

# Strategies for Treatment of Mine Impacted Waters with High Ammonia-N Feed Levels using Membrane Systems

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## Abstract

RO membranes are an attractive treatment technology for mine impacted water due to the range of pollutants which they can remove with modest energy requirement. There is lack of data on Ammonia-N removal, which is typically present in appreciable quantities and is toxic toward aquatic life. This paper reports on Ammonia-N rejection data obtained for membranes on a mine water feed. The sea water membrane obtained 27% lower Ammonia-N passage compared to brackish water membranes, but with higher energy requirement. Regressed design parameters were fed into a solution-diffusion model to describe performance of an 8-inch membrane plant. An opex study considered different plant designs treating various Ammonia-N loads, with 0.8 mg/L discharge limit. Brackish water membranes could treat a maximum feed of 7.5 mg/L. From 7.5 – 15 mg/L brackish water membranes with permeate recycle would be most cost effective. From 15 mg/L sea water membranes with permeate recycle is required and could treat up to 22.5 mg/L feed. Permeate recycle is sensitive to power costs and less effective when rejection deteriorates. Future work should consider manipulation of feed pH for better rejection and non-membrane technologies for better risk management.

**Keywords:** Mine impacted water, RO membranes, Ammonia-N, permeate recycle, capex cost, operational cost, polishing, risk management

## Introduction

Extraction of minerals in mining operations requires an explosive typically containing ammonium nitrate. Incomplete reaction allows residual ammonium nitrate to be mobilized in drainages from the site (Hallin et al. 2015; Häyrynen et al. 2009). Unionized ammonia is toxic to fish, with a mean acute toxicity level of 2.79 mg/L Ammonia-N and 1.86 mg/L Ammonia-N for freshwater and saltwater species being reported, respectively (USEPA 1985; USEPA 1989). Mining companies typically deploy membrane systems to treat affected waters due to the broad range of contaminants that can be separated (Aguiar et al. 2016). This enables the water balance over the tailings storage facility (TSF) and waste rock dumps to be managed and to satisfy permitting requirements of environmental authorities. Rejection ratios are used to quantify the extent of separation of solutes from water for different types of membranes with the parameter formally being defined as  $(1 - \frac{C_{permeate}}{C_{feed}}) \times 100\%$ . Rejection data, together with water permeability,

are the two most important parameters which dictate membrane selection during the process design phase. Ammonia-N RO membrane rejection data for feed streams emanating from mine dewatering operations are scarce. Van Voorthuizen et al. (2005) reported Ammonia-N rejections of 80-90% when treating domestic waste water with low energy brackish water RO membranes. Such technology would not be appropriate when treating mine impacted water of Ammonia-N levels > 10 mg/L and a discharge of 1 mg/L or less has been imposed.

This paper reports on ammonia-N rejection data generated for 4-inch high rejection brackish and low energy seawater RO membranes on a synthetic neutral pit lake feed matrix. Membranes considered in this study included the Toray TML10D (brackish), Hydranautics CPA7-LD-4040 (brackish) and Suez AE90 (low energy sea water). Testing enabled computation of membrane-specific ammonia-N permeability coefficients (B-values), pure water permeability coefficients (A-values) as well as calibration of a feed channel pressure

drop correlation as a function of feed spacer thickness, membrane leaf length and Reynolds number. These parameters enabled scale up to 8-inch equivalents of the tested membranes as well as prediction of rejection performance for a full-scale RO membrane system fed different levels of ammonia-N (5, 10 and 15 mg/L) and total dissolved solids (TDS) of 1400 mg/L. The operational (opex) costs associated with different RO design configurations are then evaluated to determine the most cost-effective route of producing 40 L/s of treated water meeting a discharge specification of 0.8 mg/L Ammonia-N.

Progressive separation of water causes total dissolved solids to cycle up across an element string in a pilot or full-scale membrane plant. Two consequences arise from a strengthening in feed chemistry along the string: (1) driving force for salt flux across the membrane increases and (2) the feed osmotic pressure is elevated, which combined with dynamic pressure losses across the feed channel lowers the net driving pressure for permeate flux. These two factors ultimately cause a worsening of permeate quality and hence rejection as recovery is increased. The intent of this study was to model the inherent rejection capabilities of the selected membranes under a series of operating conditions corresponding with discrete points across a full-scale element string. A-values and pressure drop characteristics supplied by membrane manufacturers enabled permeate

flux and volumetric recovery profiles to be obtained across a two-stage RO operating at 80% overall recovery, which was then used to fix hydraulic conditions for the lead and tail element rejection tests as shown in Table 2. Feed flow rates differed for each membrane for the same test type due to differences in membrane surface area. Permeate flux was assumed to be the dominant factor affecting rejection performance in this regard (Artuğ 2007). Feed chemistry for tail element rejection tests was approximated by purging 78% of lead element rejection test feed solution to permeate at fixed pump speed.

The test rig was designed and built according to the ASTM specification D4194-03 *Standard Test Methods for Operating Characteristics of Reverse Osmosis and Nanofiltration Devices* – refer to Figure 1 for further details. Major equipment included: 4"x40" single element vessel; feed and charge pumps; concentrate flow control valve; 5/20 µm cartridge filters for feed pre-treatment; feed tank temperature controller; chilled water circuit as well as pressure and flow instrumentation on feed, permeate and concentrate lines. Sampling facilities were also provided on feed, permeate and concentrate lines for water quality analyses. The ASTM specification D4194-03 was designed for characterizing nominal single salt rejections of membranes. Hence the specification could not be followed in its entirety in this study. Nevertheless, certain aspects of the specification were adopted to

**Table 1:** Targeted feed composition for synthetic mine water used in rejection tests

	General	Cations	mg/L	Anions	mg/L
pH	7.7	Ca	176	SO <sub>4</sub>	1029
Temp	30 °C	Mg	180	NO <sub>3</sub> -N	35
TDS	1670 mg/L	Na	34	Cl	39
Alkalinity as CaCO <sub>3</sub>	38 mg/L	NH <sub>4</sub> -N	9.4		

**Table 2:** Rejection test matrix

Test #	Test class	Membrane model	Area m <sup>2</sup>	Temp °C	Flux l/mh	Recovery %	Feed m <sup>3</sup> /hr	Permeate m <sup>3</sup> /hr
1-01	Lead	TML10D	6.78	30	24	10	1.64	0.16
1-02	Tail	TML10D	6.78	30	12	11	0.74	0.08
1-03	Lead	CPA7-LD-4040	7.43	30	24	10	1.80	0.18
1-04	Tail	CPA7-LD-4040	7.43	30	12	11	0.81	0.09
1-05	Lead	AE90	8.36	30	24	10	2.02	0.20
1-06	Tail	AE90	8.36	30	12	11	0.91	0.10

enhance the rigour of the test work such as: (1) a maximum variation of 1°C either side of the chosen operating temperature of 30 °C, (2) enforcing a maximum of 10% variation for three successive permeate flux, recovery, overall salt and ammonia-N rejections and (3) at least 60 minutes of stable operation between sample sets. A Hach ammonium ISE probe model ISENH4181AP (USA) was used to measure ammonia-N. Calibration curves were constructed daily using 0.08 mg/L, 0.78 mg/L, 10 mg/L, and 100 mg/L ammonia-N standard solutions to account for probe drift. As per manufacturer recommendation, 5

mL of ionic strength adjuster (ISA) solution was added to 20 mL of sample for calibration and rejection test samples. ISA solution elevates the ionic strength of the sample sufficiently such that any changes in species concentration in the range of interest will not effect the ammonia-N activity coefficient, thereby allowing for the direct conversion of mV output to concentration.

The permeability coefficient for each membrane was determined using Equation 1, while the ammonia-N and overall salt permeability coefficients were determined using Equations 2 and 3 respectively below.

$$A = \frac{J_v}{(P_{\text{feed}} - 0.5\Delta P - P_{\text{perm}} - \pi_{\text{fc}} + \pi_p)TCF} \quad \text{Equation 1}$$

$$B_{\text{amm-N}} = \frac{C_{p,\text{amm-N}}J_v}{(C_{FC,\text{amm-N}} - C_{p,\text{amm-N}})TCF} \quad \text{Equation 2}$$

$$B_{\text{salt}} = \frac{C_{p,\text{salt}}J_v}{(C_{FC,\text{salt}} - C_{p,\text{salt}})TCF} \quad \text{Equation 3}$$

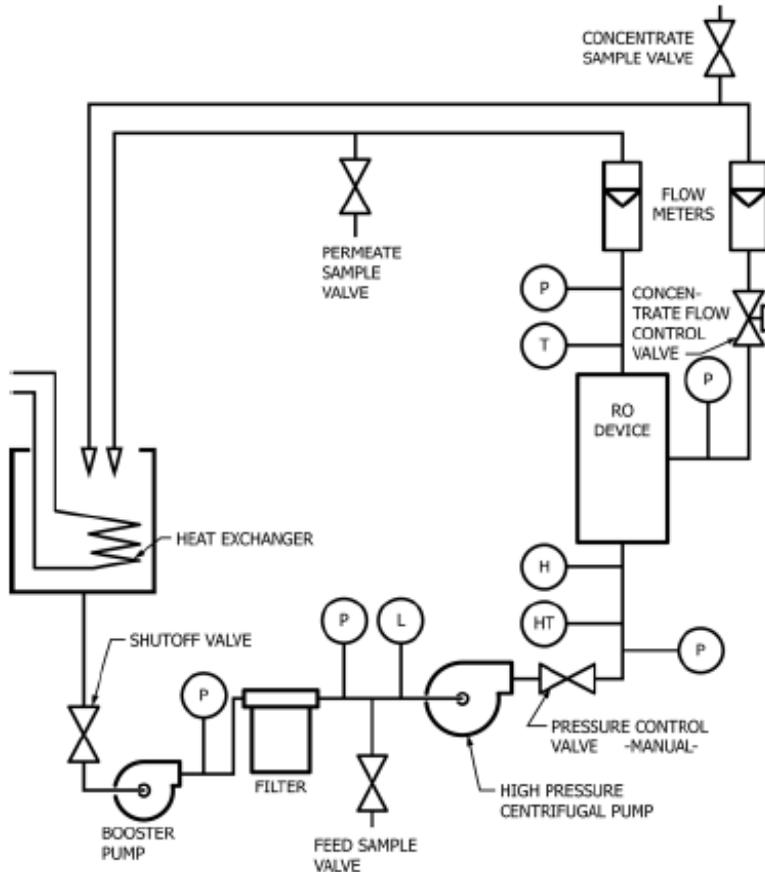


Figure 1: Diagram of test rig according to ASTM specification D4193-03 where P, T, L, H, and HT are abbreviations for pressure, temperature, low pressure, high pressure, and high temperature respectively

**Results**

*Experimental Results*

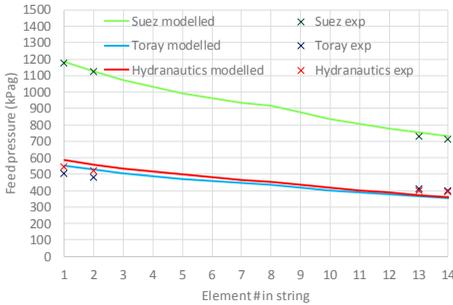
Table 3 below presents rejection data as well as the computed membrane-specific performance parameters from each rejection test. Lead and tail ammonia-N permeability coefficients for each membrane differed by <2% and 17% for the brackish water membranes and low energy seawater membrane, respectively. Ammonia-N rejection data was found to be similar for both brackish water membranes. The ammonia-N permeability coefficient was found to be 27% lower for the low energy seawater membrane, but at the expense of a 59% lower pure water permeability coefficient when compared to

the brackish water membranes. Computed membrane coefficients and feed channel pressure drop correlations for the 4-inch membranes were assumed to be the same for their 8-inch equivalents. The parameters were used in a simplified solution-diffusion model developed by Miwatek in Python to simulate full-scale system performance.

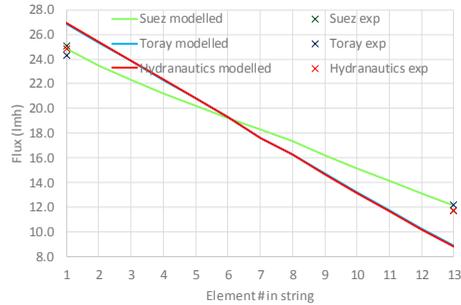
The calibrated solution diffusion model was utilized to run projections of hydraulic profiles and permeate ammonia-N loading curves across the full-scale 8 inch membrane string. Figures 2 – 5 show experimental test points super-imposed on the hydraulic profiles and ammonia-N loading curves obtained from the Python model. The

**Table 3: Rejection data and modelled membrane parameters**

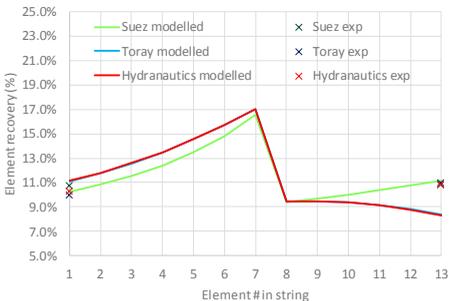
Test class	Membrane model	Feed pressure barg	Feed Cond $\mu\text{S/cm}$	Feed amm-N mg/L	Perm Cond $\mu\text{S/cm}$	Perm amm-N mg/L	A-value lmh/bar	B-salt m/s	B-amm m/s
Lead	TML10D	5.00	1902	10.8	18.6	0.46	4.74	3.6E-08	2.2E-07
Tail	TML10D	4.10	5450	33.1	102	2.66	5.09	2.5E-08	2.2E-07
Lead	CPA7-LD-4040	5.40	1873	11.0	14.5	0.46	4.46	2.8E-08	2.2E-07
Tail	CPA7-LD-4040	4.00	5460	31.4	87.1	2.65	5.17	2.0E-08	2.2E-07
Lead	AE90	11.7	1902	12.2	9.60	0.37	1.94	1.9E-08	1.6E-07
Tail	AE90	7.30	5633	37.9	61.5	1.93	1.94	1.4E-08	1.3E-07



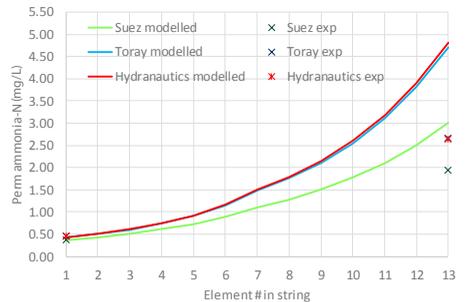
**Figure 2: Modelled feed pressure profile across element string with experimental conditions superimposed**



**Figure 3: Modelled flux profile across element string with experimental conditions superimposed**



**Figure 4: Modelled element recovery profile across element string with experimental conditions superimposed**



**Figure 5: Modelled element permeate concentration across element string with experimental conditions superimposed**

importance of the curves is for verification that experiments were executed under representative conditions.

Overall, the experimental conditions of the low energy seawater element are the most representative based on replicating projections from a calibrated solution-diffusion model. There is a substantial difference in experimentally determined and modelled tail element permeate Ammonia-N concentrations for all three membranes tested. This behaviour would be expected if insufficient permeate was purged during cycling up resulting in a less concentrated tail feed.

The ammonia-B value was found to differ by a maximum of 17% between lead and tail experiments for the three elements. As a result of a consistent ammonia-N B-value being obtained the lack of cycling up is thought to have no substantial effect on the validity of the experimental data obtained. By interpolation, it is observed that the permeate concentrations obtained experimentally lie within the element string. The experimental point can be placed approximately element 10 and 11 for the high rejection brackish and low energy seawater elements respectively.

*Opex Study*

The operational cost study utilizes the membrane parameters computed based on experimental data to predict permeate concentrations, feed pressure and feed flow-rate for feed concentrations of 5, 10 and 15 mg/L ammonia-N at a fixed feed TDS of 1400 mg/L using the calibrated solution diffusion

model. The study considered four variants of a two-stage RO system: (1) Brackish water membranes, (2) brackish water membranes with tail bank permeate recycle, (3) sea water membranes and (4) sea water membranes with tail bank permeate recycle. For each configuration, 80% overall recovery was targeted with fresh feed of 90 m3/hr to the plant. The B-values obtained for the CPA7-4040-LD and TML10D coincided close enough for the membranes to be equivalent. The data obtained from the modelling exercise is presented in Table 4. The opex study was limited to the pumping costs, i.e. electricity usage, of running the various RO configurations. The pumping costs were thought to be the difference between each of the alternatives as the remaining operating costs will remain approximately constant. In order to estimate the pumping costs, pump and motor efficiencies of 65% and 83% respectively were assumed. Utilities were costed at 0.19 \$/kWh which was obtained for a plant situated in Ghana. A discharge limit of 1.00 mg/L ammonia-N for receiving surface waters is recommended by Ghanaian EPA. The RO system is designed to maintain an operational limit of 0.80 mg/L ammonia-N to manage risks of discharging non-compliant water. Table 4 summarizes which of the configurations meet discharge guidelines for a specified ammonia-N feed concentration. Table 4 also shows the pumping costs associated which each configuration.

The high rejection brackish water elements have a lower estimated pumping cost when compared to the low energy seawater elements.

**Table 4: Modelled data from Python for different RO configurations and feed ammonia concentrations**

Configuration	Feed amm-N mg/L	Perm amm-N mg/L	Feed Pressure kPag	Feed Flow m3/h	Ops Limit	Pumping Cost \$/m3 Feed
Brackish Only	5	0.54	549	90	✓	0.05
Brackish Only	10	1.09	549	90	✗	0.05
Brackish Only	15	1.63	549	90	✗	0.05
Brackish with permeate recycle	5	0.26	649	109	✓	0.06
Brackish with permeate recycle	10	0.52	649	109	✓	0.06
Brackish with permeate recycle	15	0.79	649	109	✓	0.06
Sea water only	5	0.39	1182	90	✓	0.12
Sea water only	10	0.77	1182	90	✓	0.12
Sea water only	15	1.16	1182	90	✗	0.12
Sea water with permeate recycle	5	0.18	1500	112	✓	0.15
Sea water with permeate recycle	10	0.35	1500	112	✓	0.15
Sea water with permeate recycle	15	0.53	1500	112	✓	0.15

This behaviour is due to the lower permeability of the low energy seawater elements. Table 3 shows an experimental A-value of 1.95 l/mh/bar for the low energy seawater element which is 60% lower compared to the average A-value of 4.87 l/mh/bar for the high rejection brackish water elements. Overall the permeate recycle systems meet the operational limits for all three feed concentrations presented. On a relatively low ammonia-N concentration of 5 mg/L ammonia-N a high rejection brackish water element would provide sufficient separation to discharge water within Ammonia-N specification. A high rejection brackish element with permeate recycle is able to maintain operational limits with feed concentrations up to 15 mg/L ammonia-N. The fact that a permeate concentration of 0.79 mg/L  $\text{NH}_4\text{-N}$  is achieved at 15 mg/L ammonia-N shows a feed of 15 mg/L ammonia-N is the threshold for utilization of high rejection brackish water elements with tail bank permeate recycle. If the feed increases past a feed of 15 ammonia-N a low energy seawater element with tail bank permeate recycle would be required at a resultant increase in the cost of approximately 150%. The maximum Ammonia-N feed level which a low energy sea water element with tail bank permeate recycle configuration could handle would be 22.5 mg/L.

## Conclusions

The study presented herein revealed similar Ammonia-N rejection characteristics for both brackish water membranes. The low energy sea water membrane provided better Ammonia-N rejection, but at the expense of substantially higher energy requirement. For each of the membranes, the Ammonia-N B-values were an order of magnitude larger than the overall salt B-values confirming the fact that Ammonia-N has substantially lower rejection compared to the bulk average of ionic species in the feed. An opex study was performed considering multiple RO configurations which could be used to treat varying levels of feed Ammonia-N to a discharge specification of 0.8 mg/L. At 5 mg/L, the brackish water membrane only option would be most cost effective. Brackish water membranes would require tail bank permeate recycle to meet discharge specification above 7.5 mg/L to a maximum of 15 mg/L and

would be more cost effective than running sea water membranes only. Permeate recycle is attractive due to low initial capital expenditure and ease of operation. Nevertheless, permeate recycle has multiple drawbacks including: sensitivity to power costs; vulnerability to diminishing returns when membrane degradation becomes relevant as well as the fact that spare capacity of the system is being used to reprocess treated water whereas priority should be assigned to processing additional fresh RO feed. Future work should entail investigation of other process levers, such as manipulation of feed pH to ensure all of the dissolved ammonia species are in the ionized ( $\text{NH}_4^+$ ) form. Other types of polishing technologies should also be explored such as the use of zeolite or breakpoint chlorination. Implementation of non-membrane based technologies as a backstop would make sense from a risk management perspective.

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