Erlenmeyer flasks were used to collect the treated water at the outlet of the column (5 batches of 50ml of the treated effluent were collected in 5 different flasks). The samples were analysed for the; pH (ASTM Standard method D 1067 - Standard test method for acidity or alkalinity of water), conductivity (ASTM Standard method D 1125 Standard test methods electrical conductivity and resistivity of water) and for the determination of nitrates and ammonia concentration by using the absorbance spectrophotometer (Merck SQ 118 photometer) operating manual analysis method 14542: Determination of nitrates and operating manual analysis method 14559: determination of ammonia respectively.

3.4.3 Regeneration and rinsing of exhausted (saturated) resins

1BV (50 ml) of 15% nitric acid solution (prepared by diluting 15 ml of concentrated nitric acid in 100 ml of de-ionised water) and 1BV (50 ml) of 7% ammonia solution (prepared by diluting 7 ml ammonia solution in 100 ml of de-ionised water) were to regenerate both the columns of exhausted SAC and WBA resins respectively. Both columns were water washed with 2BV (100 ml) of deionised water and further fast washed with another 3BV (150 ml) of deionised water. Samples were frequently taken after each BV (50 ml) of solution has eluted through the column, the samples were tested for pH, conductivity, cations, (Ca^{2+}, Na^{+}, Mn^{2+}, NH^{+} and K^{+}) and anions (NO_3^- and Cl^-) respectively.

The column test operating parameters are listed in Table 3-1 below.

Table 3-1 Column test parameters.

Parameter	
Resin volume	5BV (equivalent to 250ml)
Resin bed depth	600ml
Service flow rate	1BV/h (BV/h = Bed volumes per hour)
Regenerant flow rate	1BV
Regenerant contact time	60 minutes
Slow displacement rinse	2BV
Final fast rinse	3BV

3.4.4 Instrumental Analysis

The effluent samples from the shake flask test and bench-scale resin ion exchange samples were analysed as follows; the pH of the samples was measured using the Metrohm 704 pH meter (electrode 6.0202.100) that was calibrated (using buffer pH 4 and pH 7 and 3M KCl solution) in line with the operator manual. The pH meter was stored in an electrolyte solution (potassium nitrate to prevent the membrane of the pH probe from drying out. Conductivity of the solution was measured by using the Metrohm conductivity meter. In addition inorganic non-metallic constituents such as hardness and anion concentration were measured.

In the above experiments, the various water quality parameters were determined as follows, spectrophotometrically using a Merck model SQ-118 photometer for the measurement of the concentration of nitrates and ammonia in the treated effluent. The analysis was conducted in line with operating manual method 14542: Determination of nitrates using a Merck SQ-118 photometer spectrophotometer and operating manual method 14559: Determination of ammonium.

To determine the concentration of cation metals, an instrument instruction manual method for atomic absorption spectrometer (AAS) was used. The analysis procedure was in line with the Shimadzu AAS AA-6601 instrument instruction manual method: Spectrophotometric analysis No. A274 - Analysis of environmental samples (i.e. for the determination of cations; manganese, calcium, potassium and sodium).

The data was used to plot the break-through curves for the target pollutant (nitrates and other present chemical species of interest). Three cycles of cation and anion ion exchange were completed to ensure the reproducibility of the treatment results.

CHAPTER 4: TECHNOLOGY REVIEW

In this chapter a literature review of prevalent wastewater treatment methods is undertaken, with the aim of identifying the most appropriate method of in-house treatment of wastewater produced by the N_2O plant at AFROX Northern Operations GOC.

The properties of pollutants found in wastewater are important in determining what type of treatment method should be pursued. Wastewater treatment technologies can be divided into three categories: chemical, biological and physical (Woodard & Curran, 2001: 149). A literature review of wastewater treatment methods from all three categories follows in the next section. Treatment methods are contrasted against one another in light of their advantages and drawbacks regarding their suitability for treatment of the N_2O plant wastewaters.

4.1 CHEMICAL TREATMENT METHODS

These are methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions. Chemical treatment methods take advantage of two properties: chemical characteristics of pollutants regarding their tendency to react with or interact with treatment chemicals and the chemical characteristics of the products of reaction between pollutants and treatment chemicals, regarding their solubility, volatilities, or other properties that relate to the inability of the product to remain in water solution or suspension. The settled precipitate will contain both the constituents that may have reacted with the added chemicals and the constituents that were swept out of the wastewater as the precipitate settled. Chemical treatment methods that can be used to remove substances from wastewater include precipitation, coagulation, disinfection, adsorption, absorption, chemical oxidation and biological oxidation.

The most commonly used examples of wastewater treatment methods are chemical precipitation, disinfection and chemical oxidation or reduction.

4.1.1 Drawbacks of chemical treatment methods in wastewater treatment

Chemical processes are additive, compared to physical treatment processes. Addition of chemicals to enhance removal efficiency of particulate sedimentation results in a significant increase in total dissolved solids concentration in wastewater.

The additive nature of the chemical process is a contrast to both physical and biological methods which can be described as subtractive processes in that wastewater constituents are removed from wastewater.

The handling, treatment, and disposal of large volumes of sludge that is produced pose a serious cost challenge when using the method.

Cost of most chemicals is related to the cost of energy and as a result the user has little control over chemical costs (Metcalfe & Eddy Inc., 2003: 478).

4.2 BIOLOGICAL TREATMENT METHODS

Biological treatment methods can be described as methods that involve living organisms that uses organic, or in some instances, inorganic substances as food and can completely change their physical and chemical characteristics (Woodard & Curran, 2001: 255). They involve the systematic break down of complex organic molecules and their reassembling as new cell protoplasm. The processes utilise oxygen in either the dissolved molecular form (aerobic) or in the form of anions (anaerobic) such as sulphates and nitrates. They result in a decrease in quantity of organic pollutants and increase in the quantity of microorganism, carbon dioxide, water and other by-products of microbial metabolism (Cervantes et al, 2006: 16).

4.2.1 Application

Historically biological processes have been used in municipal wastewater treatment plants. They are primarily and widely used where the bulk of the pollution load in wastewater is organic material, and is biodegradable. However their ability to remove a wide range of contaminants, both organic and inorganic, has led to their integration into various wastewater treatment systems (Cervantes et al, 2006: 16).

4.2.2 Advantages of biological treatment methods

Once the pre-requisite conditions of temperature, humidity and suitable pH range have been met, biological waste treatment methods are very tolerant to changes in wastewater composition, and the process is an on-going and effective one.
They are simpler and less expensive to operate as they do not require extremes in pH, temperature and oxidation potential (Cervantes et al, 2006: 16).

4.2.3 Disadvantages

Biological wastewater treatment processes produce large amounts of residual sludge that may have to be disposed of, with financial and/or environmental consequences, if there is no market for it in the fertiliser industry or the sludge contains metal ions.

In this study the effluent being treated has no organic matter present and contains high concentrations of metal ions and anions (dissolved inorganic cations and anions), which are all not biodegradable (i.e. nitrate is biodegradable). For the technique to be applicable an organic body (i.e.

carbon containing) must be introduced to the effluent to exchange electrons (act as an electron donor) with the anions present in the effluent (for example phosphates and nitrates). Furthermore, the presence of chlorides in the effluent inhibits the growth of the microbial population that is required breakdown the organic pollutant (Cervantes et al, 2006: 16). Therefore, for the type effluent under study, the biological treatment methods are inappropriate and incapable of producing the desired wastewater treatment results.

4.3 PHYSICAL METHODS

With physical treatment methods, change is achieved through the application of physical forces (Metcalfe & Eddy Inc., 2003: 313). The removal of dissolved and non-dissolved substances is accomplished without changing their chemical structure; instead, substances are removed by use of naturally occurring forces such as gravity, van der Waals forces, electrical attraction, and physical barriers.

Physical methods of wastewater treatment include sedimentation, filtration, flotation, adsorption, and physical barriers such as bar racks, screens, deep bed filters, and membranes. Racks, sieves and screens are considered part of the treatment plant head works or part of the primary treatment. Filters, microscreens, electrodialysis processes, and reverse osmosis are considered either secondary or tertiary treatment depending on their specific use (Woodard & Curran Inc., 2001: 322). The three physical methods that have gained industry-wide use to treat industrial wastewater with the aim of re-use are reverse osmosis (RO), electrodialysis (ED), and ion exchange (IX).

4.3.1 Reverse osmosis

Reverse osmosis is an example of a pressure driven membrane process used in conjunction with other membrane processes, such as nano-filtration, ultra-filtration and micro-filtration.

Its treatment principle is based on separating solutes by diffusion through a thin, dense, semi-permeable membrane barrier layer, as well as by sieving action. The required membrane feed-pressure generally increases as removal capability increases. The filtered stream is the “permeate” because it has permeated the membrane, the second stream is called the “concentrate” because it carries off the concentrated contaminant rejected by the membrane. Water has to be slightly acidic, pH ranging between 5 – 6, for the best operating conditions to be achieved, and also to assist in reducing membrane hydrolysis (American Water Works Association & American Society of Civil Engineers, 2005: 13.1).

RO is based on the same principles as osmosis, except for the fact that the membrane allows some compounds (like water) to pass through and rejects other large compounds through the use of a semi-permeable membrane. RO and osmosis also differ in that with osmosis pressure-difference ensures that water passes through the membrane from a dilute to a more concentrated solution. In RO, hydrostatic pressure (ranging between 50 – 100 bar) is applied to the concentrated side of the membrane (the contaminated side) thus forcing the osmotic process into reverse; by applying adequate pressure, water is forced from the concentrated (contaminated) to the dilute (treated) side (Kocher et al, 2005: 4).

Figure 4-1 shows a schematic diagram of a RO system. The membranes may be made of a dense material (without pores or void spaces), as in the case of a high-pressure reverse osmosis membrane. The permeate

stream exists at more or less atmospheric pressure, while the concentrate remains at more or less the feed-pressure (MWH, 2005: 1435).

The quantity and quality of the treated water is dependent on the type of membrane used, as well as on other operating conditions such as flow control and pressure. A slow flow rate ensures that there is enough time for water to pass through the membrane, which will result in a higher recovery rate. However, membrane fouling occurs if concentrated contaminants are not washed away rapidly enough; such fast flow rates result in low recovery rates.

The incoming feed-water line should be adequate to overcome osmotic pressure and any backpressure generated from the storage tank down the line from the membrane. Auxiliary pumps may be employed to increase the incoming water pressure. A higher-pressure difference across the membrane will result in an improved rejection of contaminants and recovery rate (Kocher et al, 2005: 5).

The reverse osmosis process

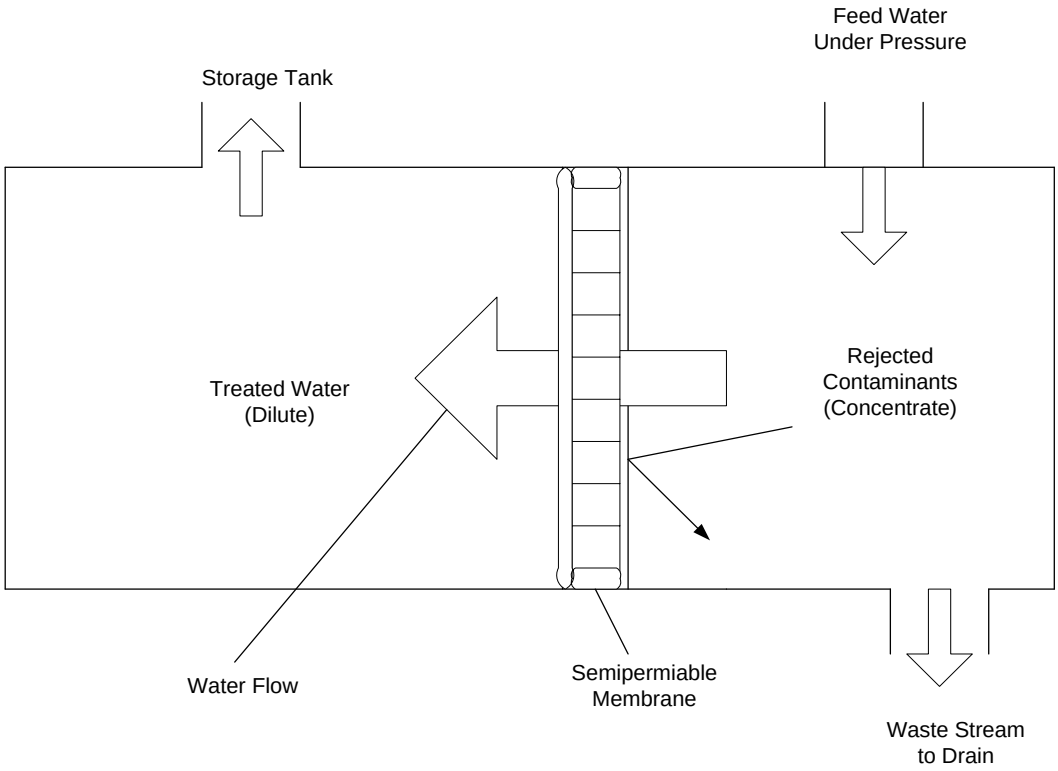

Figure 4-1 The reverse osmosis process (MWH, 2005: 1435).

4.3.2 Maintenance

Maintenance and rejection percentage need to be monitored to ensure that NO_3^- levels are below the legislated limit. Regular monitoring is important to determine fouling, scaling and other degradation of the membrane. Fouling and scaling can be removed by flushing a cleaning agent with acidic or caustic solution (for example, $NaHSO_3$) through the system at high pressure/low volume. RO stages are cleaned sequentially; the frequency of membrane replacement depends on the raw water (feed water) characteristics, pre-treatment and maintenance (Bureau of Reclamation, 1998: 2).

4.3.3 Application

RO is used in the separation of solutions with low molecular weight constituents. It is effective in removing products such as trihalomethanes (THMs), some pesticides, solvents, other volatile organic compounds (VOC's) and sizeable amounts of selected compounds such as *N*-nitrosodimethylamine (NDMA) (a compound with strong carcinogenic properties). As part of a spiral wound configuration it can be used to promote turbulence, thereby reducing concentration polarisation fouling and particle cake deposition (Zhou & Smith, 2002: 250).

4.3.4 Advantage

- Produces highest quality water.
- Can effectively treat a wide range of salts and minerals, turbidity, health and aesthetic contaminants and certain organics.
- Low pressure, compact, self-contained, single membrane units are available for small installation.
- Low energy consumption translates into low product cost and atmospheric emissions (Sagle & Freeman, 2005:11).
- Reduces the amount of treatment chemicals used (EPRI Municipal Water & Wastewater Program, 1997:5).

- Can disinfect treated water.
- Removes dissolved constituents.
- Can remove natural organic matter (a disinfection by-product precursor) and inorganic matter (Metcalf & Eddy Inc., 2003:1125).

4.3.5 Disadvantages

- Fairly expensive to install and operate.
- Frequent membrane monitoring and maintenance is required.
- Monitoring of rejection percentage for NO^-_3 removal is required.
- Pressure, temperature and pH requirements have to meet membrane tolerances and may be chemically sensitive.
- Recovery rates may be less than 100%.
- Flux rate (the rate of feed water flow through the membrane) gradually declines overtime (EPRI Municipal Water & Wastewater Program, 1997:5).
- The membrane is prone to fouling or can be easily blocked by colloidal substances and other substances in wastewater. This phenomenon is sometimes known as concentration polarisation and leads to flux inhibition or reduction in throughput (Woodard & Curran Inc., 2001: 329).
- It cannot remove all salts from water and dissolved gases such as dissolved oxygen and carbon dioxide pass through the membrane into the treated water (Kneen et al, 2005).

4.4 ELECTRODIALYSIS

Electrodialysis (ED) is an electrochemical membrane process that involves the movement of ions through anion and cation selective membranes from less concentrated solution to a more concentrated solution by the application of a direct current (DC). Direct current causes the charged ions to move in opposite direction, anions move towards the anode (+) and the cations move towards the cathode (-). Cations easily pass through the negatively charged cation exchange membrane but are retained by the positively charged anion exchange membrane. Similarly, anions pass through the positively charged anion exchange membrane but are retained by the positively charged cation exchange membrane. ED as a membrane process differs from other membrane process in that no pressure is applied, only electrical potential is used (Baker, 2000: 393).

The ion selective semi-permeable membranes placed in between the electrodes, alternatively allow only hydrogen and hydroxyl anions to pass through the respective electrodes as indicated in Figure 4-2. As migrating ions intersect the selectively permeable membrane, alternative cells of concentrated and dilute streams are produced in the spaces between the membranes, and during the process the impurities are trapped within the membranes. The recovery rate is reduced over time when the membrane process becomes saturated with the charged ions. The problem can be overcome by reversing the polarity of the electrodes every 15 minutes. Polarity reversal causes the concentrating and diluting flow streams to switch-off after every cycle and this result in cleaning of the membrane by sending high quality water into the compartment that was previously filled with reject stream (Baker, 2000: 393).

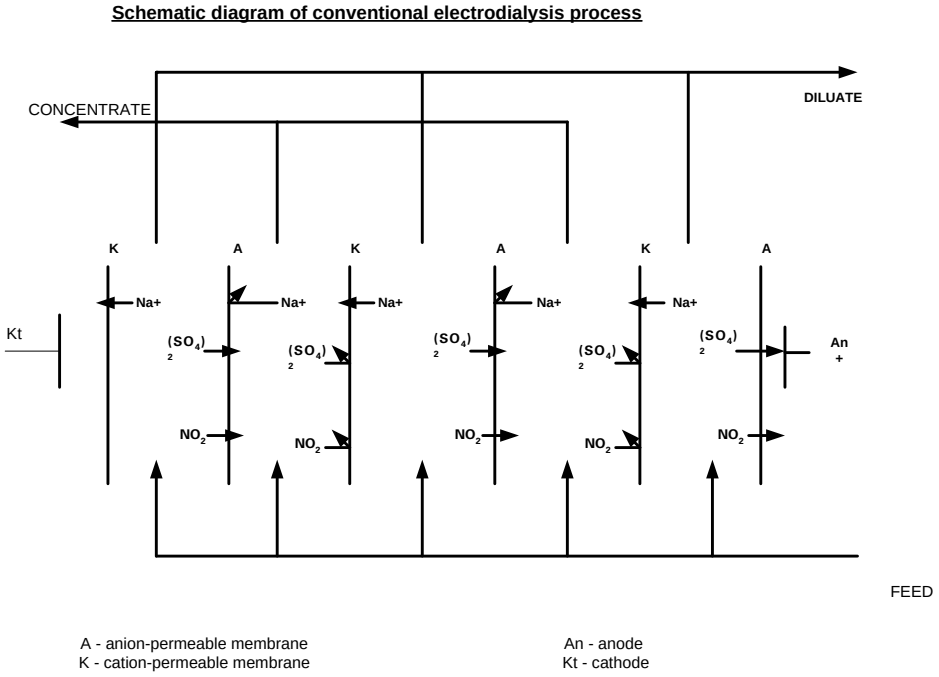

Figure 4-2 Schematic diagram of conventional electrodialysis process (American Water Works Association & American Society of Civil Engineers, 2005:13.1

4.4.1 Maintenance

The membranes are durable and can tolerate a pH range of between 1 – 10, and temperatures up to 75^0C for caning wastewater. The membranes may be removed from the unit and scrubbed. Turning off the power will allow solids to be washed off and water to be circulated through the stack. Electrode washes will flush out by-products of an electrode reaction, including hydrogen (formed in the cathode spacer), oxygen and chlorine gas (formed in the anode spacer) (American Water Works Association & American Society of Civil Engineers, 2005:13.1)

4.4.2 Application

ED process has been found to be most suitable for the separation of salt solutions and the removal of brackish water with Total Dissolved Solids (TDS) feed-water of up to 4000 mg/L. The technology is suitable for removal of organics, it has also gained a wide usage in wastewater treatment and its application include concentrating the RO reject streams, mining water reuse and cooling tower blow-down treatment (Seneviratne, 2007: 223).

4.4.3 Advantages

- It is possible to operate without fouling or scaling.
- Low pressure is required.
- Membrane life is extended by electrodialysis reversal.
- It is easy to handle, and very moderate in its demand of chemicals.
- It enables a high extent of water recovery.
- It has a very high selectivity for nitrates (depending on what type of membrane).
- It can operate without fouling or scaling, or chemical additions; it is thus suitable for TDS.
- Denitrification of water with ED is cost effective.

- Nitrate removal is 85% efficient (Rozanka & Wisniewski, 1994:12).

4.4.4 Disadvantages

- It is not suitable for high levels of iron (Fe) and manganese (Mn), hydrogen sulphide, chlorine or hardness.
- Electricity costs start increasing significantly with TDS feed-water of over 4000 mg/L.
- It has a limited current density, current leakage and back diffusion.
- At a 50% rejection of TDS per pass, the process is limited to water with 3000 mg/L TDS or less.
- Increased power demands due to internal resistance of the solution to current (especially when ED has reduced wastewater concentration to less than 200 mg/L of TDS) (Lee & Neff, 2011: 457).
- Its applicability is limited to removing only low-molecular-weight ions from wastewater and will thus require an additional technology like ultra-filtration (UF) that is capable of removing high-molecular weight ions (Woodard & Curran Inc., 2001: 333).

4.5 ION EXCHANGE

Ion exchange is a mass transfer process in which ions of a given species are displaced from an insoluble exchange material by ions of different species in solution (Metcalf & Eddy Inc., 2003: 296). It is a reversible reaction in which charged ions in solution are exchanged for similarly charged ions that are electrostatically attached to an immobile solid particle. The ions on the solid medium are associated with functional groups that are attached to the solid medium, which is immersed in the liquid or gas medium (Woodard & Curran Inc., 2001: 377).

Ions in dilute concentrations replace ions of like charges that are of lower valence state. However, ions in high concentrations replace all other ions

of like charge. For example, calcium ions or ferric ions in dilute concentration in water or wastewater replace hydrogen or sodium ions in the ion exchange medium. Similarly when a strong solution of sodium chloride is brought into contact with an anion exchange material that has nitrate ions associated with its functional groups, the chloride ions will replace the nitrate ions. The divalent ions or tri-valent ions move from the bulk solution to the surface of the ion exchange medium where they replace ions of lesser valence state, which in turn pass into the bulk solution (Woodard & Curran Inc., 2011: 383). Figure 4-3 indicates a typical ion exchange column.

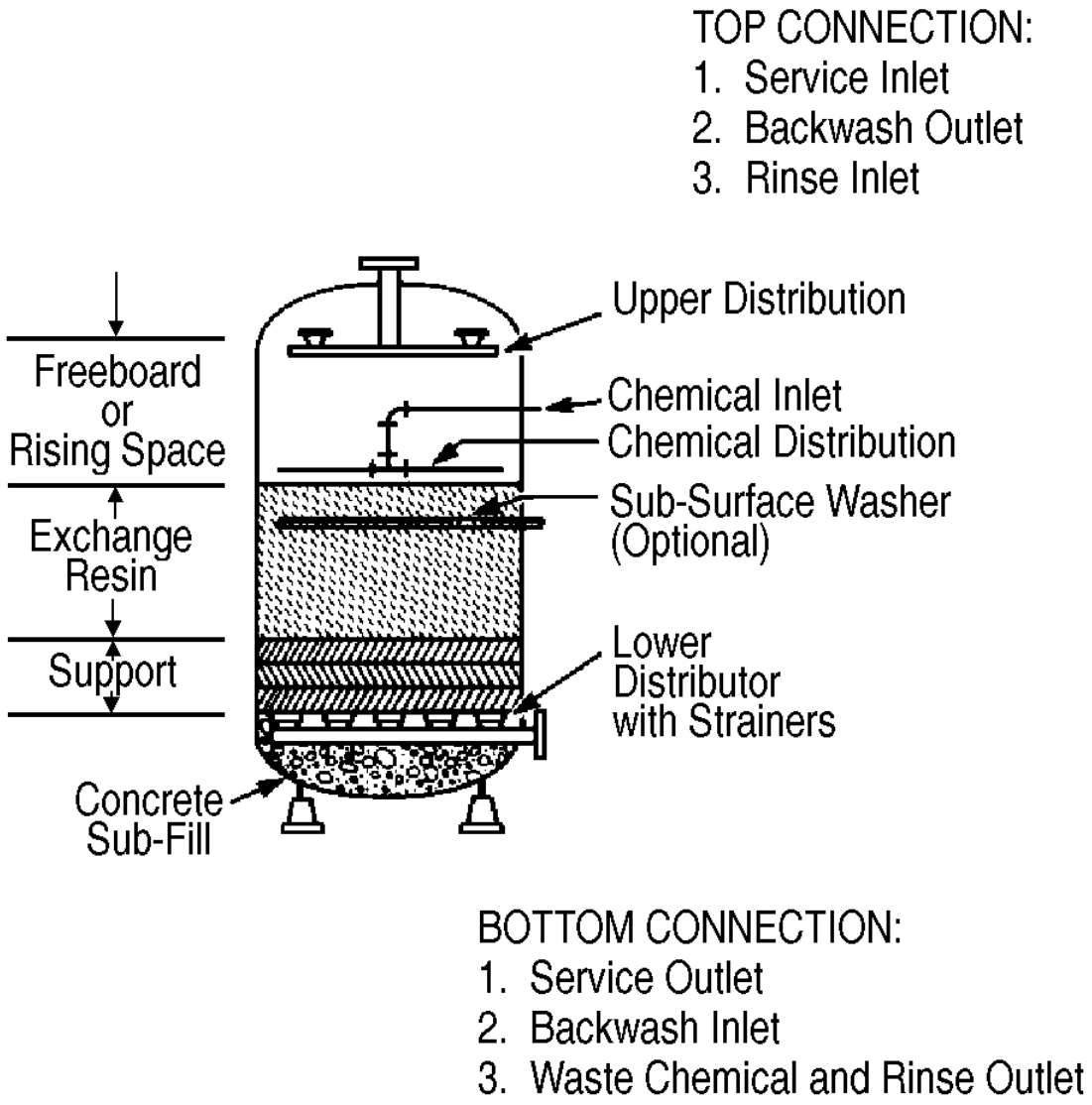

Figure 4-3 Schematic diagram of a typical Ion exchange process (American Water Works Association & American Society of Civil Engineers, 2005: 13.1).

4.5.2 Maintenance

Ion exchange resins are susceptible to fouling and require frequent regeneration of resins which can result in an increase in cost (due to regeneration) (Metcalf & Eddy Inc., 2003: 1182).

4.5.2 Application

It is commonly used in water treatment to soften water through the removal of multivalent cations. Its principal use in wastewater is to remove nitrogen and phosphorus and the removal of total dissolved solids (i.e. demineralisation) for re-use applications (Metcalf & Eddy Inc., 2003: 297). It can also be used to remove specific contaminants such as, arsenic, barium, nitrate, and radium.

Ion exchange can be used to remove undesirable ions from industrial wastewaters as a final treatment step, as treatment for isolated process streams as part of a waste minimisation programme, or as a polishing step before recycle and reuse of process water or wastewater. It can also be used to recover valuable metals or other exchangeable substances.

4.5.3 Advantages

- Substances removed by ion exchange have been successfully recycled and reused, substantially reducing the real cost for this treatment step (for example, by regenerating the strong base anions with ammonia, the resulting waste concentrate (concentrated ammonium nitrate solution) can be reused in different industries such as the fertiliser industry, ammonium nitrate manufacturing and nitrate based explosive industry (Bureau of Reclamation, 2001:2).
- Ease of operation; efficient and highly reliable.
- Lower initial costs; resins will not wear out with regular regeneration.

- Suitable for small and large installations (Bureau of Reclamation, 2001:2).
- No significant sludge disposal problem.
- No chemical feeders, mixers, etc., other than what is required to make up the feed regenerant (Woodard & Curran Inc., 2011: 387).

4.5.4 Disadvantages

- When ionic concentration is greater than 500 mg/L, ion exchange may become impractical or less attractive than other processes (American Water Works Association and American Society of Civil Engineers, 2005: 12.8).
- Cannot remove non-ionic dissolved species or microbes;
- Requires salt storage;
- Strongly basic anion resins are susceptible to organic fouling, have a reduced life span and are thermodynamically unstable (Bureau of Reclamation, 2001:2).
- The effluent to be treated must be reasonably free of un-dissolved solids
- Corrosion-resistant material of construction is required for the column containers, pumps, and piping;
- Ion exchange resins are mechanically weak, cation resins tend to be brittle and anion resins are normally soft.
- The resins are dimensionally unstable due to the variation in the amount of water imbibed into the gel in different circumstances (Noble & Stern, 1995: 233).

CHAPTER 5: TECHNOLOGY SELECTION

In this chapter the three potential wastewater treatment technologies are put through the technology selection test criteria in order to determine the most suitable technology.

From the technology literature review that was conducted in the previous chapter, three technologies, electrodialysis (ED), ion exchange (IX) and reverse osmosis (RO) were strong contenders for use in the treatment of the wastewater under study. ED was eliminated based on affordability (technology not energy efficient), availability (in South Africa the technology is not readily available thus poor technical support is a risk for continued use) and ability (technology unable to treat wastewater containing high molecular-weight ions thus requiring an additional advanced wastewater technology to treat these types of ions).

5.1 COMPARISON BETWEEN IX AND RO

RO and IX technologies were further contrasted to determine the most suitable method between them. Ion exchange is generally run on a batch basis while RO is run continuously. Ion exchange requires a high degree of operator attention; however this can be significantly reduced by automating the commercial systems. RO on the other hand requires cleaning which may be frequently based on the composition of the wastewater.

RO is sensitive to incoming suspended matter and requires comprehensive but expensive pre-treatment technologies. Ion exchange is less sensitive to suspended matter. RO is sensitive to hardness of the effluent and thus require some softening pre-treatment. Generally membranes cannot handle silica containing waters (Cheremisinoff, 2002: 401).

RO systems are sensitive to certain temperature ranges, within the temperature range of 15 – 25ºC, and as a result it has been proven to lose about 30% of its performance. The steep loss in performance can be attributed to the fact RO has increased salt passage when temperature increases. Ion exchange is insensitive to temperature changes (Cheremisinoff, 2002: 402).
Low operational cost in ion exchange can be achieved by using the new generation of high performance resins that enable ion exchange to be kept small by using short cycle times and regeneration utilisation that approaches stoichiometric theoretical values (Cheremisinoff, 2002: 402).

Due to the recovery rates that can be achieved with ion exchange, it can be classified more as a pollution prevention technology. For example the difference between net throughputs (the water produced for reuse) and gross throughput (the amount of water that is consumed) is minimal. Less water is required for dilution of regenerants and for rinsing. For medium TDS water, the wasted water is about 5% or less but with older co-flow regeneration system and high TDS water, it can reach or exceed 10%. In comparison with RO only 70 – 75% of water pumped into the system can be recovered. RO rejects large volumes of concentrate (Cheremisinoff, 2002: 403).

Ion exchange removes all ions down to extremely low residuals; it does not remove non-ionic species. RO removes all compounds based on their sizes (small ions of molecules such as Na^{+}, Cl^{-}, and CO_2 are partially removed and other molecules like Ca^{2+} and SO_4^{2} are harmful to the membrane (Cheremisinoff, 2002: 404).

RO is a partial demineralisation process whereas complete demineralisation can be achieved with a simple ion exchange plant. To achieve same salt residual as obtained with ion exchange plant, a more

expensive double-pass reverse osmosis system is required (Cheremisinoff, 2002: 404).

Difference between RO and ion exchange (IX)

Quality of treated water: IX can produce demineralised water with a conductivity of less than 0.5 µS/m from a simple SAC-SBA combination, and less than 0.1 µS/m with the addition of a mixed bed SAC/SBA unit.
Even the best performing RO plants cannot meet the treated water quality of a simple IX plant and a subsequent IX unit is required to achieve boiler feed water quality. (SAC is strong acid cation resin; SBA is strong base anion resin).

Flexibility: IX plants tend to be more flexible than RO, for example, in terms of performance over a wider range of temperature variations and the ability to recover from high suspended solids in the feed.

Plant cost/feed flow-rate: The capital cost of an RO plant is generally higher than that of an IX plant and is relatively insensitive to scale. If investment cost is the major consideration in selecting between RO and IX plants then IX will be selected.

Operating Cost: Operating costs represent 70 to 80% of the total cost of both cases. Chemical costs for ion exchange and power costs for RO are the most significant contributors to operating costs.

Membrane and resin replacement costs: The cost of membrane plus resin replacement in the RO-IX system is significantly higher than the cost of resin replacement in the IX system and this is very little affected by the ionic load and scale of operation.

Plant maintenance: RO plants have higher maintenance costs than ion exchange plants owing to the more complex nature of RO plants.

5.2 JUSTIFICATION FOR THE SELECTION OF ION EXCHANGE TECHNOLOGY

Based on the literature comparisons and contrast between IX and RO above, it can be concluded that ion exchange (IX) is the most suitable wastewater treatment technology for the type of effluent being studied. It easily satisfies the three key tests of technology selection, namely, affordability, acceptability and manageability.

Affordability

Ion exchange is least costly than other technologies (RO and ED) and requires the least amount of electrical energy during operation. The rising cost of electricity in South Africa gives IX an advantage over the other technologies which use lots of electrical energy compared to it. For RO to be economically feasible the volume of wastewater being treated must be more than tenfold the current generated volume in the N_2O production plant.

Acceptability

The criteria mainly depend on the performance of the treatment system. IX will be readily acceptable to the local municipal authorities as it demonstrates AFROX GOC's intention to comply with the local by-laws.

Manageability

It refers to both the routine operation of the plant as well as its maintenance and repairs. The ease of operation and low cost of maintenance of the IX technology also gives it an edge over the other technologies.

The preference of other IX over other wastewater treatment technologies was further supported by the characteristics of the effluent being treated. The following effluent characteristics highly influenced the preference for IX, low acidity, corrosive nature, presence of metal ions like manganese (Mn^{2+}) and higher nitrate $\left(NO_3^-\right)$ ion concentration. Both ED and RO were found to be unsuitable for handling this type of heavy industry effluent, for example both technologies can only treat low levels of nitrate ion concentration similar to that found in groundwater, at high levels nitrate concentrations, the membranes were susceptible to fouling and thus required additional costly pre-treatment steps.

On the other hand IX technology could handle this type of effluent without requiring any pre-treatment (resulting in lower operational costs). The physical characteristics of the types of resins used in the treatment of this type of effluent are strong and rugged enough to ensure removal of the anions and neutralisation of the effluent without using any additional chemicals. The most suitable type of resins that can be used to treat this type of effluent was found to be weak base anions (WBA) and strong acid cation (SAC).

CHAPTER 6: ION EXCHANGE

The following chapter takes an in-depth look at the preferred wastewater treatment technology, ion exchange (IX). The principles of the technology which are mostly similar to adsorption principles (namely, breakthrough concentration curve, columns capacity and mass transfer zone) are explained in detail. The section also expands on the selected type of resins that were used in the study by looking at their properties.

Ion exchange process is a chemical reaction between ions in solution and ions in an insoluble solid phase. The technique used in ion exchange closely resembles that of adsorption and for the majority of engineering purposes, ion exchange can be considered as a special case of adsorption (Geankoplis, 2003: 823).

In ion exchange, certain ions (solutes) are removed by the ion exchange solid (resin). Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin and the adsorbed ions replace ions that are on the resin surface on a 1:1 charge basis (Geankoplis, 2003: 823).

6.1 ION EXCHANGE PROCESS CONFIGURATION

Ion exchange process is normally conducted in a fixed bed of resins with treated effluent passed down through the packed bed of resins at a constant flow rate. When passing through the fixed packed bed, the concentrations of the ions (solute) in the effluent and that of the resin (solid adsorbent phase) within the fixed bed changes with time and position. At the start of the process, (i.e. at the inlet to the bed) the resin is assumed to contain no solute (or ions in the solution). When the treated effluent comes in contact with the inlet of the fixed bed, mass transfer and adsorption takes place. The concentration of the treated effluent drops

rapidly with distance in the bed and reaches zero before reaching the end of the bed (Geankoplis, 2003: 838).

After some time the resins near the entrance to the packed bed are almost saturated with the solute, and most of the mass-transfer and adsorption takes place at a position or point further down from the inlet. The mass transfer zone where most of the concentrations change takes place, changes its position by moving further down the fixed packed bed (Geankoplis, 2003: 839).

A similar process takes place for the concentration of the adsorbates on the resin, where the resins at the entrance will be nearly saturated. The concentration would remain almost constant down to the mass-transfer zone, where it will drop off rapidly to almost zero. The driving force for mass transfer is the difference in the concentrations (Geankoplis, 2003: 838).

6.2 BREAKTROUGH CONCENTRATION

When almost half of the fixed bed is saturated with solute, the outlet concentration is approximately zero, and the outlet concentration remains near zero until the mass-transfer zone reaches the fixed bed outlet. When the outlet concentration starts to rise again, a breakthrough point is reached; beyond this point the concentration of ions to be exchanged increases rapidly, rendering the fixed packed bed ineffective. The breakthrough point concentration represents the maximum amount of the target specie that can be discarded (Geankoplis, 2003: 838).

6.3 RESIN REGENERATION

When the fixed packed bed resins reaches saturation point, the fixed bed column is taken offline for regeneration and another column is used to supply continuous treatment. The regeneration steps of an ion exchange resin are important to the overall efficiency of the process.

There are two methods of regenerating an ion exchange resin, co-current and counter-current.

6.3.1 Co-current operations

In the co-current method, the regenerant is passed through the resin in the same direction flow as the influent (treated effluent) and usually downwards. It is the preferred method when small concentrations of the unwanted ion(s) can be tolerated in the effluent (referred to as leakage), and the exchange in the regeneration is favourable.

The method is effective in reducing leakage of unwanted ions and can handle dirty raw water (with high turbidity) better (American Water Works Association & American Society of Civil Engineers, 2005:12.35).

6.3.2 Counter-current operations

The regenerant is passed through the resin in the opposite direction as the influent (the solution being treated). It is used in situations where high-purity water is required, chemical consumption should be reduced to a minimum, least waste volume is produced, and where the raw water is cleaner. This type of operation will not be used in the laboratory testing of the treatment technology (American Water Works Association & American Society of Civil Engineers, 2005:12.35).

6.4 KINETICS OF ION EXCHANGE

Ion exchange process consists of two types of rate-controlling processes: the rate of diffusion of ions through the film (the region of water molecules surrounding the ion exchange resin material) and the rate of diffusion of the interchanging ions within the pores (or diffusion through interstitial pores of the resin particle itself) (Woodard & Curran Inc., 2001: 384). The first of these processes is called film diffusion, and the second is termed pore diffusion. If the exchange treatment process is a batch type (for example, shake flask test) in which the fusion-diffusion mechanism controls the overall rate of ion exchange, higher rates of stirring are required to minimise the retarding effects of film diffusion. In a continuous flow column system, higher flow rates minimise these effects. Larger pores can minimise the retarding effects of pore diffusion. In reality there is no film that exists, it is a hypothetical stagnant film or a hydrodynamic boundary layer that is a convenient means for representation and mathematical expression of the transport process which brings an iron into direct contact with the surface of a resin particle (Weber, 1972: 278).

There are operational differences between ion-exchange reactions which are controlled by film and those that are controlled by pore-diffusion processes:

Flow rate and/or stirring: film diffusion processes are dependent on stirring rate or flow rate. The rate of exchange increases with the rate of stirring. Pore-diffusion processes (for example, packed column) are unaffected by the stirring or changes in rate of flow (Weber, 1972: 278).

Resin particle size: for film diffusion processes, the rate of exchange varies inversely with the particle size. For pore-diffusion processes, the order of dependence of rate on the reciprocal of particle size is of a higher order.

Solution concentration: film diffusion process dominates when the concentration of the exchanging ion in solution surrounding the resin particles is very low. Pore-diffusion is more important at high solution concentration (Weber, 1972: 278).

Resin cross-linkage: the effects of cross-linkage on rate of exchange will be more marked for the pore-diffusion process than for film-diffusion processes. Film-diffusion will be affected to the extent that increased cross-linkage will decrease swelling and the resulting change in the external particle area (Weber, 1972: 278).

For pore-diffusion, the rate of exchange is proportional to the concentration of fixed charges and the effective particle-diffusion coefficient and is inversely proportional to the volume of the particle. For film-diffusion the exchange rate is proportional to the solution concentration and the effective film-diffusion coefficient of the ions (Weber, 1772: 279).

6.5 CLASSIFICATION OF ION EXCHANGE RESINS

There are five types of synthetic ion exchange resins: **strong acid cation (SAC)** – they are characterised by strong acid functional group (i.e. sulphonated polystyrene (e.g., R-SO_3H) which is obtained by: copolymerisation of styrene and divinylbenzene in emulsion form); they are highly ionised and can be used over the entire pH range. **Weak acid cation (WAC)** - characterised by a weak acid functional group (R-COOH), carboxylic group and behaves like weak organic acids that are weakly dissociated. **Strong base anion (SBA**) – characterised by a strong-base functional groups such as (R-N-OH); they are highly ionised and can be used over the entire pH range. They can also be used in hydroxide form (OH-) for water deionisation (American Water Works Association and

American Society of Civil Engineers, 2005: 12.8). **Weak base anion (WBA)** – characterised by weak base functional group (e.g., R-NH3OH or R-R'-NH2OH) in which the degree of ionisation is dependent on the pH. Heavy metal selective chelating resins – characterised by the functional group EDTA-Na compound. They have a high degree of selectivity for heavy metal cation. They have regeneration similar properties to WAC and in widely used in polishing to lower the heavy metal concentration in wastewater from a hydroxide treatment process (Bisen & Sharma, 2012: 299).

For the purpose of this study SAC and WBA types of resins were selected for usage in the column tests, their selection was based on their engineering and physical properties as detailed below in **section 6.6.1** Physical properties and **section 6.6.2** Engineering properties. The resins were found to be the most suitable resins for removing both target pollutant cations and anions in the type of effluent being treated and thus the focus of the study on them instead of other resins.

6.5.1. Strong Acid Cation (SAC)

The behaviour of SAC resins is similar to a strong acid, and are highly ionised in both the acid RSO_3H and salt $R\text{-}SO_3Na$ form, over the entire pH. Products obtained by this process are virtually mono-functional; their properties vary depending on the percentage of divinylbenzene (DVB) to styrene (this is known as degree of cross-linking) (American Water Works Association and American Society of Civil Engineers, 2005: 12.8).

The resins have a different percentage of cross-linkage; resins with higher percentage of cross-linkage are used in applications where the influent water has a higher level of chlorine or an increased water temperature. These types of resins (i.e. resins with a high percentage of cross-linkage) can be utilised in electric utility condensate polishing process and are capable of removing corrosion products from the utility condensate (Degremont, 1991: 236).

6.5.2 Weak Base Anion (WBA)

Their functional groups are usually amines; the functional groups do not have a true hydroxide form. In practice WBA types of resin retain weak acids such as carbonic acid or silica. Ionisation occurs under acidic condition as indicated in Equation 6.1 below:

$$RN(CH_3)_2 + H^+NO_3 \rightarrow RN^+H(CH_3)_2NO_3 \quad \text{.....Equation 6.1}$$

Under alkaline conditions, they exist as free bases and can adsorb acids in the same way that free ammonia reacts with nitric acid to form ammonium nitrate or free ammonia. The absence of H^+ ion to which the nucleophilic base can donate its electron to, and thus balance the anions, results in the WBA failing to adsorb strong acids and splitting the neutral salts, Equation 6.2 below indicates the phenomenon:

$$RN(CH_3)_2 + NaCl \rightarrow \text{no reaction} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{Equation 6.2}$$

This occurs because of the absence of H^+ ion.

WBA can be regenerated with both ammonia and sodium carbonate; Equation 6.3 and Equation 6.4 indicate the regeneration equations respectively:

$$RN(CH_3)_2.HNO_3 + NH_3 \rightarrow RN(CH_3)_2 + NH_4NO_3 \cdots\cdots\cdots\cdots \text{Equation 6.3}$$

$$RN(CH_3)_2.HCl + Na_2CO_3 \rightarrow RN(CH_3)_2 + NaCl + NaHCO_3 \cdots\cdots \text{Equation 6.4}$$

The resins are sensitive to hydrolysis in the form of the displacement by pure water of the anions (Degremont, 1991: 236). WBA are capable of removing contaminants such as sulphates, chlorides and nitrates ions, which are strong acids and do not remove contaminants such as silica and carbon dioxide. WBA resins have a greater capacity for mineral acids and higher regeneration efficiencies than SBA resins (Metcalf & Eddy Inc., 2003: 1182).

6.6 PROPERTIES OF ION EXCHANGE

Two major properties that are critical for ion exchange are physical and engineering properties.

6.6.1 Physical properties

They are important in selecting resins for specific water treatment applications. Physical properties of resins include: **particle size,** where particles must be large enough to minimise the column pressure drop while in operation, but small enough to enable fast mass transfer of the ions for ion exchange; **stability** – resins must be durable to undergo

swelling and shrinking during regeneration and loading. It is also an important process design consideration, under certain physical, chemical and radioactive conditions resins can be fouled thus leading to their poor performance and increased replacement costs (MWH, 2005:1477). **Swelling** is a critical design factor that must be considered in the design of the ion exchange column. It is related to the change in the volume of resins due to the differing magnitude of the resin-counter ion interactions (for example, the degree of resin cross-linking, and hydration). Swelling and shrinking of the resin bead may lead to internal osmotic pressure inside the bead which may result in the fracture of the resin bead (MWH, 2005:1379).

6.6.2 Engineering Properties

The two most significant engineering properties are exchange capacities and ion selectivity. These properties are mainly considered during column design and operation.

Exchange capacity enables the determination of the number of ionic constituents that may be retained by the resin for a given resin volume. It is important when selecting an ion exchange resin; one of the key things to consider is the quantity of counter-ions that can be exchanged onto the resin. The total capacity is dependent on the function of the functional group on a resin bead. The exchange capacity may be reported as equivalents per gram of dry resin (eq/g) or as equivalents per millilitre of wet resin eq/ml) (MWH, 2005: 1371).

Ion selectivity is defined as the preference or affinity for ions in an aqueous solution. It provides information as to which ionic constituents in the water are preferred by the resin. The forward or reverse of the ion exchange reaction depends on the resin selectivity for a particular ion system.

Physical properties such as degree of swelling or pressure within the resin bead do influence ion selectivity. Resin selectivity for ions increases with increasing atomic number. Ionic radius is increased while hydrated radius is decreased. Except for specialty resins, the preference of anions for WBA is the same as for SBA resins; the exception is that the hydroxide ion is the most preferred ion. The general rule for order of selectivity applies to ions in water with TDS values less than approximately 1000 mg/l. The preference for divalent ions over mono-valent ions diminishes as the ionic strength of the solution increases (MWH, 2005:1377).

6.7 ION EXCHANGE EQUILLIBRIUM DEVELOPMENT

Equilibrium expressions for ion exchange are reversible. The reversibility equilibrium is independent of the direction from which the equilibrium state is approached. The ratio of concentrations of various ions in the solution will be different from the concentration ratios in the resin phase equilibrium (MWH. 2005:1377).

Ion exchange equilibrium can be developed by treating ion exchange as a chemical reaction and applying the laws of mass action (as indicated in Equation 6.5) to obtain equilibrium description and developing the equilibrium description by using the principle of Donnan exclusion theory. Donnan's theory describes the behaviour of ions based on their unequal distribution across the membrane, especially when one electrolyte solution on the other side of the membrane contains ionic species that cannot diffuse through the membrane (MWH. 2005:1377).

By assuming that ion exchange is a simple stoichiometric reaction, the laws of mass action can be applied to obtain an equilibrium expression.

$$N\left[R^{\pm}\right]A^{\pm} + B^{\pm} = \left[nR^{\pm}\right]B + nA^{\pm} \quad \text{.....Equation 6.5}$$

$R^{\pm}$ - Ionic group attached to the ion exchange resin
A & B are exchanging ions.

In water treatment, ion exchange application involves a dilute solution where the ions behave independently from one another and are treated as ideal solutions (i.e. activity coefficient is assumed to be unified) (MWH. 2005:1377).

6.8 SEPARATION FACTORS

Equilibrium can be expressed in terms of equivalent fractions instead of concentration. The binary separation factor $\left(\alpha^{i}_{j}\right)$ is a measure of preference for one ion over another during ion exchange. It can be expressed as:

$$\alpha^{i}_{j} = \frac{Y_i X_i}{Y_j X_j} \quad \text{Equation 6.6}$$

X_j = equivalent fraction of presaturant ion in the aqueous phase
X_i = equivalent fraction of counterion in the aqueous phase
Y_j = resin-phase equivalent fraction of presaturant ion
Y_i = resin-phase equivalent fraction of counterions

The equivalent fraction in the aqueous phase is calculated from the following equations:

$$X_i = \frac{C_i}{C_T} \quad \text{Equation 6.7}$$

$$X_j = \frac{C_j}{C_T} \quad \text{Equation 6.8}$$

C_T = total aqueous ion concentration
C_i = aqueous-phase concentration of counterion, eq/L
C_j = aqueous-phase concentration of presaturant ion, eq/L

The equivalent fraction in the resin phase is expressed as:

$$Y_i = \frac{q_i}{q_T} \quad \text{Equation 6.9}$$

$$Y_j = \frac{q_i}{q_T} \quad \text{Equation 6.10}$$

q_T = total exchange capacity of resin, eq/L

For process design calculations, binary separation factors are primarily used in ion exchange calculations. The reason for this is that they are experimentally determined and that they account for the solution concentration and total ion exchange capacity.

In exceptional cases of mono-valent ion exchange with a mono-valent presaturant ion, the separation factor is constant and equal to the apparent equilibrium constant as indicated in Equation 6.13:

$$\propto^i_j = K_{ij} = \frac{q_i c_j}{c_i q_j} \quad \text{Equation 6.11}$$

The separation factor is not a constant; it is influenced by various factors, such as exchangeable ions (size and charge), properties of resins and water mixes. Properties of resins, includes particle size, degree of cross-linking, capacity and type of functional groups occupying the exchange sites. Due to the separation factor being influenced by various factors it can be determined by performing the equilibrium experiment (i.e. binary isotherm). Binary isotherm involves performing a batch equilibrium experiment for the binary system. Water mixes includes concentrations, type and quantities of organic compounds present in solution, reaction period and temperature. A separation factor with a value that is greater than 1 means that the ion ***(i)*** is preferred over ***(j)*** (MWH. 2005:1377).

6.9 ADSORPTION ISOTHERM

Adsorption is defined as the increase in the concentration of a particular component at the surface or interface between two phases. To determine the effectiveness with which a given adsorbent can treat wastewater, an adsorption test at constant temperature (isotherm) is conducted in the laboratory.

Isotherms are important in providing clarity on the best suitable candidate adsorbent that is efficient in terms of the amount of adsorbent required per amount of adsorbate removed as well as to provide the quality of effluent achievable (Woodard & Curran Inc., 2001: 378).

The quantity of the adsorbate (target pollutant) that can be taken up by the adsorbent (resin) is a function of both concentration of the adsorbate and the temperature. Important characteristics of the adsorbate include solubility, molecular structure, molecular weight, polarity and hydrocarbon saturation.

Adsorption isotherms are developed by exposing a given amount of the absorbate in a fixed volume of liquid to a varying amount of resins. A number of flasks or containers are used and 24 hours are allowed for the samples to equilibrate. The amount of absorbate remaining in the solution is measured at the end of the test (after 24 hours). The absorbent phase concentration data is computed using Equation 6.12 and used to develop adsorption isotherm.

$$q_e = \frac{(C_\circ \quad C_e)V}{m} \quad \text{Equation 6.12}$$

Where q_e = adsorbent (i.e., solid phase concentration after equilibrium, mg adsorbate/g adsorbent

C_0 = initial concentration of adsorbate, mg/L

C_e = Final equilibrium concentration of adsorbate after absorption has occurred, mg/L

V = volume of liquid in the flask or container, m

M = mass of adsorbent, g

Experimental isotherm data can be described by equations that were developed by the Freundlich and Langmuir isotherms. The Freundlich isotherm is most commonly used to describe the adsorption characteristics of the adsorbent in water or wastewater treatment. Freundlich model does not require any assumptions concerning the number of layers of adsorbed molecule, heat of adsorption or other conditions. It is a curve-fitting model and effectively used for industrial wastewaters. It is defined as follows:

$$\frac{x}{m} = K_f C_e^{1/n} \quad \text{Equation 6.13}$$

To determine the constants in the Freundlich isotherm, Equation 6.16 is used to plot log (x/m) versus log C.

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \quad \text{Equation 6.14}$$

A plot of q versus C_e on a log-log paper yields a straight line, the slope of which is the inverse of n, and the vertical intercept is the value of K_f. In practice the candidate adsorbent material (for example, different types of resins) are evaluated for effectiveness in treating a given industrial wastewater by constructing the Freundlich, Langmuir or BET isotherm after obtaining the appropriate laboratory data (Woodard & Curran Inc., 2001: 378).

Langmuir Isotherm

This is defined as:

$$\frac{x}{m} = \frac{abC_e}{1+bC_e} \quad \text{.....Equation 6.15}$$

$\frac{x}{m}$ = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g resin

a,b = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

It is a good generalised model for making estimates based on limited data. The Langmuir adsorption isotherm model is based on the assumption that: A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy and that adsorption is reversible.
Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of the molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is the driving force between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At equilibrium concentration the difference is zero (Woodard & Curran Inc., 2001: 378).

Constants in the Langmuir isotherm can be determined by plotting:

$\frac{C_e}{\frac{x}{m}}$ V/s C_e and using equation (6.16):

$$\frac{C_e}{\frac{x}{m}} = \frac{1}{ab} + \frac{1}{a}C_e \quad \text{.....Equation 6.16}$$

CHAPTER 7: ANALYSIS OF THE FINDINGS

In this chapter the results of different laboratory experiments, chemical analysis are compiled, analysed and interpreted in support of the preferred treatment technology. The aim of the section is to understand various constitutive elements of the collected data through an inspection of the relationship between concepts, variables and to identify trends that can establish themes in the data. By interpreting the data collected from the tests that were carried out, study seeks to relate the results and findings to existing theoretical framework. The data is analysed to show levels of support that the data provides for the preferred technology.

Wastewater chemical analysis

Wastewater samples were collected in line with the methodology described in Chapter 3 and sent to an accredited laboratory for chemical analysis. Table 7-1 below, indicates the chemical analysis results for the influent samples that were sent to the laboratory for analytical characterisation

Table 7-1 N_2O plant wastewater analysis report.

Lab No. / Sample I.D.		45/04 Effluent Tank 2	48/04 Effluent Tank 1
PHYSICAL ANALYSIS			
pH @ 20°C	pH units	7.9	1.2
Conductivity @ 25°C	uS/cm	34900	35800
T.D.S (By Calculation) @ 25°C	mg/l	24430	25060
CATIONS			
Total Hardness	mg/l $CaCO_3$	21	54
Calcium Hardness	mg/l $CaCO_3$	13	50
Magnesium Hardness	mg/l $CaCO_3$	8	4
Total Iron	mg/l Fe	0.3	0.5
Sodium	mg/l Na	700	900
Ammonium	NH_4	4592	4792
Potassium	mg/l K	70	69.0
ANIONS			
P-Alkalinity	mg/l $CaCO_3$	0	0
Total Alkalinity	mg/l $CaCO_3$	100	0
OH-Alkalinity	mg/l $CaCO_3$	0	0
Chlorides	mg/l Cl	710	0
Nitrate	mg/l NO_3	10090	10000
Phosphates	mg/l PO_4	100	500
Sulphates	mg/l SO_4	<0.1	<0.1
Silica	mg/l SiO_2	100	225.0

Interpretation of the analytical results for the N_2O plant effluent tanks

As indicated in the methodology chapter, Chapter 3, the wastewater stream of interest in which the treatment of the wastewater will be focused in are the two effluent storage tanks where the final wastewater was collected, effluent tank 1 (ET 1) and effluent tank 2 (ET 2).

Analytical results indicate that the elements of interest which characterises the effluent and will guide the proposed treatment of wastewater are, for Effluent Tank 1 (ET 1):

pH= 1,6; conductivity= 35,800 µS/m, $NO_3^- = 10{,}000 mg/l$ and $NH_4^+ = 4{,}792 mg/l$.

The solution was found to be very acidic as a result of the presence of nitric acid (HNO_3). The high conductivity indicated the high salt content of the wastewater solution, and the concentration of hydrogen ions (acidity). The high concentration of ammonium ions was as a result of the high strength of liquid ammonium nitrate used as the main raw material in the production of N_2O gas.

The anions present in the solution owed their existence to the acidic nature of the solutions. For example, sulphates were present in the solution due to the formation of sulphuric acid, similarly for phosphates in the form of phosphoric acid. At low pH, nitrates are present together with free acid and the amount of free base on the resin (for example, when pH = 1 and free base = 0) is minimum. At high pH, the amount of free base on the resin is very high.

Adsorption isotherm testing results

A standard laboratory procedure for determining the suitability of the selected resin to remove the target pollutant (nitrate ion) and the adsorption capacity of the selected resin was conducted as described in the methodology chapter, section 3.4.1). Table 7-2 below indicates the results of the adsorption isotherm shake flask test, the results were used to construct a plot Figure 7-1, indicating the relationship between the concentrations of the adsorbate in solution after equilibrium has been reached and the quantity of adsorbate adsorbed per unit mass of adsorbent. The plot indicates the maximum amount of nitrate that can be adsorbed. At equilibrium the amount of nitrates adsorbed increased with the amount of resin in the flask. Equilibrium was reached quickly when a small amount of resins was added into the solution in the flask. The plot had an as S-shape which indicated that the reaction of the anions during the shake flask test tend to follow Langmuir isotherm.

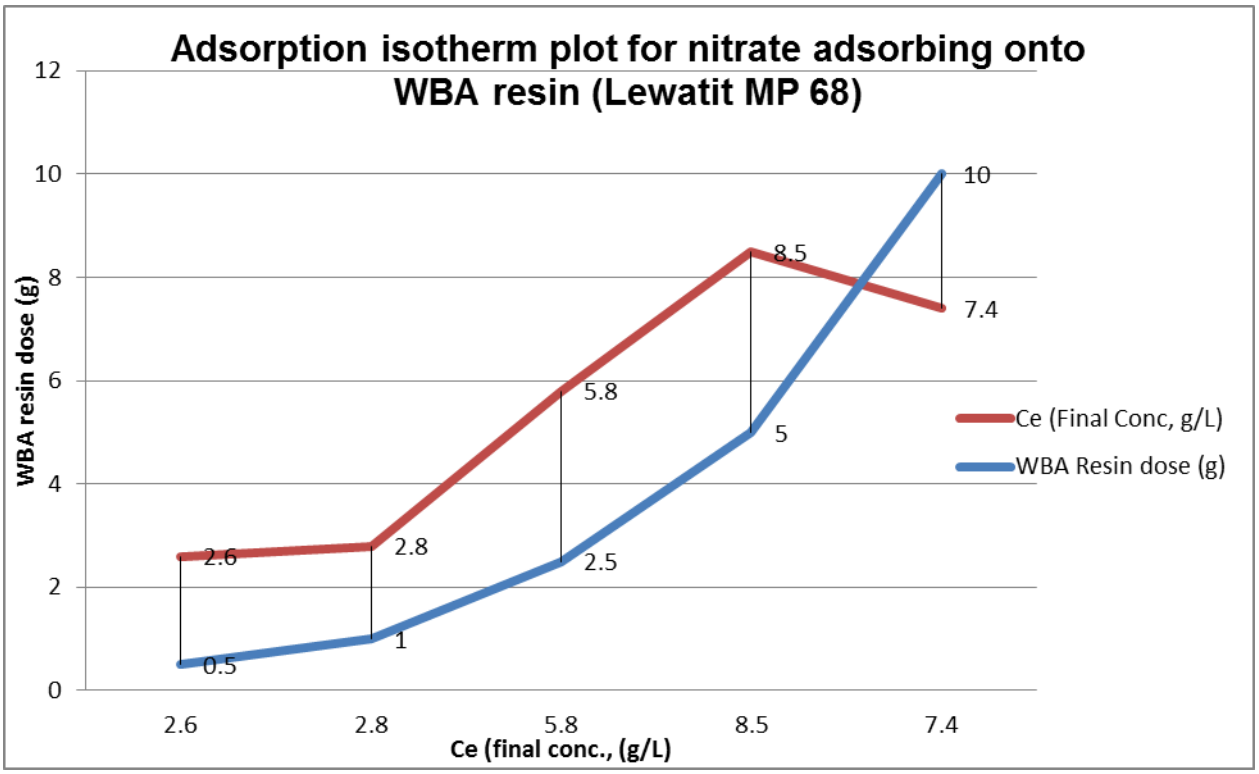

Figure 7-2 Adsorption isotherm plot for nitrate adsorbing onto WBA resin (Lewatit MP 68)

Table 7-2 Adsorption Isotherm laboratory testing results

	Initial $\left(NO_3^-\right)$ Conc. of untreated wastewater		Final $\left(NO_3^-\right)$ Conc.	Final Conductivity	Final pH
	C_0 (g/L)	Resin dose (g)	C_{NO_3} (g/L)	Conductivity (µS/cm)	pH
Flask 1	10	0.5	2.6	1888	2.31
Flask 2	10	1.0	2.8	1890	2.70
Flask 3	10	2.5	5.8	1890	3.48
Flask 4	10	5.0	8.5	1900	8.49
Flask 5	10	10	7.4	1894	5.32

Analysis of WBA adsorption data

The values required for plotting the Freundlich and Langmuir adsorption isotherms were determined by using the adsorption test data indicated below in Table 7-3. The absorbent phase concentration after equilibrium was determined by using Equation 6.16.

Table 7-3 Batch adsorption test data.

Adsorbate concentration (Nitrate) mg/l			**Mass of resin**	**Capacity of resin for component of interest**			
C_o (g/L)	C_e (g/L)	$C_o - C_e$ (g/L)	X (g)	C_a	q_e (g)	$\frac{C_e}{q_e}$	$Log\, q_e$ (g)
10	10	-	-		-	-	-
10	2.6	7.4	0.5	0.74	1.48	1,75	0.17
10	2.8	7.2	1.0	0.64	0.720	3.89	-0.14
10	5.8	4.2	2.5	0.42	0.168	34.52	-0.77
10	8.5	1.5	5.0	0.15	0.03	283	-1.52
10	7.4	2.6	10	0.26	0.026	284	-1.58

The Freundlich isotherm coefficients can be determined by plotting a curve of Log (x/m) versus Log C_e as indicated in Figure 7-2. The resulting curve indicates the feasibility of the selected WBA resin (MP 68) to perform the desired nitrate ions removal under the testing conditions. The capacity of the resin is exhausted after removing about 8,5 g/L of the target pollutant (nitrate ions), after which the dumping process starts, resulting in the increased concentration of nitrate ions in the wastewater that is being treated.

Maximum adsorbate that can be adsorbed onto the surface can be determined by using the slope and intercept of the Langmuir isotherm plot (see Figure 7-2), this indicated the adsorption capacity of the selected WBA resin (Lewatit MP 68) compared to the theoretical capacity of the WBA resin as supplied by the manufacturer.

The curvilinear nature of the graph makes the use of Langmuir adsorption isotherm inappropriate. The values of correlation coefficient (R^2) listed in Figure 7-2 indicate that nitrate retention is not well represented by Langmuir isotherm model since $R^2<1$ (i.e. $R^2 = 0.806$). This means that the resin surface is not made of homogeneous retention patches.

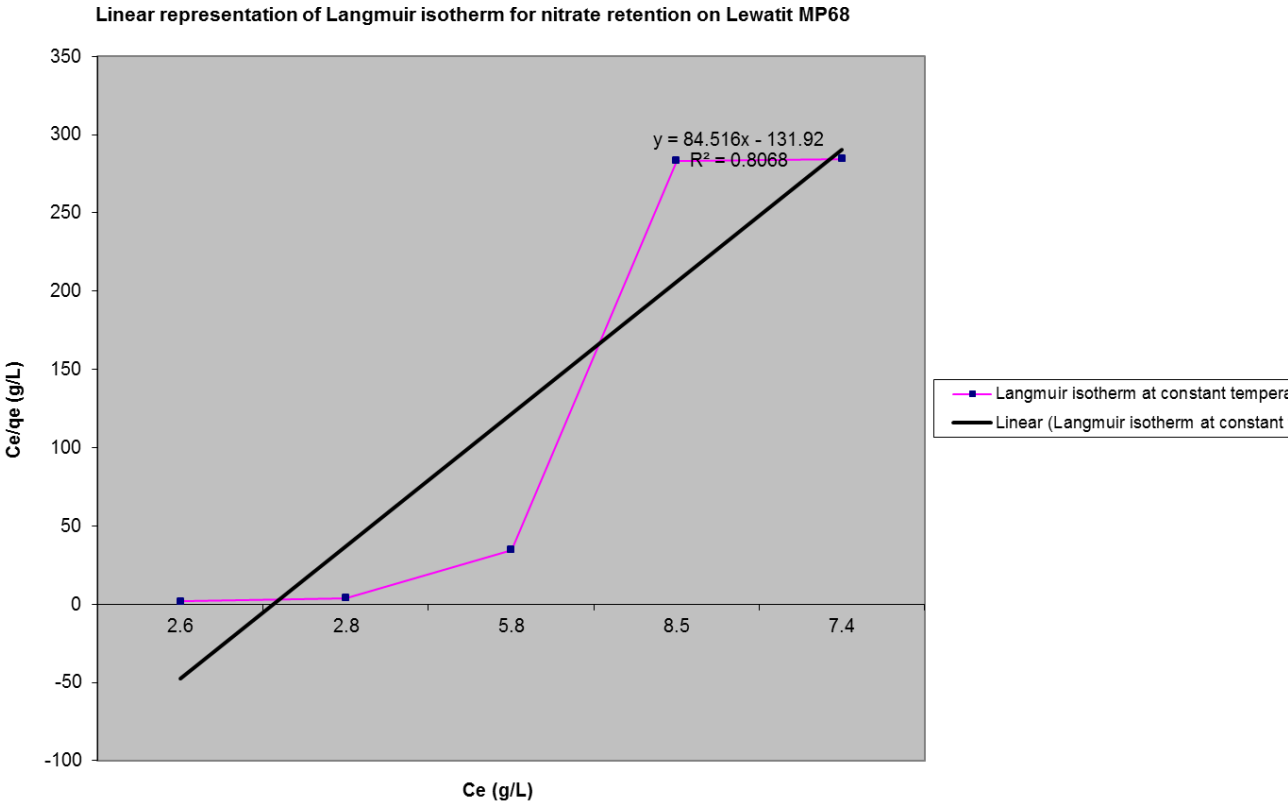

Figure 7-3 Linear presentation of Langmuir isotherm for nitrate retention on Lewatit MP 68 resin.

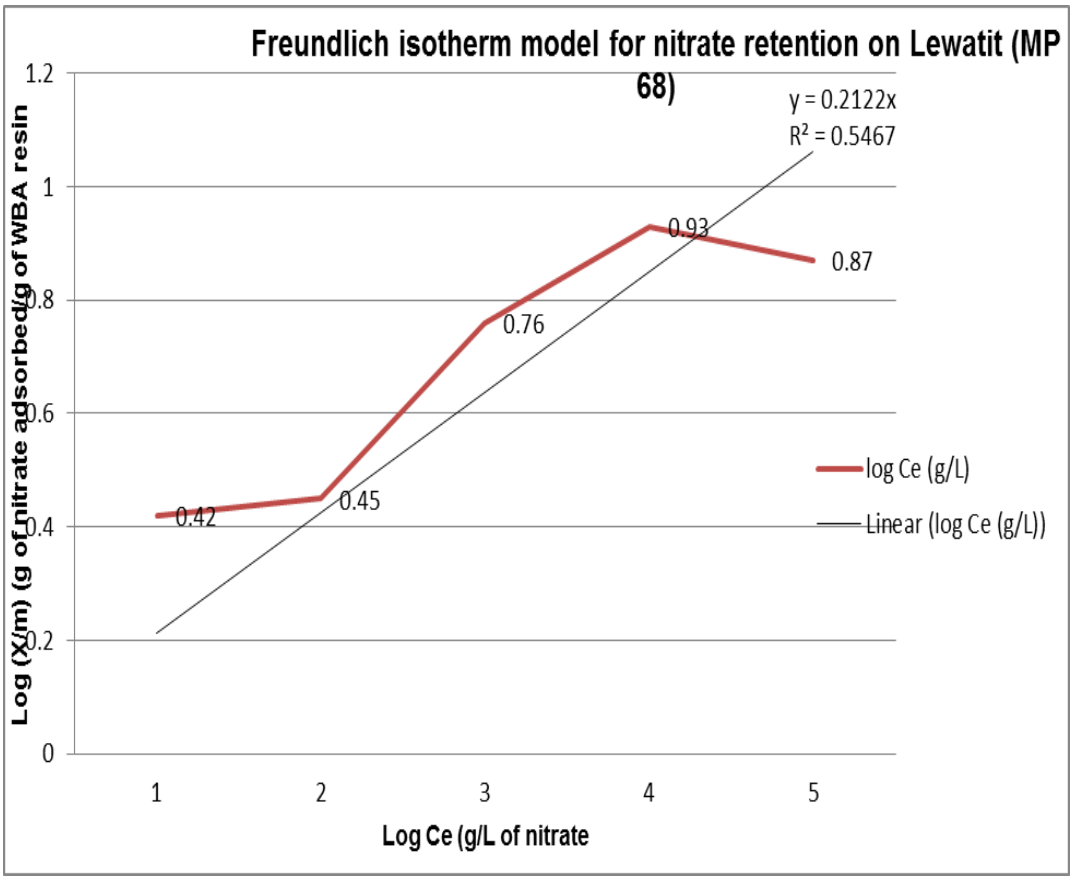

Figure 7-4 Freundlich isotherm model for nitrate retention on Lewatit MP 68

$$\text{Log}\frac{x}{m} = \log K_f + \frac{1}{n}\log C_e \quad \text{.....Equation 7.1}$$

$$y = c + mx$$

$$0.85 = 0.55 + \frac{1}{n}(0.45)$$

$$\frac{1}{n} = 0.67$$

$$n = 1.48$$

$$q_e = K_f \times C_e^{\frac{1}{n}} \quad \text{.....Equation 7.2}$$

$$1.48 = K_f \times (2.6)^{0.67}$$

$$K_f = \frac{1.48}{1.89}$$

$$K_f = 0.87$$

Freundlich constant (n) which estimate the retention intensity of nitrate ions on the resins surface is greater than 1 (n>1), this indicates favourable ion exchange process despite the high nitrate concentration.

The above mentioned isotherm graphs are of high importance when a number of different resins are tested for their capability to treat wastewater, however in this study only one type of resin was available and the manufacturer's information was provided for theoretical adsorption capacity and the operating capacity was determined by conducting a bench-scale column test.

Table 7-4 Ion exchange bench-top testing results.

Initial					After			
	Nitrate		Ammonium		Nitrate		Ammonium	
Bed volume (BV, ml)	C_o g/l	Initial pH	C_o g/l	Initial Conductivity (µS/m)	C_e g/l	pH	C_e mg/l	Conductivity (µS/m)
1BV	10	1.67	2.43	1895	1.50	9.11	0.559	1901
2BV	10	1.67	2.43	1895	4.85	9.31	10.437	1900
3BV	10	1.67	2.43	1895	5.60	8.87	13.307	1921
4BV	10	1.67	2.43	1895	11.40	8.71	18.958	1905
5BV	10	1.67	2.43	1895	10.60	8.92	19.37	1954

Nitrate breakthrough curve

The nitrate ion breakthrough curve below in Figure 7-4 indicated that the WBA resins used in the column test were exhausted after 3 Bed Volumes (3BV). The entire capacity of the resin was used up and resulted in a nitrate dumping effect at about 4BV (the nitrate ions were released back into solution). Nitrate dumping resulted in the increased concentration of the nitrate ion, and was also caused by the presence of phosphate $\left(PO_4^{3-}\right)$ ions which displaced the nitrates in solution.

The amount of treated water recovered was lower than expected; this meant that a large volume of resins would have to be used to treat small quantities of water thus increasing the operational costs.

The early breakthrough of nitrate had some implication on the capability of the Lewatit MP 68 WBA resin to produce enough treated water for reuse in the plant. Based on results of the bench scale column test, the water mass balance can also be used to determine whether the desired benefits of the selected treatment technology were realised (i.e. to production of sufficient treated (clean) water for reuse in the N_2O production plant).

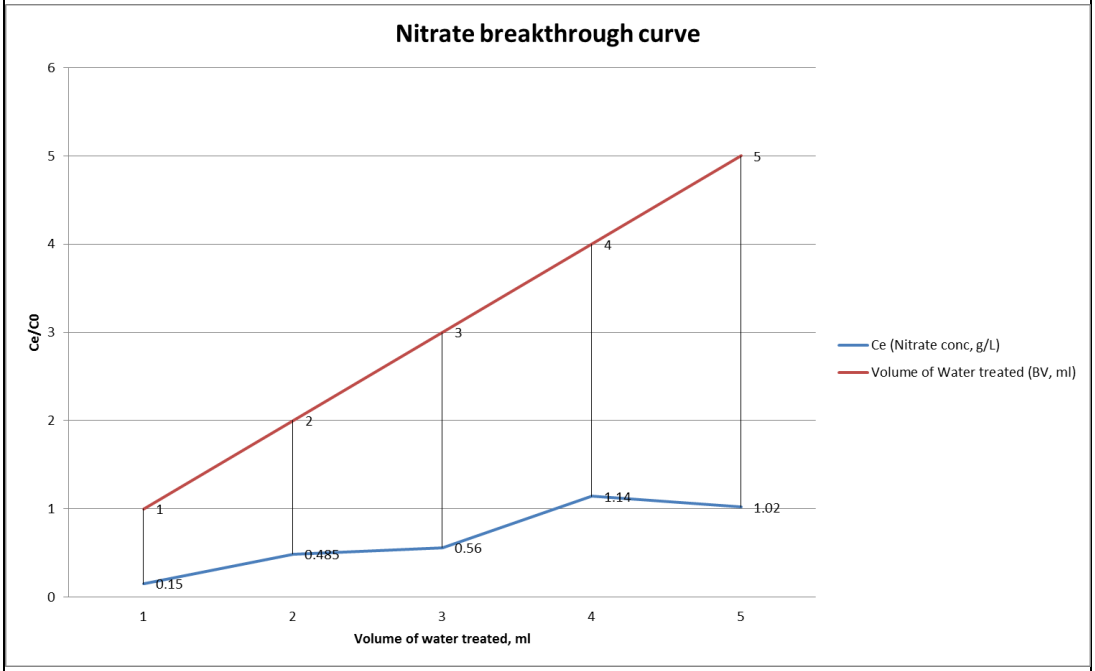

Figure 7-5 Ion exchange nitrate breakthrough curve.

Water mass balance

A water mass balance was conducted, the results of the water mass balance indicated that the high concentration of nitrate ions in the wastewater negatively impacted the effectiveness of resins in treating the wastewater. As a result the production of clean water was very low in volume. The amount of water produced was sufficient for use in the preparation of the regeneration reagent (regenerants) and for water rinse (3BV recovered and 3BV used for regeneration and water rinse), as demonstrated in Figure 7-5 below. .

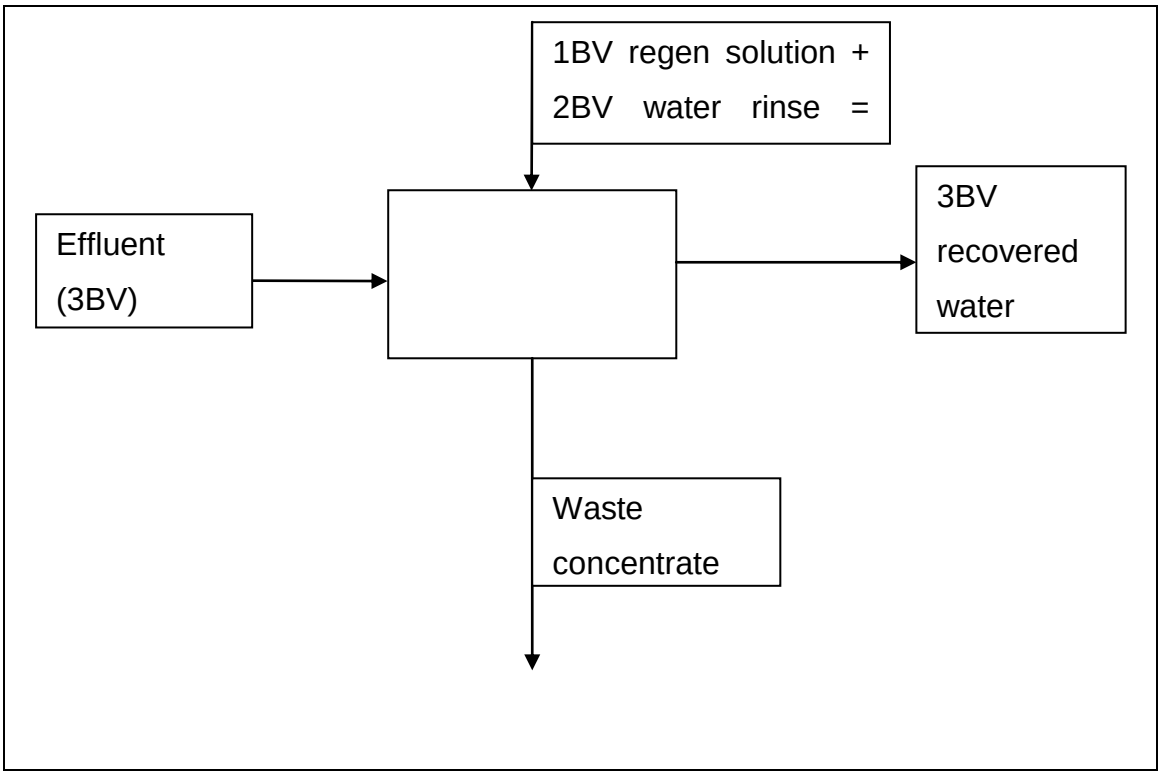

Figure 7-6 Ion exchange water balance using LEWATIT MP 68 resin.

Cation exchange breakthrough curves

The breakthrough curve for depicted in Figure 7-6 below, indicates that SAC resin (Lewatit S108) reached equilibrium with the influent water after 3BV before reaching its exhaustion state during removal of the ammonia.

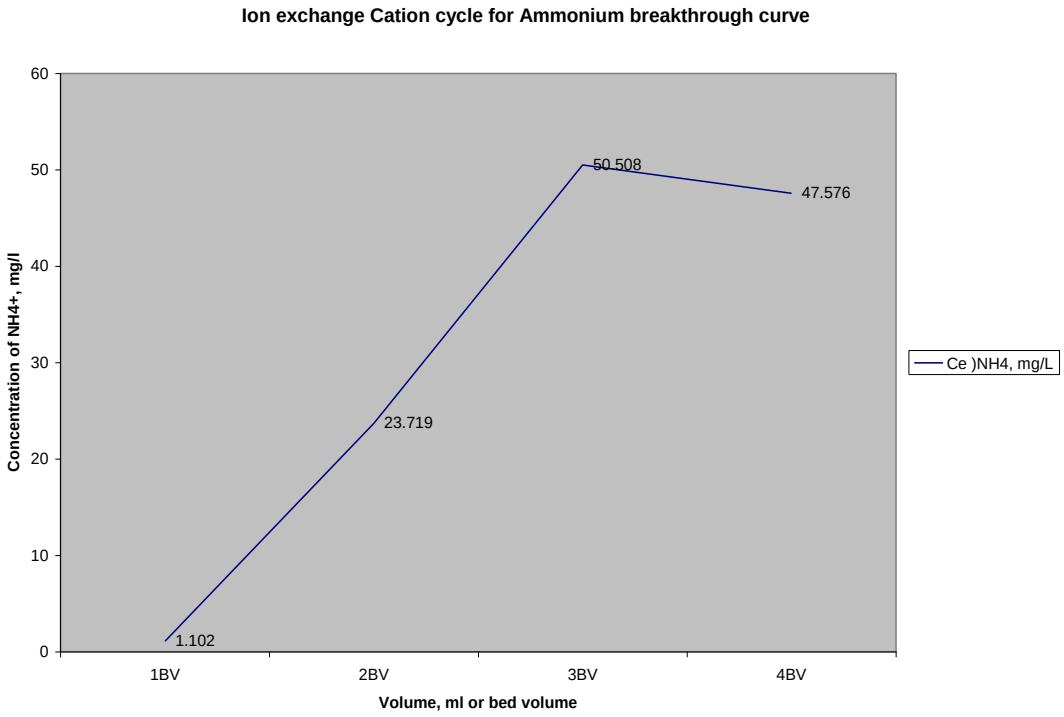

Figure 7-7 Cation exchange breakthrough curves.

Conversion of analytical results from mg/L to meq/L

Table 7.7 and Table 7.6 indicate the conversion of the concentration units from mg/L to meq/L. These are the correct units for working with ion exchange concentrations.

Table 7-5 Conversions of analytical results of Effluent Tank 2 (ET 2) from mg/l to meq/L.

Cation	Conc. (mg/l)	MW (g/mol)	Meq/L	Anion	Conc. (mg/l)	MW (g/mol)	Meq/L
Ca^{2+}	13	(40.08/2)=20.04	0.65	HCO_3^-	100	61.02	1.64
Mg^{2+}	8	(24.4/2)=12.5	0.64	SO_4^{2-}	0.1	48.03	0.002
Na^+	700	23	30.34	Cl^-	710	35.45	20.03
K^+	70	39.1	1.79	NO_3^-	10000	62.01	161.3
NH_4^+	4592	18.01	255	SiO_2	100	60	1.66
				PO_4^{3-}	100	31.6	3.16
			A_{nion}= 288				Σ_{cation}= 187

Table 7-6 Conversions of analytical results of Effluent Tank 2 (ET 1) from mg/l to meq/L.

Cation	Conc. (mg/l)	MW (g/mol)	Meq/L	Anion	Conc. (mg/l)	MW (g/mol)	Meq/L
Ca^{2+}	50	40.08	1.24	NO_3^-	10090	62.00	163
K^+	69	39.10	1.77	NO_2^-	0.1	46.01	0.002
Na^+	680	22.99	29.56	Cl-	760	35.45	21.4
Mg^{2+}	4	24.31	0.32	SO_4^{2-}	0.1	96.06	1.04
NH_4^+	4792	18.04	266	HCO_3^-	100	61.02	1.66
				PO_4^{3-}	500	31.6	3.16
Total			A_{nion}= 298				Σ_{cation}= 190

To remove the anion pollutants from the wastewater, an anionic resin with a standard exchange capacity of 1.3 eq/L and a density of 0.7 kg/L was used.

The selectivity coefficient and separation factor for various anions are listed in Table 7-7. Selectivity coefficient indicates the different preferences for ions in water that characterises the resin and can be used to describe ion exchange equilibrium. At equilibrium ions do not occupy the same amount of resin; the resin preferred ions with a higher valence. The relationship for selectivity of the resin for different ions in water can be written as follows:

$$SO_4^{2-} > Cl^- > NO_3^-$$

Separation factor indicates the preference of ion exchanger for one of the two counter-ions and it is practically used to calculate the performance of the column (Helfferich, 1995:153).

Table 7-7 Selectivity coefficient and separation factor for strong base anionic resin (example, Lewatit MP68) (Metcalf & Eddy Inc., 2003: 1187).

Anion	Selectivity Factor $K^{i}_{Cl^-}$	Separation factors $\alpha^{i}_{Cl^-}$
Cl –	1.0	1.0
SO_4^{2-}	0.15	9.1
NO_3^-	4.0	3.2

K^{i}_{cl} selectivity coefficient for anion i exchanging with $Cl-$ onto the resin

α^{i}_{Cl} separationfactor for anionic exchanging with Cl onto the resin

The different separation factors for an ion with respect to the other were determined by using Equation 7.2:

$$\alpha^{i}_{k} = \alpha^{i}_{j}.\alpha^{j}_{k} \quad \text{.....Equation 7.2}$$

α^{i}_{k} separationfactor for counterioni withrespectto ion

α^{i}_{j} separationfactor for counterioni withrespectto ion j

α^{j}_{k} separationfactor for ion j withrespectto ionk

Separation factor for NO^{-}_{3} with respect to both SO^{2-}_{4} and Cl^{-} were determined by using Equation 7.2:

$$\alpha^{SO^{2-}_{4}}_{Cl^{-}} = \alpha^{SO^{2-}_{4}}_{NO^{-}_{3}} \times \alpha^{NO^{-}_{3}}_{Cl^{-}}$$

$$\alpha^{Cl-}_{NO^{-}_{3}} = \frac{\alpha^{Cl-}_{Cl^{-}}}{\alpha^{NO^{-}_{3}}_{Cl^{-}}}$$

$$= \frac{1}{3.2}$$

$$= 0.3$$

$$\alpha^{NO_3^-}_{NO_3^-} = \frac{\alpha^{NO_3^-}_{Cl-}}{\alpha^{NO_3^-}_{Cl-}}$$

$$= \frac{3.2}{3.2}$$

$$= 1$$

$$= 1$$

$$\alpha^{SO_4^{2-}}_{NO_3^-} = \frac{\alpha^{SO_4^{2-}}_{Cl^-}}{\alpha^{NO_3^-}_{Cl-}}$$

$$= \frac{9.1}{3.2}$$

$$= 2.8$$

Separation factor for SO_4^{2-} with respect to both NO_3^- and Cl^- were also determined by using Equation 7.2 as the following:

$$\alpha^{Cl-}_{SO_4^{2-}} = \frac{\alpha^{Cl-}_{Cl-}}{\alpha^{NO_3^-}_{Cl-}}$$

$$= \frac{1}{9.1}$$

$$= 0.1$$

$$\alpha^{NO_3^-}_{SO_4^{2-}} = \frac{\alpha^{NO_3^-}_{Cl^-}}{\alpha^{NO_3^-}_{Cl^-}}$$

$$= \frac{3.2}{9.1}$$

$$= 0.4$$

$$\alpha^{SO_4^{2-}}_{SO_4^{2-}} = \frac{\alpha^{SO_4^{2-}}_{Cl}}{\alpha^{SO_4^{2-}}_{Cl^-}}$$

$$= \frac{9.1}{9.1}$$

$$= 1.0$$

The equilibrium capacity of the resin for was determined by using the separation factors calculated above:

$$q_{Cl^-} = \frac{EC \times \left[Cl^-\right]}{\alpha^{Cl^-}_{Cl^-} \times \left[Cl\right] + \alpha^{SO_4^{2-}}_{Cl^-} \times \left[SO_4^{2-}\right] + \alpha^{NO_3^-}_{Cl^-} \left[NO_3^-\right]}$$

$$= \frac{1.3 \times 20.3}{1 \times 20.3 + 9.1 \times 0.002 + 3.2 \times 161.3}$$

$$= 0.77\,eq/L$$

$$q_{SO_4^{2-}} = \frac{EC \times [SO_4^{2-}]}{\alpha^{Cl^-}_{SO_4^{2-}} \times [Cl^-] + \alpha^{SO_4^{2-}}_{SO_4^{2-}} \times [SO_4^{2-}] + \alpha^{NO_3^-}_{SO_4^{2-}} [NO_3^-]}$$

$$= \frac{1.3 \times 0.002}{0.1 \times 20.3 + 1.0 \times 0.002 + .35 \times 161.3}$$

$$= 0.00005 \text{ eq/L}$$

$$q_{NO_3^-} = \frac{EC \times [SO_4^{2-}]}{\alpha^{Cl^-}_{NO_3^-} \times [Cl^-] + \alpha^{SO_4^{2-}}_{NO_3^-} \times [SO_4^{2-}] + \alpha^{NO_3^-}_{NO_3^-} [NO_3^-]}$$

$$= \frac{1.3 \times 161.3}{0.32 \times 20.3 + 2.8 \times 0.002 + 1 \times 161.3}$$

$$= 0.003 \text{eq/L}$$

The sum of the equilibrium capacities of the resins for different anions determined above can be used as a control to confirm if they are equal to the theoretical total exchange capacity of the resin which was equivalent to 1.3 eq/L.

$$q_{eqIm} = q_{Cl^-} + q_{SO_4^{2-}} + q_{NO_3^-}$$

$$= (0.77 + 00005 + 0.0038) \text{eq/L}$$

$$= 0.77 \text{eq/L} \equiv 0.8 \text{eq/L}$$

Therefore, from the calculation above, it was determined that the sum of the equilibrium capacities occupied by the different ions were less than the total exchange capacity of the resin.

The maximum volume of water that can be treated per litre of resin before breakthrough occurs:

$$V_{max(Cl^-)} = \frac{q_{Cl-}}{[Cl-]\times 10^{-3}}$$

$$= \frac{0.05}{20.3\times 10^{-3}}$$

$$= 2.46\,L_{water}/L_{resin}$$

$$V_{max(SO_4^{2-})} = \frac{q_{SO_4^{2-}}}{[SO_4^{2-}]\times 10^{-3}}$$

$$= \frac{0.00005}{0.0002\times 10^{-3}}$$

$$= 2.5\,L_{water}/L_{resin}$$

$$V_{max(NO_3^-)} = \frac{q_{NO_3^-}}{[NO_3^-]\times 10^{-3}}$$

$$= \frac{161.3}{161.3\times 10^{-3}}$$

$$= 1000\,L\ water/L\ resin$$

The maximum volume (V_{max}) calculated above indicated that saturation for chloride ion occurred after treating 2.46 L of wastewater and that 1000 L of wastewater per litre of resin can be treated before breakthrough for nitrate ions occurred.

The percentile repartition of the occupied sites in the resin was determined as follows:

$$\%q_{Cl-} = \frac{q_{Cl-}}{q_{equi}} \times 100$$

$$= \frac{0.05}{1.4} \times 100$$

$$= 3.57\%$$

$$\%q_{SO_4^{2-}} = \frac{q_{SO_4^{2-}}}{q_{equi}} \times 100$$

$$= \frac{0.00005}{1.4} \times 100$$

$$= 0.0036\%$$

$$\%q_{NO_3^-} = \frac{q_{NO_3^-}}{q_{equi}} \times 100$$

$$= \frac{1.34}{1.4} \times 100$$

$$= 95.7\%$$

The percentile distribution for the different concentrations of ions in the N_2O plant wastewater was determined as:

$$\%[Cl-] = \frac{[Cl-]}{[C_{total\,ions}]} \times 100$$

$$= \frac{20.03}{181.3} \times 100$$

$$= 11.05\%$$

$$\%\left[SO_4^{2-}\right] = \frac{\left[SO_4^{2-}\right]}{\left[C_{total\,ions}\right]} \times 100$$

$$= \frac{0.002}{181.3} \times 100$$

$$= 0.0011\%$$

$$\%\left[NO_3^-\right] = \frac{\left[NO_3^-\right]}{\left[C_{total\,ions}\right]} \times 100$$

$$= \frac{161.3}{181.3} \times 100$$

$$= 88.97\%$$

By determining the percentile repartition of the occupied sites in the resin it was found that the percentile distribution for concentration was not the same as the percentile distribution for the occupied sites in the resin at equilibrium. This was caused by the selectiveness of the resin for certain ions. The results of the above calculations were summarised in Table 7-8.

Table 7-8 Comparative table of the percentile distribution for concentration and percentile distribution for the occupied sites in the resin at equilibrium.

Anion	% [Concentration]	% q_{equi}
Cl^-	11.05	3.57
SO_4^{2-}	0.0011	0.0036
NO_3^-	88.97	95.7

CHAPTER 8: PRELIMINARY DESIGN AND ECONOMIC BENEFIT ANALYSIS

8.1 PRELIMINARY DESIGN

In designing an ion exchange system for nitrate removal, wastewater quality analysis and bench-scale testing of the preferred technology were conducted. The design parameters were determined from the bench-scale testing; this included the determination of the type of resin, resin capacity, bed dimensions, and regenerant requirements or quantities.

The following basic data must be known: design flow-rate through the exchanger, influent water quality, total anions, and operating conditions for the resin selected (normally provided by resin manufacturers). Water quality analysis should include nitrate, sulphates, chlorides, bicarbonates, calcium carbonates, iron, total suspended solids and total organic carbon.

The resin requirements for WBA were estimated using Effluent Tank 2 (ET 2) analysis results:

Flow rate for the plant = 4.3 $m^3/d \equiv 0.179\ m^3/h$

Type of resins that were used in the columns bench-scale test were LEWATIT MP 68 weak base anions (WBA) and the LEWATIT S108 strong acidic cation (SAC) resins (see Appendix G & H for their technical specifications).

The stoichiometric equation for the WBA resins can be written as:

$$\left[R^{+}\right]OH \ + NO_3^- \leftrightarrow \left[R^{+}\right]NO_3^- \ + OH^- \quad \text{.....Equation8.1}$$

Therefore, the selectivity expression for the above equation can be written as:

$$K_{Cl-}^{NO_3^-} = \frac{q_{NO_3^-} \times C_{Cl-}}{C_{NO_3^-} \times q_{Cl-}} \quad \text{.....Equation8.2}$$

The total theoretical resin capacity of the LEWATIT MP 68 weak base anion (WBA resin) was listed as being equal to 1.3 eq/L in the manufacturer's material specification data sheet (see Appendix G). The following theoretical separation factors to be used in determination of the operating capacity of the Lewatit MP 68 resin was taken from Table 7-7

$$\alpha_{Cl-}^{NO_3^-} = 3.2$$

Determining the maximum volume of water that may be processed per litre of WBA resin with an exchange capacity of 1.3 eq/L (using WBA LEWATIT MP 68)

NO_3^- and SO_4^{2-} levels were required to calculate the operating capacity of the nitrates removal unit. These parameters were converted to their milli-equivalent per litre. Typically, sulphate was expressed as SO_4^{2-} in water analysis. Sulphates were also converted to their milli-equivalent per litre. The conversion calculation was done by dividing the element's ionic weight by its ionic charge as indicated in both Table 7-5 and Table 7-6.

The selectivity coefficient of the following anions was assumed to be:

Nitrates (NO_3^-) = 4.0; HCO_3^- = 0.4; Cl^- = 1.0

$$K_{HCO_3^- \rightarrow NO_3^-} = \frac{4.0}{0.4}$$

$$= 10$$

$$K_{Cl- \rightarrow NO_3^-} = \frac{4.0}{1.0}$$

$$= 4$$

$$K_{[HCO_3^- (Cl^-) \rightarrow NO_3^-]} = 7.0 \text{ (estimated)}$$

For equilibrium conditions $C_e/C_o = 1.0$

The nitrate equivalent fraction in solution was as follows:

X_{NO3}^- = 161.3/220 = 0.733

$$X_{NO_3^-} = \frac{161.3}{220}$$

$$= 0.733$$

$$\frac{X_{B^+}}{1 - X_{B^+}} = \left[K_{A^+ \rightarrow B}\right]\left[\frac{X_{B^+}}{1 - X_{B^+}}\right]$$

$$\frac{X_{NO_3^-}}{1 - X_{NO_3^-}} = [7.0]\left[\frac{0.733}{1 - 0.73}\right]$$

$$= 7.0\left[\frac{0.73}{0.0907}\right]$$

$$X_{NO_3^-} = 69.69\left[1 - X_{NO_3^-}\right]$$

$$X_{NO_3^-} = \frac{69.69}{70.69}$$

$$X_{NO_3^-} = 0.98$$

Therefore, 98% of the exchange site in the resin can be used for the removal of the nitrate NO_3^- ions.

Determining the limiting operating capacity of the resin for removal of nitrates $\left(NO_3^-\right)$.

$$\text{Limiting capacity} = \frac{\text{operating capacity of the resin}}{\text{number of sites available for adsorption}}$$

$$= \frac{1.3\ \text{eq/L}}{0.98}$$

$$= 1.32\ \text{eq/L of resin}$$

Volume of treatable water during a service cycle

$$V = \frac{NO_3^-\ \text{removal capacity of resin, eq/L of resin}}{NO_3^-\ \text{in solution, eq/L water}}$$

$$= \frac{1.32\ \text{eq/L of resin}}{161.3E^{3}}$$

$$= 3.14\ \text{L of water/ L of resin}$$

The low volume of effluent treated during a service cycle can be attributed to the high concentration of nitrate ions in the effluent tank (approximately = 10 000 mg/l).

Ion exchange column design

$$\text{Plant effluent flowrate} = 4300\ \text{L/day} \equiv 4.3\ \text{m}^3/\text{d} \equiv 179\ \text{l/hour}$$

Determining the volume of resin required

Assume a typical Service Flow Rate (SFR) ≈ 1 BV/h (3 hr loading cycle time) and 1 hour regeneration time

$$\text{Total volume of resin required} = \frac{Q_{\text{flow rate}}}{SFR}$$
$$= \frac{179\,L/h}{1}$$
$$= 179L$$

Therefore, 179L of resins per column were required for each column.

Determining the depth of the column

$$\begin{aligned} B &= \text{Area} \times \text{Depth} \\ &= \pi r^2 \times \text{Depth} \\ 1 &= \pi r^2 \times (1) \\ r^2 &= 0.32 \\ r &= \sqrt{0.32} \\ r &= 0.56m \end{aligned}$$

H: D = 2 m; Bed Volume = 1 BV/h; assume that bed depth (height) ≈ 1 m

B = Area x depth

$$\begin{aligned} B &= \text{Area}\,(A) \times \text{Depth}\,(d) \\ &= \Pi(d^2) \times (H) \\ 1 &= \frac{1}{4}\Pi(d^2) \times (1) \\ d &= 0.44\,m \end{aligned}$$

Number of columns

If the area of one column is divided into the total required area, the required number of columns = 1

A 0.44 m column diameter is chosen for the design.

Total equivalent per day to be removed:

$$= Q_{\text{flowrate per hour}} \times \text{Operating Capacity of a resin}$$

$$= 179\,\text{L/d} \times 1.3\,\text{eq/L}$$

$$= 232.7\,\text{eq/cycle}$$

$$= \frac{C_{NO_3^-} \times Q}{1000}$$

$$= \frac{161.3\,\text{eq/L} \times 4300\,\ell\text{/day}}{1000}$$

$$= 693\,\text{eq/day}$$

Determining the number of regeneration cycles per day:

$$= \frac{\text{eq/day}}{\text{eq/cycle}}$$

$$= \frac{693\,\text{eq/day}}{232.7\,\text{eq/cycle}}$$

$$= 4.84\,\text{cycle/day}$$

Total NO_3^- removed per day

$$= \frac{C_{NO_3^-} \times 1000}{Q}$$

$$= \frac{161.3\,\text{eq/L} \times 1000}{4300\,\ell\text{/day}}$$

$$= 37.51\text{eq/day}$$

Determining the amount resin requirements per cycle per day:

Exchange capacity of resin = 1.3 eq/L and the operating capacity is 1.3

Ion exchange capacity is pH dependent (it increases with the pH). The experimentally determined capacity may include inner-spherically bound cations (Stumm & Morgan, 1996:587).

$$\text{resin requirements} = \frac{\text{Total } C_{NO_3^-} \times \text{Regenerations cycles}}{\text{Operating capacity of the resin}}$$

$$= \frac{37.51\text{eq/day} \times 4.84\text{ days/cycles}}{1.3\text{ eq/L}}$$

$$= 140\text{ L of resin/cycle per day}$$

Select a column diameter of 0.44m and calculate the required depth of resin bed.

$$\text{Cross section} = \pi r^2 = 0.16$$
$$= \pi(0.05) = 0.16$$
$$= \frac{0.16}{\pi}$$
$$r^2 = 0.05\text{m}$$
$$r = \sqrt{0.05}$$
$$r = 0.22\text{m}^2$$

The required depth of the resin bed is = 2 m.

Column Size

$$\text{Column size} = Q_{\text{hourly flowrate}} + \left(Q_{\text{flowrate}} \text{ x } 50\%\right)$$

$$= 179\,\text{L/day} + (179\,\text{L/day} \times 50\%)$$

$$= 179\,\text{L/day} + 89.5\,\text{L/day}$$

$$= 269\,\text{L}$$

The size of the column was determined to be 269 L and this included 50% free board space to make allowance for bed expansion of the resin or swelling of the resin and back-washing of the resins.

It was also determined that a set of cations and anions columns in parallel are required for use in the proposed wastewater treatment plant. Each column would be 2m in height. The rationale behind using two columns in parallel was to enable the continuous use of the system during the regeneration of one of the columns.

Determining the amount of the required regenerant solution

The exhausted resins for the cation and anion columns were regenerated by using 10% solution of HNO_3 resin and 7% solution of NH_3 respectively. The amount of regeneration solution required for regenerating the exhausted resins were obtained from the product information sheet (see Appendix O). The laboratory trial guide recommended 1BV of 10% HNO_3 solution for regenerating the cation resins and 1BV of 7% NH_3 solution for regenerating the anion resins.

The amount regenerant required per day was determined as follows:

Determining the cation regenerant:

$$\begin{aligned}&\text{Amount of cation regenerant require}\\&= Q_{\text{hourly flowrate}} \times \text{Mass fraction of } HNO_3 \times \text{regeneration cycle/day}\\&= (179\,\text{L/hour} \times 0.1) \times 6.2\,\text{cycles/day}\\&= 111\,\text{L/cycle}\end{aligned}$$

Anion regenerant:

$$\text{Amount of anion regenerant require} = Q_{\text{hourly flow rate}} \times \text{Mass fraction of } NH_3 \times \text{regeneration cycle/day}$$

$$= (179\,\text{L/hour} \times 0.07) \times 6.2\,\text{cycles/day}$$

$$= 78\,\text{L/cycle}$$

The nitrate ions loaded column can be regenerated fully by using a 7% NH_3 solution.

Total amount of chemicals used in the regeneration of resins

The total quantity of HNO_3 and NH_3 required on an annual basis was calculated by multiplying the number of regenerations in a year with the quantity of regeneration solution required per regeneration. The number of regenerations was calculated by dividing the number of hours in a year by the loading cycle time per column.

SAC resin regenerations using HNO_3:

$$\text{loading cycle time per column} = Q_{\text{flow rate per hour}} \times \frac{\text{strength of cation regenerant}}{\text{number of regeneration}}$$

$$= 179\,\text{l/hr} \times \frac{10\%}{3}$$

$$= 5.96 \equiv 6\,\text{cycles per column}$$

$$\text{Number of regenerations per year (anion regeneration)} = \frac{\text{number of hours in a year}}{\text{Loading cycle time per column}}$$

$$= \frac{365 \times 24}{6}$$

$$= 1460 \quad \text{regenerations per year}$$

WBA (LEWATIT MP 68) resins regenerations using NH_3:

Loading cycle time of Anion regeneration:

$$\text{loading cycle time per column} = Q_{\text{flowrate per hour}} \times \frac{\text{strength of anion regenerant}}{\text{number of regeneration}}$$

$$= 179\,\text{l/hr} \times \frac{7\%}{3}$$

$$= 4.18 \equiv 4 \text{ cycles per column}$$

Loading cycle time of cation regeneration:

$$\text{loading cycle time per column} = Q_{\text{flowrate per hour}} \times \frac{\text{strength of Cation regenerant}}{\text{number of regeneration}}$$

$$= 179\,\text{l/hr} \times \frac{10\%}{3}$$

$$= 5.96 \equiv 6 \text{ cycles per column}$$

Number of regenerations per year (anion regenerations)

$$= \frac{\text{Number of hours in a year}}{\text{loading cycle time per year}}$$

$$= \frac{365(24)}{4}$$

$$= 2190$$

Number of regenerations for each column per year

$$= 365\ \text{d/yr} \times 78\ \text{l/d}$$

$$= 28470\ \text{L/year}$$

Determining the amount of rinse water required after regeneration:

From the manufacturer specifications and material safety data sheet, 2 BV rinse water were required for slow rinse.

$$\text{Rinse volume per column}$$

$$= \frac{1\text{m resin}}{\text{BV}} \times (2\,\text{BV})$$

$$= 2\,\text{BV/ column}$$

Regeneration cycle time

The cycle time for the regeneration was calculated by multiplying the empty bed contact time (EBCT) by the number of bed volumes of generation's solution per column. The EBCT is first calculated by dividing the resin depth in the column by the superficial velocity as shown:

$$\text{EBCT} = \frac{\text{Column height}}{1\text{BV/hour}}$$

$$= \frac{1\text{m}}{1\,\text{BV/hour}}$$

$$= 1\text{hour}$$

$$\text{Regeneration time per column} = \text{EBCT} \times \frac{\text{Bed Volume}(BV)}{\text{Regeneration frequency}}$$

$$= 60\,\text{min} \times \frac{3BV}{1}$$

$$= 180\,\text{minutes}$$

Total of 3 BV = 1 acid regeneration, 2 water rinse

$$180\,\text{min} = 3\,\text{hours}$$

$$1\,\text{year} = 365 \text{ x } 24$$

$$\text{Total regeneration possible} = \frac{365 \times 24}{3}$$

$$= 2920$$

Typical backwash times ranges from 5 – 20 minutes, therefore a backwash time of 10 minutes will be used, backwash was done only when required (not per cycle), it was measured as change in pressure (ΔP) across the bed), this is normally indicated by the controls e.g. water gauge.

Therefore, the total time that a column would be out of service for the regeneration was estimated to be 20 minutes. In the cases where the effluent was found to be turbid, pre-filtration step was required to prevent clogging and fouling of resins.

Volume of rinse water required

At slow rinse, rinse water requirements ≈ 2B ≈ 0.935 m^3/m^3

At slow rinse, rinse water requirements $\sim 2B \equiv 0.935 m^3/m^3$

$=$ Rinse water $\times$ Resin requirement

$= 0.935 m^3/m^3 \times 0.279 m^3$

$= 0.260 m^3$

The design of the wastewater treatment plant indicated by Figure 8-1 was based on practical consideration, in practice it takes approximately 4 hours to load the resin and complete a single regeneration cycle. The resin can be loaded over 3 hour period with an additional hour required for regeneration of the resin.

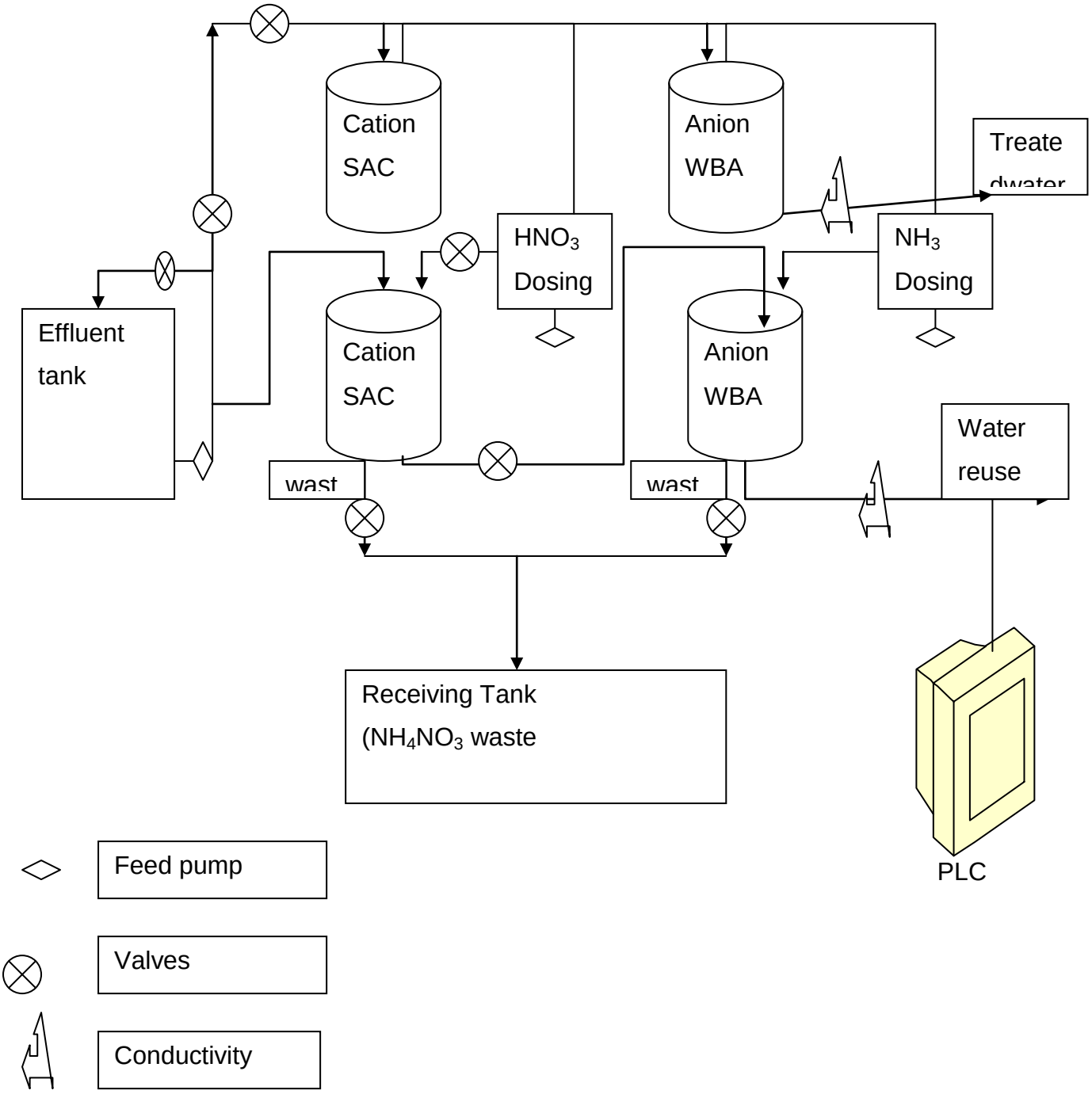

Figure 8-1 Typical diagram for the removal of cations and anions using ion exchange resins.

8.2 ECONOMIC BENEFIT ANALYSIS

This section uses the plant sizing and operating parameters data that was determined in the previous section above to demonstrate the financial feasibility of the proposed in-house wastewater treatment plant. A cost-benefit analysis and sustainability benefits of the preferred in-house wastewater treatment method over the existing practice of outsourcing wastewater removal and disposal was also conducted. Industry standard quotes were obtained from various equipment suppliers and the potential costs of the required equipment were summarised in Figure 8-1~~Figure 8-1~~. The obtained data was also used to determine the cost of the proposed in-house wastewater treatment plant.

Table 8-1 Ion exchange wastewater treatment plant equipment costs and quantities

Equipment	Quantity	Cost (ZAR)	Total (ZAR) (Exclude VAT)
Feed Pumps	3	21 667	65 000
Valves	7	642.85	4 500
Programmable Logic Control (PLC)	1	100 000	100 000.00
Columns (rubber-lined stainless steel)	4	1 972.00	7 888
Receiving Tank (20 m^3) (plastic)	1	70 000	70 000
Dosing system	3	15 000	45 000
Water Flow meter	1	4 000	4 000
Construction costs		220 000	220 000
Orion star A215 pH/Conductivity meter, BT, Kit (online pH and conductivity meter combination)	2	18 510.00	37 020.00
Total (ZAR)			490 408

Table 8-2 Running costs for the proposed wastewater treatment plant

	Frequency	Quantity	Unit price (ZAR)	Total costs (ZAR) (excl. VAT)
HNO_3	annually	24309	3.22 ZAR /kg	78 275
NH_3	annually	7972	2.88 ZAR /kg	22 959
Labour	monthly	1	5 500	66 000
Analyser	6 monthly	2	3 000	6 000
Anion exchange resins (Lewatit MP 68)		2x 179Lx7	55	68 915
Cation exchange resins (S108)		2x 179Lx7	25	31 325
Energy (electricity)	Annual costs			4 898.83
Flow meter (calibrations 6 monthly)	6 monthly	2	2 500	5 000
Preventative maintenance on valves, pump, electrical equipment, mechanical equipment	monthly	monthly	4 000	48 000
Total (ZAR)				331 373

The cost of resins per column were determined by multiplying the amount of resins in a column by the cost per litre of the resins and the design factor for the vessel (in practice the size of the vessel has to be seven times the amount of resins required to factor in the effects of swelling (i.e. the volume of resins change due to the differing magnitude of the resin-counter ion interactions)) see Equation 8.3 and Equation 8.4 below.

Anion resin costs:

$$= (\text{Total volume of resin required per column} \times \text{Costs of resins per liter}) \times \text{design factor for the column} \quad \text{Equation 8.3}$$

$$= (\text{Total volume of resin required per column} \times \text{Cost of resins per liter}) \times \text{design factor for the column}$$

$$= (179\,\text{L/hours} \times \text{ZAR } 55) \times 7$$

$$= \text{ZAR } 68915$$

Cation resin costs:

$$= (\text{Total volume of resin required per column} \times \text{Cost of resins per liter}) \times \text{design factor for the column} \quad \text{Equation 8.4}$$

$$= (179\,\text{L/hours} \times \text{ZAR } 25) \times 7$$
$$= \text{ZAR } 31325$$

To determine the economic benefits of the proposed project, the present values (PV) of the proposed in-house N_2O production plant wastewater treatment were determined first and compared to present value (PV) of the existing practice of using a contractor to dispose of the effluent (see Appendix E).

Total cost of discharging wastewater using a contractor = ZAR 1,872,000

Initial Investment Costs = ZAR 490,408

Operating Costs = ZAR 331,373 per annum

Cost of money (*r*) = 10%

T = 20 years

Inflation rate (g) = 6.5%

$$PV = \frac{C}{r-g}\left(1 - \frac{(1+g)^T}{(1+r)^T}\right) \quad \text{.....Equation 8.3}$$

(Grinblatt & Titman, 2002: 320)

PV = Present value

c = cash flow = 331373

r = investment interest rate (cost of capital) = 10%

g = inflation rate = 6.5%

T = number of years = 20

Determining PV for the wastewater treatment option:

Present value

c = cash flow = 490,908

r = investment interest rate (cost of capital) = 10%

g = inflation rate = 6.5%

T = number of years = 20

$$\text{Present Value} = \frac{-404{,}933}{0.1-0.065}\left(1 - \frac{(1+0.065)^{20}}{(1+0.1)^{20}}\right)$$

$$= \text{ZAR } -5{,}137{,}210$$

Net Present Value

$$= PV_0 + PV(\text{proposed project})$$

$$= (490408) + (5{,}137{,}210)$$

$$= (5{,}627.618)$$

Determining PV for the current used method wastewater disposal method using a contractor:

PV = Present value

c = cost (annual costs of effluent disposal) = 1,872,000.00

r = investment interest rate (cost of capital) = 10%

g = inflation rate = 6.5%

T = number of years = 20

$$\text{Present Value} = \frac{-1,872,000.00}{0.1 - 0.065}\left(1 - \frac{(1+0.065)^{20}}{(1+0.1)^{20}}\right)$$

$$= \frac{1,872,000.00}{0.035}\left(1 - \frac{(1.065)^{20}}{(1.1)^{20}}\right)$$

$$= 54385714.0\left(1 - \frac{3.524}{6.627}\right)$$

$$= 54385714.00\ (0.532)$$

$$= \text{ZAR}\ -27,354,078$$

To determine the savings accruing from the proposed wastewater treatment plant project:

$$\text{Saving} = NPV_{\text{new project}} - NPV_{\text{old project}}$$

$$= (-5,627,618) - (-27,354,078)$$

$$= 21,726,397.00$$

By installing a wastewater treatment plant, AFROX GOC stand to make a saving of ZAR 21,726,397.00 over twenty years of the expected life span of the wastewater treatment plant compared to the option of continuing with the practice of outsourcing wastewater removal and disposal.

Payback Period

$$\text{Payback period} = PV_{\text{new project}} - PV_{\text{old project}}$$

$$= (-368,120) - (-1,701,818)$$

$$= 1,333,698$$

Therefore, the payback period for the project is 1 year.

Further areas of savings

Further financial savings could be achieved by re-using the treated (clean) water in the N_2O production process, this has a potential of greater saving in the consumption of potable water that is supplied from the municipality.

From the bench scale column testing results above, 3 BV out of 5 BV of wastewater were treated before breakthrough was reached or resins were exhausted. At 4300 L/day of wastewater generated and treated, this was equivalent to 60% water recovery and the remaining 40% was concentrated ammonium nitrate waste.

A 60% water recovery meant is equivalent to 2570 L/day of treated water recovered from the wastewater treatment process.

The Ekurhuleni Metropolitan Municipality currently charges water users in the scale of AFROX GOC an approximate amount of ZAR 11.69 per kilolitre (kL) of water used.

$$\text{Water savings will thus be} = \frac{2580}{1000\,\text{L/d}} \times (11.69\,\text{ZAR/kL})$$

$$= 30\,\text{ZAR/day}$$

$$\text{Total water savings per year} = (30\,\text{ZAR/day} \times 30\,\text{days} \times 12\,\text{months})$$

$$= \text{ZAR } 10858 \text{ per annum}$$

Waste trading benefits

A 40% concentrated ammonium nitrate waste was generated a result of regeneration of the saturated resins, this is equivalent to 1720 L/day of ammonium nitrate waste). AFROX GOC can potentially obtain an additional income (estimated ZAR 40/ton) by trading on ammonium nitrate waste with other organisations that require the waste as an input to their production processes.

Possible additional income as a result of waste trading

$$= \left(\frac{1720\text{l/day}}{100}\right) \times \text{ZAR } 40$$

$$= \text{ZAR } 688 \text{ per day}$$

$$\text{Total waste trading income per year} = (\text{ZAR } 688/\text{day} \times 30 \text{ days x } 12)$$

$$= \text{ZAR } 247{,}860$$

CHAPTER 9: CONCLUSION AND RECOMMENDATION

9.1 CONCLUSION

The study indicates that ion exchange does provide benefits as the best technological approach in treating N_2O production plant wastewater despite the limited capacity of the mono-amine-based WBA resins that was used. Based on the outcome of the bench-scale tests, WBA resins with a single amine functional group were found to be limited in treating the high strength N_2O production plant wastewater. Due to the high concentration of nitrates in the wastewater, the anions occupied all the available sites on the WBA resin thus exhausting the resins capacity within 3 BV of effluent treated. As a result small amounts of water were produced, most of which can be used to prepare regeneration chemicals, thus leaving no water for reuse in the N_2O production plant processes.

It is thus concluded that more test must be conducted using specialised type of ion exchange resins (Lewatit A356) which has a high exchange capacity and excellent regeneration efficiency due to their polyamine weak base functional group. The resins have high total exchange capacity of 3.2 eq/L and will thus have an operating capacity of approximately 1.9 eq/L which is three times the capacity of the LEWATIT MP 68 used in the study (the resin can process 9BV of the treated wastewater).

Alternatively a technology that involves a combination of neutralisation and evaporation needs to be considered in order to achieve the effective treatment of N_2O production plant wastewater. The process has the ability to produce fertiliser that is neutral in pH and high quality distilled water. The other feasible technology is hybrid technology or freezing technology as it is commonly known. This technology also offers an opportunity of a closed loop by freezing and concentrating the pollutant and producing clean water that can be reused in the plant processes.

The cost benefit analysis for the proposed in-house treatment method far outweighs the existing practice of outsourcing wastewater disposal. The payback period for the proposed project is 1 year.

9.2 RECOMMENDATIONS

To enable effective treatment of the N_2O production plant wastewater, it is recommended that the permanganate caustic scrubber be drained into separate containers. This will result in reduction of the chemical load and also eliminate pH variation of the effluent.

Ion exchange regeneration process produces ammonium nitrate which can be used in various industries like the fertiliser industry, explosives industry and LAN manufacturing industry. It is recommended that AFROX GOC management investigates the opportunity of trading the waste to reap the full benefits of the waste generated by the proposed ion exchange treatment plant.

AFROX GOC must consider installing a water meter at the N_2O production plant to enable it to quantify the amount of potable water consumed during the N_2O production process. Currently only wastewater generated as a result of the production process can be quantified and does not reflect the amount of water lost through evaporation in the plant.

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APPENDIX A: COMPREHENSIVE N_2O PLANT WASTEWATER ANALYSIS REPORT

Lab No. Sample I.D.		44/04 Sump Effluent	45/04 Effluent Tank 2	46/04 Washing Tower 1	47/04 Washing Tower 4	48/04 Effluent Tank 1	49/04 After cooler	50/04 Washing Tower 2	51/04 Washing Tower 3
PHYSICAL ANALYSIS									
pH @ 20°C	pH units	1.0	7.9	1.6	10.4	1.2	1.0	14.2	14.3
Temperature	°C								
Conductivity @ 25°C	uS/cm	40500	34900	10310	248	35800	39300	635000	733000
T.D.S (By Calculation) @ 25°C	mg/l	28350	24430	7217	173.6	25060	27510	444500	513100
Suspended Solids	mg/l								
CATIONS									
Total Hardness	mg/l $CaCO_3$	36	21	112	44	54	0	41	0
Calcium Hardness	mg/l $CaCO_3$	4	13	16	20	50	0	0	0
Magnesium Hardness	mg/l $CaCO_3$	32	8	52	24	4	0	41	0
Total Iron	mg/l Fe	0.8	0.3	0.4	0.2	0.5	0.5	10.00	10.00
Sodium	mg/l Na	1000	700	10	90	900	10	150000	150000

Ammonium	NH_4	'1.25	4592	1058	'0.58	4792	'0.27	774	593
Potassium	mg/l K	10	70	6.0	15.0	69.0	6.0	3000.0	2600.0
ANIONS									
P-Alkalinity	mg/l $CaCO_3$	0	0	0	16	0	0	114800	119200
Total Alkalinity	mg/l $CaCO_3$	0	100	0	52	0	0	118800	123600
OH-Alkalinity	mg/l $CaCO_3$	0	0	0	12	0	0	52000	40000
Chlorides	mg/l Cl	248	710	71	18	760	3905	0	0
Nitrate	mg/l NO_3	21472	10090	3124	4.8	10000	18480	7040	<0.1
Phosphates	mg/l PO_4	0.3	100	0.3	0.1	116	0.2	2300.0	1800.0
Sulphates	mg/l SO_4	<0.1	<0.1	10	12	<0.1	<0.1		
Silica	mg/l SiO_2	0.4	100	9.0	14.0	115.0	<0.1	24800	12000

APPENDIX B: ION EXCHANGE CATION REMOVAL ANALYSIS RESULTS

Sample (2^{nd} cycle)	Manganese as Mn (mg/l)	Calcium as Ca (mg/l)	Potassium as K (mg/l)	Sodium as Na (mg/l)
Effluent Tank	4.8	1	140	1110
First Cycle Column Cation removal testing				
Cation Sample 1st 50ml (1BV)	0.12	0.75	13	105
Cation Sample 2nd 50ml (2BV)	0.19	4.1	43	160
Cation Sample rd 50ml (3BV)	0.26	<1	24	125
Cation Sample 4th 50ml (4BV)	0.29	<1	33	285
Cation Sample 5th 50ml (5BV)	0.36	6.3	11	667
Second Cycle Column Cation removal testing				
Cation Sample 1st 50ml (1BV)	<1	<1	32	125
Cation Sample 2nd 50ml (2BV)	0.6	<1	32	180
Cation Sample 3rd 50ml (3BV)	0.5	<1	30	120
Cation Sample 4th 50ml (4BV)	0.7	<1	39	350
Cation Sample 5th 50ml (5BV)	1.3	<1	97	780
Third cycle of Column Cation removal testing				

Acid Regeneration	2.7	<1	51	370
Cation Sample 1st 50ml (1BV)	0.6	<1	22	98
Cation Sample 2nd 50ml (2BV)	3.7	<1	37	230
Cation Sample 3rd 50ml (3BV)	4	<1	61	310
Cation Sample 4th 50ml (4BV)	4.6	<1	82	640
Cation Sample 5th 50ml (5BV)	5.2	<1	91	740
Water rinse cycle				
Cation water wash 1st 50ml (1BV)	1.3	<1	110	98
Cation water wash 2nd 50ml (2BV)	0.52	<1	37	230
Cation water wash 3rd 50ml (3BV)	0.44	<1	0.4	5.1
Cation Exchange 3rd 50ml (3BV)	0.42	<1	8.1	10020
Cation Regenerate solution	1	<1	350	1990
NH4+ Regenerant Solution	0.39	<1	13	1870

APPENDIX C: EQUIPMENT POWER SUPPLY DATA

POWER CALCULATIONS				
	LOAD LIST			
PRIMARY	POWER SUPPLY DATA			MOTOR DATA
EQUIPMENT #	VOLTAGE	PHASE	FREQ	INSTALLED
				POWER
				P
	V		Hz	kW
Pump Motor	380	3	50	2.2
Pump Motor	380	3	50	2.2
PLC	380	3	50	4
Conductivity Meter	220	1	50	0.5
PH Meter	220	1	50	0.5
Flow Meter	3	1	50	0.5
Instruments	220	1	50	0.5
Instruments	220	1	50	0.5
				10.9

APPENDIX D: ESTIMATED ELECTRICITY CONSUMPTION COSTS

For 24 Hours Operation , 7 days a week and for 352 days		
Estimated Electricity Consumption Costs for the Period		
Total KW	Energy Charge (c/kWh)	
	Peak	Off-peak
10.9	0.894	0.537
	432192.50	57690.12
Total Consumption (ZAR)		R4 898.83

APPENDIX E: ALTERNATIVE METHOD TO DETERMINE THE ECONOMIC BENEFITS OF THE PROJECT.

Wastewater treatment option

	Constants	Yr 0	Yr 1	Yr 2	Yr 3	Yr 4	Yr 5	Yr 6	Yr 7	Yr 8	Yr 9	Yr 10	Yr 11	
Interest Rate	0.1													
Inflation	0.065													
NPV Calculation														
CAPEX		-490,408	-	-	-	-	-	-	-	-	-	-		
operating cost			-331,373	-352,912	-375,851	-400,282	-426,300	-454,009	483,520	514,949	548,420	584,068	622,032	
Depreciation			-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	
Interest			-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	
Total			-404,933	-426,472	-	473,842	-499,860	-	-	588,509	-	-	-695592	

					449411,			527,569	557,080		621,980	657,628	
Discount Factor			1.10	1.21	1.33	1.46	1.61	1.77	1.95	2.14	2.36	2.59	2.85
			1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
Present Value		-490,408	-368,120	-352,456	-337,903	-324,549	-310,472	-298,061	-285,682	-275,004	-263,550	-253,910	-244,067
NPV			-5,627,618										

Yr 12	Yr 13	Yr 14	Yr 15	Yr 16	Yr 17	Yr 18	Yr 19	Yr 20
-	-	-	-	-	-	-	-	-
-662,465	-705,525	-751,384	-800,224	-852,238	-907,634	-966,630	-1,029,461	-1,096,376
-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520	-24,520
-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040	-49,040
-736025	-779,085	824,944	873,784	-925,798	-981,194	-1,040,190	-1,103,021	-1,169,936
3.14	3.45	3.80	4.18	4.59	5.05	5.56	6.12	6.73

12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00
-234,402	-225,821	-217,090	-209,039	-201,698	-194,295	-187,084	-180,232	173,838

NPV Calculation for the existing method of wastewater disposal

	Constants	Yr 0	Yr 1	Yr 2	Yr 3	Yr 4	Yr 5	Yr 6	Yr 7	Yr 8	Yr 9	Yr 10	Yr 11
Interest Rate	0.1												
Inflation	0.065												
NPV Calculation													
operating cost		-1,872,000	-1,872,000	1,993,680	-2,123,269	-2,261,281.70	-2,408,265	-2,564,802	-2,731,514	-2,909,062	-3,098,151	-3,299,531	-3,514,001
Depreciation		-	-	-	-	-	-	-	-	-	-	-	-
Interest		-	-	-	-	-	-	-	-	-	-	-	-
Total		-	-	-	-	-	-	-	-	-	-	-	-

		1,872,000	1,872,000	1,993,680	2,123,269	2,261,281.70	2,408,265	2,564,802	2,731,514	2,909,062	3,098,151	3,299,531	3,514,001
Discount Factor		1	1.10	1.21	1.33	1.46	1.61	1.77	1.95	2.14	2.36	2.59	2.85
		0	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
Present Value		-1,872,000	-1,701,818	-1,647,669	-1,596,443	-1,548,823	-1,495,817	-1,449,041	-1,400,776	-1,359,375	-1,312,776	-1,273,950	-1,232,983
NPV			-27,354,078										

Yr 12	Yr 13	Yr 14	Yr 15	Yr 16	Yr 17	Yr 18	Yr 19	Yr 20	
-3,742,411	-3,985,668	-4,244,736	-4,520,644	-4,814,486	-5,127,427	-5,460,710	-5,815,657	-6,193,674	
-	-		-	-	-	-	-	-	
-	-	-	-	-	-	-	-	-	

-3,742,411	-3,985,668	-4,244,736	-4,520,644	-4,814,486	-5,127,427	-5,460,710	-5,815,657	-6,193,674	
3.14	3.45	3.80	4.18	4.59	5.05	5.56	6.12	6.73	
12.00	13.00	14.00	15.00	16.00	17.00	18.00	19.00	20.00	
-1,191,851	-1,155,266	-1,117,036	-1,081,494	1,048,908	-1,101,332	-982,141	-950,270	-920,308	

APPENDIX F: MATERIAL SAFETY DATA SHEET FOR THE SAC TYPE OF RESINS (LEWATIT MONOPLUS S108).

Lewatet
Monoplus S108.pc

APPENDIX G: PRODUCT INFORMATION - LEWATIT MONOPLUS S108.

Lewatit-MonoPlus-S-108-H-L.pdf

APPENDIX H: PRODUCT INFORMATION - LEWATIT MONOPLUS 68.

Lewatit-MP-68-L.pdf

APPENDIX I: MATERIAL SAFETY DATA SHEET FOR THE WBA TYPE OF RESINS (LEWATIT MP 68).

MP 68.pdf

APPENDIX J: QUOTATIONS FOR INSTRUMENTS TO BE USED IN THE WASTEWATER TREATMENT PLANT


B.P.doc

APPENDIX K: QUOTATIONS FOR WASTEWATER ANALYSIS AND MONITORING INSTRUMENTS (CONDUCTIVITY BENCHTOP METERS)

S-STARA215-E-1
011-RevB_WEB.pc

APPENDIX L: QUOTATIONS FOR WASTEWATER ANALYSIS AND MONITORING INSTRUMENTS (CONDUCTIVITY PORTABLE METER)

S-STARA325-E-1
011-RevB_WEB.pc

APPENDIX M: MERCK SQ-118 PHOTOMETER - OPERATING MANUAL ANALYSIS METHOD 14542: DETERMINATION OF NITRATES

mERCK sq-118
PHOTOMETER NITRAT

APPENDIX N: MERCK SQ-118 PHOTOMETER - OPERATING MANUAL ANALYSIS METHOD 14559: DETERMINATION OF AMMONIUM

Merck SQ 118
photometer Ammoniu

APPENDIX O: INSTRUCTION FOR LABORATORY TRIAL WITH LEWATIT SELECTIVE ION EXCHANGE RESIN