Electrodialysis in zero liquid discharge systems for sustainable brine management

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Abstract

According to the latest environmental requirements, zero liquid discharge must be considered in all modern manufacturing processes. In principle, solid waste can be achieved only by evaporation plus crystallization, and therefore reverse osmosis is usually applied to decrease the operation expenses by pre-concentrating the evaporator feed.

However, reverse osmosis can generally only achieve concentrates of about 70 to 75 g/kg, still leaving a significant gap before saturation of common salts is reached. Electrodialysis can double this concentration, thus cutting the evaporator operating expenses or even eliminating the evaporator at all, providing the concentrate can be fed directly to crystallization.

In this work, an array of the most common brines was tested on a lab-scale electrodialysis unit, and salt transport, electricity consumption and electric current efficiency was evaluated. No performance drop in either scale-up factor was observed at the maximum concentrations, suggesting that under right operating conditions, integrated membrane processes should significantly decrease the evaporator costs and provide economic feasibility of zero liquid discharge process in waste brine treatment.

Keywords: Zero liquid discharge; ZLD; electrodialysis; saturation; supersaturation, evaporation

1. Introduction

Recent environmental requirements have been pushing waste water treatment into zero liquid discharge (ZLD). Evaporation (EV) and crystallization (CR) have been the traditional operations, even though the ZLD feasibility has been compromised by the operating costs. The balance can be improved by a pre-concentration step such as reverse osmosis (RO). Electrodialysis (ED) is not limited by osmotic pressure and can achieve much higher concentrations than RO, thus minimizing both investment and operation cost of the thermal step. An array of laboratory ED tests was carried out, investigating the operational limits of the most typical inorganic salts present in industrial waste waters. Also a study of economic feasibility is presented, justifying the overall significance of integrated membrane processes.

2. Materials and Methods

Feed-and-bleed experiments were carried out on a laboratory ED unit P EDR-Z/10-0.8 (MemBrain, s.r.o), with ten pairs of heterogeneous cation (CMH-PES) and anion (AMH-PES) exchange membranes RALEX® (MEGA a.s.). A potential gradient of 1 V per cell pair was applied with a current density limiter corresponding to 250 A /m^2.

The feasibility was calculated for a case study of a uranium mine waste water in Dolní Rožínka, Czech Republic. Its tailing pond contains primarily sodium sulphate (app. 27.5 g/kg) with a capacity close to 230 000 m^3/year. The new line would operate at 90% capacity (maintenance, chemical cleaning, etc.). The RO plant was projected using LewaPlus™ (LANXESS), and the ED line was calculated in cooperation with MEGA a.s. The EV part was based on commercial offers, provided by suppliers of mechanical vapour recompression evaporators (MVR). Two green field installations were projected:

- RO pre-concentrates the feed to EV (i.e. RO-EV)
- Optimized project with ED operated to the maximum concentration (i.e. RO-ED-EV)

3. Results and Discussion

3.1. Maximum Concentrations

Two principal mechanisms limited the maximum achievable salt concentration via ED -- water transport (due ion hydration) and salt solubility in water (due to nucleation barrier), see Figure 1 and Figure 2.

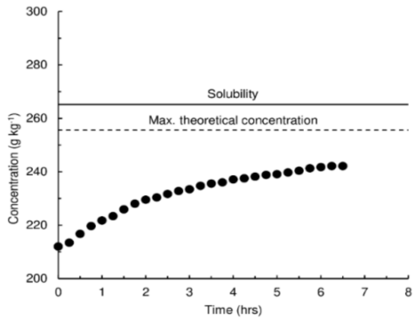

Figure 1. Concentration of $KHCO_3$.

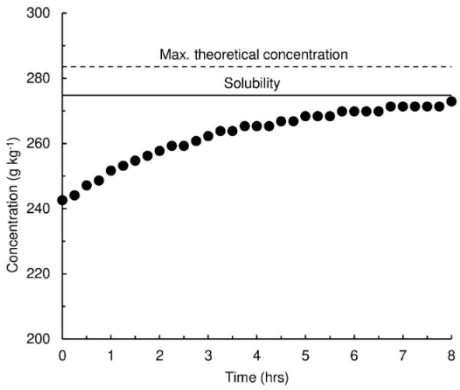

Figure 2. Concentration of KNO_3.

No limit, beyond which the operation would not be feasible was found. From the tested array of salts (such as NaCl, Na_2SO_4 and their mixtures, KCl, $MgCl_2$, NH_4Cl, $NaNO_3$, KNO_3, $Ca(NO_3)_2$, NH_4NO_3, $NaHCO_3$, $KHCO_3$, or NH_4HCO_3), most behaved predictably with a maximum achievable concentration ranging from 160 to 190 g/kg. The notable exceptions were nitrates whose concentration was above 200 g/kg and in the case of KNO_3 it peaked at app. 265 g/kg. On the contrary, with $MgCl_2$ concentrations of only 110 g/kg were achieved. The salt transport intensity did not vary over time and typically ranged between 6 and 7 eq/m^2/h. Energy consumption typically ranged between 0.36 and 0.40 Wh/g$_s$, with the current efficiency usually being between 70 and 80%.

3.2. Comparison of Process Alternatives

When RO concentrate is fed directly to EV, the following EV then treats nearly 23 t/h of 77 g/kg solution. When ED is placed between RO and EV, the ED effluents are split to EV and back to RO. This arrangement allows for much smaller EV, due to more concentrated feed. The scale-up resulted in four ED lines, each consisting of three ED-IF modules with 250 membrane pairs, each module with 125 m^2 of active membrane area. Since the thermal step of the first alternative covered almost 98% of the total cost, the overall process cost was 13.03 € per ton of treated water, whereas the second alternative resulted only to 2.51 €/t. And even though the second RO is bigger (the feed is mixed with ED diluate), and even though the ED unit has twice the energy consumption per ton of treated feed compared to RO, the capacity of EV can be reduced dramatically, thereby reducing the energy consumption of the thermal step more than eight times (Figure 3).

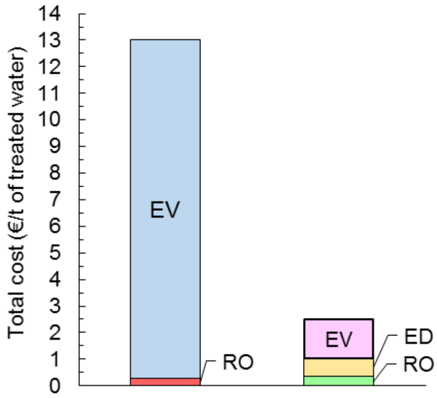

Figure 3 | Comparison of total costs.

4. Conclusions

The integration of membrane processes can substantially improve the overall ZLD feasibility, by considerably decreasing the capacity requirements of EV. No technological obstacle was observed (membrane scaling, stack leakage due to membrane swelling, etc.) while searching for the maximum concentration limit for ED. In real industrial conditions, there is usually a need for further process optimisation, such as polarity reversal frequency or chemical cleaning frequency, given that the feed is rarely a pure inorganic salt.

References

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