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Scaling prediction in electrodialytic desalination

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ABSTRACT

The application of thin intermembrane spacers with densely distributed membrane abutments allows the single-pass electrodialysis with different linear velocities in the diluate and concentrate compartments, which results in the increase in recovery ratio. When applied to the desalination of sparingly soluble salts solutions, such method allows achieving high supersaturation in the concentrate stream, which increases the risk of the membrane scaling. To avoid the scaling, the limiting condition, binding apparatus hydrodynamic conditions and scaling kinetics, can be assumed during module design. In the previous research, the condition was that the crystallization induction time has to be larger than the sum of the electrodialyzer's mean residence time and its standard deviation. Experiments with electrodialysis reversal (EDR) showed however, that even with this assumption unfulfilled, there is no significant decrease in the performance between the polarity cycles. Thus, a new limiting condition was proposed, based on the assumption of additivity of mean residence time and a square root of its variance, and linear increase of saturation level along the concentrate channel. The presented algorithm for evaluation of scaling risk turn out to be successful in case of calcium sulfate solutions, but not in case of calcium carbonate solutions.

Keywords: Electrodialysis; Electrodialysis reversal; Scaling; Calcium sulfate; Calcium carbonate; residence time distribution

1. Introduction

Electrodialysis reversal (EDR), an electrodialysis (ED) performed with periodic reversal of electrodes' polarity, can be used for brackish water desalination, that is., as RO discharge brines concentration step [1–4], or even as alternative to reverse osmosis. Some case studies have shown that application of EDR over RO can result in a lower desalination costs due to energy and chemical consumption [5,6] or less frequent shutdowns when the feed brackish river water is of poor quality [7]. The composition of feed water used in electrodialytic desalination causes the risk of the calcium sulfate and carbonate crystallization on the membrane surface, which leads to the decrease of process efficiency. Korngold et al. [1,2] presented the idea of reducing EDR scaling probability by controlled precipitation of recirculated (to achieve high recovery ratio) concentrate, oversaturated with calcium sulfate. The relative supersaturation in recirculated brine after precipitator was less than 10% and no gypsum crystallization inside ED stack was observed. Higher concentration of brine stream would probably not be possible, because of the excess turbidity of precipitator effluent. Korngold et al. pointed that this indicates the presence of small, difficult to remove crystals, which accelerate the gypsum precipitation. The idea was applied in

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a pilot-scale desalination plant [3], which showed the possibility of stable work with gypsum oversaturation in brine at the exit of EDR stack reaching 35%. Korngold, Oren et al. used antiscalants in BWRO stream, which is left in the diluate stream and would not be transported into concentrate brine stream, since such additive would be problematic in the controlled crystallization step. If, however, the BWRO retentate stream was to be directly passed through the EDR unit to the crystallizer [4], there should be no antiscalants in the system.

Authors' earlier research [4,8–10] showed that the high recovery ratio could be achieved not by concentrate recycle, but by the application of thin spacer (inter-membrane distance 0.16–0.25 mm) having densely distributed membrane abutments. Such spacers allow different linear velocities of diluate and concentrate stream without membrane bulging. Thus, a single-pass EDR can be performed with relative $CaSO_4$ saturation of factor 4 and LSI of + 2.4. To determine the maximal saturation conditions in ED process, the appearance of self-growing crystal nuclei was assumed a limiting point of the process. Thus, the ED should be performed in a manner prohibiting the creation of such crystal nuclei inside the ED module, meaning that the residence time of majority (90% or more) of the particles should be smaller than the crystallization induction time:

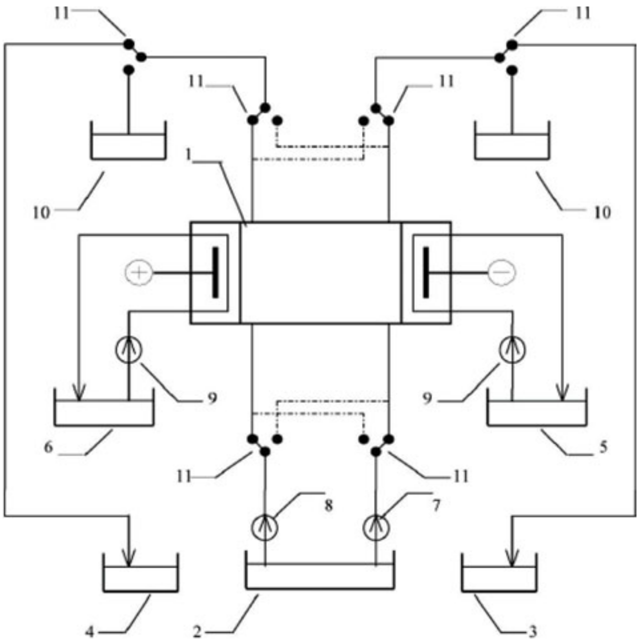
$$t_{ind} > \bar{t} + \sqrt{\sigma^2}$$

where t_{ind} denotes the induction time, denotes mean residence time and σ^2 denotes its variance. During EDR however, as shown later in this paper, the sum of mean residence time and a square root of its variance can be much larger than crystallization induction time with no significant decrease in process performance between each polarity change cycle. This arises the necessity of new limiting condition for EDR process.

2. Experimental

An ED module presented in Fig. 1 was used. A thin, 0.19 mm spacers, Neosepta® AMX and CMX membranes were placed in a manner resulting in four pairs of diluate and concentrate channels – *see* Fig. 2. The membrane working length was 51 cm.

Residence time distribution was determined in a manner described in previous paper [8]–stimulus-response method with injection of 2 ml of 0.5 M NaCl solution into the diluate or concentrate stream fed with water, next normalization of conductivity at the outlet and calculation of mean residence time and its variance. The resulting mean residence time was $\bar{t}$ = 426 s, and its standard deviation (calculated as square root of variance) σ = 334 s.



1 electrodialysis unit
2 feed tank
3 diluate tank
4 concentrate tank
5 catholyte tank
6 anolite tank
7,8 peristaltic pumps
9 centrifugal pumps
10 off-spec tank
11 three-way electronically actuated valve

Fig. 1. Schematic diagram of EDR measuring equipment.

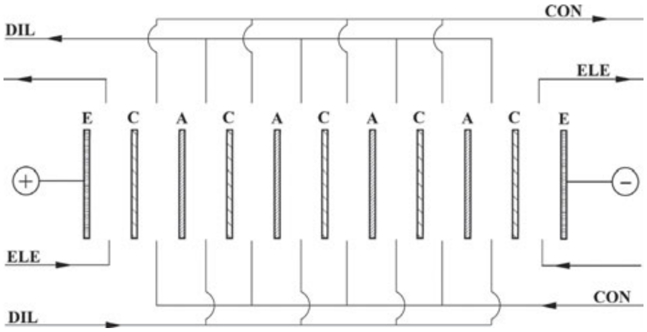


Fig. 2. The membrane stack configuration: C – cation-exchange membrane, A – anion-exchange membrane, E – platinum-coated titanium electrode, ELE – electrode rinse solution, CON – concentrate, DIL – diluate.

A model calcium sulfate solutions were used to perform single-pass ED with polarity changes at constant current density of 29 A m^{-2}. The limiting current density was determined in the earlier experiments for the as 35.4 A m^{-2} (diluate linear flow velocity 8.16 cm s^{-1}) and 35.7 A m^{-2} (8.9 cm s^{-1}). The test solution for limiting current density determination was saturated calcium sulphate. The concentration of calcium, sulphate and chloride ions in the feed, diluate and concentrate solutions are shown in Table 1. The saturation level *S* was calculated using the algorithm proposed by Lancia et al. [11]. The voltage drop across membrane stack was

Table 1
Composition of feed, diluate and concentrate in ED and respect saturation levels

No.	Linear flow velocity [cm s^{-1}]		Concentration [mg dm^{-3}]									Saturation		
			Feed			Diluate			Concentrate			Feed	Diluate	Concentrate
	Diluate	Concentrate	Ca^{2+}	SO_4^{2-}	Cl^-	Ca^{2+}	SO_4^{2-}	Cl^-	Ca^{2+}	SO_4^{2-}	Cl^-			
1	8.16	0.6	514	1233	0	325	779	0	2244	5375	0	0.74	0.38	4.34
2	8.9	0.65	349	838	0	151	362	0	2669	6220	0	0.47	0.12	5.20
3	8.9	0.65	349	838	252[a]	151	362	50.6	2669	6220	2260	0.45	0.12	4.08

[a] In case of solution no. 3, the sodium chloride was added to the feed.

measured until rapid increase of voltage was observed, indicating $CaSO_4$ crystallization on the membrane surface.

3. Results

Results show that EDR desalination of supersaturated calcium sulfate solution of given concentration can be performed in 20 min cycles of electrodes polarity reversal. It was confirmed by experimental EDR of solution no. 1 (*see* Fig. 3). The conditions were the same as in case of earlier described ED experiment and the electrodes polarity was changed each 20 min. The results, presented in Fig. 4, show no significant difference of the membrane stack voltage drop between each cycle.

3.1. Prediction of calcium sulfate scaling

In the presented experiment of EDR of solution no. 1, the sum of mean residence time and its standard deviation was 760 s ($\bar{t}$ = 426 s, σ = 334 s). The induction time was calculated by semi-empirical correlation [12]:

$$t_{ind} = K \cdot S^{-r}$$

where S denotes the saturation level, $K = 1.3 \times 10^5$ [s] and r = 5.6 [13]. The calculated induction time was 71.23 s. Thus, limiting condition $t_{ind} > \bar{t} + \sqrt{\sigma^2}$ is not fulfilled, however process still can be performed. The reason is the simplification leading to a large margin of safety. Comparing only residence time distribution (by definition an exit age distribution at the module outlet) and the induction time calculated based on the saturation of solution leaving the electrodialyzer, we silently imply that the concentrate solution was supersaturated throughout the whole time it was inside the module. In reality, the solution does not become supersaturated at the very first point along the concentrate compartment, but the concentration increases as the solution flow through the compartment. Based on the presented experimental data, a new limiting condition for ED was proposed.

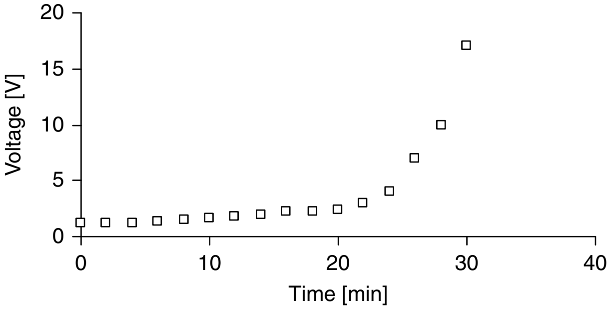


Fig. 3. Voltage drop across membrane stack during electrodialysis of solution no. 1.

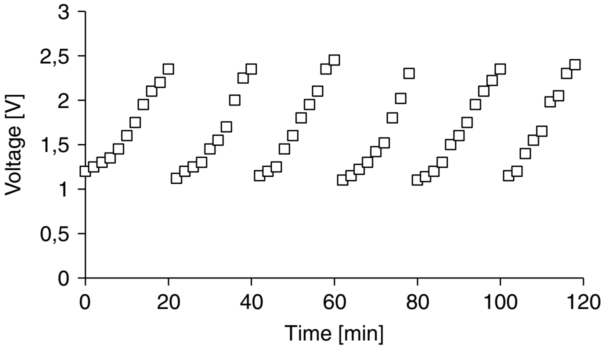


Fig. 4. Voltage drop across membrane stack during electrodialysis reversal of solution no. 1.

3.2. Discussion

Assuming the additivity of residence time and its standard deviation, one could calculate the residence time between the given point of concentrate channel and the concentrate outlet (and corresponding standard deviation) as a function of relative position along the channel:

$$t = \bar{t}\,\frac{l}{L} + \sqrt{\sigma^2\,\frac{l}{L}}$$

where t denotes the sum of residence time at its standard deviation calculated as a function of relative position, l denotes the distance between the given point of concentrate channel and the concentrate outlet and L denotes the length of concentrate channel.

The saturation level was calculated based on feed and outlet concentrations, assuming linear change along the concentrate channel. The results of calculations for solution nos. 1, 2 and 3 are presented in Tables 2, 3 and 4.

Table 2
Induction time and residence time calculations for solution no. 1

l [cm]	t [s]	S	t_{ind} [s]
50 (inlet)	760	0.74	701,852
25	449.2	2.54	702.9
20	381.6	2.90	334.6
15	310.7	3.26	173.7
10	234.6	3.62	96.6
5	148.2	3.98	56.8
0 (outlet)	0	4.34	35.0

Table 3
Induction time and residence time calculations for solution no. 2

l [cm]	t [s]	S	t_{ind} [s]
50 (inlet)	760	0.47	8,916,519
25	449.2	2.84	379.9
20	381.6	3.31	160.1
15	310.7	3.78	75.7
10	234.6	4.25	39.1
5	148.2	4.73	21.7
0 (outlet)	0	5.20	12.7

Table 4
Induction time and residence time calculations for solution no. 3

l [cm]	t[s]	S	t_{ind} [s]
50 (inlet)	760	0.45	11,375,049
25	449.2	2.72	479.0
20	381.6	3.17	201.9
15	310.7	3.63	95.5
10	234.6	4.08	49.3
5	148.2	4.54	27.3
0 (outlet)	0	4.99	16.0

The induction time and residence time can be compared on the plot – *see* Figs. 5, 6 and 7. The residence time and induction time curves enclose the area, which is proportional to the probability of calcium sulfate crystallization inside electrodialyzer. The calculated enclosed areas for solution no. 1, 2 and 3 are respectively 2085.7, 4313.7 and 3677.2 cm·s. Solution no. 1 is the least likely to crystallize, because the final concentrate supersaturation is the lowest one – 4.34, compared to 5.20 and 4.99 in case of solution nos. 2 and 3. Solution no. 3 is less likely to crystallize than solution no. 2 because of the presence of chloride anions, which increase the induction time [13].

3.3. Predictions of calcium carbonate scaling

Earlier described procedure for scaling prediction was applied for calcium bicarbonate solution ED. The results of EDR experiments at current density 23 A m^{-2} and diluate recovery 94.6% are presented in Fig. 8.

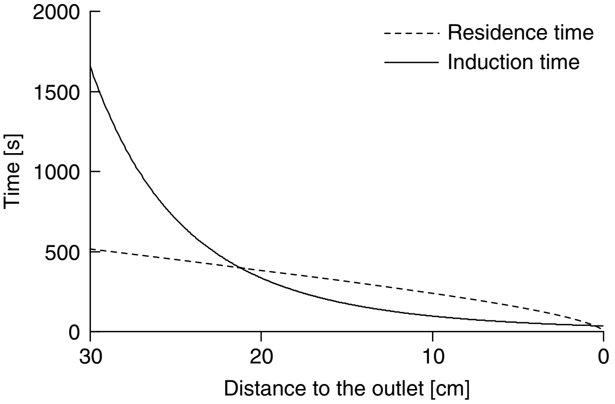


Fig. 5. Comparison of induction time and residence time for electrodialysis of solution no. 1.

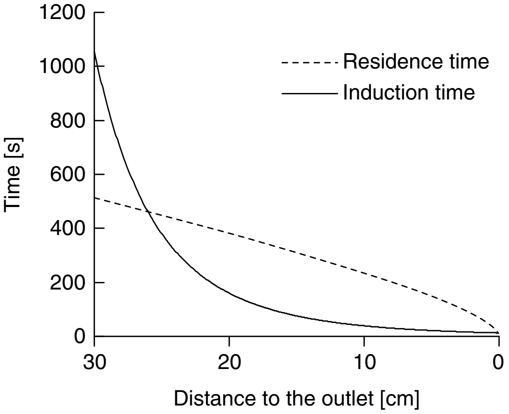


Fig. 6. Comparison of induction time and residence time for electrodialysis of solution no. 2.

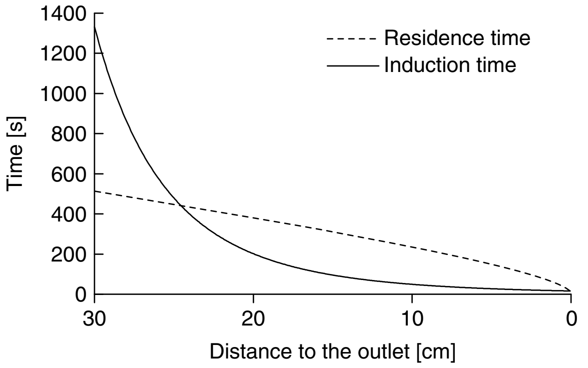


Fig. 7. Comparison of induction time and residence time for electrodialysis of solution no. 3.

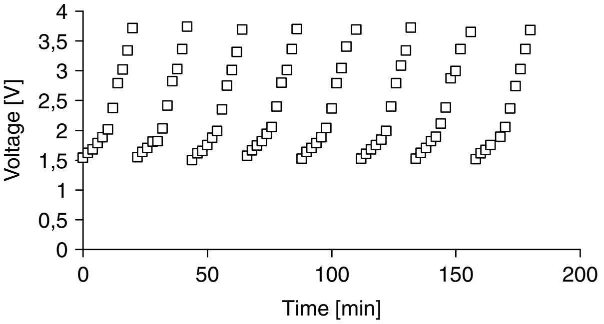


Fig. 8. EDR voltage drop across membrane stack over time, calcium carbonate feed at current density 23 A m^{-2} and diluate recovery 94.6%.

Polarity change cycle was 20 min; off-spec time was 4 min. The composition of feed, diluate and concentrate is presented in Table 5. In case of calcium carbonate traditionally the Langelier Saturation Index (LSI), not the crystallization induction time, was being used for assessment of crystallization risk. Only recently, papers investigating the relation between the LSI and the calcium carbonate crystallization induction time started to appear. Thus, data were recalculated according to the procedure given by Waly et al. [14]. According to the author, the feed water LSI was 0.41, however recalculation showed feed LSI of 0.8 and concentrate LSI of 2.3. The results of calculations of induction time and residence time are presented in Fig. 9.

Contrary to the calcium sulfate solutions, calcium bicarbonate solution's residence time and crystallization induction time curves do not intersect, which indicate no scaling. The experiments showed however, that scaling—observed as an increase in voltage drop across membrane stack, *see* Fig. 8 – does take place. The kinetic aspects of $CaCO_3$ crystallization are not as well described as in the calcium sulfate case. The calculated induction time in this case have a large margin or error and may be highly overestimated. Simultaneously, the simplifications of our method—linearity of saturation increase and additivity of mean residence time and its variance—may be the problem.

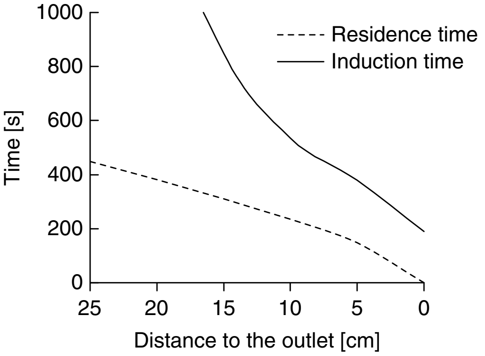


Fig. 9. Comparison of induction time and residence time for calcium bicarbonate solution.

4. Conclusions

We propose an algorithm for prediction of scaling during EDR, which is based on the two variables: sum of mean residence time and square root of its variance and crystallization induction time, both given as a function of relative position along the concentration compartment. Assuming linear increase in the saturation level along the concentrate compartment, the crystallization induction time can be given as a function of the relative position along the concentrate compartment. Assuming linear increase in the mean residence time and its

Table 5
Composition of feed, diluate and concentrate in EDR of calcium bicarbonate solution

No.	Linear flow velocity [cm s^{-1}]		Concentration [mg dm^{-3}]											
	Diluate	Concentrate	Feed				Diluate				Concentrate			
			Ca^{2+}	HCO_3^-	pH	LSI	Ca^{2+}	HCO_3^-	pH	LSI	Ca^{2+}	HCO_3^-	pH	LSI
1	7.87	0.45	184	275	7.7	0.8	48	134	7.5	0.0	1322	1224	8.0	2.3

variance, as well as additivity of mean residence time and its standard deviation, the residence time (defined as a sum of mean residence time and square root of its variance) can be given as a function of the relative position along the concentrate compartment. These two functions can be drawn as curves on the time-relative position plane, with scaling probability proportional to the area enclosed by the curves. Presented algorithm showed successful with calcium sulfate solutions, however was not suitable for analyzing the risk of calcium carbonate crystallization on the membrane surface–curves do not intersect, however voltage increase shows crystallization is observed. This can be explained by inaccurate method of crystallization induction time estimation; further investigations on calcium carbonate crystallization kinetics would probably result in more precise calculation of induction time. In addition, the method of residence time calculation is simplified and can be fully applied only in case of relatively small dispersion. The assumed limiting condition (induction time larger than residence time and its standard deviation) may be an oversimplification of complex crystallization process. Despite all simplifications, the proposed limiting condition can be to some extent applied in design of electrodialyzers and EDR installations and can lead to increase the desalination efficiency, allowing longer work without the polarization change.

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