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Removal of metal contaminants from salts and brines

Summary of Ph.D. Thesis

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1. Introduction, aim of the research work

Chlorine production in chemical plants is generally based on the electrolysis of sodium chloride (NaCl) solution, yielding hydrogen gas and NaOH solution as co-products, which are highly important chemical feedstocks. In the past, mercury-cell electrolysis was widely used; however, under the provisions of the Minamata Convention, it has been phased out in most countries and largely replaced by membrane-cell electrolysis.¹ This latter method represents the Best Available Techniques (BAT) for chlorine production and offers both economic and ecological advantages over the mercury-cell and diaphragm-cell processes.^{2,3,4}

Membrane-cell technology, however, requires brine feedstocks of significantly higher purity than those used previously – specifically, brines containing metallic impurities only in the parts-per-billion (ppb, mass-based) range. Even below ppm (mg/kg) concentrations of metal contaminants can severely damage the cell membranes, leading to shortened membrane lifespans, contamination of the products, and increased specific energy consumption.³ The main metallic impurities to be removed include Al, Ca, Mg, Sr, Ba, and Fe, in addition to silicon dioxide (SiO₂).

Our investigations were carried out in a real industrial environment, in cooperation with Hungary's leading chlorine producer, BorsodChem Ltd., ensuring that the scientific results are followed by practical industrial implementation. During problem identification, it was revealed that aluminum content posed the most significant issue for the company, as it most significantly deviated from BAT reference values. The novelty of our research lies in the fact that, while most studies in the literature focus primarily on the removal of alkaline earth metal ions, the present work places special emphasis on the removal of other ions – particularly Al³⁺ – from concentrated brines.

The purification procedures primarily involve the formation of poorly soluble hydroxide or carbonate salts from Fe³⁺, Ca²⁺, and Mg²⁺ ions, which are then removed by sedimentation and filtration. Residual alkaline earth metal ions remaining in solution are typically removed by ion exchange.³

Our main goal was to achieve the most complete possible removal of contaminants from brine used in membrane-cell electrolysis and to optimize the removal processes. This required, above all, the development or adaptation of analytical methods capable of determining impurities – especially dissolved aluminum content – in the ppb range within highly saline matrices, in a manner suitable for industrial application, yet offering high sensitivity and low detection and quantification limits. Following the development of suitable analytical methods, we aimed to identify the impurities present in the salts and saturated brines used for electrolysis (including recycle streams from other plants within BorsodChem Ltd.) and to determine which contaminants require further removal process improvements to enhance overall efficiency.

Subsequently, we sought to optimize the first major step in purification: precipitation, along with the subsequent coagulation, flocculation, and sedimentation of the precipitate. This included the removal of key metallic impurities (alkaline earth metals, aluminum, iron) as well as silicon dioxide. We aimed to conduct extensive experiments on how various process parameters – such as pH, temperature, type and concentration of flocculant, and brine composition – affect purification efficiency, thereby improving removal effectiveness.

Furthermore, we intended to study ion exchange methods for removing residual impurity ions, with a particular focus on optimizing Al³⁺ removal. This involved assessing the aluminum-binding capacity of ion exchange resins from various manufacturers, with different functional groups, while examining the

¹H. Selin, S. E. Keane, S. Wang, N. E. Selin, K. Davis, D. Bally (2018) *Ambio* 47:198-215.

²P. Schmittinger, T. Florkiewicz, L. C. Curlin, B. Lüke, R. Scannell, T. Navin, E. Zelfel, R. Bartsch (2012) Chlorine. *Ullmann's Encyclopedia of Industrial Chemistry* 8th edition, 532-621, Wiley, Weinheim, Germany.

³European Commission (2014) JRC Publications Repository - Best Available Techniques (BAT) Reference Document for the Production of Chlor-alkali. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control) [Online] <https://publications.jrc.ec.europa.eu/repository/handle/JRC91156>. [Date of access: January 15, 2025.]

⁴G. Pátzay, A. Tungler, L. T. Mika (2011) A klór-alkáli elektrolízis. *Kémiai Technológia*, 61-64, Typotex, Budapest, Hungary.

effect of pH on the capacity. After that, we optimized further operational parameters such as temperature, resin bed geometry, and flow conditions. Our findings may contribute to extending the service life of electrolysis membranes. In addition to binding capacity, we also aimed to optimize resin regeneration methods to determine the longest feasible operational cycle between regenerations, and to identify the most effective regeneration conditions (type, concentration, and flow rate of regenerant, etc.).

Our experimental work was also intended to be complemented by simulation analysis and sensitivity studies. A further goal was to simulate the purification units of the brine circuit at the system level, allowing for the detection of interactions between different technological units. Additionally, we planned to simulate the ion exchange step in detail to support experimental work by selecting the most promising experimental parameters, thereby shortening development time and facilitating scale-up studies.

2. Literature background

Although numerous methods are available for the accurate determination of trace levels of aluminum, these typically involve high capital and operational costs (e.g., GF-AAS, ICP-AES).⁵ Spectrophotometric techniques offer a promising alternative for aluminum measurement as well. These methods generally employ organic complexing agents that selectively form colored complexes with the target metal. Based on our literature review, the bidentate ligand eriochrome cyanine R (ECR) stands out in terms of sensitivity; although several authors have studied it, to the best of our knowledge, it has not yet been applied in highly saline media.⁶

Shokrollahi et al.⁶ developed a spectrophotometric method capable of determining dissolved aluminum concentrations between 4 and 400 ppb. However, their study found that at $\text{Na}^+/\text{Al}^{3+}$ or $\text{Cl}^-/\text{Al}^{3+}$ molar ratios above 500:1, the method was no longer applicable due to significant interference effects. The authors increased the sensitivity of the measurement by adding a cationic surfactant. This method served as the foundation for our own method development. During the investigation of pH dependence, it was crucial to use buffer systems that would not engage in unwanted side reactions with the components present, while maintaining appropriate acid dissociation constants and sufficient solubility. An acetic acid–sodium acetate buffer was suitable around pH 5, but above this pH, other buffers were required. The biological buffers developed by Good and colleagues appeared promising for this purpose.⁷

Various authors have investigated options for purifying salts and brine solutions. These approaches are typically based on precipitation, filtration, coagulation, flocculation, sedimentation, adsorption, and ion exchange.^{8,9,10,11,12,13,14,15} However, there are also studies that employ ultra-, micro-, and nanofiltration,¹² membrane operations, steam distillation, extraction, stripping, photochemical oxidation, flotation,^{9,16} electrocoagulation, reverse osmosis, and membrane distillation.¹² Some of these methods are not feasible for scale-up,¹⁶ others involve prohibitively expensive steps,¹² and some employ aluminum-based flocculants or coagulants,^{9,15,16,17} or increasing the aluminum content of the system to promote

⁵M. Frankowski, A. Ziola-Frankowska, I. Kurzyca, K. Novotny, T. Vaculovic, V. Kanicky, M. Siepak, J. Siepak (2011) *Environmental Monitoring and Assessment* 182:71-84.

⁶A. Shokrollahi, M. Ghaedi, M. S. Niband, H. R. Rajabi (2008) *Journal of Hazardous Materials* 151(2-3):642-648.

⁷N. E. Good, G. D. Winget, W. Winter, T. N. Connolly, S. Izawa, R. M. Singh (1966) *Biochemistry* 5(2):467-477.

⁸M. A. Aghdam, F. Zraick, J. Simon, J. Farrell, S. A. Snyder (2016) *Desalination* 385:69-74.

⁹M. A. Marcin, T. R. Sage (2017) U.S. Patent No. 9,719,179 B2, August 1, 2017.

¹⁰S. Harrison, J. Burba (2020) U.S. Patent No. 10,829,676 B2, November 10, 2020.

¹¹X. Luo, C. Wei, X. Li, Z. Deng, M. Li, G. Fan (2022) *Separation and Purification Technology* 296:121367.

¹²R. Chidambaran, N. S. Bisht, P. Raina (2014) WO Patent No. 2014/088826 A1, June 12, 2014.

¹³X. Luo, X. Li, C. Wei, X. Shi, S. Zheng, Z. Deng (2021) *Separation and Purification Technology* 267:118676

¹⁴M. J. Adelman, R. Newman, H. Seshan, M. Z. Afifi, M. Dornfeld, J. R. Quicho (2018) The impact of brine on primary settling of wastewater. *Water Environment Federation* [Online] <https://www.accesswater.org/publications/proceedings/-299530/the-impact-of-brine-on-primary-settling-of-wastewater>. [Date of access: May 10, 2024.]

¹⁵C. H. Lee, Y. J. Kim, S. H. Moon, S. H. Kwon, K. H. Ahn (2022) *Journal of Environmental Science International* 31(1):1-8.

¹⁶B. Abada, S. Joag, R. Sharma, S. Chellam (2022) *Water Research* 226:119241.

¹⁷S. Kvech, M. Edwards (2002) *Water Research* 36(17):4356-4368.

precipitation.^{10,18} Consequently, the effective removal of aluminum from electrolytic brines required a novel approach and extensive experimental development.

The chemistry of dissolved aluminum in dilute aqueous solutions has been extensively studied. Aluminum generally precipitates as a colloidal solid between pH 4 and 10. In mildly acidic environments, the precipitate typically forms a stable sol that does not settle, whereas in mildly alkaline conditions, sedimentation becomes dominant, as surface-adsorbed ions no longer stabilize the sol particles.^{19,20} Kvech and Edwards¹⁷ demonstrated that sulfate ions significantly destabilize positively charged aluminum hydroxide sols in dilute aqueous media, thereby promoting aggregation of the colloidal precipitate. Additionally, above pH 9.5, they experimentally confirmed that the presence of magnesium, aluminum, and silicon mutually reduced each other's solubility. According to the literature, the conventional method for silicon dioxide precipitation is co-precipitation with magnesium,²¹ although the presence of iron, aluminum, or calcium ions can also be beneficial.²² These findings provided the basis for the design of our own experiments.

Studies on the ion exchange removal of aluminum are scarce in the literature. However, Virolainen et al.²³ applied an ion exchange resin with aminomethylphosphonic acid (AMP) functional groups (Lewatit TP260) for removing Al, Fe, Mn, and Cu from leachates of lithium-ion batteries. Elution of iron and aluminum from the resin beads was achieved with 0.4 M potassium oxalate, while manganese and copper were eluted with 2 M sulfuric acid. In terms of regeneration, they also tested sulfuric acid, nitric acid, hydrochloric acid, a mixed hydrochloric acid–sodium chloride solution, sodium citrate and ethylenediaminetetraacetate, but these were significantly less effective than potassium oxalate. Compared to other ion exchangers with iminodiacetate, sulfonic acid, and carboxylic acid functional groups, the AMP resin was highly efficient for aluminum binding at 60 °C, with an optimal pH of 3. However, the initial aluminum concentration was 1.3 g/l, which is three orders of magnitude higher than in our brine solution and four to five orders of magnitude above the desired threshold, making direct comparison difficult. Nevertheless, we selected ion exchange resins with AMP groups for our experiments.

System-level simulation of brine purification or other water treatment processes can be achieved using appropriate process simulation software such as Aspen Plus, ChemCAD, or UniSim Design. Alternatively, individual units can be simulated using custom code.^{24,25} A relevant example for the system-level simulation of a brine purification circuit is the study conducted by Fengmin et al.²⁴ using Aspen Plus. Ma et al.²⁵ investigated Ni²⁺ removal from wastewater using an iminodiacetate ion exchange resin and their own custom simulation code. Their program described intraparticle transport in resin beads using the Homogeneous Surface Diffusion Model (HSDM). This method appeared promising for the detailed modeling of the ion exchange process used in brine purification.

3. Experimental and computational methods

During the development of an analytical method for the determination of trace amounts of aluminum in brine solutions, I investigated a spectrophotometric procedure based on complex formation with the promising ECR ligand. To this end, an ECR reagent solution was prepared, and cetyltrimethylammonium bromide (CTAB) was used to further enhance the sensitivity. Calibration was performed using brine

¹⁸E. T. Nurmesniemi, T. Hu, K. Rajaniemi, U. Lassi (2021) *Desalination and Water Treatment* 217:195-202.

¹⁹A. J. Rubin, L. Hayden (1973) *Studies on the hydrolysis and precipitation of Aluminum(III)*, Ohio State University, Columbus, Ohio, USA.

²⁰J. D. Hem, C. E. Roberson (1967) *Form and stability of aluminum hydroxide complexes in dilute solution*, United States Government Printing Office, Washington, USA.

²¹P. Meyers (1999) *IWC* 99(64):1-10.

²²D. M. Thomas (1992) Silica recovery and control in Hawaiian geothermal fluids. Final report. *U.S. Department of Energy Office of Scientific and Technical Information* [Online] <https://www.osti.gov/servlets/purl/10179299>. [Date of access: April 15, 2025.]

²³S. Virolainen, T. Wesselborg, A. Kaukinen, T. Sainio (2021) *Hydrometallurgy* 202:105602.

²⁴D. Fengmin, D. M. Warsinger, T. I. Urmi, G. P. Thiel, A. Kumar, J. H. V. Lienhard (2018) *Environmental Science & Technology* 52(10):5949-5958.

²⁵A. Ma, A. Abushaikha, S. J. Allen, G. McKay (2019) *Chemical Engineering Journal* 358:1-10.

solutions with known aluminum content under various conditions. In the course of the method development, I studied the effects of salt concentration, pH, temperature, wavelength, and elapsed time after reagent addition on the measured absorbance signals, the sensitivity of the method, and the correlation coefficient (R^2) of the calibration curve. Under optimized conditions, I determined the analytical performance characteristics of the method using various buffer systems (acetate, HEPES, MOPS, Tris), and validated the method with standard solutions of known concentrations. Proper photometric methods was also successfully adapted for the determination of magnesium and silicon.

For the investigation of brine purification via precipitation, coagulation, flocculation, and sedimentation, a nearly saturated (25 w%) solution was prepared from Transylvanian rock salt, the same type used by BorsodChem Ltd. The pH of the solution was adjusted to the desired value at 60 °C. In certain experiments, a polyacrylamide-type flocculant was also added to the system. The brine was then placed in a thermostated reactor, and sedimentation was studied for 4 hours. Removal efficiency was evaluated based on the decrease in contaminant concentrations in samples taken from the surface of the solution. Dissolved aluminum was measured using the spectrophotometric method I developed, while total concentrations of other metal contaminants were monitored by ICP-AES. This approach allowed for the optimization of pH, flocculant type and concentration, and sedimentation time. The interactions between different metal contaminants during precipitation were investigated through model experiments following a similar methodology. For these experiments, pre-treated brine obtained from the industrial process was used, and varying amounts of contaminant ions were added. For the removal of SiO_2 , plastic apparatus was employed. Additional model experiments were conducted with laboratory-grade chemicals to study the effects of flocculant concentration and the mutual influence of metal ions on each other's removal. The morphology and composition of precipitates were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD); aggregation processes were studied by dynamic light scattering (DLS), and microphase charge characteristics were assessed via zeta potential measurements. The solubility of the precipitates was also investigated in brine solutions at different pH values.

In the investigation of ion exchange processes, I first characterized the ion exchange resins and then studied the aluminum-binding capacities of the most promising ones. To this end, a known volume of resin was agitated with brine solutions of known weight and aluminum content, buffered to different pH values. The unbound aluminum content was measured under equilibrium conditions using the developed photometric method, and the resin capacity was calculated using component balance equations. At the optimized pH values, both batch and dynamic sorption experiments were conducted. From batch experiments, I determined the overall mass transfer coefficient and kinetically compared the performance of the tested resins. In the dynamic sorption experiments, I studied the aluminum-binding behavior of resins at various levels of saturation relative to their total capacity, at the optimal pH and under thermostated conditions, recording breakthrough curves at different temperatures and for different resin types. Additionally, the effect of resin bed geometry was assessed by loading the same amount of resin into columns with different diameter-to-height ratios while keeping all other parameters constant. Finally, I optimized the regeneration conditions of the aluminum-binding resins, including cycle time, type, concentration, volume, and flow rate of regenerants, as well as the sequence of regenerant application. Aluminum content in regenerant solutions were determined using the photometric method I developed.

For the system-level simulation of the brine circuit, Aspen Plus software was used. The model incorporated brine recirculation; precipitation processes facilitated by NaOH and Na_2CO_3 ; sedimentation and filtration; two-step ion exchange for alkaline earth metal removal; one-step ion exchange for aluminum removal; and the recycling of regenerants formed during resin regeneration. Using the developed model, sensitivity analyses were performed to evaluate the impact of brine composition, dosage of precipitant reagents, and temperature on removal efficiency. A custom-built Python program, based on the Homogeneous Surface Diffusion Model (HSDM) and employing the Crank-Nicolson algorithm, was used for detailed modeling of the ion exchange process. This program enabled comprehensive sensitivity analyses by mapping the influence of various parameters, such as feed brine composition, resin quantity, column geometry, and flow rate. Breakthrough curves, as well as isotherms, isoplanes, and isochrons, were generated under different conditions. The cyclic operation of the resin bed was also investigated.

4. Results

4.1. Development of a spectrophotometric method for the determination of trace aluminium in concentrated saline media

Based on our experiments, it was found that dissolved aluminum can be determined spectrophotometrically in high-concentration NaCl samples using ECR reagent as a complexing ligand in the presence of a cationic surfactant, within a trace concentration range of 5.9–690 ppb. Not only is the measurement feasible in concentrated saline media, but increasing the salt concentration significantly enhances the method's sensitivity (see Figure 1). Thus, despite using liquid reagent solutions – rather than solid reactants – for ease of handling, which results in sample dilution, a similar dynamic range can be achieved as with diluted solutions using solid-phase reagents.

In summary, the analytical procedure can be performed as follows:

- Add a volume of ECR reagent solution corresponding to one-sixth of the sample mass, with a concentration of 0.08000 w%.
- Add a volume of CTAB-buffer solution corresponding to one-third of the initial sample mass. The CTAB concentration in this solution is 0.546 w%. The buffer concentrations are as follows:
 - Acetate: 35.8 w% CH₃COONa · 3H₂O, 2.37 w% acetic acid
 - Tris-HCl: 22,5 w% 22.5 w% Tris, with pH adjusted to 7.0 using hydrochloric acid.
 - MOPS-NaOH: 13.5 w% MOPS, with pH adjusted to 6.5 using NaOH solution
 - HEPES-NaOH: 18 w% HEPES, with pH adjusted to 6.2 using NaOH solution
- After mixing, the absorbance of the sample should be measured after the following waiting periods, depending on the buffer system: 15-90 min for acetate, 2-8 h for MOPS, 4-24 h for HEPES, 4-8 h for Tris. The aluminum concentration can then be determined using the appropriate calibration curve – previously recorded for the relevant salt content – taking into account the dilution factor.

The analytical performance characteristics obtained for the procedure using each buffer system are summarized in Table 1.

Table 1: Analytical performance characteristics of the spectrophotometric method developed for Al determination.

	Acetate (pH 5.0)	HEPES (pH 6.2)	MOPS (pH 6.5)	Tris (pH 7.0)
Limit of detection	2.5 ppb	1.8 ppb	2.0 ppb	1.9 ppb
Limit of quantification	8.4 ppb	5.9 ppb	6.8 ppb	6.3 ppb
Sensitivity (<i>S</i>)	2.897 ppm ⁻¹	3.846 ppm ⁻¹	3.911 ppm ⁻¹	4.001 ppm ⁻¹
Molar absorption coefficient	1.05 · 10 ⁵ Lmol ⁻¹ cm ⁻¹	1.39 · 10 ⁵ Lmol ⁻¹ cm ⁻¹	1.42 · 10 ⁵ Lmol ⁻¹ cm ⁻¹	1.45 · 10 ⁵ Lmol ⁻¹ cm ⁻¹
Dynamic range	8.4-690 ppb	5.9-469 ppb	6.8-470 ppb	6.3-349 ppb

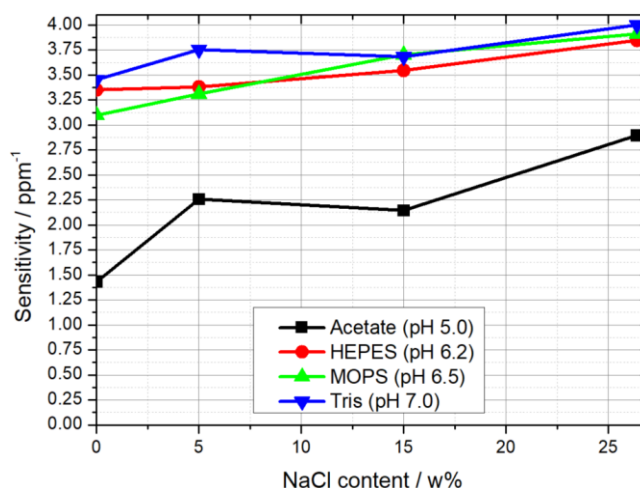


Figure 1: Effect of the NaCl content of the sample on the sensitivity of the measurement for each buffer system.

Compared to measurements performed at pH 5 in an acetic acid–sodium acetate buffer system, adjusting the pH to 6.2–7.0 using suitable biological buffers (HEPES, MOPS, Tris) increases the measurement sensitivity by 32.8–38.1%, depending on the buffer type, in high-salt-content samples. An additional advantage of procedures using biological buffers is that sensitivity is much less affected by variations in salt concentration compared to the acetic acid–sodium acetate buffer system. This makes it possible to perform preliminary measurements even without first determining the sample's salt content or preparing a specific calibration curve for it (some calibration required). However, unlike the acetic acid–acetate buffer where an adequate signal develops within 15–20 minutes, it takes about 2 hours with MOPS buffer and approximately 4 hours with both HEPES and Tris buffers. Although this prolongs the measurement, the resulting signal remains stable for a significantly longer period than in a pH 5 environment. Examining the influence of temperature, it was found that accurate results require the measurement to be performed at the calibration temperature, or at most a few °C from it. Temperature-related disturbances were most pronounced with the Tris buffer. Another disadvantage of using Tris is its higher blank absorbance, which narrows the dynamic range.

Among the three biological buffers examined, the use of MOPS buffer is considered most advantageous. A further benefit of the MOPS system is that no variation in the optimal measurement pH was observed across different aluminum concentrations. Comparing the characteristics of the method using MOPS buffer to that using the acetic acid–acetate buffer system in concentrated saline media, it can be concluded that both approaches offer certain advantages over the other. The acetic acid–sodium acetate system yields faster results and uses a more common and cost-effective buffer. In contrast, the MOPS buffer ensures greater sensitivity and provides lower limits of detection and quantification. The selection of the applied method should always be based on the specific goals and available resources. We confirmed that both the acetic acid–acetate system and the three biological buffers tested allow for the determination of trace-level (ppb-range) aluminum content even in high-salt matrices. The developed measurement method offers advantages in its simplicity, speed, and minimal equipment requirements, as it can be implemented using a standard UV-Vis spectrophotometer, unlike ICP-AES or GF-AAS methods. This approach is suitable for both industrial applications and scientific research purposes.

4.2. Optimization of the precipitation, coagulation, flocculation and sedimentation steps of the brine purification process

The first major step of the brine purification procedure – precipitation, coagulation, flocculation, and sedimentation – was studied in the pH range of 3 to 12. We found that aluminum precipitation is most effective at pH 5 and pH 11 in a 25 w% solution of the studied rock salt, as the lowest dissolved aluminum concentrations were measured at these values. Although aluminum precipitates with similar efficiency at both pH levels, the resulting precipitate sediments significantly more effectively at pH 11 than at pH 5. This is indicated by a much more rapid decrease in the total aluminum content, which closely follows the decline in dissolved aluminum concentration. This phenomenon is illustrated in Figure 2.

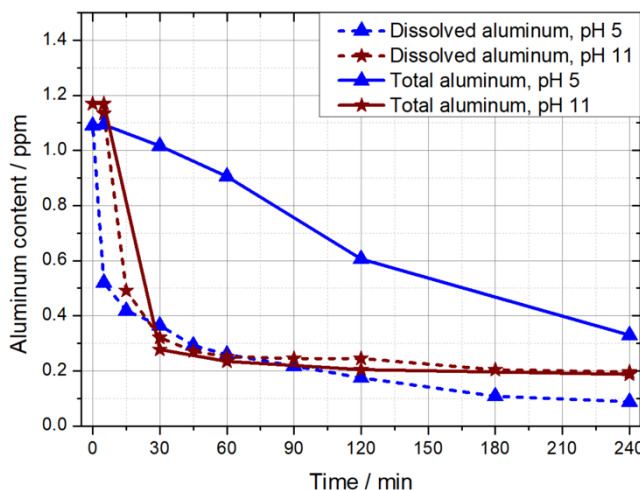


Figure 2: Effect of aluminum precipitation and sedimentation on the dissolved and total aluminum concentrations measured in the upper 1 cm layer of the solution at the optimal pH values.

We also investigated the behavior of other metals. Calcium did not sediment below pH 11; at pH 11, its concentration stabilized at 100–110 ppm after 30 minutes, and at pH 12 it dropped below 10 ppm after 2 hours. Magnesium did not sediment below pH 9, but with increasing pH, lower Mg concentrations were measured. For example, at pH 11, after 2 hours, the Mg concentration stabilized below 0.2 ppm. Strontium and barium did not sediment at any point within the studied conditions (pH 3–12, 60 °C), with starting concentrations of Sr at 1.8–2.1 ppm and Ba at 25–30 ppb. The behavior of iron was somewhat similar to that of aluminum, with alkaline pH values between 10 and 12 being most favorable. At the optimal pH of 11, the initial iron concentration of 1.29 ppm decreased to 0.33 ppm after 30 minutes, 0.11 ppm after 120 minutes, and 0.04 ppm after 240 minutes. Even pH 6 showed a moderately favorable effect, although slightly less so than alkaline conditions.

The behavior observed for aluminum was inconsistent with known solubility limits in dilute solutions – limits that result from its amphoteric nature and the formation of aluminate complexes – as well as with our own solubility measurements in concentrated saline media. However, we demonstrated that aluminum’s altered behavior is caused by the presence of Ca and Mg. Based on our model experiments, Ca and Mg significantly reduce aluminum solubility under the examined conditions, and the resulting precipitates sediment well, as shown in Figure 3. In the absence of Ca and Mg, but with the presence of other ions (e.g., iron, silicate), we observed no such effect under otherwise identical conditions.

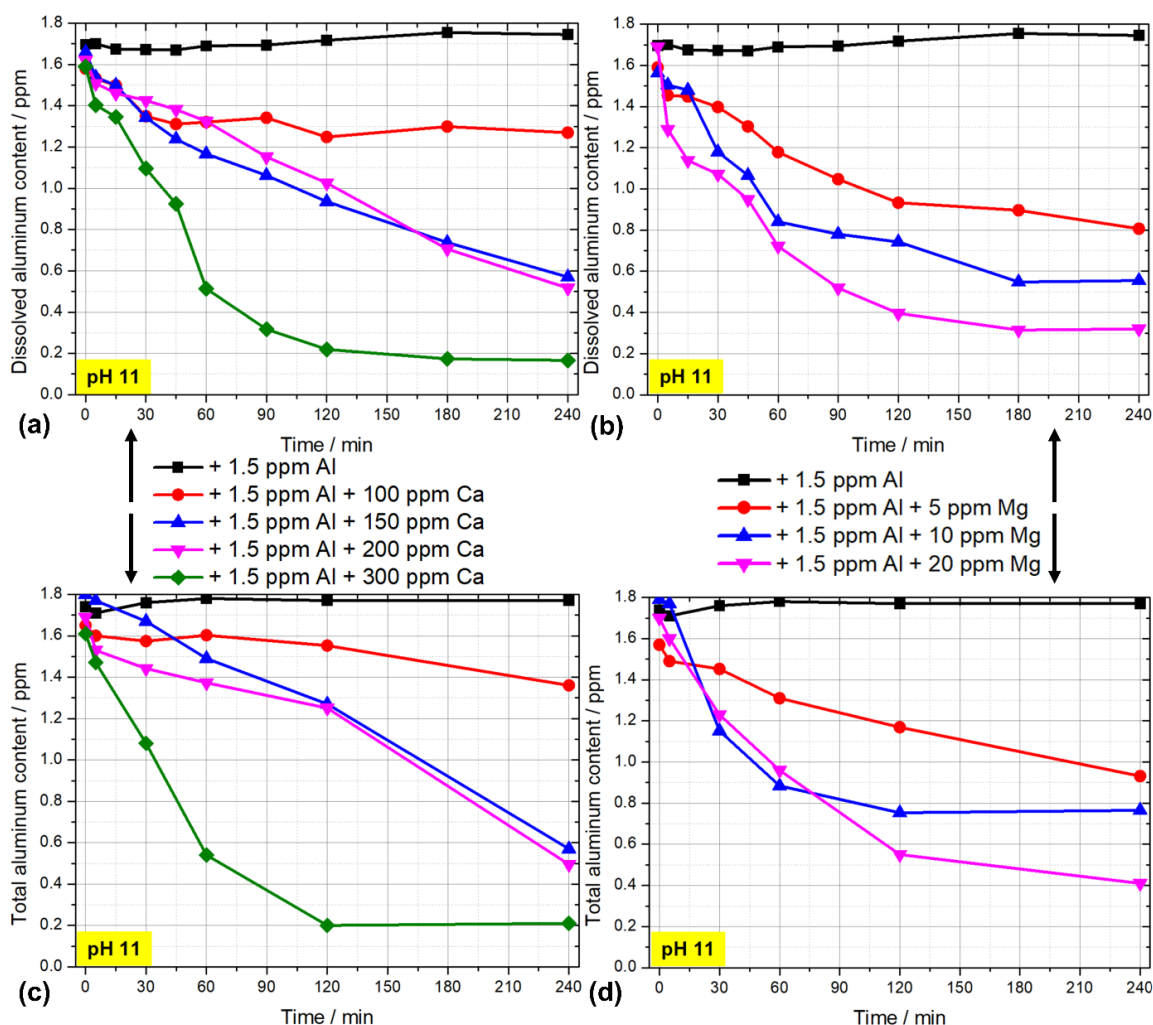


Figure 3: Effect of calcium (a, c) and magnesium (b, d) on the surface Al content (pH 11, 60 °C).

XRD analysis of the precipitates confirmed the formation of mixed compounds of aluminum with calcium and magnesium, specifically hydrocalumite and hydrotalcite (see Figure 4). This proves that calcium and magnesium facilitate aluminum precipitation by forming poorly soluble, co-precipitating compounds. Moreover, calcium also promotes the removal of SiO₂ (see Figure 5). The pH dependence of calcium, magnesium, and iron removal in the presence of Na₂CO₃ was studied using Aspen Plus simulations (see Figure 6), which indicate that the optimal pH for removal is above 10.

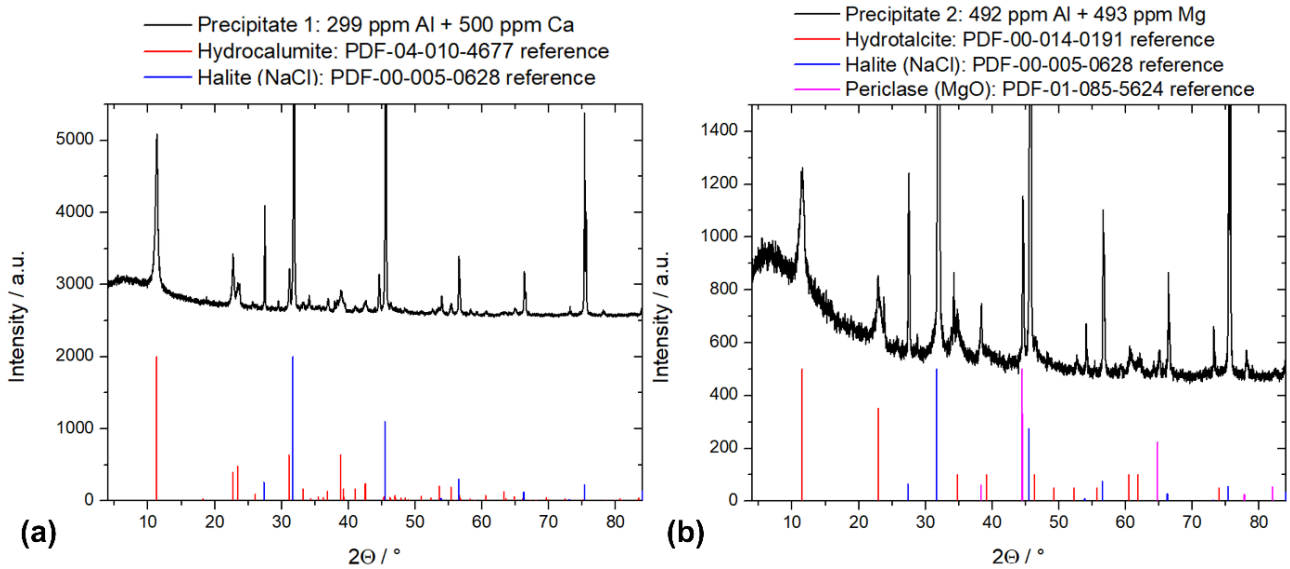


Figure 4: XRD diffractograms and identification of isolated precipitates at pH 11. Initial brine composition: 299 ppm Al + 500 ppm Ca (a); 492 ppm Al + 493 ppm Mg (b).

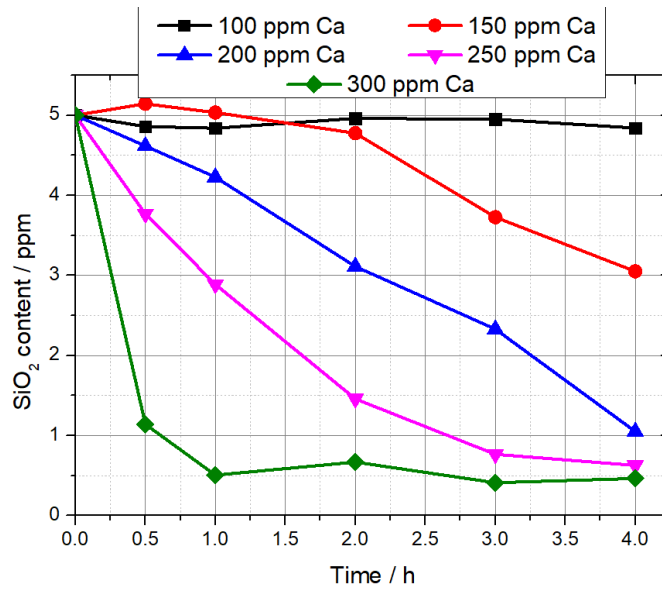


Figure 5: Effect of calcium on the reduction of silica content of concentrated brine by precipitation at pH 11 and 60 °C.

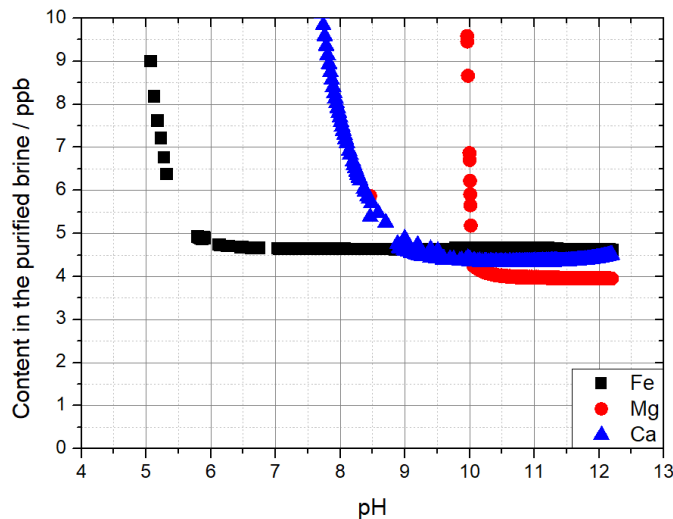


Figure 6: Removability of each metal contaminant as a function of pH in the presence of Na₂CO₃, based on Aspen Plus simulation.

We also showed that the calcium and magnesium content of the starting brine – and thus of the resulting precipitate – not only enhances the precipitation and sedimentation process but also inhibits redissolution of the precipitate. This inhibition occurs in both acidic (pH 3) and alkaline (pH 11) brine due to the formation of precipitates that are less soluble than $\text{Al}(\text{OH})_3$. These findings are promising from an industrial perspective, as they suggest that modifying only the pH during the precipitation and sedimentation steps may significantly improve aluminum removal without the need to add external reagents or introduce foreign substances into the system, since calcium and magnesium ions are already naturally present in the raw rock salt. According to our results, the very impurities themselves support each other's precipitation under appropriately chosen conditions.

4.3. Optimization of the ion exchange step of the brine purification process

Following the precipitation-based removal, we also investigated the ion exchange removal of metal ions remaining in solution. To this end, several ion exchange resins were characterized. We found that ion exchange resins with aminomethylphosphonic acid functional groups are effective for aluminum removal. For these resins, the optimal pH for aluminum binding is between 2.5 and 3.0, where the maximum capacity is observed. This optimal pH differs significantly from the mildly alkaline conditions ideal for the removal of alkaline earth metals using resins with iminodiacetate functional groups. Therefore, a separate ion exchange column is required for aluminum removal, as simultaneous removal with alkaline earth metal ions using a mixed resin in a same column is not feasible.

We tested various aminomethylphosphonic acid functional group resins from different suppliers and recorded breakthrough curves as a function of temperature, which are shown in Figure 7. Our results demonstrated that a capacity utilization exceeding 50% can be achieved while maintaining the aluminum concentration limit of 0.1 ppm required for membrane cell technology. The extended cycle time reduces fluctuations in the Al content of brine fed to the cell (as the column spends less time in the regeneration step) and lowers the amount of chemicals needed for regeneration, leading to significant cost savings.

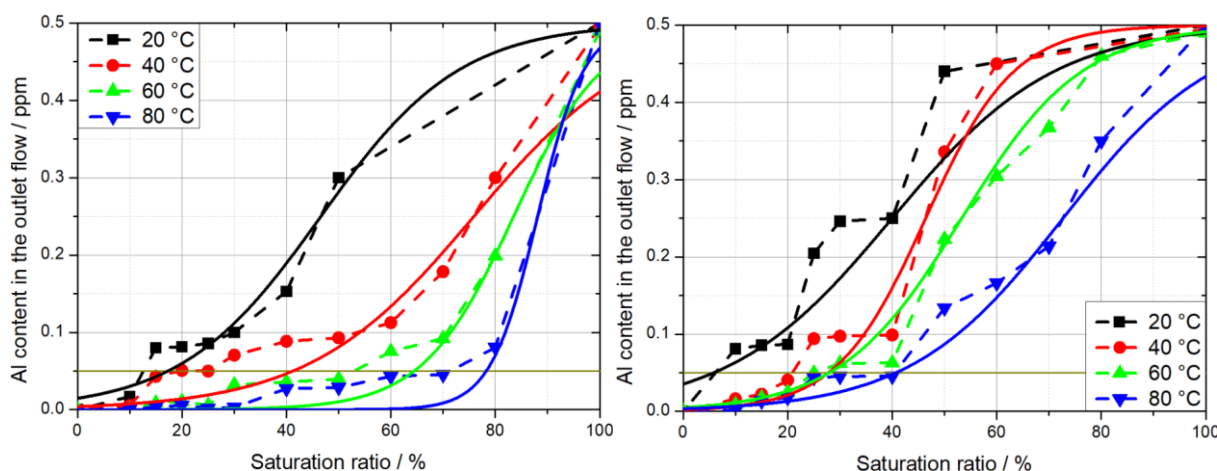


Figure 7: Effect of temperature and degree of saturation on the Al-binding capacity of aminomethylphosphonic acid functional group ion exchange resins, left for the European producer and right for the Asian producer. The dashed line is used only to guide the eye, while the solid line indicates the fit according to the logistic function.

In optimizing the regeneration method for the aminomethylphosphonic acid resins used for aluminum binding, we found that hydrochloric acid – used previously for regeneration – can generally be omitted (though a hydrochloric acid rinse is still recommended every 10 cycles to remove other bound metal ions). Aluminum is effectively eluted during the alkaline washing step. To our knowledge, no previous studies have examined a similar regeneration method, which offers additional savings in chemical usage and costs, as well as a reduction in regeneration time.

The ion exchange process was thoroughly simulated using a custom-built program based on the homogeneous surface diffusion model. The effects of the brine composition, flow rate, resin quantity, and bed geometry were investigated, including modeling for scale-up to industrial dimensions. The resulting breakthrough curves, isoplans, and isochrones were consistent with our experimental data. We

demonstrated that the ion exchange column can still fulfill its function even if the current brine flow rate of 30 BV/h (bed volumes per hour) is doubled. Furthermore, we showed that an increase in the inlet aluminum concentration causes only a minor decrease in breakthrough time (see Figure 8), which we attribute to the increased driving force for mass transfer at higher liquid-phase concentrations.

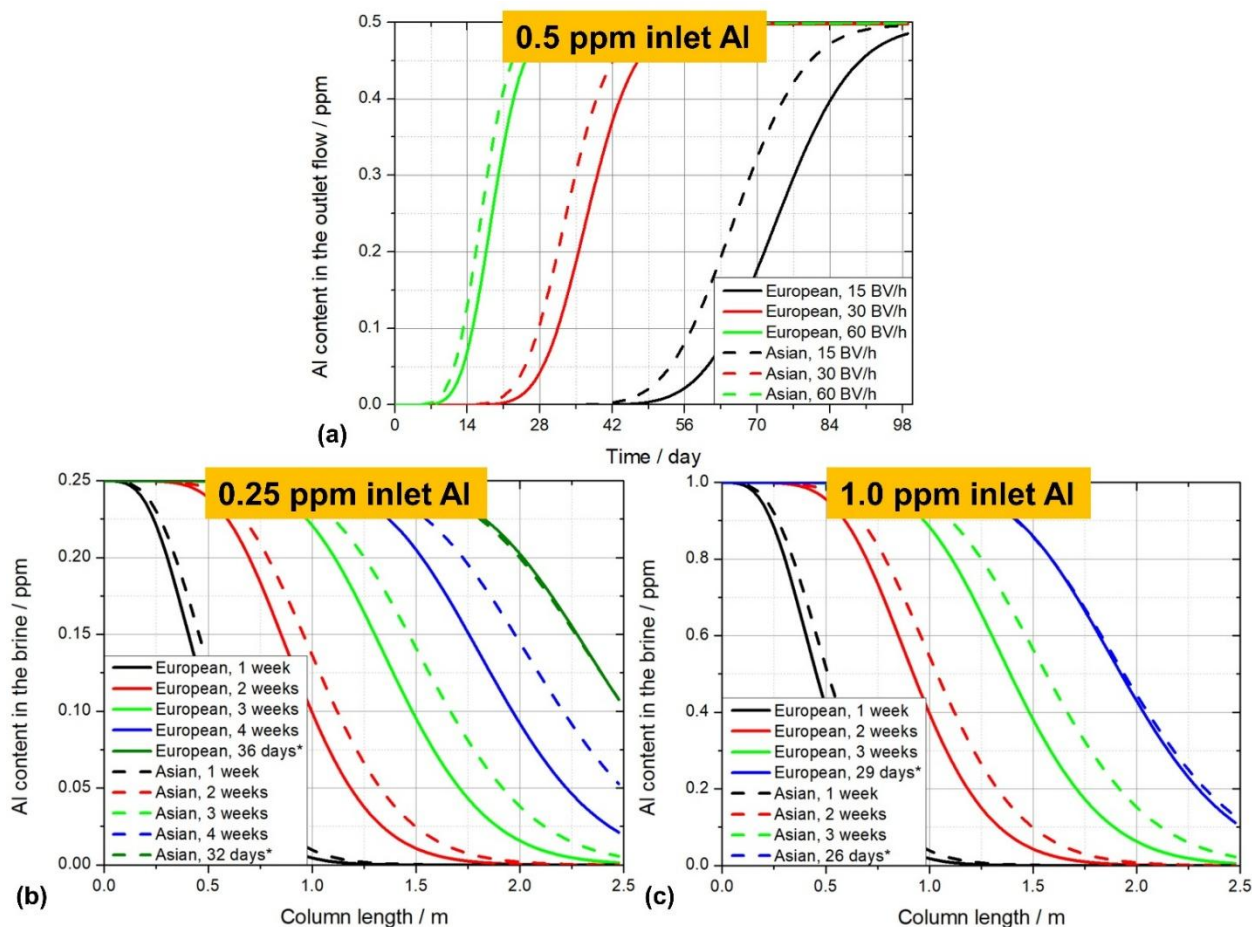


Figure 8: Simulation results based on the HSD model for plant-scale ion exchange: effect of inlet brine flow rate (top) and Al content (bottom). The breakthrough is marked with *.

5. Application

The results of my research are directly applicable in industrial practice. They have been presented quarterly to the Senior management of BorsodChem Ltd., and were also showcased during the Technological Forum in 2023, where the company’s executive leadership was in attendance. In addition to these formal presentations, the results were communicated quarterly to plant experts as well, supplementing other regular consultations. In recognition of the industrial relevance of my achievements, I received the “For Exemplary Work” award from the CEO of BorsodChem Ltd. for the year 2023.

The spectrophotometric method developed for the determination of trace dissolved aluminum content in concentrated brine solutions has been continuously used in subsequent developmental work about aluminum removal and various industrial measurements and monitoring tasks. I am also aware that our published method is being applied in the laboratory of another European chlor-alkali company.

Some of the optimization results regarding brine purification have already been implemented by the Chlorine Plant of BorsodChem Ltd. For example, the installation and commissioning of a new ion exchange column dedicated exclusively to aluminum removal – separated from alkaline earth metal binding – has already been completed. Other developments, such as the system required to establish and maintain the optimal pH conditions for the aluminum-binding column, are currently underway. Of course, some improvements are only expected to be implemented in the future.

I hope that my results will contribute to the advancement of the chlor-alkali industry and, by extension, to the growth of the Hungarian economy.

6. Thesis findings

1. I developed a spectrophotometric measurement method for determining trace amounts (in the ng/g range) of dissolved aluminum in concentrated brine solutions. Through experimental work, I demonstrated that the interference caused by Na^+ and Cl^- ions can be eliminated during spectrophotometric determination of dissolved aluminum using eriochrome cyanine R (ECR) as the complexing reagent, even in highly concentrated NaCl solutions. Furthermore, the sensitivity of the measurement increases significantly with the NaCl concentration of the medium. (P.I)
2. I experimentally demonstrated that the sensitivity of the spectrophotometric method for dissolved aluminum determination using ECR as the complexing agent and CTAB as a cationic surfactant – performed in a pH 5 medium buffered with acetic acid–sodium acetate – can be further improved, and its detection and quantification limits reduced, by replacing the acetate buffer with the Good's buffer MOPS (3-(N-morpholino)propanesulfonic acid) at pH 6.5. (P.II)
3. I experimentally verified that, in concentrated rock salt solutions used as raw materials in the chlor-alkali industry, the presence of certain metallic impurities in sufficient concentrations can significantly promote the precipitation-based removal of each other solely by adjusting the pH to an optimal value (pH 11 at 60 °C). In the presence of calcium (at least 150 mg/kg) and/or magnesium (at least 5 mg/kg), the residual aluminum concentration in the supernatant can be reduced to as low as 0.2 mg/kg. Furthermore, the calcium content of the brine also facilitates the precipitation-based removal of iron and silica. (P.III)
4. I experimentally confirmed that the pronounced aluminum sedimentation observed at pH 11 and 60 °C in concentrated industrial brines is due to co-precipitation processes where aluminum precipitates jointly with calcium and/or magnesium as hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2 \text{H}_2\text{O}$) and hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$). Moreover, the calcium and magnesium content of the initial solution – and thus of the precipitate – significantly reduces the re-dissolution tendency of the aluminum content. (P.III)
5. Through experimental investigations, I demonstrated that ion exchange resins with aminomethylphosphonic acid functional groups are suitable for removing trace amounts of dissolved aluminum from concentrated NaCl solutions, achieving residual aluminum concentrations below 0.01 mg/kg. Due to the significantly different optimal pH values required for the binding of aluminum and for the binding of alkaline earth metals on iminodiacetate-functionalized resins – commonly used for the latter – a dedicated ion exchange column is necessary for the selective removal of aluminum. Under typical operating conditions of the chlor-alkali industry, the extended cycle time of several weeks achievable between two regeneration steps results in low chemical consumption, which is advantageous from both sustainability and economic perspectives.
6. I experimentally verified that ion exchange resins with aminomethylphosphonic acid functional groups – effective for removing trace dissolved aluminum from concentrated brines – can be regenerated using NaOH solution with a minimum concentration of 3.5 w%, and an acid regeneration step is not necessary.

7. Publications

7.1. Scientific articles related to this Ph.D. dissertation

- I. **B. Csorba**, L. Farkas, A. Mihalkó, R. Z. Boros, I. L. Gresits (2023) Photometric Determination of Trace Amounts of Aluminum in Nearly Saturated Rock Salt Solutions Used by Chlor-alkali Industry. *Periodica Polytechnica Chemical Engineering* 67(3):442-451. <https://doi.org/10.3311/PPch.22051> (CsB: 100%; IF: 1.4; Q3; C:4; IC:2)
- II. **B. Csorba**, L. Farkas, M. Csécsi, L. T. Mika, I. L. Gresits (2024) Facile Determination of Aluminum Content in Industrial Brine by Investigating the Effects of Buffer Systems. *ChemistryOpen* 13(12):e202400038. <https://doi.org/10.1002/open.202400038> (CsB: 85%; IF: 3,1; Q2; C:0; IC:0)
- III. **B. Csorba**, L. Farkas, M. Csécsi, Z. Hórvölgyi, T. Szabó, J. Madarász, A. Mihalkó, Z. Keresztes, R. Z. Boros, I. L. Gresits (2025) Removal of aluminum content of concentrated salt solutions by precipitation, coagulation and sedimentation. *Chemical Papers* 79:4109-4130. <https://doi.org/10.1007/s11696-025-03942-8> (CsB: 90%; IF: 2,5; Q2; C:0; IC:0)

7.2. Oral presentations related to this Ph.D. dissertation

- I. **B. Csorba**, A. Mihalkó, L. Farkas, R. Z. Boros, I. L. Gresits (2021) Az elektrolízisipar által használt kősóoldatok nyomnyi mennyiségű alumíniumtartalmának meghatározása fotometriás úton [Photometric determination of trace amounts of aluminum in rock salt solutions used by the electrolysis industry]. *Nemzetközi Vegyészkonferencia*, online.
- II. **B. Csorba**, A. Mihalkó, L. Farkas, R. Z. Boros, M. Csécsi, I. L. Gresits (2022) A klór-alkáli ipar által használt elektrolizáló kősóoldatok nyomnyi mennyiségű alumíniumtartalmának meghatározása fotometriás úton [Photometric determination of trace amounts of aluminium in electrolytic rock salt solutions used by the chlor-alkali industry]. *Szent-Györgyi Albert Konferencia*, Budapest, Hungary.
- III. **B. Csorba**, A. Mihalkó, L. Farkas, R. Z. Boros, M. Csécsi, I. L. Gresits (2022) A klór-alkáli ipar által használt elektrolizáló kősóoldatok nyomnyi mennyiségű alumíniumtartalmának meghatározása fotometriás úton [Photometric determination of trace amounts of aluminium in electrolytic rock salt solutions used by the chlor-alkali industry]. *Tavaszi Szél Konferencia*, Pécs, Hungary.
- IV. **B. Csorba**, A. Mihalkó, L. Farkas, R. Z. Boros, M. Csécsi, I. L. Gresits (2022) Photometric determination of trace amounts of Al in cc. NaCl solutions used by the chlor-alkali industry - Coagulation and sedimentation studies. *Chemical Research in Flanders - Chemistry Conference for Young Scientists (CRF - ChemCYS)*, Blankenberge, Belgium.
- V. **B. Csorba**, J. Madarász, L. Farkas, R. Z. Boros, A. Mihalkó, M. Csécsi, I. L. Gresits (2023) Elektrolízisipari tömény kősóoldatok nyomnyi szennyező fémtartalmának eltávolítása koaguláció, szedimentáció útján [Removal of trace amounts of polluting metals from concentrated electrolytic rock salt solutions by coagulation and sedimentation]. *Műszaki Kémiai Napok*, Veszprém, Hungary.
- VI. **B. Csorba**, J. Madarász, A. Mihalkó, L. Farkas, R. Z. Boros, M. Csécsi, P. Bazsányi, I. L. Gresits (2023) A klór-alkáli iparban használt tömény kősóoldatok flokkulációval, szedimentációval és ioncseréléssel történő tisztítási lehetőségeinek feltérképezése [Mapping of the purification possibilities of saturated brine solutions used in the chlor-alkali industry by flocculation, sedimentation and ion exchange]. *Nemzetközi Vegyészkonferencia*, Târgu Mureș, Romania.
- VII. **B. Csorba**, J. Madarász, L. Farkas, R. Z. Boros, A. Mihalkó, M. Csécsi, I. L. Gresits (2023) Removal of trace amounts of polluting metals from concentrated electrolytic rock salt solutions

by coagulation, sedimentation and ion exchange. *AIChE Annual Meeting*, Orlando, Florida, USA.

- VIII. **B. Csorba**, J. Madarász, L. Farkas, R. Z. Boros, A. Mihalkó, M. Csécsi, I. L. Gresits (2024) Sólé tisztítási módszer fejlesztése csapadékképzés és ioncserés eljárás útján (klórgyártás) [Development of a brine purification method by precipitation and ion exchange (chlorine production)]. *Symposium on Polymer(s) Innovation (SPI)*, Miskolc, Hungary.
- IX. **B. Csorba**, L. Farkas, P. Bazsányi, Z. M. Martinkó, A. Mihalkó, R. Z. Boros, I. L. Gresits (2024) Purification of Concentrated Brines Used in the Chlor-Alkali Industry By Ion Exchange: Experimental Study and Simulation. *AIChE Annual Meeting*, San Diego, Amerikai Egyesült Államok.
- X. **B. Csorba**, L. Farkas, M. Csécsi, J. Madarász, R. Z. Boros, A. Mihalkó, I. L. Gresits (2024) Sólé tisztítási módszer fejlesztése csapadékképzés és ioncserés eljárás útján [Development of a brine purification method by precipitation and ion exchange]. *Borsodi Vegyipari Nap*, Miskolc, Hungary.
- XI. **B. Csorba**, P. Tóth, Z. Hórvölgyi, J. Madarász, A. Mihalkó, L. Farkas, R. Z. Boros, I. L. Gresits (2025) Klóralkáli elektrolízishez használt sóoldatok csapadékképzéses, flokkulációs, ülepitéses és ioncserés tisztításának optimalizálása [Optimization of precipitation, flocculation, sedimentation and ion exchange purification of salt solutions used for chlor-alkali electrolysis]. *Műszaki Kémiai Napok*, Veszprém, Hungary.

7.3. Poster presentation related to this Ph.D. dissertation

- I. **B. Csorba**, L. Farkas, M. Csécsi, Z. Hórvölgyi, Z. Keresztes, J. Madarász, A. Mihalkó, T. Szabó, R. Z. Boros, I. L. Gresits (2024) Removal of aluminum content of concentrated salt solutions by precipitation, coagulation and sedimentation. *International Conference of Slovak Society of Chemical Engineering – SSCHE 2024*, Tatranské Matliare, Slovakia.

7.4. Publication not strictly related to this Ph.D. dissertation

- I. **B. Csorba**, P. Szabó, S. Góger, G. Lendvay (2021) The Role of Zero-Point Vibration and Reactant Attraction in Exothermic Bimolecular Reactions with Submerged Potential Barriers: Theoretical Studies of the $R + HBr \rightarrow RH + Br$ ($R = CH_3, HO$) Systems. *The Journal of Physical Chemistry A* 125(38):8386–8396. <https://doi.org/10.1021/acs.jpca.1c05839> (IF: 2.944; Q2; C:8; IC:4)

7.5. Poster presentation not strictly related to this Ph.D. dissertation

- I. P. Bozsó, K. Várnagy, **B. Csorba**, P. Szabó, L. Farkas, A. Mihalkó, R. Z. Boros (2022) Valerolakton gyűrűnyitási reakciójának tanulmányozása, és a képződött anyagok felhasználása biobázisú poliuretánok előállításához [Study of the ring-opening reaction of valerolactone and the use of the resulting materials for the production of bio-based polyurethanes]. *Nemzetközi Vegyészkonferencia*, Oradea, Romania.