Treatment of a Thickener Overflow in Metal Mining Using Membrane Separation Technologies

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Abstract

In this study, the feasibility of treating a thickener overflow stream from a North American copper and nickel concentrator was evaluated using membrane separation technologies. Performances of pressure driven technologies including a combined ceramic membrane microfiltration (MF) and reverse osmosis (RO), and an electrochemically driven technology, electrodialysis (ED), were compared.

The results show that both RO and ED technologies were effective at reducing the concentration of the major salts and contaminants in the thickener overflow (including calcium and magnesium) below the detection limit of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). This can result in a significant alleviation of the built-up of salts in the recycled water stream, and will reduce its negative impact on the effectiveness of the flotation process in the recovery of nickel and copper. During RO separation, the permeate flux decreased over the time. This could be attributed to membrane fouling caused by a high concentration of calcium sulfate in the thickener overflow streams. This negative phenomenon could be minimized via electrodialysis reversal (EDR). The results of this study showed that both RO and ED are potential candidates for mine water treatment applications in milling operations. In addition, ED can be a promising alternative to RO, as ED requires less pre-treatment in applications for water streams having high scaling potentials.

Introduction

Milling processes including grinding, flotation and thickening are the most water intensive parts of the mining industry. The overflow stream from thickening process is normally recycled and reused in grinding and flotation. This is done to minimize the demand of fresh water. The remainder of the water balance is made up of process water that comes from the tailings treatment process. The thickener tank overflow water has a much higher total dissolved solids (TDS) than that of the process water (Di Feo et al., 2020). While the recycling of this stream reduces the intake of fresh water, it also results in a build-up of salts and contaminants. This in turn leads to a decreased effectiveness of the flotation process. It has been shown in laboratory tests that the nickel + copper grade versus nickel recovery curve decreased when thickener overflow was used (Di Feo et al., 2021). More precisely, the nickel + copper grade of the primary rougher concentrates decreased relative to that obtained with process water (Di Feo et al., 2021).

The objective of this work was to evaluate the effectiveness of two membrane separation technologies including reverse osmosis (RO) and electrodialysis (ED) to treat the thickener overflow stream. Reducing the concentration of salts and contaminants in a thickener overflow stream can result in maintaining the grade of nickel + copper in the flotation process. Figure 1 presents the flowsheet diagram of a copper and nickel concentrator with the proposed membrane separation stage to treat the thickener overflow stream before being recycled and reused in grinding and flotation.

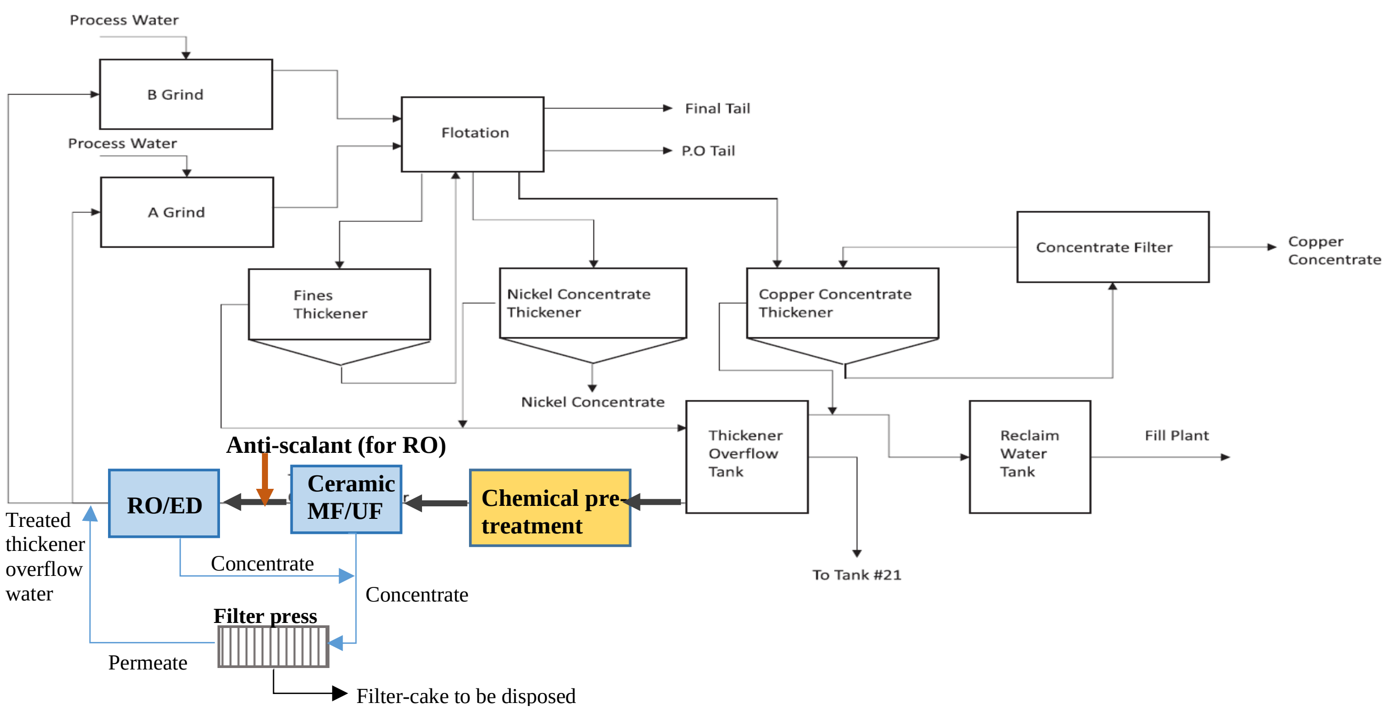

Figure 1. Flow diagram of a copper and nickel concentrator (modified from Di Feo et al., 2020)

Methodology

Two test systems were used in this study: a) pilot-scale RO system, manufactured by BluMetric Environmental Inc., Canada, containing a standard GE-Osmonics RO membrane with a Molecular Weight Cut-off (MWCO) in the range of 200-250 Daltons and maximum operating pressure of 400 psi (Figure 2); and b) pilot-scale ED system manufactured by Electrocell North America Inc., USA, with 10 pairs of

Neosepta anion exchange (CEM) and cation exchange membranes (AEM), stacked in an alternating configuration (Figure 3). The systems were utilized to treat the thickener overflow samples from a North American copper and nickel concentrator. As a pre-treatment step, a single ZrO_2/Al_2O_3 ceramic microfiltration (MF) membrane with 19 channels and a pore size of 110 nm was employed to remove suspended solids (SS). The detailed description of ED and RO operations were presented in previous publications (Di Feo et al., 2021; Mosadeghsedghi et al., 2020). During ED, operation polarity was switched to reversal mode at specific intervals for 15 seconds.

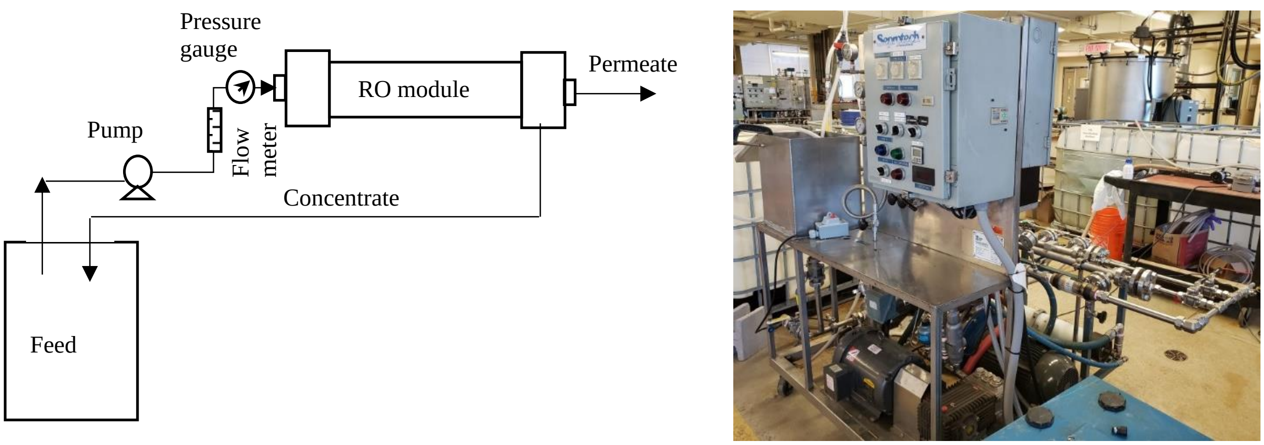

Figure 2. Schematic of the BluMetric Environmental RO system

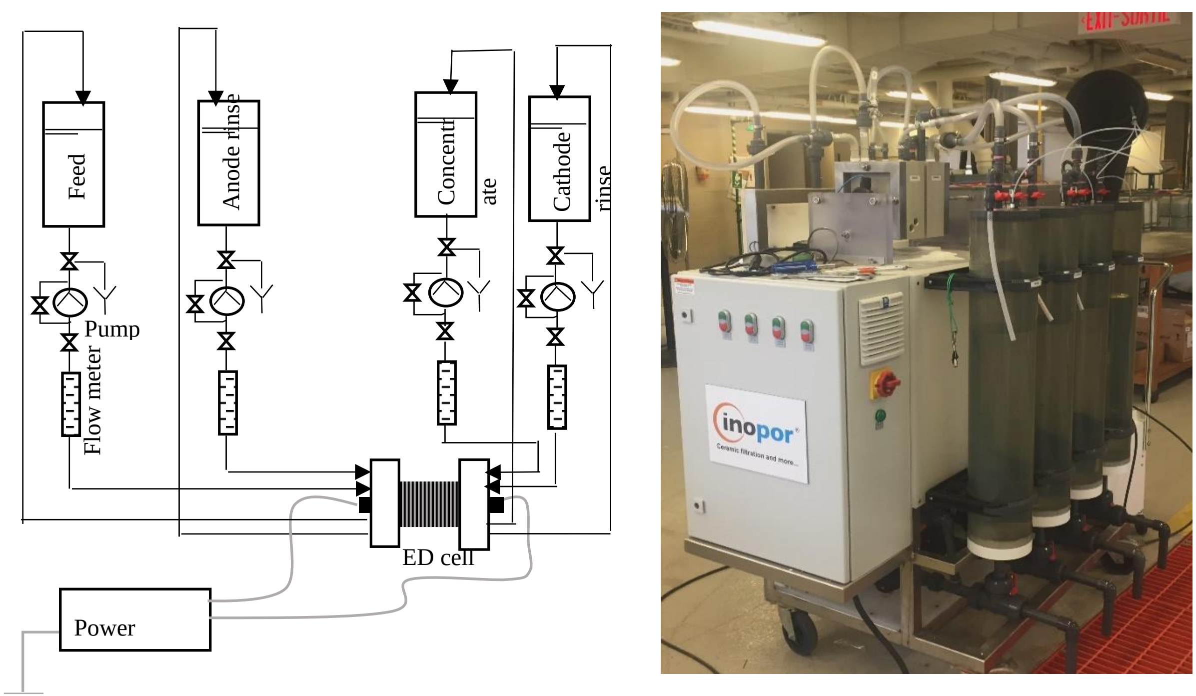

Figure 3. Schematic of the ElectroCell lab-scale ED system

In both operations, samples of 50 mL were taken in specific intervals for Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis. The percentage of ion rejection (R) was calculated using the following equation:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \ \ (\%)$$

Where, C_0 represents the concentration of a specific element in the initial thickener overflow feed sample. C_t represents the concentration of a specific element at t minutes of operation, in the permeate and in the feed respectively for RO and ED operations. To measure the permeate flow rate in RO operation, the time for collecting 500 mL of permeate is measured at specific intervals. Permeate flux describes the quantity of permeate produced during RO separation per unit of time and membrane area (Alonso et al., 2020). The permeate flux was calculated using the following equation:

$$P_v = \frac{F_P}{S}$$

where P_v, permeate flux; F_p, permeate flow rate; and S, area of the membrane, which was 7.9 m^2 for GE-Osmonics RO.

Results and Discussion

The elemental composition of the raw thickener overflow as well as the treated samples using RO and ED is presented in Table 1.

Table 1. ICP-AES elemental composition data for the raw and treated thickener tank overflow

Element	Raw feed concentration (mg/L)	Concentration after RO (mg/L)	Concentration after ED (mg/L)
Al	0.295	<0.077	<0.077
B	<0.096	<0.096	<0.096
Ba	0.114	0.003	<0.003
Bi	<0.430	<0.430	<0.430
Ca	701.000	6.310	1.230
Cd	<0.023	<0.023	<0.023
Co	<0.120	<0.120	<0.120
Cr	<0.053	<0.053	<0.053
Cu	0.032	<0.008	<0.008
Fe	<0.026	<0.026	<0.026
K	48.660	21.130	<0.058
Li	<0.042	<0.042	<0.042
Mg	0.027	0.007	0.001
Mn	<0.004	<0.004	<0.004
Mo	<0.048	<0.048	<0.048
Na	112.000	32.230	0.560
Ni	<0.140	<0.140	<0.140

P	<1.530	<1.530	<1.530
Pb	<0.140	<0.140	<0.140
S (ICP)	792.000	<17.500	<0.730
Sb	<0.090	<0.090	<0.090
Se	<0.340	<0.340	<0.340
Si	0.931	<0.096	<0.096
Sr	1.650	0.0132	<0.010
Te	<0.170	<0.170	<0.170
Zn	<0.024	<0.024	<0.024
Zr	<0.014	<0.014	<0.014
TDS (mg/L)	2416.000	247.000	189.000

The ICP-AES results (Table 1) show that the raw thickener overflow (before membrane treatment) contained calcium and sulfur (in the form of sulfate salts) at concentrations of around 700 mg/L and 790 mg/L, respectively. Membrane scaling will occur during RO treatment at these concentrations, and will result in permeate flux decline over time (Ashfaq et al., 2020). This phenomenon was observed during treatment of the thickener overflow using RO (Figure 4).

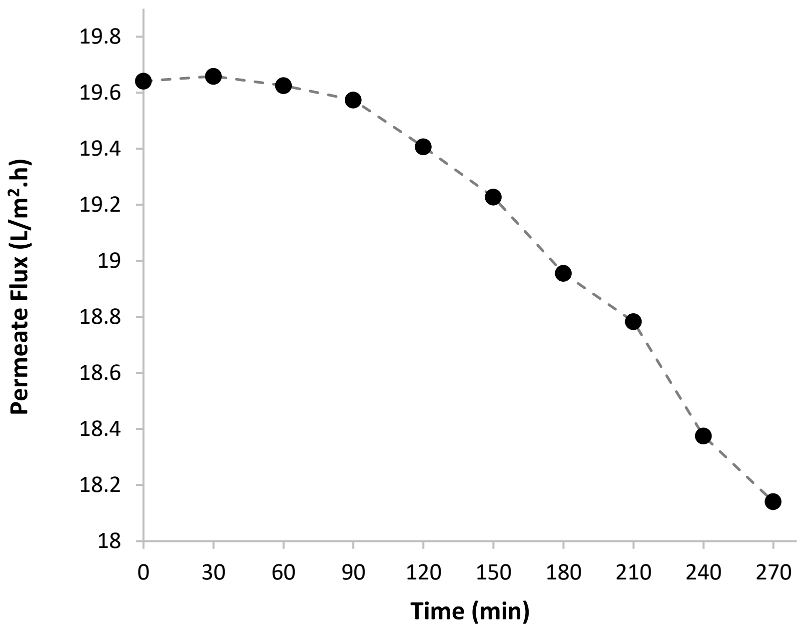

Figure 4. Permeate flux vs time during RO separation

Scanning Electron Microscopy (SEM) images of scaling layer on RO membrane are shown in Figure 5. It was suggested that the addition of polyphosphates such as sodium hexamtaphosphate (SHMP) as anti-scalants can retard the precipitation of the scale-forming sulfate and carbonate salts. However, their use can cause the formation of phosphate scaling (Mortazavi et al., 2008).

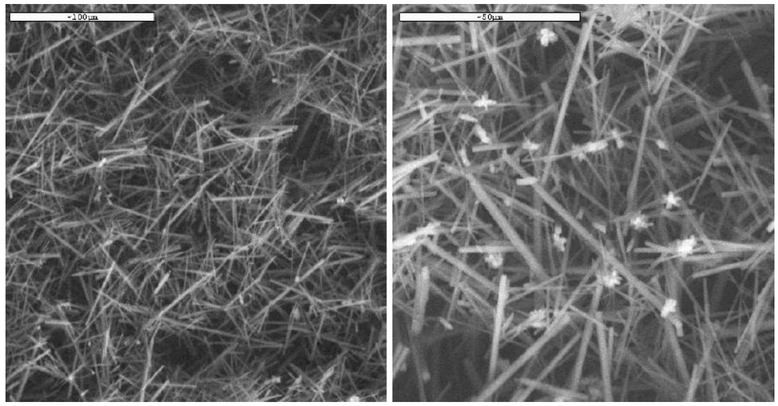

Figure 5. SEM of a scaling layer deposited on the surface of the RO membrane

This negative phenomenon was minimized via electrodialysis reversal (EDR) and the reversal polarity mode of ED operation. Due to its scaling-prevention feature, ED was suggested to be used before membrane separation technologies. This can significantly reduce the scaling and fouling issues during nanofiltration (NF) and RO operations (Geluwe et al., 2011). Figure 6 shows that using both RO and ED, high removal rates were obtained for most dissolved components of the thickener overflow.

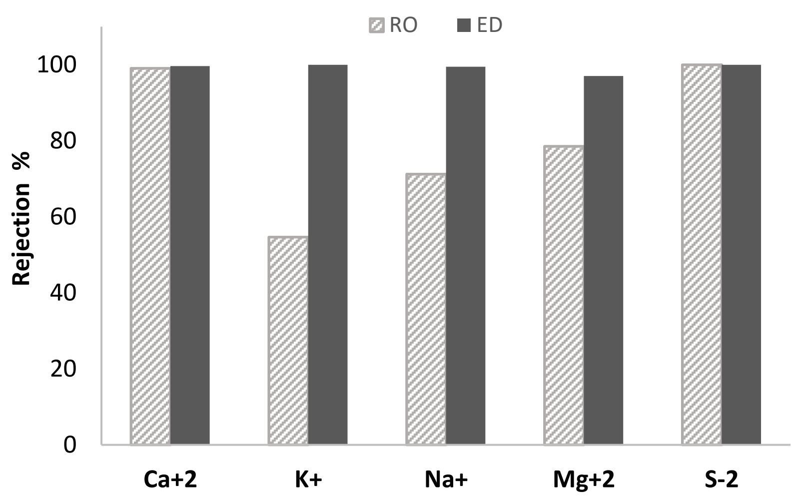

Figure 6. The percentage of ion rejection using RO and ED treatments

The quantities of calcium and sulphur, the two most concentrated constituents in the feed, removed using RO were 99% and 100%, respectively. In comparison, the quantities removed by ED were 99.6% and 100%, respectively. In addition to calcium and sulfur, potassium was present in feed water samples at considerable concentration. The concentration of potassium in initial samples was approximately 49 mg/L, and a complete removal of 100% was achieved by ED, which was around 45 percentage points higher than that of 54.6% obtained by RO. Accordingly, the total dissolved solids concentration (TDS) of the thickener overflow stream was effectively reduced by more than 90% using either technology.

Conclusion

The thickener overflow stream of a North American copper and nickel concentrator was effectively treated using membrane separation technologies including RO and ED before being recycled and reused in grinding and floatation. The TDS content of the thickener overflow was reduced by over 90% after being treated by either of the two discussed technologies. Membrane scaling occurred during RO operation due to high calcium sulfate concentrations in thickener overflow samples. This negative phenomenon could be prevented via ED due to its reverse polarity feature (EDR).

Conclusively, both RO and ED can be used to reduce the accumulation of contaminants in recycled streams in milling operations. ED seems to be more advantageous than RO as it is more resistant against scaling and organic fouling. ED is also advantageous from operating cost point of view as it does not rely on pressure

Recommendations for Future Work

The present study focuses on minimizing the constituents in the thickener overflow stream in order to alleviate their negative impact on the nickel + copper grade in the floatation process. However, there are still gaps in the understanding of how the chemistry of recycled water can influence the recoveries and grade of nickel + copper. A detailed study on the effect of constituents' concentrations of thickener overflow stream on floatation is the subject of our future studies. The ultimate objective is not to fully treat the thickener overflow recycled stream, but to maintain certain concentrations of the constituents within the operating limits of the flotation process. In order to obtain the operating limits of flotation for the constituents' concentrations, the following approaches will be taken: a) partially treat the entire thickener overflow stream to different levels of constituents concentrations, b) completely treat a split stream (20%-70%) of the thickener overflow stream and recombine the treated split with the untreated stream. Ultimately, the treated thickener overflow stream from the above-mentioned approaches will be combined with process water at different ratios (20%-50%) and will be recycled to grinding and floatation circuit.

References

Alonso G, del Valle D, Ramon Ramirez J, 2020. "Desalination in Nuclear Power Plants", Woodhead Publishing Series in Energy, UK.

Ashfaq MA, Al-Ghouti MA, Da'na DA, Qiblawey H, Zouari N, 2020. "Effect of concentration of calcium and sulfate ions on gypsum scaling of reverse osmosis membrane", Materials Research and Technology 9:13459-13473

Di Feo A, Mortazavi S, Langley S, Morin L, Prabhakar G., Demers A., Bedard I., Volchek K., 2020. "The Effects of Water Recycling on Flotation at a North American Concentrator-Part 1", Minerals and Materials Characterization and Engineering 8: 240–276.

Di Feo A, Hill-Svehla C.M, Hart B.R, Volchek K, Morin L, 2021. "The effects of water recycling on flotation at a North American concentrator ", Minerals Engineering 170:1-25.

Geluwe SV, Braeken L, Robberecht Th, Claude MJ, Van der Bruggen B, 2011. "Evaluation of electrodialysis for scaling prevention of nanofiltration membranes at high water recoveries", Resources, Conservation and Recycling 56:34-42.

Mosadeghsedghi S, Sauber M, Issa S, and Mortazavi S, 2020. "Electrodialysis Separation of Light Rare Earth Elements from Their Binary Solutions". Conference of Metallurgists COM 2020 – Hydrometallurgy: Processing of Critical Materials, CIM Academy Online, October 14-15.