Methodology for the Performance Monitoring of an Unconventional Acidic RO

Jivesh Naidu, Sebastian Franzsen, Johan Espach

Miwatek, Ebene, Mauritius, jiveshn@miwatek.co.za

Abstract

The option to feed ARD directly to a UF and RO system is an attractive treatment technology due to the higher solubility of minerals and the potential to reduce equipment sizes of downstream precipitation systems. The monitoring of such an RO system would require performance normalisation. This paper presents a method to modify conventional performance monitoring equations to develop an acid RO performance monitoring method. Modifications to the performance monitoring equations included calculating TDS / EC ratios specific to ARD using PHREEQC and the PHREEQC.dat database. Further, the osmotic pressure was calculated using a modified version of the Van't Hoff equation for the osmotic pressure of non-ideal solutions. The osmotic pressure coefficient was calculated in PHREEQC using the SIT.dat database.

Data from an acid RO pilot study was used to determine TDS / EC ratios and osmotic pressure coefficients and for the testing of the acid RO method versus vendor-provided performance monitoring methods. TDS / EC conversion factors were found to range from 0.82 to 1.45 and 0.12 to 0.48 for the feed and permeate respectively. It was found that the TDS / EC conversion factor of the feed increased with an increase in EC. The osmotic coefficients were found to be 0.84, 0.97 and 0.80 for feed, permeate and concentrate respectively. Vendor-provided methods compared favourably to the acid RO method in terms of normalised permeate flux plots however differences in the osmotic pressure calculated were observed. The acid RO method provided a more accurate estimate of the osmotic pressure as the method is calibrated to the chemistry of ARD.

Keywords: Acid Rock Drainage, Reverse Osmosis, Performance Monitoring, PHREEQC

Introduction

It is technically feasible to feed acid rock drainage (ARD) directly to ultrafiltration (UF) and reverse osmosis (RO) membrane systems. This unconventional membrane application takes advantage of the higher solubility of the sparingly soluble minerals of iron, aluminium and copper at solution pH values approximately less than 3.5, and is limited by the stability of ferric species and the clean-in-place (CIP) procedures implemented. The application of a RO system to ARD can serve as an economiser to reduce the size of downstream precipitation equipment and pre-concentrate the influent to the precipitation system for improved sulphate reduction. Potential precipitation systems include high-density sludge (HDS) or lime precipitation.

The surface of the RO membranes is subject to fouling or scaling which negatively impacts the performance of the RO system. The performance of an RO system is affected by variables such as feed water, feed pressure, temperature and recovery (Kucera 2015). Determining whether changes in performance are a result of one of these variables or as a result of fouling or scaling requires performance normalisation (Kucera 2015). Performance monitoring is typically conducted by normalising performance to a past operating point to determine how the performance has improved or deteriorated (Boulahfa *et al*. 2019).

Performance monitoring spreadsheets from vendors are readily available using equations and correlations developed for brackish and seawater applications. This paper presents a method to modify conventional performance monitoring equations for use in the unconventional membrane application. The acid RO performance monitoring method intends to provide accurate and robust normalisation of operational data gathered from an unconventional acid RO application. The method was tested and compared to vendor-provided normalisation methods using data from an acid RO pilot plant.

Methods

Input data into acid RO performance monitoring method

The acid RO performance monitoring method has been developed on the basis that performance monitoring will be required daily with operational data recorded at a frequency of at least 8 times a day, while full-suite analytical data of the feed, permeate and concentrate streams are available at a frequency of at least once a month. The operational parameters required for performance monitoring are the flow rates of the permeate and concentrate streams; feed, concentrate and permeate stream pressures, electrical conductivity (EC) of the feed and permeate streams, and the feed stream temperature.

Test data for acid RO performance monitoring method

Data from a pilot scale acid RO application was used to test the acid RO performance monitoring method. In the pilot plant, the RO pre-treatment consists of a 500 µm prefilter screen, a single UF rack consisting of up to four outside to inside Suez Zeeweed 1500 (ZW1500) UF modules and 2 x 10 µm cartridge guard filters. The RO is a two-stage system consisting of 24 Hydranautics CPA5-LD-4040 elements with sixteen elements in the lead bank and eight elements in the concentrate bank. The UF typically operated at 7.8 m^3/h feed and a volumetric recovery of 92% and the RO was typically operated at 4.5 m^3/h feed with the recovery adjusted between 60% and 70% based on feed chemistry. The feed water quality to the pilot has been summarised in Table 1.

Acid RO performance monitoring method

The methodology used for performance monitoring is: the calculation of feed and permeate total dissolved solids (TDS) from field EC readings using TDS / EC conversion factors, calculation of the osmotic pressure of the feed-concentrate channel and permeate stream, calculation of the net driving pressure

Table 1 *Average feed chemistry for acid RO pilot plant*

Parameter	Unit	Average	Range
pH		2.6	2.0 – 3.4
Temperature	˚C	13.9	11.2 – 20.3
Total dissolved solids	mg/L	3420	1100 – 8928
Electrical conductivity	µS/cm	3635	1696 – 5610
Aluminium as Al	mg/L	49.9	15.4 – 85.5
Calcium as Ca	mg/L	215	87.7 – 389
Chloride as Cl	mg/L	12.4	0.72 – 39.6
Copper as Cu	mg/L	45.0	1.92 – 200
Iron as Fe	mg/L	361	19.0 – 1405
Potassium as K	mg/L	6.78	2.35 – 12.2
Magnesium as Mg	mg/L	30.3	10.7 – 53.7
Manganese as Mn	mg/L	9.47	2.46 – 20.1
Sulphate as SO_4	mg/L	2347	802 - 7125

(NDP), temperature correction factor, and membrane permeability coefficient at 25 ˚C, and the calculation of the normalised permeate flux.

The acid RO performance monitoring sought to find a method to determine the TDS/ EC conversion factors for ARD. The aqueous solubility calculation capabilities of PHREEQC (PHREEQC Version: 3.7.3-15968) with the PHREEQC.dat database were used to calculate the EC and TDS from analytical data of the feed and permeate solutions. Through PHREEQC, the specific conductance of a solution is calculated by summing the products of the specific conductivity and molal concentrations of all the specifies in the solutions (Parkhurst and Appelo 1999). PHREEQC also corrects the molal concentration with an electrochemical activity coefficient that is derived from a combination of Kohlrausch's law and the Debye-Hückel equation (Parkhurst and Appelo 1999). The EC was calculated by adjusting the solution temperature to 25˚C. The calculated EC and TDS determined using PHREEQC were used to determine TDS / EC conversion factors for each data point. Trends of the field measured EC and PHREEQC calculated TDS / EC conversion factors for the feed and permeate streams were generated. These trends were used to determine the conversion factors for each data point and convert the field-measured EC into TDS.

The Van't Hoff equation for the osmotic pressure of non-ideal solutions, shown in Equation 1, was used as a starting point to calculate the osmotic pressure of the feed-concentrate channel and the permeate stream. Using Equation 1 requires the molal concentrations (c) and solute activity coefficients (ϒ) of solutes (i) as inputs. This data is obtained through full-suite analytical data which is available once a month. Performance monitoring is required daily therefore modifications to Equation 1 were required. The modified version of the Van't Hoff equation used for the acid RO method has been shown in Equation 2. In Equation 2, the sum of the product of the activity coefficients and concentrations of the solutes in a stream (j) has been replaced by the EC of the stream divided by the product of the EC / TDS conversion factor and the average molar mass of the stream (M). The solute activity coefficients have been omitted as they have already been accounted for in the EC / TDS ratio obtained from PHREEQC.

$$\pi = \varnothing RT \textstyle\sum_i \gamma_i c_i \qquad \text{Equation 1}$$

$$\pi_j = \varnothing_j RT \frac{EC_j}{\lambda_j M_j} \qquad \text{Equation 2}$$

The osmotic pressure coefficient (Ø) for the feed, permeate and concentrate streams were calculated from analytical data using PHREEQC with the Pitzer.dat and SIT.dat databases. Trends of the field measured EC and calculated osmotic pressure coefficients for the feed, concentrate and permeate streams were generated. These trends were used to determine the osmotic pressure coefficient. The average molar mass of the feed, concentrate and permeate streams were calculated based on the laboratory data. The average molar mass for the feed, permeate and concentrate streams were found to be 67.2 g/mol, 57.3 g/mol and 68.4 g/mol respectively. The average of the feed and concentrate average molar masses were used for the feed-concentrate average molar mass.

The calculation of EC / TDS conversion factors and osmotic pressure coefficients was completed with the aid of Python. A Python code (Python version: 3.9.7) was developed which imported and sorted analytical data for the feed, permeate and concentrate streams, created a PHREEQC script file for each dataset, ran each dataset through PHREEQC with a loop using the PHREEQC COM module (IPhreeqcCOM Module version 3.7.3-15968) and exported the EC, TDS and osmotic pressure coefficient data to excel for each dataset. The code was run on the PHREEQC.dat, Pitzer.dat and SIT.dat databases and the data was exported as one consolidated dataset.

The NDP is calculated using Equation 3 and requires the calculation of the osmotic pressure of the feed-concentrate channel. Equation 4 is used for the calculation of the feed-concentrate channel mass concentration where R is the recovery of the system. Equations 2 and 4 are combined (Equation 5) to calculate the osmotic pressure of the feed-concentrate channel.

$$NDP = P_F - 0.5\,(P_F - P_C) - P_P - \pi_{FC} + \pi_P$$ Equation 3

$$C_{FC} = C_F \frac{\ln\left(\frac{1}{1-R}\right)}{R}$$ Equation 4

$$\pi_{FC} = \emptyset_{FC} RT \frac{EC_F}{\lambda_F M_{FC}} \frac{\ln\left(\frac{1}{1-R}\right)}{R}$$ Equation 5

The temperature correction factor was calculated using Equation 6 to correct the operating conditions to a reference temperature of 25 ˚C. The membrane permeability coefficient at 25˚C is calculated using Equation 7, where J_W is the flux of water through the membranes at a point in time (k). The normalised permeate flux ($J_{W,\ norm}$) was calculated using Equation 8 where "ref" is the reference point for normalisation.

$$TCF = e^{3020\left(\frac{1}{298} - \frac{1}{273+T}\right)}$$ Equation 6

$$A_k = \frac{J_{w,k}}{NDP_k \times TCF_k}$$ Equation 7

$$J_{w,norm} = A_k \times NDP_{ref} \times TCF_{ref}$$ Equation 8

Generation of vendor performance monitoring curves

Vendor-provided performance monitoring methods were used to generate normalised flux curves for the operational data generated from the pilot plant. The methods used were LG Chem Normalization from LG Water Solutions, FT Norm from Dow and RO DataXL 8.2 from Hydranautics. The spreadsheets provided calculate the normalised permeate flow rates based on vendor equations and inputs from the users. Normalised permeate flow rates were adjusted to permeate flux by accounting for the surface area of the system. The inputs were broken up into discrete runs with each having a fixed reference point and fed into the vendor spreadsheets. The inputs required were feed temperature, flow rates of the permeate and concentrate streams, pressures of the feed, permeate and concentrate streams and EC of the feed and permeate streams. Single-stage array vendor spreadsheets were used.

Results

Inputs into acid RO performance monitoring method

TDS / EC ratio for feed and permeate streams

Figure 1 shows a plot of the calculated TDS / EC conversion factors for the analytical data using PHREEQC versus field-measured EC readings of the respective data points for the feed stream. A plot of the same data for the permeate stream is shown in Figure 2. The data shows that calculated conversion factors for the feed have a range from 0.82 to 1.45 whilst the permeate factors have a range from 0.12 to 0.48. These factors differ from the values used for the feed and permeate streams in brackish water application which are typically in the range of 0.5 – 0.75.

Second-order polynomials were fitted to the TDS / EC conversion factors versus EC for each of the feed and permeate streams. It was observed that the feed conversion factor increased with an increase in EC. The polynomial fitted for the feed conversion factor was used to estimate the conversion factor for the acid RO method. The polynomial fit would not be ideal for data gathered from a scientific experiment but was found to be suitable for data gathered from a pilot study. No trend was observed for the permeate conversion factors. The average permeate TDS / EC conversion factor of 0.24 was used for the acid RO method.

Osmotic pressure coefficient for feed, concentrate and permeate streams

Figure 3 shows a plot of the calculated osmotic pressure coefficient for the analytical data using PHREEQC with both the Pitzer.dat and SIT.dat databases versus field-measured EC readings of the respective data points for the feed stream. Similar plots for the permeate and concentrate streams are shown in Figures 4 and 5 respectively. The calculated osmotic pressure coefficient for the feed stream has an average value of 0.75 with a range from 0.65 to 0.83 using the Pitzer.dat database and an average value of 0.84 with a range from 0.79 to 0.88 using the SIT.dat database. The concentrate stream has an average value of 0.68 with a range from 0.59 to 0.79 using the Pitzer.dat database and an average value of 0.80 with a range from 0.76 to 0.86 using the SIT.dat database. The permeate stream has an average value of 0.97 with a range from 0.92 to 0.99 using the Pitzer database.dat and an average value of 0.97 with a range from 0.94 to 0.99 using the SIT.dat database.

Fitting of the second-order polynomials to the data shows no trends or best-fit line is possible for all streams irrespective of the database used. The SIT.dat database reports higher osmotic pressure coefficients when compared to the Pitzer.dat database. The Pitzer.dat database was found to have a limited set of master species and does not include aluminium which is typically elevated for ARD. Due to these limitations in the Pitzer.dat database, the averaged values for the osmotic pressure coefficient calculated using SIT.dat databases were used for the acid RO performance monitoring method.

Comparison between acid RO and vendor-provided performance monitoring methods

Operational data from an acid RO pilot plant has been broken up into discrete runs for the comparison of the acid RO performance monitoring method to the vendor-provided performance monitoring methods. The performance monitoring curves for Run 1 are shown in Figure 6, this includes the normalised permeate flux for the various methods, the normalised flux reference point as well as a line showing when a 10% decline in flux from the reference has occurred. Data

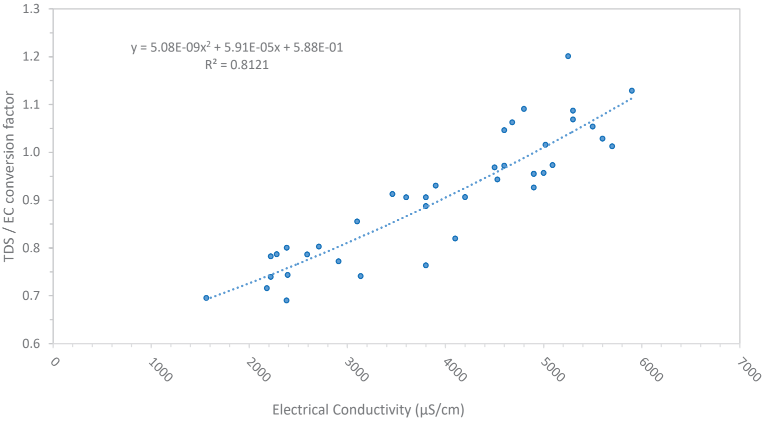

Figure 1 *Plot of TDS / EC conversion factor versus EC for the feed*

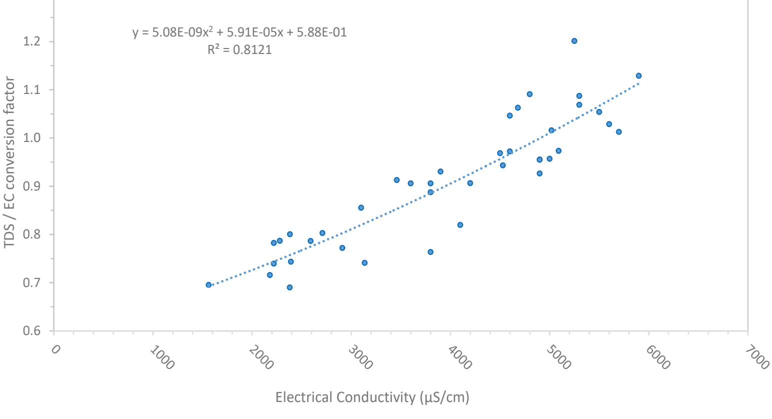

Figure 2 *Plot of TDS / EC conversion factor versus EC for the permeate*

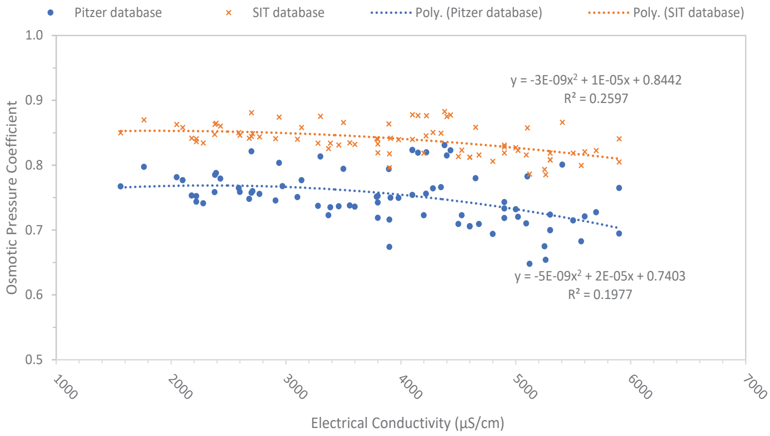

Figure 3 *Plot of osmotic pressure coefficients calculated using the Pitzer and SIT databases versus EC for the feed*

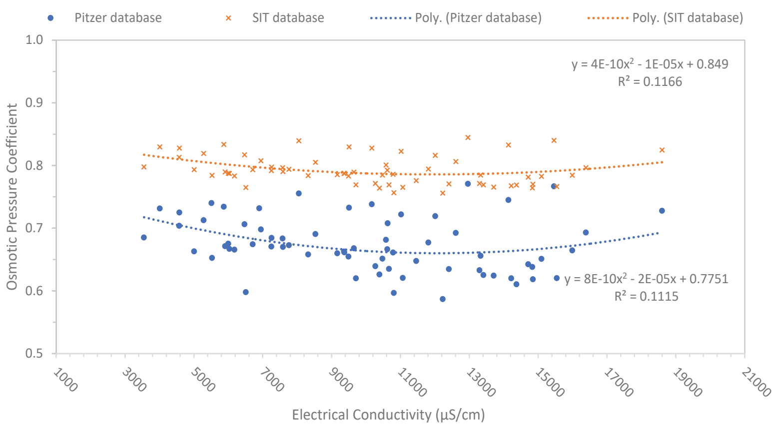

Figure 4 *Plot of osmotic pressure coefficients calculated using the Pitzer and SIT databases versus EC for the concentrate*

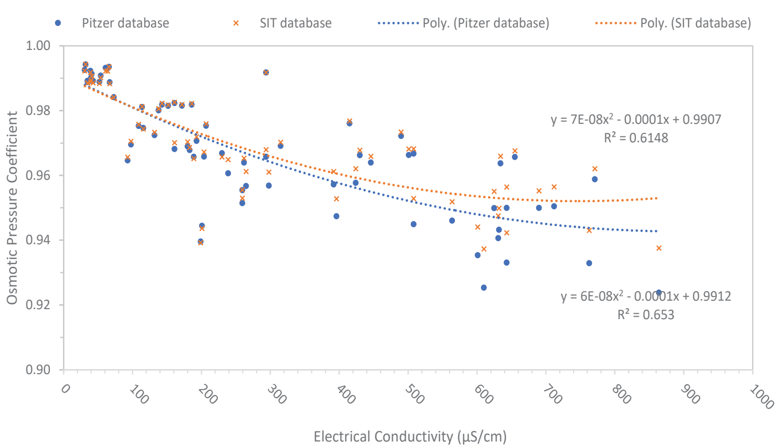

Figure 5 *Plot of osmotic pressure coefficients calculated using the Pitzer and SIT databases versus EC for the permeate*

labels have been included to show CIP points and changes in the recovery of the system. Figure 7 shows the NDP calculated by the various methods for Run 1 data. Similar comparisons of permeate flux and NDP for Run 2 are shown in Figures 8 and 9.

The performance monitoring curves produced for Runs 1 and 2, Figures 6 and 8 respectively, show there is a similarity in the normalised permeate flux calculated by the acid RO method and methods used by LG Water Solutions and Hydranautics. The normalised permeate flux calculated by Dow differs from the values produced through the other methods. Overall, the data further shows that the normalised flux calculated by the acid RO method is lower.

A comparison of the NDP calculated for Runs 1 and 2, Figure 7 and 9 respectively, using the various methods show that the acid RO method calculates a NDP which is higher than vendor-provided methods. NDP values calculated by LG Water Solutions, Hydranautics and Dow are similar. The NDP for all methods is calculated using Equation 3. A difference in the NDP is a result of the feed-concentrate channel osmotic pressure as the permeate osmotic pressure is not high enough to affect the calculations and all other inputs are the same across the methods. The higher NDP from the acid RO method is a result of the modified Van't Hoff equation (Equation 2) calculating a lower feed-concentrate channel osmotic pressure compared to the vendor-provided methods. Vendor-provided methods generally estimate the osmotic pressure using correlations specific to brackish water or seawater. The unsuitability of these correlations to the chemistry of ARD results in a less accurate estimate of the osmotic pressure.

Conclusions

TDS / EC conversion factors and osmotic pressure coefficients were calculated using PHREEQC which were used as inputs into the acid RO performance monitoring method. The data shows that TDS / EC conversion factors for ARD differ from those observed for brackish water. It is possible to predict the feed TDS / EC conversion factor for ARD based on the feed EC. Osmotic pressure coefficients were found to be higher when using the SIT.dat database compared to the Pitzer.dat database. The osmotic pressure coefficient calculated using the SIT.dat database was selected as the input to the acid RO method.

The acid RO method produced normalised permeate flux curves which were similar to those produced by vendor-provided spreadsheets from LG Water Solution and Hydranautics. The normalised permeate flux curves produced by Dow differed from those produced by the other methods. The NDP calculated using the vendor-provided methods was lower compared to the values calculated using the acid RO method. The difference is attributed to the acid RO method calculating a lower feed-concentrate channel osmotic pressure. The acid RO method used a first principles approach which had been calibrated to analytical data to estimate the osmotic pressure. This approach results in a more accurate estimation of the osmotic pressure when compared to correlations used by vendor-provided methods. A potential improvement to the acid RO method is more regular calibrations of the TDS / EC conversion factors and osmotic pressure coefficients as the chemistry of the ARD changes.

References

Boulahfa H, Belhamidi S, Elhannouni F, *et al* (2019) Demineralization of brackish surface water by reverse osmosis: The first experience in Morocco. J Environ Chem Eng 7:102937

Kucera J (2015) Reverse osmosis: industrial processes and applications. John Wiley & Sons

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations