

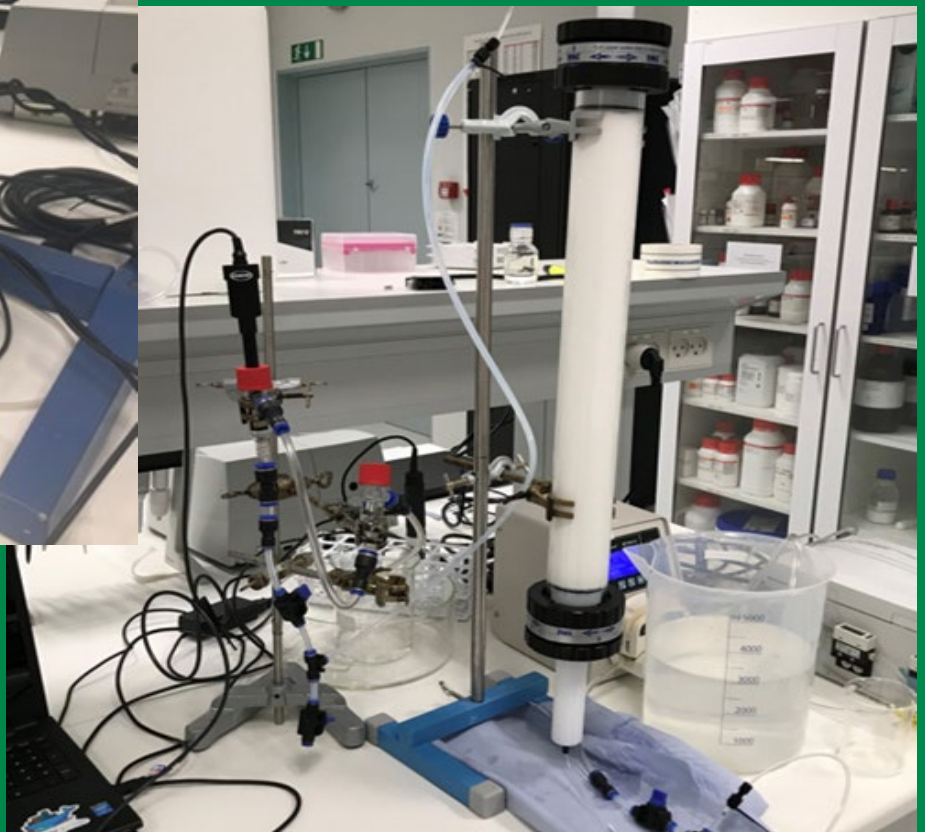
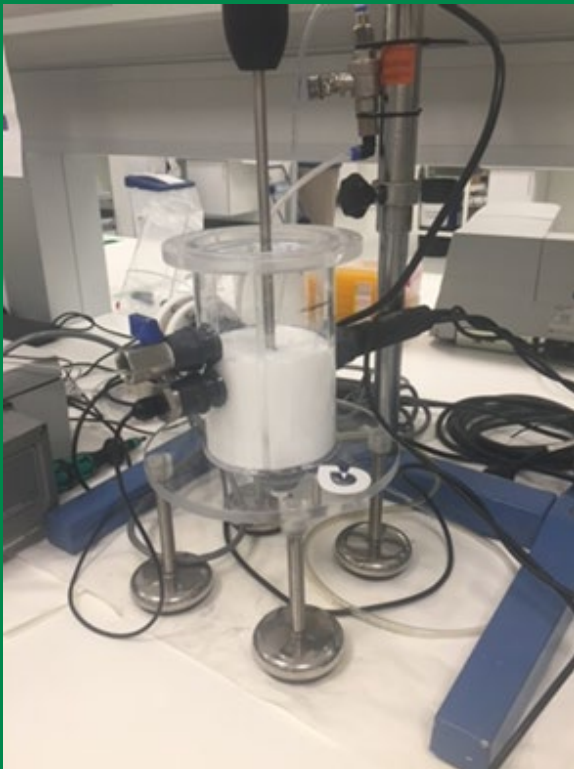


Ministry of Environment  
of Denmark  
Environmental  
Protection Agency

# Investigations of a possible novel desalination technology

MUDP Report

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# 1. Summary

Basic research on a new potential desalination process was conducted at University of Copenhagen. The research was based on the observation that introduction of  $CO_2$  to an aqueous solution of diamine and NaCl resulted in a rapid decrease in conductivity in the solution. Extensive experimental work was conducted, and a hypothesis was established resulting in a proposed mechanism comprising a series of complex reactions where the end products are protonated diamine, stabilized by chloride and sodium bicarbonate. The fundamental research at University of Copenhagen had primarily been focused on the capture-molecule structure-performance optimization and experimental proof-of-concept. The work comprised investigations on different chain-length diamines to assess the aggregation and decrease in conductivity. Based on these basic observations the process was patented and the patent fully assigned to the start-up company CowaTech ApS which was setup in 2018 with the purpose of developing an affordable, scalable, and green water desalination technology. Together with Ultraaqua A/S, CowaTech ApS received funding for the present MUDP project with the objective of undertaking a comprehensive technical feasibility study for clarifying the possibilities of transferring the research results into a viable future large-scale technology concept.

The MUDP project initially comprised a thorough scrutinization of the experimental results from the fundamental research investigations conducted at University of Copenhagen resulting in the identification of several intrinsic process parameters and knowledge necessary for the further technology development and upscaling. These comprised knowledge on salt and diamine concentration stoichiometry, of diamine and  $CO_2$  concentration stoichiometry, on the effect of stoichiometry on process kinetics and finally, on the verification of salinity drop representing desalination by aggregate separation and specific ion analysis. Based on the identified knowledge gaps, a dedicated experimental reactor was developed, and a matrix of experimental investigations performed resulting in a large dataset enabling a deep analysis of the hypothesis of the process mechanism and performance.

The conclusions on the investigations on the hypothesis of the original idea was that the potentially new disruptive desalination technology process was in fact not a desalination process removing both cations and anions, rather it was shown to be an anion exchange process where the  $CO_2$  activated diamine was able to exchange the formed bicarbonate with chloride anions in solution.

During the initial experimental work, the problem of separating the treated water from the polymers/diamine for evaluation of the process efficiency had shown to be a major issue. Thus, it was decided to continue the experimental work based on a system with immobilized diamines. With the system based on immobilized diamines the separation issue was solved through the design of the technology concept.

It was decided to investigate the possibility of immobilizing the diamine on an available epoxide functionalized resin to produce an anion exchange resin that could be commercialized in the drinking water treatment market as well as the industrial water market. The first CowaTech resin was produced by coupling 3-dimethylamino-1-propylamine to an available commercial resin and the performance of the CowaTech resin was tested with a column of 1000 mL bed volume. The test program encompassed screening of the sorption capability and capacity for ion exchange of chloride, fluoride, and nitrate.

Based on the experimental work on ion exchange on resin in a test column it was found that the  $CO_2$  activated immobilized diamine was able to exchange bicarbonate with chloride, fluo-

ride, and nitrate. The capacity for ion exchange of the three anions tested turned out to approximately match the expected capacity as calculated based on the estimated concentration of epoxide for the applied resin.

Thus, the experimental work with the immobilized diamines confirmed the hypothesis regarding the ion exchange mechanism, where target anions were removed from the feed solution through exchange with bicarbonate ions. All three tested anions are problematic anions for which a considerable global market exist.

Based on the experimental data obtained for chloride and fluoride ion-exchange of the CowaTech resin, a 1D Advection-dispersion reactive pellet bed model was successfully setup in COMSOL Multiphysics to simulate the ion-exchange process and elution of the two ions. The model description enables the virtual scaling up of the column from laboratory scale to industrial scale. By using the forward and reverse ion-exchange rate constants as fitting parameters the model was able to simulate the removal and elution of the two ions according to the observed data. As such, the model results indicated a higher affinity of the CowaTech resin towards chloride than fluoride resulting also in a lower capacity of the CowaTech resin for fluoride removal compared to the chloride removal.

However, these conclusions are made based on only one dataset for each ion, why one should be very cautious to generalize based on these limited data. In fact, the future development of the CowaTech resin concept will need considerable future experimental work regarding optimization of the resin capacity, testing of selectivity of the ion exchange capability in complex water matrices, and investigation into regeneration of the resin.

These future investigations are fundamental in fully elucidating and determining the potential commercial viability and environmental sustainability of a technology based on the CowaTech resin concept. Due to the limited resources of CowaTech ApS, further development of the technology will be discontinued under the auspices of CowaTech ApS.

## 2. Background and objective

**The following report presents results of an MUDP project that was undertaken to provide a comprehensive technical feasibility study of a possible new disruptive desalination technology of which fundamental proof-of-concept research results were previously obtained at Department of Chemistry at Copenhagen University.**

### 2.1 Technology hypothesis and concept

Recent fundamental research results obtained by the Lee Group at Department of Chemistry at Copenhagen University (<https://www.leeegroup.dk/>) has revealed possibilities for development of a new disruptive desalination technology which could potentially reduce the energy consumption and thereby the CO<sub>2</sub> footprint from sea water desalination considerably. The basic principle and hypothesis behind the proposed technology, is based on a novel physico-chemical mechanism whereby mixing specific recyclable organic capture molecules and carbon dioxide (CO<sub>2</sub>) into saline water (such as sea water) initiates a complex chemical reaction that results in the complexation and aggregation of salts that can subsequently be separated from the desalinated water – e.g. by filtration.

Results from lab-scale investigations with model test water have indicated that the addition of CO<sub>2</sub> activates the complexation and aggregation of salts with the organic capture molecules in high salinity water resulting in a fast decrease in the conductivity of the water. After separation a desalinated liquid phase and suspended aggregate phase expectedly would be the result where subsequently, the aggregates could be separated into a salt brine (for discharge) and a stream with regenerated capture molecules.

### 2.2 Project objective

The objective of the MUDP project has been to undertake a comprehensive technical feasibility study for clarification of the possibilities for transfer of the research results into a viable future technology concept. The intention was therefore to create a solid knowledge-based platform for decisions regarding the direction of future RDI (Research, Development, and Innovation) activities. The project goal was to move the technology from TRL1-2 to TRL4 - thereby creating a bridge to future technology development and commercialization.

### 2.3 Project execution

The project was completed in the period of October 2019 to November 2021 as a collaboration between CowaTech ApS and Ultraaqua A/S with IN-Water ApS as subcontractor. Project leader was CowaTech ApS with Camilla de Thiersant as project manager.

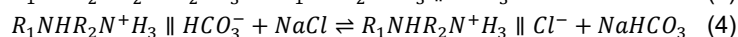
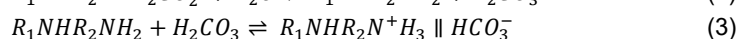
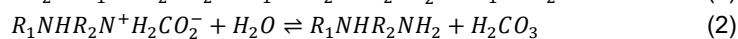
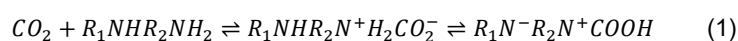
Based on a deep analysis of the recent research findings a dedicated lab-scale experimental program was designed and executed to ensure a solid data base for design and preparation of a virtual prototype of the new desalination technology. Based on laboratory and model results a technical, economic and sustainability assessment was conducted as part of the feasibility analysis. Further, a preliminary toxicity assessment and a preliminary technology viability analysis in the global water treatment market were part of the project.

# 3. Review of existing knowledge

This chapter summarizes the result of the review of existing knowledge presented in more detail in Appendix 1. The proposed mechanism behind the observations done through the comprehensive laboratory investigations at KU is outlined and identified knowledge gaps and missing information are summarized.

## 3.1 Proposed mechanism of desalination

The fundamental research of the desalination process conducted at University of Copenhagen, was based on the proposed mechanism that is shown in the below four reactions.

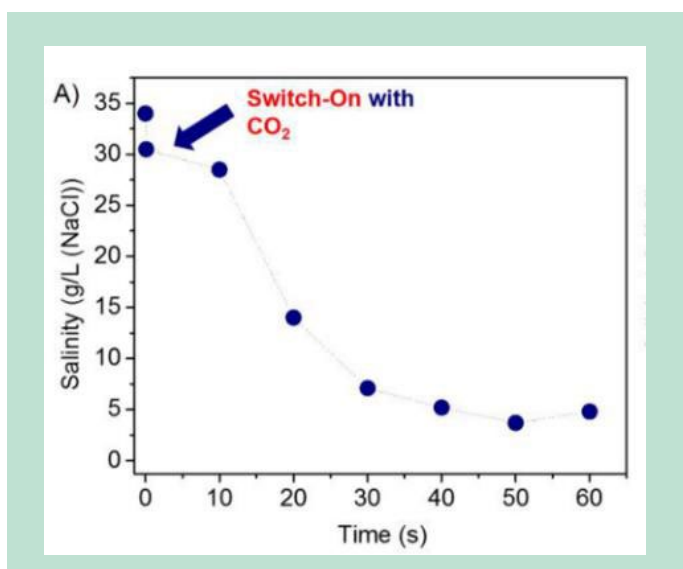


From the equations, the proposed mechanism states that by introducing  $CO_2$  to an aqueous solution of diamine, the tertiary amine is protonated, forming a carbamate salt. This can further react, via a proton transfer reaction, resulting in the formation of carbamic acid and protonation of the secondary amine, equation 1. Due to the reaction taking place in an aqueous solution, carbamic acid will react with water, resulting in diamine and carbonic acid, equation 2. From this, the diamine can react with the carbonic acid, forming protonated diamine and bicarbonate, equation 3. If salts are present, in this example NaCl, the protonated diamine will exchange the bicarbonate ion with chloride, as chloride has higher affinity for electrostatic stabilization by the nitrogen. The end products are therefore protonated diamine, stabilized by chloride and sodium bicarbonate.

The fundamental research at University of Copenhagen had primarily been focused on the capture-molecule structure-performance optimization and experimental proof-of-concept. This work comprised investigations on different chain-lengths of  $R_1$  to assess the aggregation and decrease in conductivity as shown in the below example, Figure 1.

Based on extensive experimental work conducted in beakers, where the exact  $CO_2$ -flow was unknown it was preliminary concluded that an alkyl chain modified diamine with a chain length of 12 carbon atoms was the most promising candidate to facilitate the  $CO_2$ -responsive autonomous aggregation (or precipitation) process that would lead to desalination – see more details in Appendix 1.





**FIGURE 1.** Lab-scale demonstration of the novel desalination process. Salinity measured as conductivity.

### 3.2 Identified knowledge gaps and needed information

Based on a thorough scrutinization of the experimental results from the fundamental research investigations conducted at University of Copenhagen (Appendix 1), it was clear that several intrinsic process parameters and knowledge necessary for the further technology development and upscaling were missing. These comprised the following:

- Effect of salt and diamine concentration stoichiometry on extent of desalination
- Effect of diamine and CO<sub>2</sub> concentration stoichiometry on extent of desalination
- The effect of the above on process kinetics
- Verification of salinity drop representing desalination by aggregate separation and specific ion analysis

From the identified knowledge gaps, a matrix of experimental investigations needed to be performed to acquire these fundamental data was developed, along with specifications for design of an experimental reactor suitable for obtaining credible data.

## 4. Experimental investigations on suspended diamine polymers

**A dedicated reactor was constructed to investigate details in the observed mechanism as well as determine process kinetics and stoichiometry data. To this end a comprehensive investigation matrix for selected combinations of salt and diamine concentrations was defined and experimental work carried out. The conclusion on the comprehensive data analyses of the experimental results was that the observed conductivity reduction reflected micelle formation and therefore that the process was in fact not a desalination process. Rather, it was shown to be an anion exchange process where the CO<sub>2</sub> activated diamine was able to exchange the formed bicarbonate with chloride anions in solution.**

### 4.1 Design of dedicated experimental reactor

A specialized reactor (Figure 2) was designed and constructed to study the process in detail to establish data on process kinetics and stoichiometry.

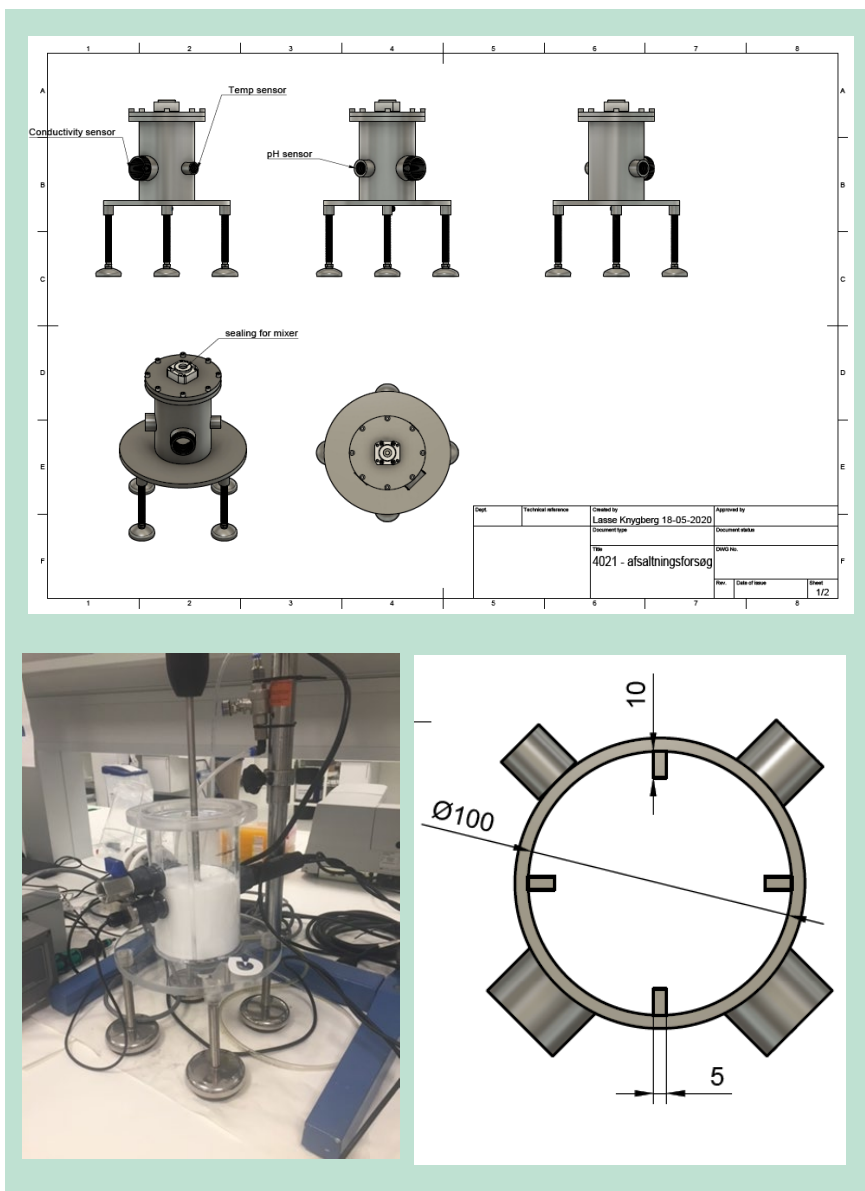
The reactor consisted of a transparent plastic reactor with a gas-tight lid and with sensors for monitoring pH, conductivity and temperature mounted on the side of the reactor house. Four baffles for securing adequate mixing were placed symmetrically on the inside wall of the cylindrical reactor. A specialized stainless-steel diffuser with 2 µm pores was mounted in the center of the bottom of the reactor to ensure adequate mass-transfer of the injected CO<sub>2</sub> gas into the liquid. In the lid, a paddle stirrer was mounted with the shaft placed in a gas tight ball bearing to ensure that CO<sub>2</sub>-gas exiting the water phase could only escape the reactor through the dedicated sampling hole mounted in the lid. The CO<sub>2</sub> gas entering and exiting the reactor was measured externally by low-flow CO<sub>2</sub>-flow sensors with a measuring range 0-1 L/min. The inlet gas flow was regulated by an ultrafine manual needle valve mounted on the pressure reduction valve on the CO<sub>2</sub> gas cylinder.

Data acquisition was established to collect all sensor data with a time resolution of eight seconds to monitor the process in near real-time.

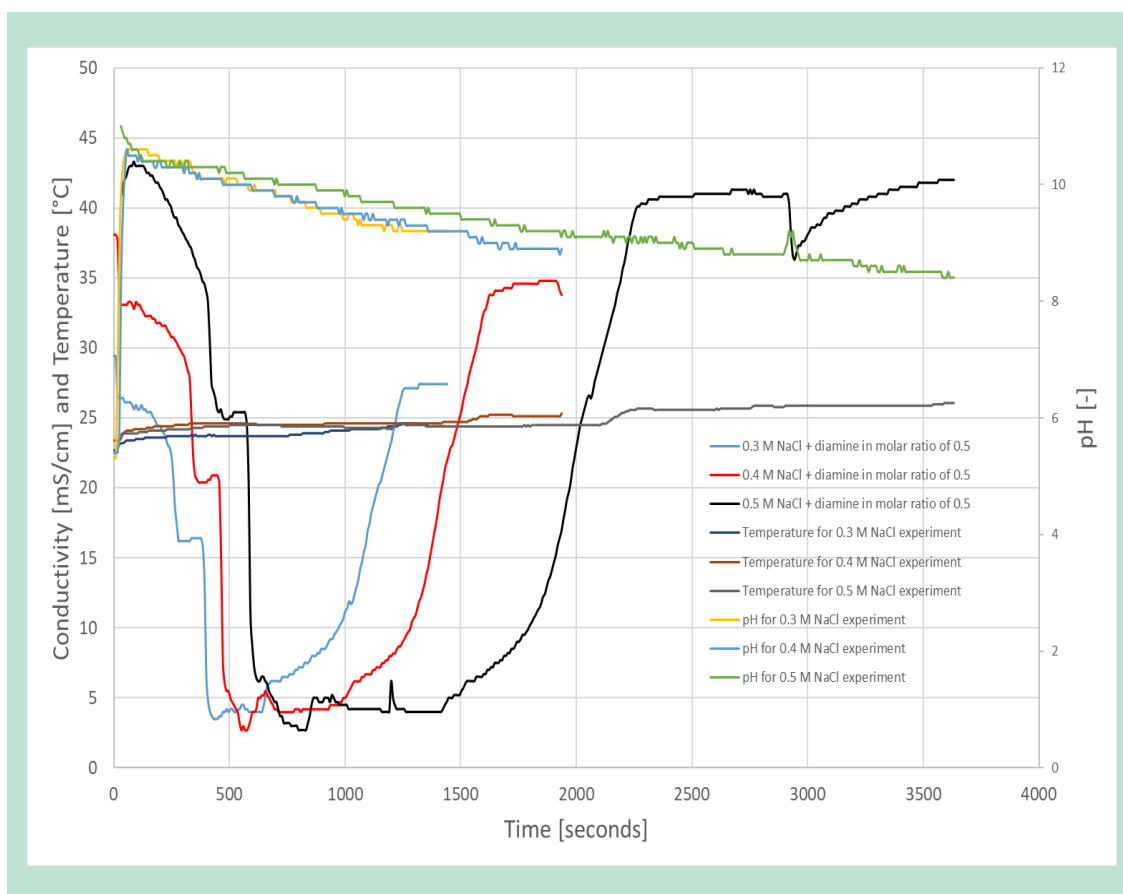
#### 4.1.1 Experimental procedure and investigation matrix

Experiments were performed by adding 1 L of sodium chloride solution to the reactor followed by addition of C-12 diamine in a predefined molar ratio to the sodium chloride molar concentration. Subsequently the lid was closed, and the stirring of the solution was started. The experiment was then started by initiating the injection of CO<sub>2</sub> gas and the immediate start of the data acquisition.

All experiments except the experiment with a salt concentration of 0.6M were run until conductivity increased again because of the de-aggregation, after passing the low conductivity phase corresponding to the self-aggregation of the diamine polymer. Examples of process curves for initial salt concentrations of 0.3, 0.4 and 0.5 M are shown in Figure 3.



**FIGURE 2.** Specialized reactor for systematic studies on diamine aggregation desalination process.



**FIGURE 3.** Example of results of process monitoring during diamine aggregation experiments.

To obtain data for a solid understanding of the process stoichiometry and kinetics, the following comprehensive investigations matrix for the combination of salt and diamine concentration was defined – Table 1.

**TABLE 1.** Experimental matrix for the investigation of process stoichiometry and kinetics

Salt concentration [g/L]	Salt concentration [M]	Diamine conc. [M]
4	0.068	0.007; 0.021; 0.034
8	0.137	0.014; 0.041; 0.068
12	0.205	0.021; 0.062; 0.103
18	0.308	0.154
24	0.411	0.205
30	0.513	0.257
35	0.599	0.299

The molar ratio of diamine to salt concentration for the lower concentrations (4-12 g/L) was investigated at 0.1, 0.3 and 0.5 while for all other salt concentrations it was fixed at 0.5. A molar ratio of 0.5 corresponded to an equivalent number of active sites and chloride entities, as each diamine molecule has two active amine groups for exchanging chloride. A molar ratio of 0.5 would therefore correspond to a theoretical complete removal of chloride.

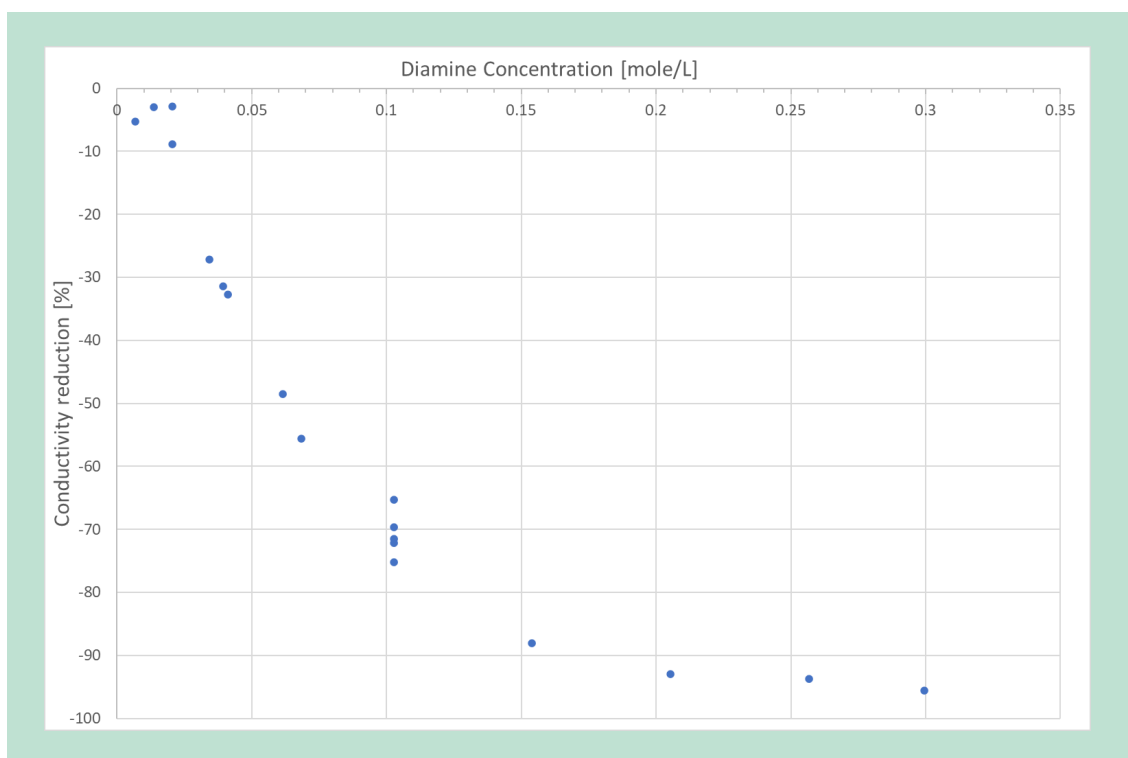
## 4.2 Results of conducted experiments

For all the combinations of salt and diamine concentration, the process monitoring results showed the same trend with an initial decrease in conductivity during the CO<sub>2</sub>-dosing, corre-

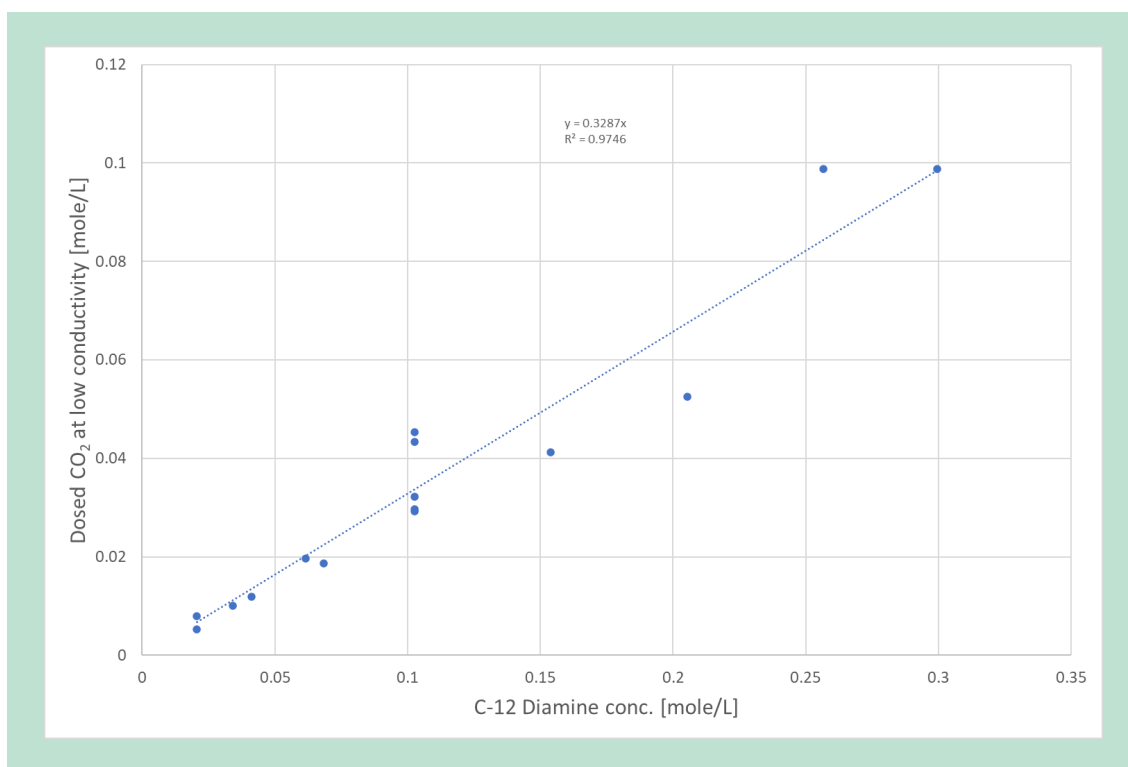
sponding to the self-aggregation of the diamines. This was followed by a phase with an increase in conductivity due to the stabilization and de-aggregation of the aggregates as the CO<sub>2</sub> dose continued. The conductivity measurements during the experiments showed between 3-90% conductivity reduction - depending on initial conductivity - with the lowest conductivity reductions obtained with the lowest initial salt concentration. Based on the obtained data, plots of diamine concentration versus conductivity reduction as well as of amount of dosed CO<sub>2</sub> at the point of minimum conductivity versus diamine concentration were made as shown in Figure 4 and Figure 5.

From Figure 4 can be seen that the observed conductivity reduction was directly related to the diamine concentration across all initial salinities up to around 0.2 M diamine after which the conductivity reduction became independent of the diamine concentration.

From Figure 5 can be seen that the dosed amount of CO<sub>2</sub> at the point of minimum conductivity corresponded to a fixed molar ratio of around 0.33 mole CO<sub>2</sub>/mole diamine. This stoichiometry was much lower than expected based on the molar concentration of amine groups and necessary amount of activated diamine groups to achieve complete desalination. To come to an understanding of the reasons behind these contradictory data, a short review of literature on micelle formation and its impact on conductivity was conducted to assist in understanding the observed results.



**FIGURE 4.** Observed conductivity reduction versus initial diamine concentration across all initial salinities.



**FIGURE 5.** Dosed CO<sub>2</sub> amount at minimum conductivity versus diamine concentration across all initial salinities.

From the micelle literature review it was found that during micelle formation, the drag forces of micellar aggregates slow down ionic mobility and at the point of maximum micelle aggregation, conductivity would decrease dramatically. This could therefore indicate that the observed desalination from the conductivity measurements was merely a result of the impact of the micelle formation on measured conductivity and not a result of ion removal. This could also support the observed linear relationship between conductivity reduction and diamine concentration as a higher diamine concentration would increase the micelle aggregate concentration and lead to a higher impact on the measured conductivity.

To further understand the mechanism of the process based on the observed data, the experiment with 12 g/L NaCl was selected for studies on separation of the micelle aggregates by membrane filtration. The conductivity measurements from the aggregation experiment showed around 75% reduction while conductivity measurements on the permeate from the membrane filtration of the micelle aggregates showed only 20% conductivity reduction as can be seen in Table 2.

**TABLE 2.** Measured conductivities of 12 g/L NaCl solution prior to aggregate experiment, after reaching micelle aggregation and of the permeate after micelle separation.

Salinity [g/L]	Initial conductivity [mS/cm]	Conductivity after micelle aggregation [mS/cm]	Conductivity of permeate after micelle separation [mS/cm]
12	22.1	5.54	18.1

To understand this discrepancy, a deeper data analysis was conducted on the data based on a hypothesis that the change in conductivity between the original solution and the permeate after aggregate separation was alone governed by exchange of chloride ions with bicarbonate ions formed from the added amount of CO<sub>2</sub>. Based on this hypothesis, molar conductivities of involved ionic species and their temperature dependence was found in literature and together with physical-chemical models for ionic strength and activity coefficients, theoretical calculations of the expected conductivity change from ion exchange of chloride with the formed bicarbonate were made. Results are shown in Table 3.

**TABLE 3.** Theoretically calculated conductivity of a 12 g/L NaCl solution and after ion exchange with added amount of bicarbonate

Calculated initial conductivity [mS/cm]	Calculated conductivity after ion exchange [mS/cm]
22.5	17.3

As seen, the calculated conductivities of the original solution and in the permeate fitted well with the actual measured conductivities assuming ion exchange as the governing mechanism of the process. This was subsequently further supported by measurements of bicarbonate in the permeate. From this data analysis and the micelle literature support, it could be concluded that the measured conductivity reduction observed was misinterpreted as desalination and instead reflected micelle formation.

The conclusions on the investigations on the hypothesis of the original idea was therefore that the potentially new disruptive desalination technology process was in fact not a desalination process, rather it was shown to be an anion exchange process where the CO<sub>2</sub> activated diamine was able to exchange the formed bicarbonate with chloride anions in solution.

# 5. Experimental and transport modelling investigations on immobilized diamine polymers

The technology set-up for testing of the CO<sub>2</sub> activated ion exchange with immobilized diamines was developed and a first generation of CowaTech resin was prepared. The resin was packed in a one liter column and a test-rig was established. Tracer experiments were applied to investigate the hydraulic flow through the column and a model was established to simulate flow pattern and species transport. Experimental testing of ion exchange of the anions: chloride, fluoride, and nitrate, confirmed the ion exchange mechanism and documented efficient sorption of the tested anions in exchange for release of bicarbonate. Further, column regeneration with KOH was demonstrated.

## 5.1 Immobilized ion exchange

Based on the conclusions that the process mechanism was an anion exchange of bicarbonate with chloride anions, it was decided to investigate the possibility of immobilizing the diamine on an available epoxide functionalized resin to produce an anion exchange resin that could be commercialized in e.g. the drinking water treatment market.

Traditionally, applications of ion exchange (IX) resins in the drinking water treatment market are for the removal of inorganic anions such as sulfate, uranium, arsenic, fluoride, nitrate, removal of natural organic matter (NOM) and most recently polyfluorinated compounds (PFAS). Application of IX has received considerable attention because of its effectiveness, ease of operation, large available exchange capacities, small foot-print and regenerative capabilities. Anionic IX resins are often categorized based on intrinsic properties such as functional group (quaternary ammonium or tertiary ammonium), polymeric matrix (acrylic vs styrenic) and extent of cross-linking (gel-base or macro-porous).

Fundamental characteristics include exchange capacity (expressed in equivalent (eq) per L of resin), particle size and water content. IX resins adopted for drinking water treatment can also be broadly classified in two categories, strong- and weak-base IX resins, respectively.

Briefly, an IX resin with quaternary ammonium functional group is termed as strong-base IX resin. These resins are typically categorized in terms of chemical structure as Type I (trimethyl ammonium group) and Type II (dimethylethanol ammonium group). These resins show an excellent physical and chemical stability, and they can exchange different anions under a broad range of pH-values. Weak-base IX resins with primary, secondary, tertiary or mixed amine as functional groups offer excellent regenerative and reuse capabilities (>90% regeneration efficacy over multiple cycles) and are highly resistant to organic fouling. However, these are mostly operated only in low pH ranges (below neutral pH).

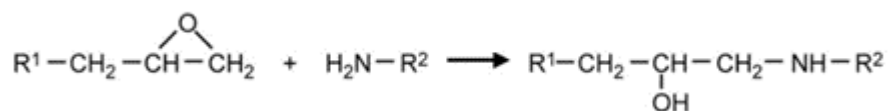


By comparison to the characteristics of traditional anion exchange resins, a future CowaTech resin would differ in the *type of functional group* (diamine vs quaternary ammonium or tertiary ammonium), *capacity* as it would be possible to obtain larger capacity due to the double amount of functional groups per linking site on the basic epoxide resin (potential for double capacity compared to current commercially available anion exchange resins) and *exchange of anions with bicarbonate* rather than hydroxide (OH<sup>-</sup>) or chloride (Cl<sup>-</sup>) which would be beneficial for the pH stability of the produced water. Further, the CowaTech resin would be best characterized as a weak-base IX resin with regenerative and reuse capabilities.

### 5.1.1 Preparation of a first generation CowaTech resin

The following procedure was applied for preparation of a first generation CowaTech resin. The first generation of the resin was produced by the assistance of MipSalus ApS. The principle behind the diamine immobilization was as follows.

We selected an epoxide-based resin to prepare the CowaTech resin with reactive epoxide functional groups. A primary amine, as in 3-dimethylamino-1-propylamine, will under suitable conditions react with the epoxide with the following reaction giving a secondary alcohol and a secondary amine. The number of epoxide groups is approx. 50 µmol/g wet resin.



First step in the resin preparation was preparation of the coupling solution:

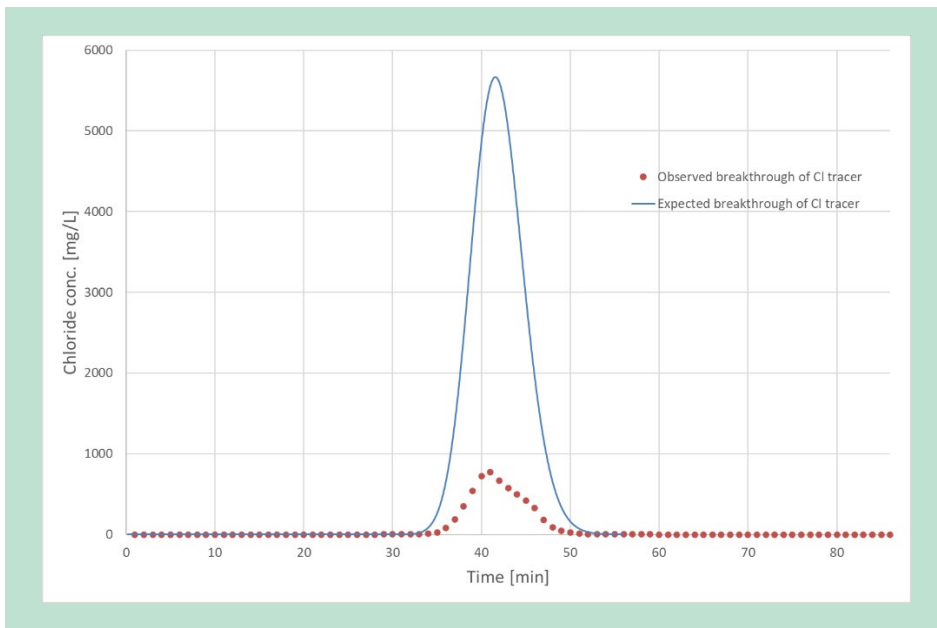
Diamine was mixed with DI water and epoxide-based resin was filled into a column. The resin was wetted with DI water, and the column was filled and packed. The resin was then washed on a 2 CV (column volume) DI water with 20 mL/min. Then 1 CV of the diamine coupling solution was fed to the column – downflow at 20 mL/min. Then both ends of the column were blocked and after coupling under soaking conditions and the resin was washed for testing.

## 5.2 Characterization of column flow and species transport with CowaTech resin

Initially, a series of tracer experiments with impulse dosing of a fixed amount of chloride on a non-CO<sub>2</sub>-activated column was planned and conducted to enable characterization of the transport properties of the column in terms of establishing a numeric value for the mechanical dispersion coefficient. Chloride concentrations were monitored in the column effluent by use of a HACH Chloride probe, See Appendix 2 for further information and results from an experiment designed to evaluate the quality of the probe signal.

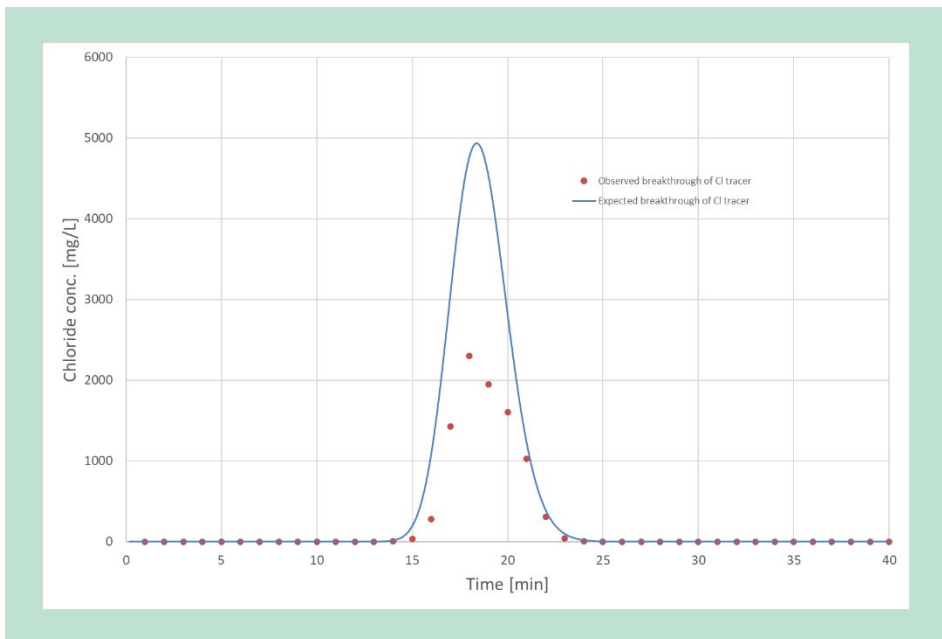
The mechanical dispersion coefficient was estimated through modelling in COMSOL Multiphysics based on a setup of the column as a reactive pellet bed in which the transport of diluted species is modelled in two domains comprising the transport of species in the interstices between the resin particles and inside the porous pellets as an extra dimension where the transport is modelled in the radial microscale dimension inside each pellet. This model setup of the column would allow for later adding the ion exchange chemical process to occur on the inside of each pellet for the description of the column performance.

However, it turned out to be difficult to keep the column non-activated and thus the first tracer experiments revealed significant removal of chloride through ion exchange as exemplified in Figure 6.

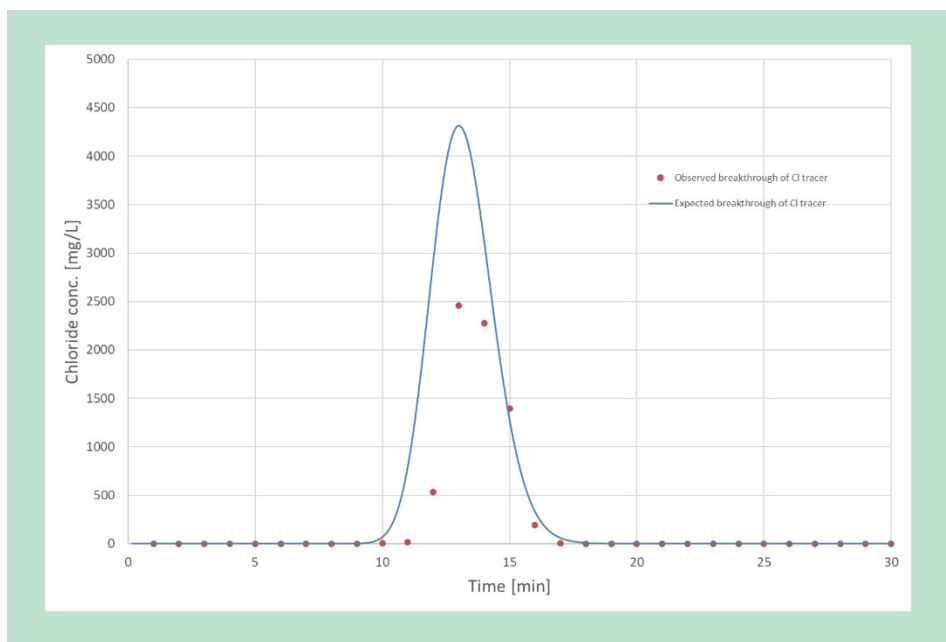


**FIGURE 6** Expected and observed breakthrough curves of chloride from initial tracer experiments at a flow of 20 mL/min.

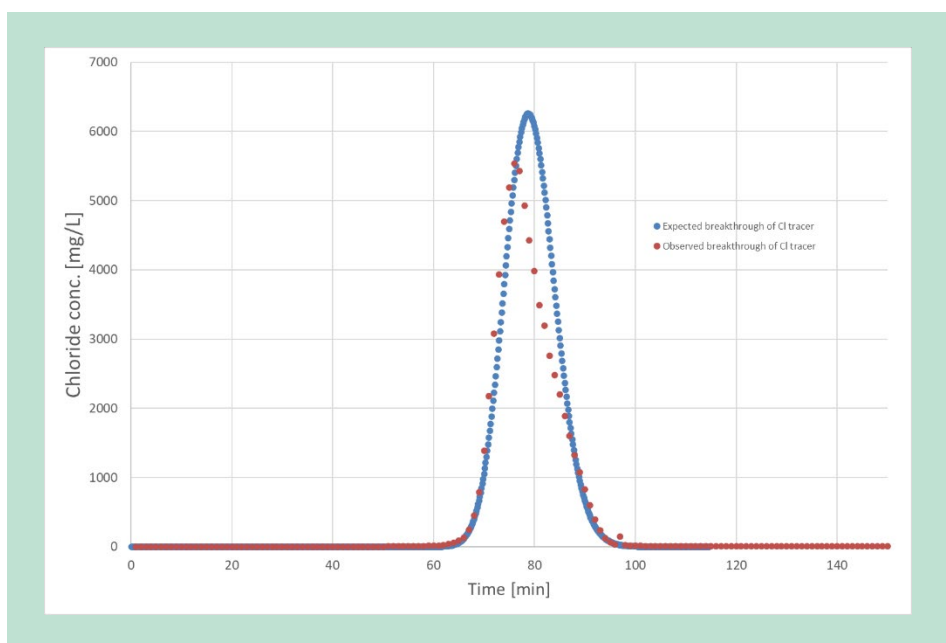
It was concluded that CO<sub>2</sub> from the wash water between experiments with pulse dosing of chloride contributed to activation of the diamine. It was observed that continued repetition of chloride tracer experiments at different flows on the column with only limited flushing between experiments resulted in smaller and smaller removals of chloride as shown in Figure 7-9.



**FIGURE 7.** Expected and observed breakthrough curves of chloride from initial tracer experiments at a flow of 40 mL/min.

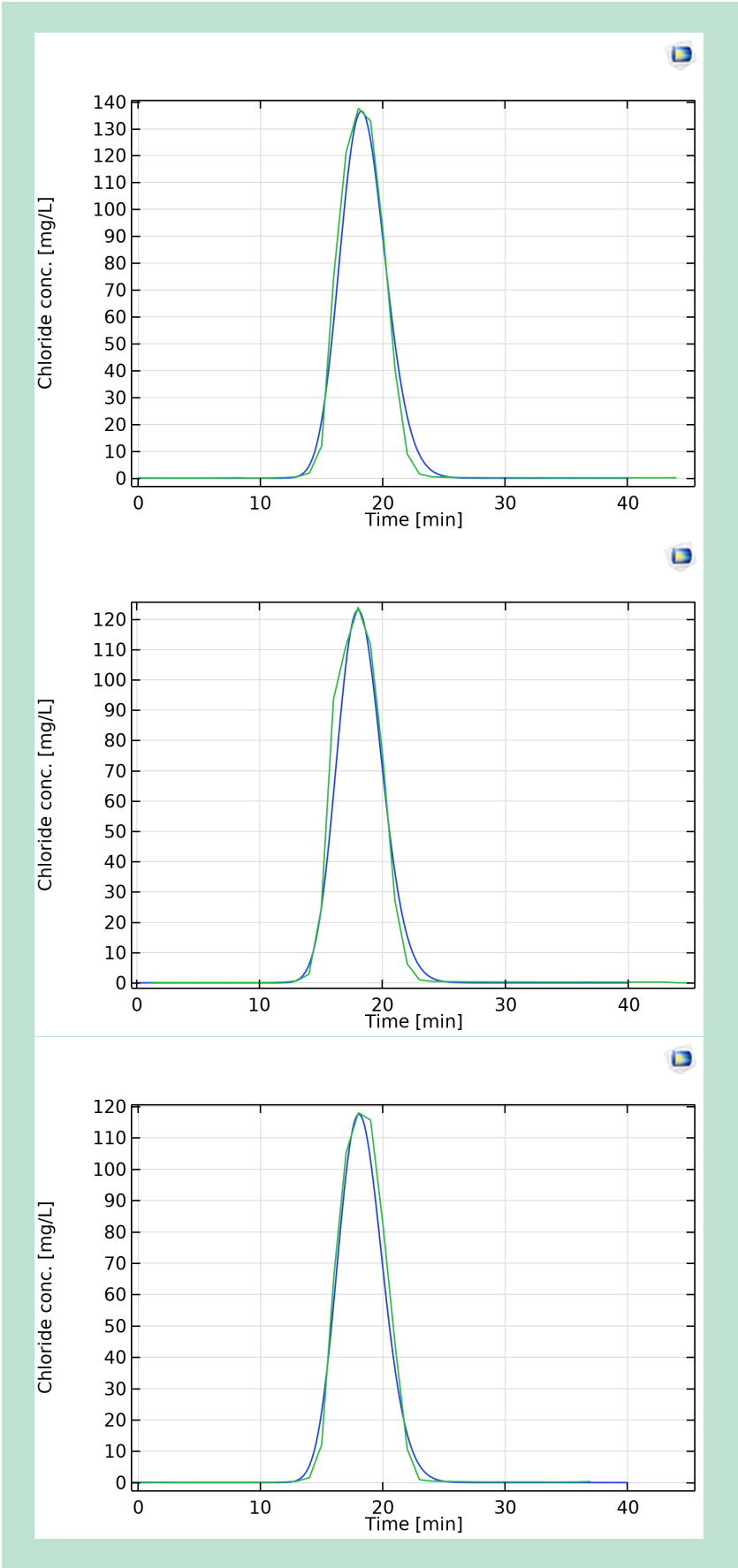


**FIGURE 8.** Expected and observed breakthrough curves of chloride from initial tracer experiments at a flow of 60 mL/min.



**FIGURE 9.** Expected and observed breakthrough curves of chloride from initial tracer experiments at a flow of 10 mL/min.

Based on these results, a procedure for completely saturating the column with chloride prior to performing the tracer experiments was established, with the purpose of establishing numerical values for the mechanical dispersion coefficient. The procedure consisted of soaking the column for 1 hour in a concentrated salt solution of 10 g/L chloride. Subsequently, several tracer experiments were run consecutively, and the obtained data used for modelling the mechanical dispersion coefficient in COMSOL Multiphysics. The experimental and model results of the tracer experiments are shown in Figure 10.



**FIGURE 10.** Observed (green) and modelled (blue) breakthrough curves of chloride from final tracer experiments at a flow of 43 mL/min.

Tortuosity of the flow paths in a porous media (e.g., differences in pore size and path lengths), as well as friction with pore walls, makes water molecules and the ions that they carry move differently within the porous medium. This process, known as mechanical dispersion, causes mechanical mixing and dilution effects along the direction of the flow. Based on the modelling of the chloride transport the mechanical dispersion coefficient for the CowaTech resin was fitted to the experimental data with a numerical value of  $6 \times 10^{-7} \text{ m}^2/\text{s}$ . With the determination of the mechanical dispersion coefficient the fundamental transport properties of dilute ionic species in the CowaTech resin column can be described and this forms the basis for the subsequent description of the ion exchange process when coupling the ion exchange reactions with the transport model.

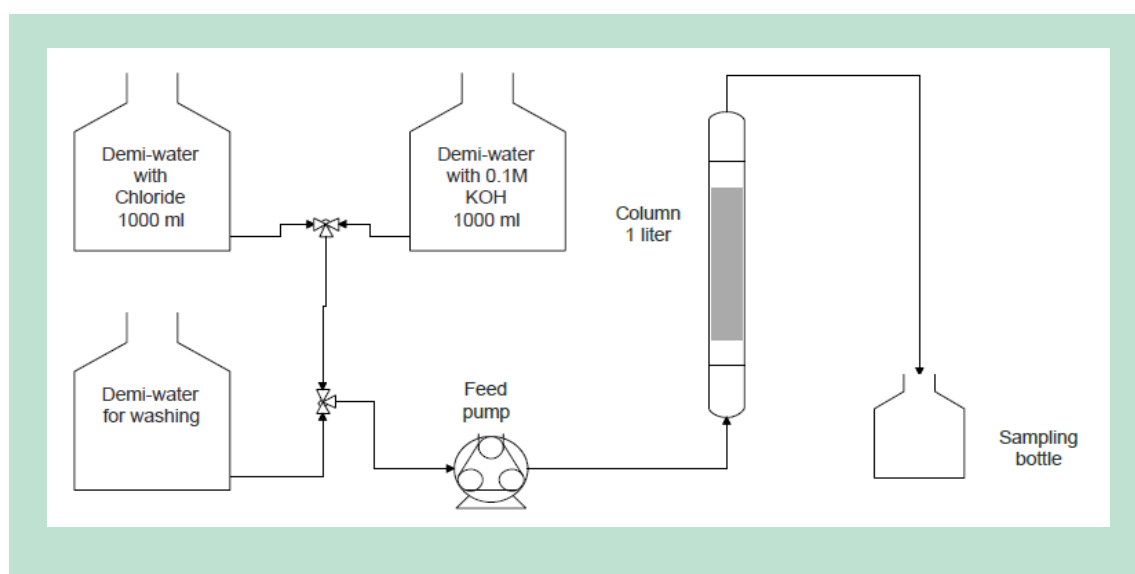
### 5.3 Experimental test of chloride, fluoride, and nitrate ion exchange

To design an ion exchange column based on the CowaTech resin it is necessary to be able to describe the ion exchange reactions on the surface of the resins. The ion exchange process in the column is a reversible reaction and is as such described by a forward and reverse rate constant. For design purposes it is necessary to establish values for these rate constants for the different anionic species in water. Three experiments with chloride, fluoride, and nitrate ions, three anions for which a commercial potential was identified, were designed, and conducted to generate data for the modelling and determination of the forward and reverse ion exchange rate constants for the three ions respectively. The experiments and results are described in the following.

#### 5.3.1 Experimental set-up

Figure 11 shows a schematic drawing of the set-up used for testing the chloride, fluoride, and nitrate ion exchange process of the CowaTech resin. The column was filled with 980 mL diamine coupled resin. The applied experimental set-up and experimental procedure was identical for the three tested anions: chloride, fluoride, and nitrate.

For details regarding the testing of each of the three anions see Appendix 3-5. The overall procedure was to first activate the resin with  $\text{CO}_2$  - then to pump a well-defined mass of anion (sodium salt) in one liter of solution through the column, wash the column and finally to eluate the exchanged anions (the column capacity) with  $\text{KOH}$ . Below the procedure is described in more detail.

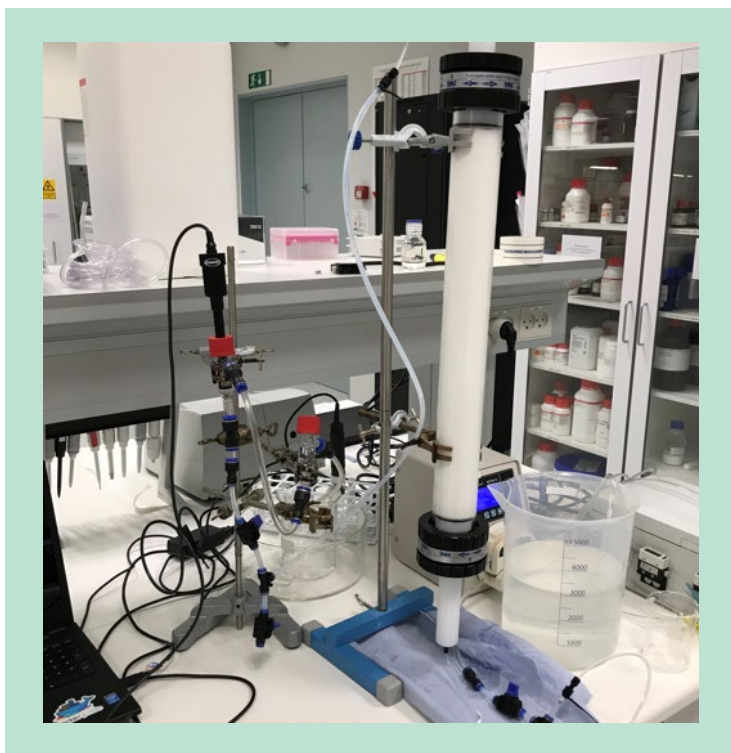


**FIGURE 11.** Experimental set-up for testing of the ion exchange capacity – here illustrated with ion exchange of chloride.

For each anion the following experimental procedure was followed:

1. Initially the diamine coupled resin was activated with CO<sub>2</sub> by up-flow recycling through the column with CO<sub>2</sub> saturated demineralized water. Recycling and CO<sub>2</sub> activation took place over 3 hours. CO<sub>2</sub> saturation was ensured by recycling of the demineralized water through a column aerated with pure CO<sub>2</sub> dosed by a micro-porous diffusor
2. After CO<sub>2</sub> activation 1000 ml of a solution with a known mass of the target anion dissolved in demineralized water was pumped through the column with a pump flow of 20 mL/min.
  - Sample A: Feed solution.
3. Following this the input was switched to demineralized water.
4. Sampling of the column effluent was planned according to the observed retention time distribution for the applied flow. The objective was to collect all effluent anion mass in one sample, C, containing the effluent peak and took place as follows:
  - Sample B: Effluent from the column for the period 0-20 min (approx. 400 ml)
  - Sample C: Effluent from the column for the period 20-100 min (approx. 1600 ml)
  - Sample D: Effluent from the column for the period 100-120 min (approx. 400 ml)
5. Subsequently, the column was washed with 0.1 M KOH to eluate the exchanged anion and the following effluent samples were taken to identify the ion exchanged mass - i.e. the capacity of the ion exchanger towards the target anion:
  - Sample E: Effluent from the column for the period 0-20 min. (approx. 400 mL)
  - Sample F: Effluent from the column for the period 20-100 min. (approx. 1600 mL)
  - Sample G: Effluent from the column for the period 100-120 min. (approx. 400 mL).

Figure 12 shows a photo of the 1 L column with diamine coupled resin used for the experimental work.



**FIGURE 12.** Experimental set-up for 980 mL column with diamine-coupled resin applied for ion exchange test.

Samples for the chloride ion exchange experiment were analyzed at KU. Sodium was determined by NMR and chloride was determined by silver titration.

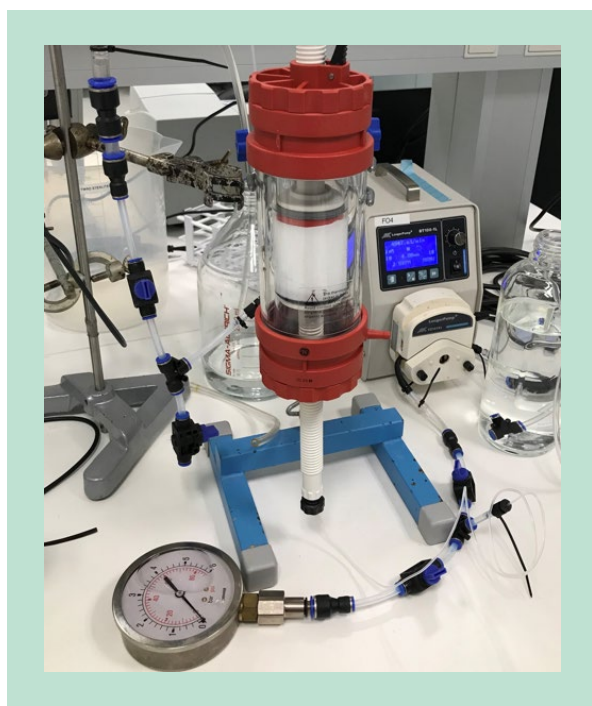
Feed sample and samples with fluoride peaks showing break-through of fluoride through loading and fluoride eluted with KOH were analyzed with AquaPorin's HACH meter (Type DR3900) using HACH reagents for determination of fluoride.

Feed sample and samples with nitrate peaks showing break-through of nitrate through column loading and nitrate eluted with KOH were analyzed with a HACH meter (Type DR3900) using HACH reagents for determination of nitrate.

Inorganic carbon released from the resin during the anion exchange was analyzed at Ultraqua's laboratory with a Shimadzu TOC-L CSH instrument.

### 5.3.2 Experimental setup for testing non-diamine coupled resin

For chloride an experiment was conducted to investigate whether the resin structure itself – without diamine coupling – was able to retain chloride. The experimental setup is shown in Figure 13.



**FIGURE 13.** Experimental set-up for 140 mL non-coupled resin test.

A sodium chloride solution with a well-defined mass of sodium and chloride was fed to a 140 ml column with non-diamine-coupled resin. The effluent volume was collected, and sodium and chloride were analyzed at KU.

Table 4 shows the results from the experiment with the 140 mL non-diamine-coupled resin column investigating potential sorption of chloride to the resin structure itself.

**TABLE 4.** Results from experiment with the 140 mL column resin not coupled with diamine.

Inlet and effluent	Mass Na <sup>+</sup>	Mass Cl <sup>-</sup>	Volume
Pulse Input: 5 mL 80 g Cl/L	263 mg	400 mg	5 mL
Effluent 5 mL/min	284 mg	428 mg	400 mL
Effluent 10 mL/min	293 mg	407	300 mL
Recovery 5 mL/min	108%	107%	
Recovery 10 mL/min	111%	102%	

The data shows complete recovery of chloride, and it could thus be concluded that there is no unspecific sorption related to the resin itself – and that the observed reversible sorption on the diamine coupled resin is related to ion exchange with the coupled diamine groups.

### 5.3.3 Experimental results for chloride

Detailed description and data for the experiment with exchange of chloride in the CO<sub>2</sub> saturated column are shown in Appendix 3. Table 5 gives a summary for the chloride mass balance data resulting from chemical analysis at KU.

**TABLE 5.** Main data from chloride ion exchange experiment.

Chloride Mass Balance		
Chloride mass fed to the column	2910	mg Cl
Chloride mass passing the column	574	mg Cl
Chloride mass eluted	2354	mg Cl
Total chloride mass re-covered	2928	mg Cl

As can be seen, the Cl removal under the actual experimental conditions was close to 80%. From the data, a chloride ion exchange capacity of 0.066 eqv/L of bed volume could be calculated. The overall chloride mass balance fits well for the chloride experiment. Sodium in the peak sample passing the column was determined at KU by NMR to 1.27 g Na/L. When calculating the sodium mass in the sample and comparing to the sodium mass in the feed volume of 1000 mL this shows a very fine agreement. Thus, no sodium was retained in the column when Cl was ion exchanged.

The chemical analyses from the chloride ion exchange experiment results showed that significant inorganic carbon (bicarbonate) was released from the resin during sorption of chloride – as also expected from the mechanistic hypothesis for the understanding of the process. The released inorganic carbon amounted to 0.094 eqv inorg-C, which is somewhat higher than expected from calculation of the ion exchanged chloride which amounted to 0.066 eqv Cl. However, it can be concluded that the experimental data supports the overall mechanistic hypothesis – and that more experimental work with resin with considerably higher capacity will be better suited for more detailed investigation of the mechanism and evaluation of the commercial possibilities.

### 5.3.4 Experimental results for Fluoride

Details regarding the experiment with ion exchange of fluoride with the CO<sub>2</sub> activated resin are given in Appendix 4. A summary of results is shown in Table 6.

**TABLE 6.** Mass balance data from fluoride ion exchange experiment

Fluoride	Value	Unit
Fluoride mass fed to the column	1460	mg F
Fluoride mass passing the column	552	mg F
Fluoride mass eluted	988	mg F
Total fluoride mass recovered	1540	mg F

From the table can be seen that 1460 mg fluoride was fed to the column. The effluent fluoride which was not exchanged in the column amounted to 552 mg while the captured fluoride amounted to 988 mg. The 552 mg fluoride not exchanged in the column was eluted in the effluent fraction corresponding to 0.4 and 1.6 column volumes (400-1600mL). While the mass



and concentration of fluoride in the effluent fractions 0-0.4 and 1.6-2 column volumes was below detection limit. This distribution of the non-exchanged fluoride was used later in the modeling of the fluoride ion exchange kinetics.

The sum of the fluoride detected in the effluent during loading and during the subsequent KOH wash amounted to 1540 mg – and when compared to the input fluoride the balance shows recovery of 105% of the influent. Thus, within acceptable uncertainty in the chemical analyses, all fluoride could be accounted for in the mass balance. As can be seen from the data, the removal of fluoride under the test conditions amounted to 68% of the incoming fluoride. From the data, the observed capacity under the test conditions for the 980 mL column for ion exchange removal of fluoride was calculated to be 0.052 eqv F/L of bed volume which is slightly less than for chloride. Analysis of inorganic carbon in the sample corresponding to the exchanged fluoride showed a bicarbonate release capacity of 0.040 eqv/L of bed volume.

### 5.3.5 Experimental results for nitrate

Details regarding the experiment with ion exchange of nitrate with the CO<sub>2</sub> activated resin are given in Appendix 5. A summary of results is shown in Table 7.

**TABLE 7.** Mass balance data from nitrate ion exchange experiment

Nitrate	Value	Unit
Nitrate mass fed to the column	5159	mg NO <sub>3</sub>
Nitrate mass passing the column	0	mg NO <sub>3</sub>
Nitrate mass eluted	3045	mg NO <sub>3</sub>
Total nitrate mass recovered	3045	mg NO <sub>3</sub>

From the table can be seen that 5159 mg nitrate was fed to the column. The effluent samples collecting the nitrate, which was not ion exchanged, amounted to zero, while the captured nitrate amounted to 3045 mg. Thus, the sum of the nitrate detected in the effluent during loading and during the subsequent KOH wash amounted to 3045 mg. Thus, the mass balance showed that 2114 mg was missing – apparently absorbed in the column by a mechanism not reversible through KOH washing. As can be seen from the data, the reversible ion exchange removal of nitrate under the test conditions amounted to 60% of the incoming nitrate. From the data, the observed capacity under the test conditions for the 980 mL column for ion exchange removal of nitrate was calculated to 0.049 eqv NO<sub>3</sub>/L of bed volume.

Analysis of inorg-C in the sample corresponding to the exchanged nitrate showed a bicarbonate release capacity of 0.091 eqv/L of bed volume.

### 5.3.6 Summary of results from ion exchange of chloride, fluoride, and nitrate

Summing up on the experimental work with ion exchange of chloride, fluoride, and nitrate on the first diamine coupled CowaTech resin after activation with CO<sub>2</sub> it can be concluded that all three tested anions can be exchanged. The observed ion exchange capacities are shown in Table 8. It should be noted that the observed sorption capacities are based on a non-optimized preliminary ion exchange material. Thus, the capacities are not to be compared with commercial ion exchange resins as it is expected that the capture capacities can be increased significantly through a commercial optimization program.

**TABLE 8.** Ion exchange capacities for the first CowaTech resin

Ion exchange capacities	Value	Unit
Chloride	0.066	eqv/L bed volume
Fluoride	0.052	eqv/L bed volume
Nitrate	0.049	eqv/L bed volume

The experimental work showed that the fundamental ion exchange mechanism involved exchange of the anions with bicarbonate from the CO<sub>2</sub> activated diamines. The mass of inorganic carbon released during loading with the three anions was analyzed. The observed bicarbonate data to be compared with the observed ion exchange capacities for the tested anions are shown in Table 9.

**TABLE 9.** Observed release of bicarbonate during ion exchange for the first CowaTech resin.

Bicarbonate release during maximum anion sorption	Value	Unit
Chloride	0.094	eqv/L bed volume
Fluoride	0.040	eqv/L bed volume
Nitrate	0.091	eqv/L bed volume

In conclusion it was demonstrated that the diamine coupled resin after activation with CO<sub>2</sub> performed as an ion exchanger with affinity towards sorption of chloride, fluoride, and nitrate. Thus, the hypothesis of ion exchange as the governing process for anion removal was confirmed. In exchange for sorption of the three tested anions, bicarbonate was released to the water. Ion exchange capacities were found to be in the range of 0.049-0.066 eqv/L bed volume. Corresponding released bicarbonate values were found in the range of 0.040-0,094 eqv/L bed volume.

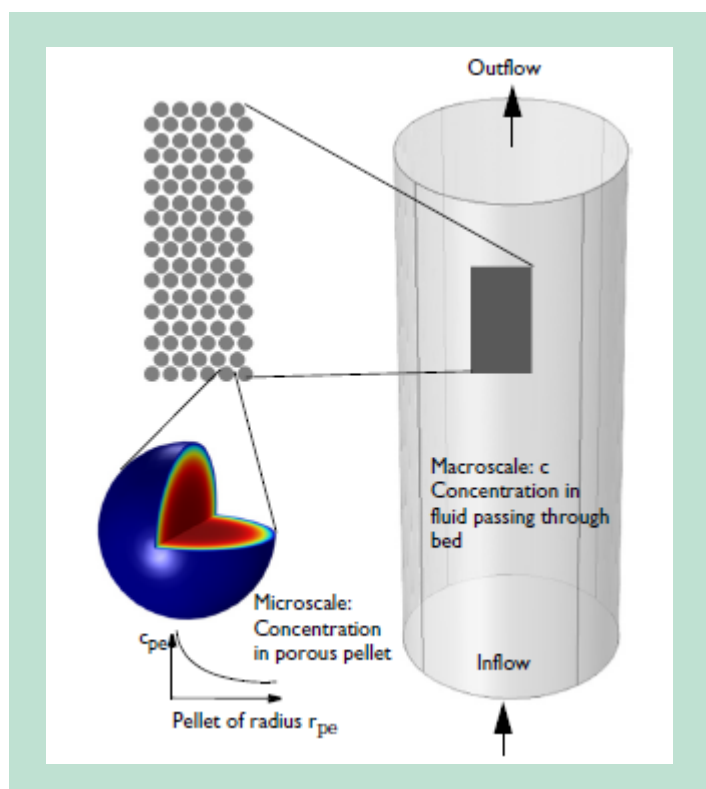
The results were found based on a single experiment with each anion. Thus, there is a need for further testing to confirm the calculated capacities. Furthermore, the experimental work does not demonstrate the relative affinity between the three anions. The selectivity towards specific anions is commercially interesting and will have to be investigated through a series of experiments with ion exchange in various mixed water matrices. Ion exchange material which shows high selectivity in complex water matrices towards problematic drinking water pollutants present in low to moderate concentrations – like e.g. fluoride or nitrate - will give ion exchange technology a market advantage in comparison with existing competing technologies.

## 6. Modelling of diamine-based ion-exchange column

The following chapter contains the description and results of using a 1D Advection-dispersion reactive pellet bed model setup in COMSOL Multiphysics. The developed model was applied to simulate the ion-exchange process and elution of the two ions based on the data obtained for chloride and fluoride in the CowaTech resin column investigations described in the previous chapter.

### 6.1 Modelling ion exchange kinetics in COMSOL Multiphysics

To establish the forward and reverse rate constant for the ion exchange of the different anions used in the experimental investigations with the first diamine coupled CowaTech ion exchange resin, a model of the column was setup in COMSOL Multiphysics. The model was setup to simulate transport of diluted species in porous media with the reactive pellet bed feature, that allows the simulation of regions filled with reactive pellets, as in packed bed ion exchange reactors. The pellets are simulated with the extra dimension technology that adds a radial microscale dimension inside each pellet as illustrated in Figure 14.



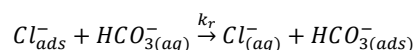
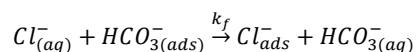
**FIGURE 14.** Schematic showing the macroscale (bed volume) and the microscale (pellet) [COMSOL, 2019, Chemical reaction engineering user guide].

On the macroscale the transport of diluted species is modelled through solving the advection-dispersion equation for the transport in between the individual pellets using the previously

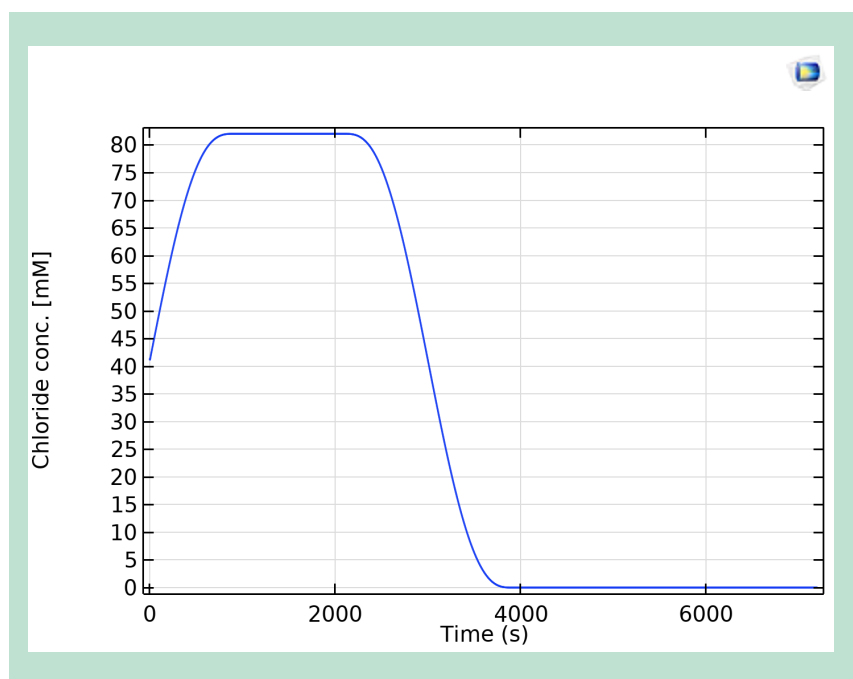
model determined mechanical dispersion coefficient. At the microscale, the transport(diffusion) and reaction equations inside the pellets are solved on an extra dimension attached to the macroscale physics interface. The model assumes that all resistance to mass transfer to/from the pellet is within the pellet and no resistance to pellet-fluid mass transfer is on the bulk(macroscale) fluid side. The concentration in the fluid will thus be equal to that in the pellet pore just at the pellet surface. Looking inside a pellet, assuming only concentration variations in the radial direction of the spherical pellet allows the setup of a spherically symmetric reaction-diffusion transport equation inside the pellet. Surface reactions are simulated inside the pellet. Surface species are introduced onto the pellets by adding them in the surface species section when defining the chemical reactions in the COMSOL chemical reaction engineering module.

### 6.1.1 Modelling the chloride anion exchange experiment

Using the geometrical data of the column, the size, surface area, porosity, and theoretical capacity of the resin particles as well as the molecular diffusion coefficients of chloride and bicarbonate, a 1D reactive pellet bed model was setup to simulate the data from chloride ion exchange experiment shown in table 5. The ion exchange process was setup in the chemical reaction engineering module of COMSOL as shown below:



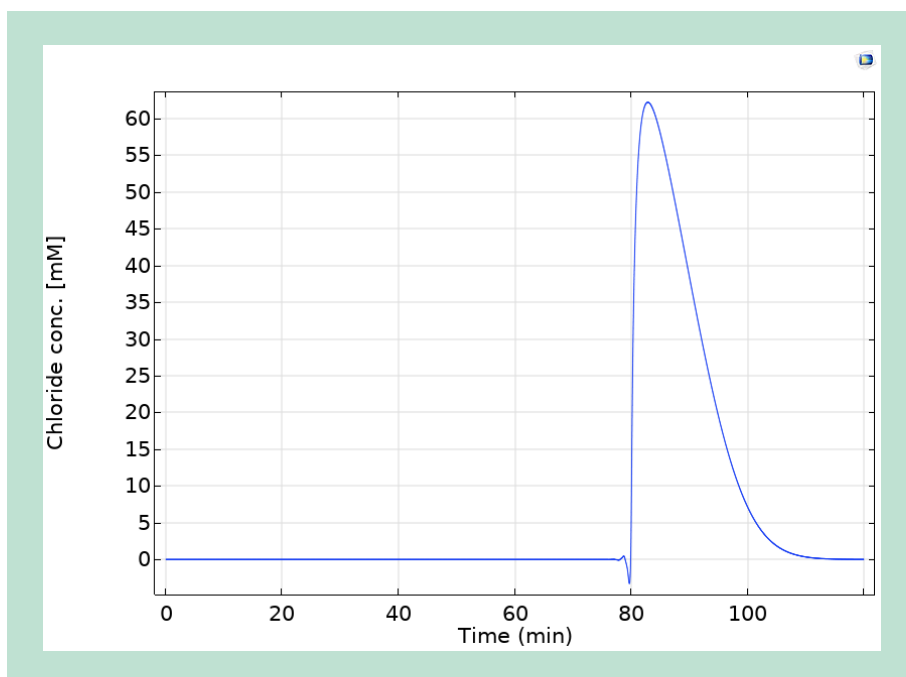
Where,  $k_f$  and  $k_r$  are the forward and reverse rate constants of the ion exchange process used as fitting parameters. The inlet dosing of the 1 liter 3 g/L chloride solution was simulated as a rectangular function with smooth transition zones to avoid steep gradients that can cause numerical errors as shown in Figure 15.



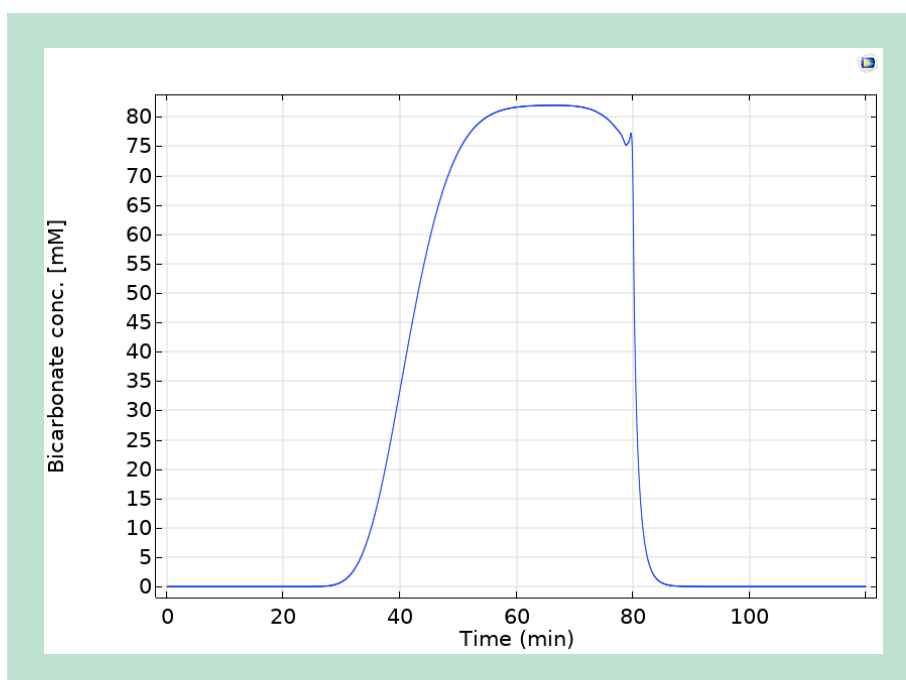
**FIGURE 15.** Chloride inlet condition used in the COMSOL model of the chloride ion exchange experiment.

The forward and reverse reaction rate constants of the ion exchange process was fitted so that the total amount of chloride leaving the column corresponded to the experimentally observed amount in the corresponding eluted volume fraction. With a forward reaction rate constant of  $50 \text{ M}^{-1}\text{s}^{-1}$  and a reverse rate constant of  $1 \text{ M}^{-1}\text{s}^{-1}$  the amount of chloride was the same as the

experimentally observed amount in the same elution volume fraction. This gave the below modelled elution curves for chloride and bicarbonate – see Figure 16-17.



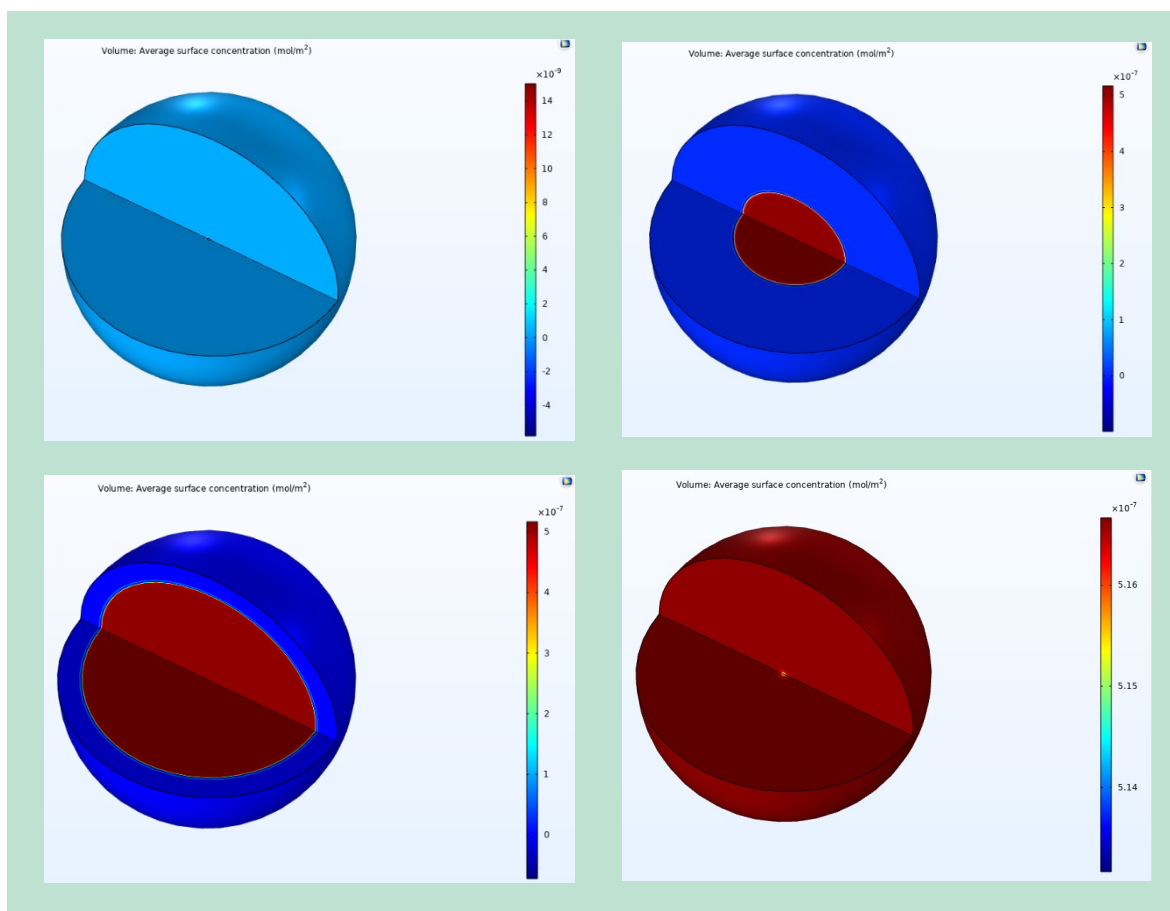
**FIGURE 16.** Modelled elution curve for chloride.



**FIGURE 17.** Modelled elution curve for bicarbonate.

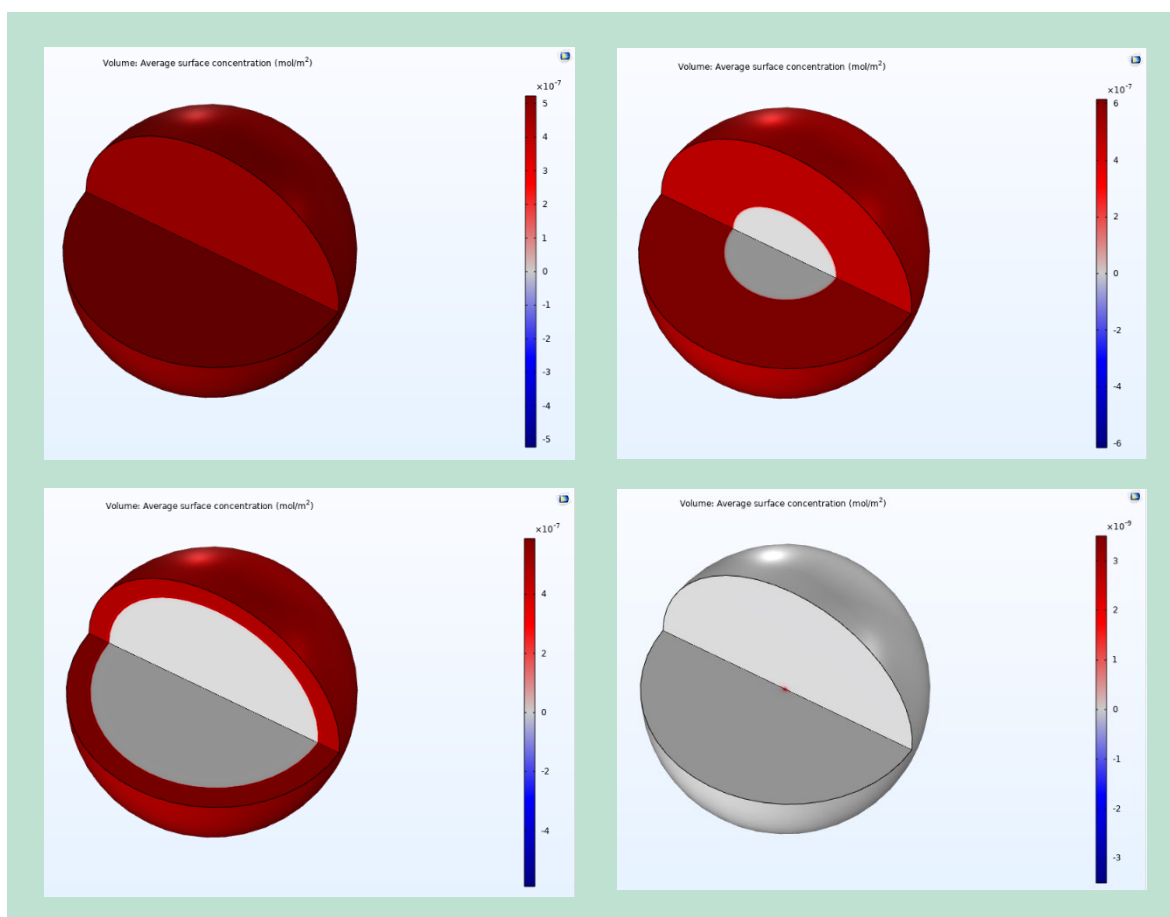
As seen from the modelled curves, the kinetics of the ion exchange process is fast enough to allow complete removal of chloride for  $1\frac{1}{2}$  column volumes after which the capacity of the column is close to exhausted, and the chloride starts to increase in the effluent until all non-removed chloride has passed the column. Simultaneously, the exchanged bicarbonate is eluted with increasing concentration over a period from around half a column volume until around  $1\frac{1}{2}$  column volumes after which the column capacity is exhausted.

On the microscale, the continuously increasing exhaustion of the resin pellet ion exchange capacity can be visualized through a 3D plot of the chloride surface concentration distribution within the individual resin pellets at different elution times as shown in Figure 18.



**FIGURE 18.** Average chloride surface concentration in resin particles at t=0s (top-left); t=2000s (top-right); t=4000s (bottom-left) and t=7200s (bottom-right).

As seen, the ion exchange capacity of the resin pellets is gradually consumed from the interior of the pellet towards the outer surface, due to the intra particle diffusion, until all capacity is consumed. On a macroscale this means that initially, all resin pellets in the top of the column starts to be saturated according to the evolution shown in Figure 18. On a macroscale this fits with the chloride elution curve in Figure 16, where all chloride is removed during the first 1½ column volumes corresponding to that the zone of unused resin pellet moves further down the column until the ion exchange capacity of all the resin particles has been consumed and the chloride concentration in the outlet starts to increase.

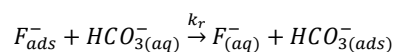
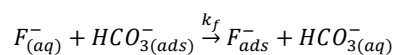


**FIGURE 19.** Average bicarbonate surface concentration in resin particles at  $t=0s$  (top-left);  $t=2000s$ ;  $t=4000s$  and  $t=7200s$ .

Conversely, the surface concentration of bicarbonate experiences a completely opposite process with a lowering of the surface concentration as the ion exchange process proceeds as shown in Figure 19.

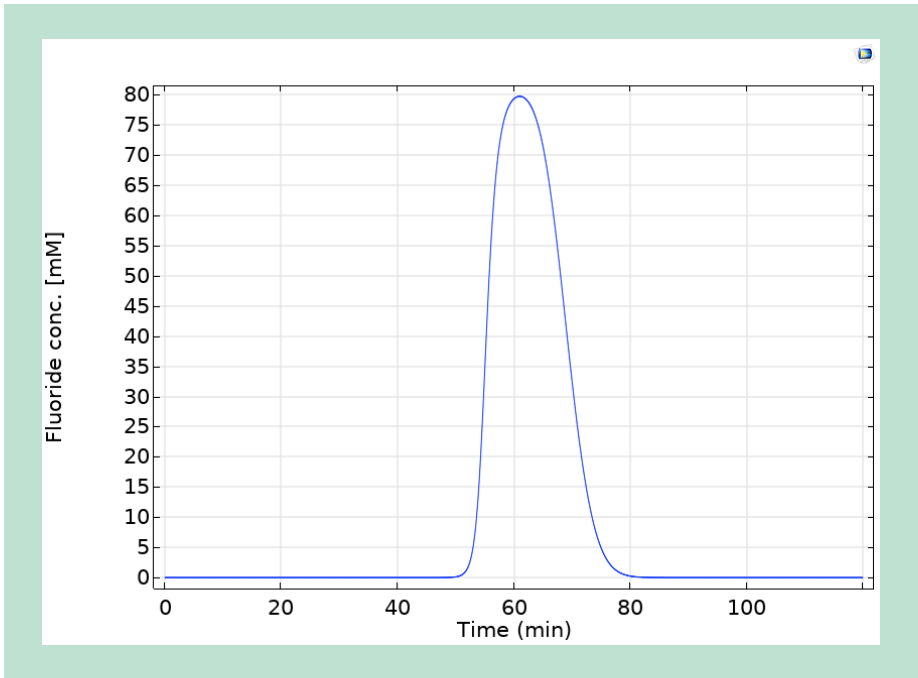
### 6.1.2 Modelling the fluoride anion exchange experiment

Using the same 1D reactive pellet bed model, the data from fluoride ion exchange experiment shown in Table 6 was modelled to establish the forward and reverse ion exchange rate constants for fluoride. The ion exchange process was setup in the chemical reaction engineering module of COMSOL as shown below:

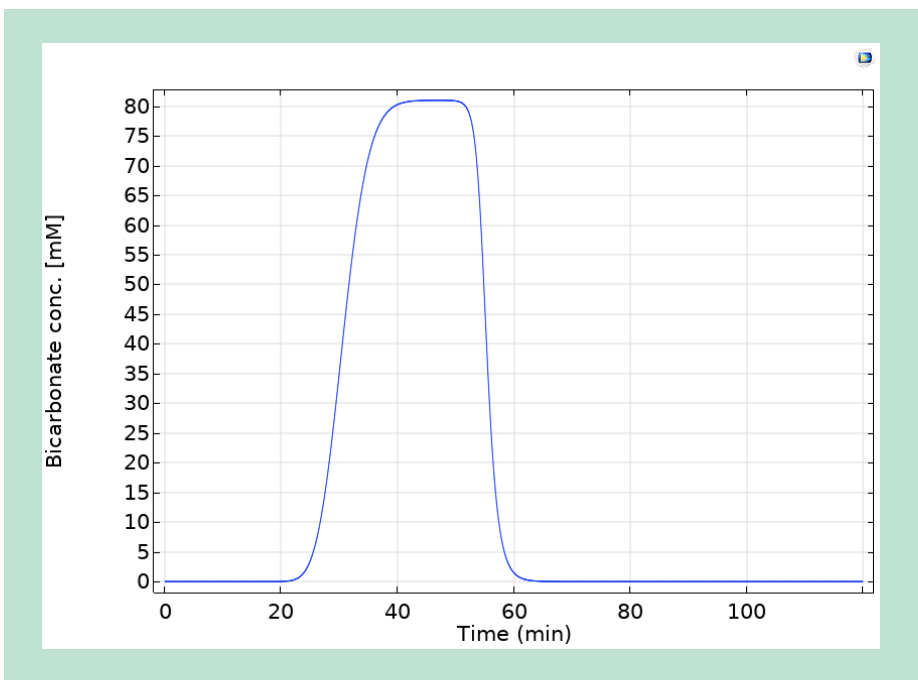


The inlet to the model column consisted of a 1 liter 1.55 g/L fluoride solution corresponding to approximately the same molar equivalents as the chloride experiments. The inlet was again simulated as a rectangular function with smooth transition zones.

The forward and reverse reaction rate constants of the ion exchange process was fitted so that the total amount of fluoride leaving the column corresponded to the experimentally observed amount in the corresponding eluted volume fraction. With a forward reaction rate constant of  $3 \text{ M}^{-1}\text{s}^{-1}$  and a reverse rate constant of  $1 \text{ M}^{-1}\text{s}^{-1}$ , the amount of fluoride was the same as the experimentally observed amount in the same elution volume fraction. This gave the below modelled elution curves for fluoride and bicarbonate – see Figure 20.



**FIGURE 20.** Modelled elution curve for fluoride.



**FIGURE 21.** Modelled elution curve for bicarbonate.

The eluted amount of fluoride was around 29 millimole while the corresponding eluted amount of chloride in the previous experiment was only 15 millimole. As such the capacity of the CowaTech column for fluoride ion exchange seems lower and in addition the ion exchange rate constant is also lower which could indicate lower selectivity towards fluoride ion exchange. The lower capacity and rate of fluoride ion exchange also result in that the non-exchanged fluoride ions are eluted from the column at much fewer column volumes as can be seen by comparing Figure 16 and Figure 20. The fact that fluoride is removed to a lower degree and at a lower rate than chloride means that when using the resin for treating real drinking water where the two ions are both present, the chloride ions would lower the capacity of



the column for fluoride removal. However, at the present stage of resin development, care should be taken in concluding too much on the selectivity of the resin towards the two ions as the observed data is only based on one dataset for each ion.

## **6.2 Conclusion and further investigations**

Based on the data obtained for chloride and fluoride ion-exchange in the experimental CowaTech resin column investigations, a 1D Advection-Dispersion reactive pellet bed model was successfully setup in COMSOL Multiphysics to simulate the ion-exchange process and elution of the two ions. By using the forward and reverse ion-exchange rate constants as fitting parameters the model was able to simulate the removal and elution of the two ions according to the observed data. The fitted second-order forward rate constants had values of 50 and 3  $\text{M}^{-1}\text{s}^{-1}$  for chloride and fluoride respectively indicating a higher affinity of the resin towards chloride than fluoride. This, lower affinity also resulted on lower capacity of the resin for fluoride removal compared to the chloride removal.

However, these conclusions are made based on only one dataset for each ion, why one should be very cautious to generalize based hereof. In fact, it is recommended to continue with further experimental and modelling investigations using the same approach as used in the current project to gain a more solid data for the observed ion exchange selectivity of the CowaTech resin and also to expand the investigation with other relevant anions and also to investigate real water matrices with different anion mixtures and also organic anions.

# 7. Preliminary toxicity assessment

The following preliminary toxicity assessment aims at estimating whether the use of the ion exchange technology based on the CowaTech resin as described in the previous sections could be limited due to concerns related to human consumption or contact or due to impact to the environment. The basis for the assessment is the physical-chemical properties and the diamine form (free diamine or bound to the resin), the toxicity and ecotoxicity as they are stated in the safety data sheet for the 3-dimethyl-1-propylamine (see Appendix 6) and a preliminary assessment of the potential exposure routes which could result in exposure of humans and the environment.

## 7.1 Concern related to human consumption or contact

The potential exposure routes related to human consumption and contact are:

- 1) Exposure to diamine and resin during the handling of these during the reaction of the free diamine with the resin in the ion exchange column
- 2) Exposure during the operation of the ion exchange column and during regeneration of the column, where the resin due to age/wear/regeneration with chemicals can be released from the column
- 3) Final disposal of column material at the end of the lifetime of the column, where the diamine will also be chemically bound to the resin.

3-dimethyl-1-propylamine is a strong base and exposure to skin, eyes and inhalation should be avoided. It is non cancerogenic and has a low toxicity if consumed. The resin itself is considered inert. It is assessed that human exposure and contact to the diamine and the resin can be avoided/limited in both situation 1 and 3, as it is assumed that good production procedures and the use of personal precautions and protective equipment can be followed. Further, disposal procedures can follow the safety precautions stated in the safety data sheet, see Appendix 6.

During the operation of the ion exchange column there will be a loss of ion exchange material, due to wear-out and the impact of regeneration chemicals. However, since the diamine will form a very strong C-C bond to the resin, neither the diamine nor the resin will be lost from the ion exchanger in a free form. When the ion exchange column loses material, it will be in the form of the diamine bound to the resin which can be considered inert.

It is expected that the binding between the resin and the diamine may hydrolyze if the regeneration is done at high pH -  $\text{pH} > 13$  - and high temperature. This might result in release of the diamine and resin in a different form. If the ion exchange column is used for drinking water purposes, very high pH combined with high temperature should be avoided during regeneration. However, regeneration of the CowaTech ion exchange material do not need strong base - and no high temperature is needed either.

If the safety precautions of the 3-dimethyl-1propyl amine and the resin are followed, and regeneration is performed as recommended, the use of the technology based on the immobilized CowaTech ion exchange technology should not lead to concern related to human concern and contact.

## **7.2 Concern related to impact on the environment**

The potential exposure routes related to impact on the environment are:

- 1) Spill of diamine and resin to the wastewater system, during the handling of these during the reaction of the free diamine with the resin in the ion exchange column
- 2) Exposure during the operation of the ion exchange column and during regeneration of the column, where the resin due to age/wear/regeneration with chemicals can be released from the column
- 3) Final disposal of column material at the end of the lifetime of the column, where the diamine will also be chemically bound to the resin.

It is assessed that spills of the diamine and the resin can be avoided/limited in both situation 1 and 3 using good production procedures securing that spill is avoided and contained. Further, disposal procedures can follow the safety precautions stated in the safety data sheet (Appendix 6). If 3-dimethyl-1propylamine eventually should reach the environment it is easily degradable in the environment and has a low toxicity to algae and fish. Based on its octanol/water distribution coefficient it has a very low bioaccumulation potential. The resin is assessed to be environmentally inert.

Thus, if the safety precautions of the 3-dimethyl-1propyl amine and the resin are followed - as well as recommended operational procedures - the CowaTech technology as tested in this study should not lead to concern related to impact on the environment.

## **7.3 Conclusions**

Based on the above preliminary toxicity assessment, it can be concluded that if the safety precautions and recommended operational procedures are followed, the here developed and tested immobilized CowaTech ion exchange technology does not give rise to serious concern regarding toxicity related to human contact or consumption and the same can be concluded regarding toxicity related to impact on the environment.

It should be stressed that the above comprises a preliminary toxicity assessment and that activities to document a more comprehensive toxicity assessment will be a necessary component in a potential future development and optimization of the technology which might include other resin material, other diamines, and various polymeric substances.

## 8. Market opportunities for the CowaTech technology

**The global market for water treatment technology based on ion exchange is large and growing. The market includes applications in industry as well as in public water supply. The global market for adsorbents for drinking water treatment is expected to grow by 5% per year in the coming years. Despite there are numerous players in the market, there is still a need for new adsorbents and room for new players. Market opportunities for ion exchange technology for removal of chloride, fluoride, and nitrate are illustrated. Maximum capacity and selectivity are important parameters to be investigated to identify the technology's future competitiveness in the market.**

### 8.1 Chloride control in closed cooling water systems

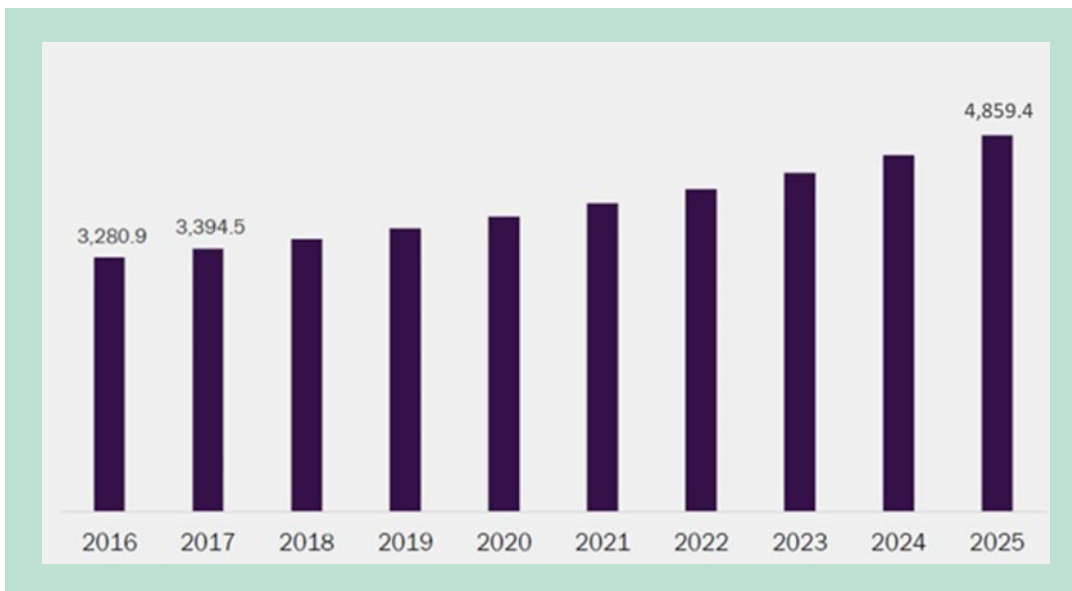
Evaporative cooling towers are used to remove excess heat from various sources like industrial manufacturing facilities, oil and gas production, thermo-electric power stations and office buildings and complexes (heating as well as A/C and ventilation). Evaporative cooling towers is a highly used technology which is applied world-wide.

Cooling water is circulated in pipes connecting the facility's excess heat generating unit operations and finally the collected excess heat is released in the connected open cooling tower through evaporation. The evaporation of cooling water causes the salt content of the cooling water to increase, and the increased salt concentration might cause corrosion problems in the cooling water piping and heat exchanger system. Further, the increased salt concentration might result in problems meeting environmental effluent standards for discharge of the "bleed off" of cooling water needed to maintain an acceptable salt concentration in the cooling water.

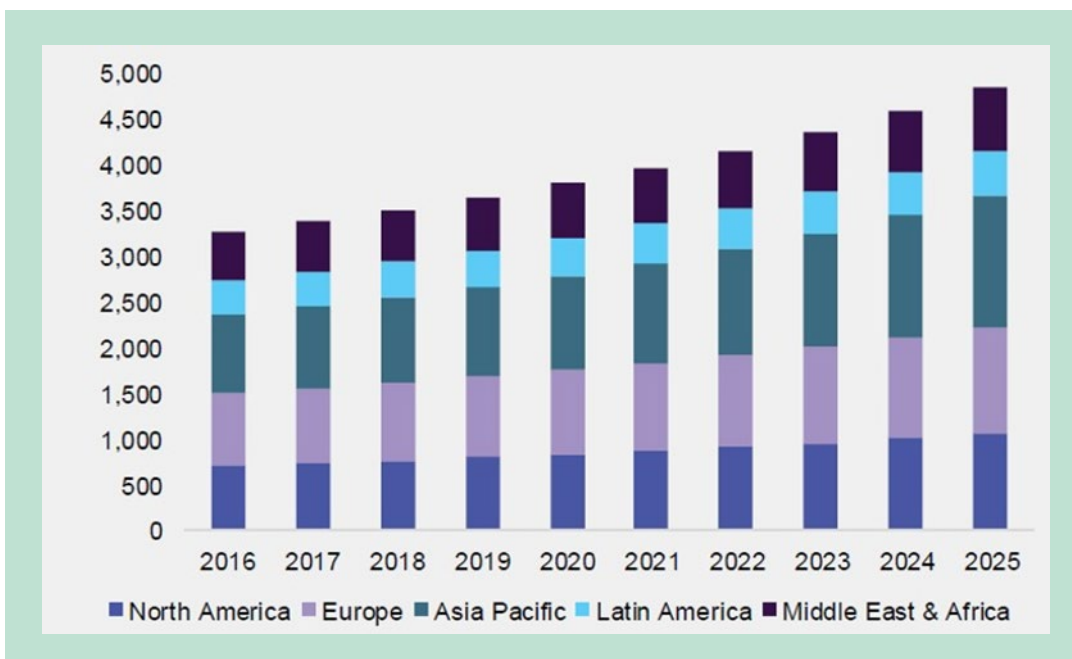
It is here expected that the CowaTech technology can be applied for control of the chloride level – and potentially other anions - in the cooling water. Further, the technology can be applied to increase water efficiency of existing systems. This means that the market potential for the CowaTech technology might be closely connected to the market for cooling towers and evaporative cooling water technology. Thus, an overview for this market is given below.

The global market for cooling towers and cooling water technology amounted to 3.3 billion USD in 2016 and is expected to grow to 4.9 billion USD in 2025, see Figure 22. This corresponds to a CAGR of 4.9% driven by increased industrialization worldwide.

The cooling tower market is global and with expected growth in all regions. It is particularly foreseen that the Asia Pacific region will have a higher growth rate than other regions – expected CAGR is 6.5%, see Figure 23.



**FIGURE 22.** Cooling towers market, 2016-2025 (USD Million). Source: [www.grandviewresearch.com](http://www.grandviewresearch.com).



**FIGURE 23.** Cooling towers – market size and growth prospect mapping. Source: [grandviewresearch.com](http://grandviewresearch.com).

The most frequently applied types of cooling tower systems comprise open-circuit, closed-circuit and hybrid systems. Especially the hybrid cooling tower systems are expected to show the highest growth rate since they are more water efficient than the other types. It is expected that the CowaTech technology will be applicable for cooling tower systems for reduction of chloride concentrations – and potentially other accumulation anions – from the cooling water. The technology might be used for installation in the cooling water loop to maintain a certain low level of chloride in the cooling water loop as dictated by the standards of the materials applied in the piping and heat exchangers – or it might be installed as a treatment technology to ensure compliance with effluent standards prior to discharge of the needed “bleed-off” to receiving water bodies.

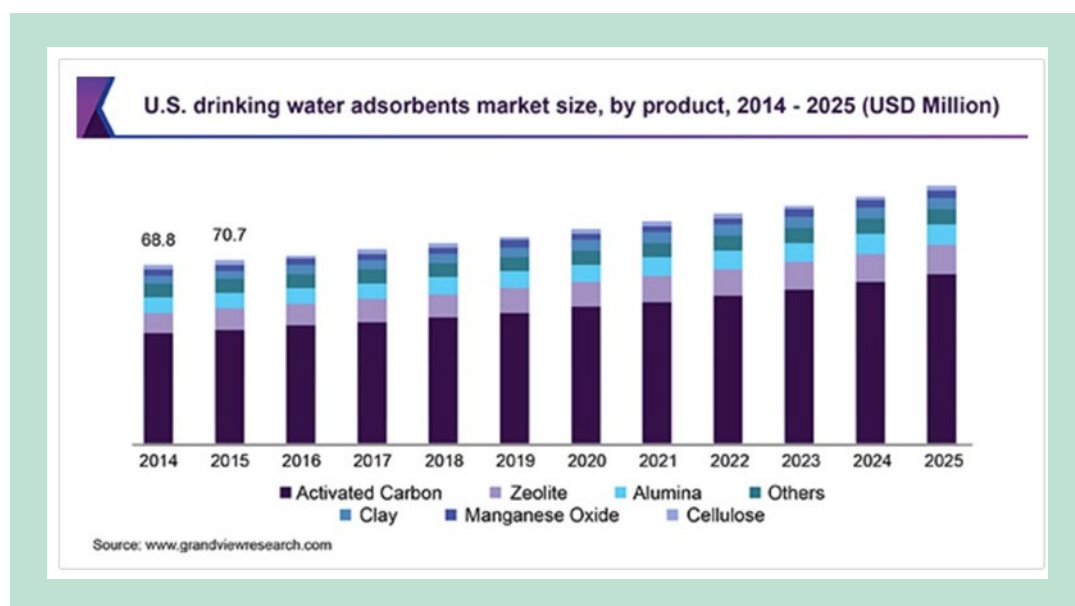
A number of large players at the global market can be mentioned, e.g. SPX Corporation, Baltimore Aircoil Company (BAC), Evapo Inc. and Paharpur Cooling Towers. In Denmark a number of local water treatment companies offer products and services within water based cooling tower systems – e.g. Silhorko (Grundfos company), BWT, Niras, Dansk Køl, Krüger.

## 8.2 Market opportunities in drinking water treatment

The global market for adsorbents for drinking water treatment amounted in 2018 to 459 million USD and is expected to grow by 5% per year in the coming years. USA is one of the largest markets and like for the rest of the global market activated carbon is the dominating adsorbent, see Figure 24.

In spite of the fact, that there is a huge number of commercial players in the field, there is still a need for new adsorbents and room for new players as also noted by the market analysis company grandviewresearch:

*” Rising demand for adsorbents for the filtration of drinking water offers huge opportunities for new manufacturers to enter the market. Furthermore, this surging demand coupled with growth opportunities in developing countries is expected to play a significant role in paving the way for local players to expand their business portfolio.”*



**FIGURE 24.** Water market size by product for drinking water adsorbents in USA.

To investigate preliminarily the potential role for the CowaTech technology in the global drinking water adsorbent market it was decided in the project to screen the technology’s performance towards three selected problematic anion drinking water components – chloride, fluoride, and nitrate.

In the following is given a brief description of the background for drinking water problems with chloride, fluoride, and nitrate.

Problems related to chloride in drinking water can arise from numerous reasons. A typical scenario might be intrusion of salt water to the groundwater basin in coastal areas – often caused by overexploitation of the fresh groundwater due to the increased urbanization and industrialization often taking place in coastal zones. In the same way overexploitation of water from inland wells has in many places globally caused increased levels of chloride creating increased need for desalination, where the concentration of chloride has passed the limit for salty taste – typically around 250 mg/L. In such situations with low to moderate salt increases ion exchange

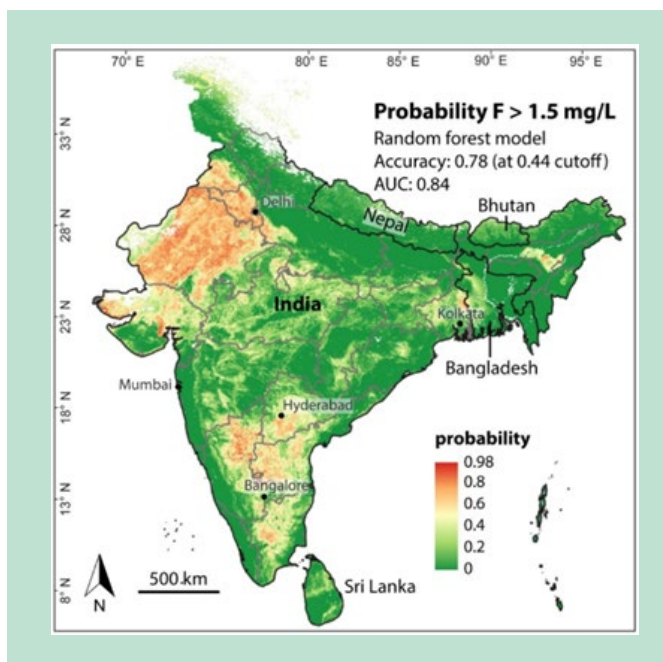
will often be relevant due to the low to moderate level of salt to be removed. For water qualities with high salt content – like seawater or salty brackish water – other solutions like reverse osmosis or evaporative technologies will most often be more attractive.

However, without going into details, the market for technology to cope with low to moderate chloride levels is huge. The commercial viability for this technology for chloride removal applications will to a high degree depend on the chloride sorption capacity for the technology.

Fluoride is found in groundwater based on natural sources – soil composition etc. - but might also reach increased levels based on pollution from industrial waste. In small concentrations fluoride is a healthy component in drinking water. However, elevated levels of fluoride intake through food or drinking water is an unwanted component, which can lead to fluorosis – an illness resulting in damage to teeth, bone deformations and disturbances in body growth.

Fluorosis is a health threat in many countries and affects the life of around 200 million people globally – mainly in India and surrounding countries. WHO considers the upper limit for a healthy drinking water to be a concentration around 1.5 mg/L fluoride. However, already at fluoride concentrations of 0.9-1.2 mg per liter initial signs of fluorosis can be observed.

In India approximately 62 million people is suffering from fluorosis – hereof 6 million children. It is estimated that 120 million people are living in areas where the fluoride content in the drinking water exceeds the recommended WHO maximum level, see Figure 25.



**FIGURE 25.** Map showing the probability distribution of groundwater in India exceeding the recommended maximum of 1,5 mg/L fluoride.

The Indian government has decided that facilities for fluoride removal from drinking water must be installed in the affected regions and has initiated this huge task. Large reverse osmosis plants are under construction in densely populated highly urbanized areas. However, this technology is not feasible in less densely populated urban or even rural areas where a variety of other technologies might be relevant. More than ten different technologies exist, however, most of them show low efficiency in large scale installation or they have high CAPEX and OPEX.

Thus, there is a real need and market pull for a better and more cost-effective technology for fluoride removal, and this is the reason behind the testing of the CowaTech technology's efficiency and capacity towards fluoride removal. Due to the low concentration level of fluoride in

groundwater – a few mg/L – the CowaTech technology would be very attractive if the ion exchange mechanism turns out to be selective towards fluoride when compared to competing anions that are harmless but present in much higher concentrations. The experimental work has shown that the capacity of the CowaTech technology for fluoride removal is comparable to chloride removal – but the topic of selectivity remains to be investigated.

Nitrate in the groundwater originates mainly from human activities – a main source in developed countries is the application of nitrogen fertilizer or manure in farming. In some arid regions where irrigation with untreated or poorly treated wastewater has been practiced for decades this activity has caused the nitrate level in the ground water to increase to critical levels. Nitrate is easily dissolved in water and is transported by rainwater to the groundwater.

WHO's guideline value for the content of nitrate in drinking water is 50 mg/L – corresponding to 11 mg/L of nitrate-nitrogen. The guideline value is based on a wish to protect bottle-fed babies from the “blue baby” phenomenon, where the oxygen carrying capacity of a bottle-fed baby is reduced visibly by the nitrate in the water turning the skin blueish.

*“The guideline value for nitrate of 50 mg/l as nitrate is based on epidemiological evidence for methaemoglobinaemia in infants, which results from short-term exposure and is protective for bottle-fed infants and, consequently, other population groups.”*

There is an ongoing discussion regarding the potential long-term effect on humans of high nitrate levels in drinking water. The potential long-term effects from the nitrate would be related to long-term body response to nitrite originating from the nitrate intake. In a Danish study published in 2018 – J. Schullehner et al, *Int J Cancer*. 2018 Jul 1;143(1) - researchers found a correlation between the concentration of nitrate in drinking water and colon and rectal cancer – even if the nitrate concentration is much smaller than the European norm of 50 mg/l. The study included a total of 2.7 million Danes during the period 1978-2011, Based on the results the researchers behind the study plea to lower the norm of nitrate in the Drinking Water Directive.

Two technologies are dominating when it comes to removal of nitrate from drinking water – reverse osmosis and ion exchange.

Ion exchange is the cheapest solution, but it has issues relating to selectivity. The existing ion exchangers are strongly alkaline ion exchangers and prefer to take up divalent anions like sulphate. This reduces - significantly - the capacity for sorption of the monovalent nitrate which causes increased need for regeneration – and thus reduces the overall cost-efficiency of the technology.

The experimental work has indicated that the capacity for nitrate sorption of the CowaTech technology is comparable to the sorption capacity of fluoride. However, the selectivity of the CowaTech technology towards nitrate sorption in a mixed water matrix remains to be investigated.

### 8.3 Conclusions

Globally, the market for water treatment by ion exchange technology is large and growing. The market covers applications in industry as well as public water supply.

Ion exchange based on CowaTech's technology has demonstrated efficient removal of the anions: chloride, fluoride, and nitrate. During the ion exchange the anions were exchanged with bicarbonate released to the treated water. Exchange of chloride, fluoride, and nitrate with bicarbonate will be attractive in many applications in the global water market.

The experimental work has been targeting mainly documentation of the fundamental mechanism for the technology and providing documentation for the ability of the technology to capture three anions for which a known market exists. Expectedly, the technology will be able to capture several other anions.



The experimental work has not covered investigation of the potential maximum capacity for the ion exchange technology after optimization of the coupling of diamines to a more optimal resin than applied here. Further, the experimental work has not included investigation of the selectivity of the ion exchange technology in mixed water matrices – i.e. the preference for the ion exchanger to capture certain anions to a higher degree than other anions. Both maximum capacity and selectivity are important parameters for the technology's competitiveness in the market. Thus, there are still important issues which need to be investigated and considerable RDI work that needs to be undertaken before an assessment can be done regarding this new technology's commercial and environmental viability and overall potential in the water technology market.

## 9. Conclusions and recommendations

The conclusions on investigations undertaken in a specially designed test reactor was that the potentially new disruptive desalination technology process was in fact not a desalination process removing both cations and anions. Rather it was shown to be an anion exchange process where the CO<sub>2</sub> activated diamine was able to exchange the formed bicarbonate with chloride anions in solution.

During initial experimental work in lab-scale based on this hypothesis, the problem of separating the treated water from the polymers/diamine for evaluation of the process efficiency turned out to be a major issue. Thus, it was decided to continue the experimental work based on a system with immobilized diamines coupled to resin in a column. With the column test system, the separation issue was solved through the design of the technology concept.

Based on the experimental work on ion exchange with the test column it was found that the CO<sub>2</sub> activated immobilized diamine was able to exchange bicarbonate with chloride, fluoride, and nitrate. For the test column the ion exchange capacity was determined for the three anions. The following values were found:

Ion exchange capacities	Value	Unit
Chloride	0.066	eqv/L bed volume
Fluoride	0.052	eqv/L bed volume
Nitrate	0.049	eqv/L bed volume

The identified capacities are not to be compared to capacities for commercial ion exchange resins as the resin has not been optimized. The experimental work showed that bicarbonate was exchanged with the target anions. It was demonstrated that the column could be regenerated with KOH.

Based on the experimental data obtained for chloride and fluoride ion-exchange of the CowaTech resin, a 1D Advection-dispersion reactive pellet bed model was successfully setup in COMSOL Multiphysics to simulate the ion-exchange process and elution of the two ions. The model description enables the virtual scaling up of the column from laboratory scale to industrial scale.

The market for water treatment technology based on ion exchange is large and growing. In spite of the fact that there is a huge number of commercial players in the field, there is still a need for new adsorbents and room for new players.

A future development of the CowaTech resin concept will need considerable experimental work regarding optimization of the resin capacity, testing of selectivity of the ion exchange capability in complex water matrices, and investigation into regeneration of the resin. The investigations are fundamental in fully elucidating and determining the potential commercial viability and environmental sustainability of the new technology based on the CowaTech resin concept.

# Appendix 1. Review on existing knowledge

## Appendix 1.1 Preface

The review report is part of the MUDP-funded RDI-project: Innovative and energy efficient desalination technology – CowaTech technology. The MUDP-project was started in 2019 and is building on previous research results from Copenhagen University, Dept. of Chemistry. The objective of the Appendix is to summarize the existing knowledge at the initiation of the MUDP project regarding the process under investigation: Carbon dioxide driven ion separation for desalination; and to identify RDI needs for further experimental RDI to clarify the fundamental mechanism, process design and technology selection and dimensioning as a background for establishing a proper viability assessment for the technology.

## Appendix 1.2 Introduction

Water is arguably the most important molecule on Earth. All forms of life consist of water, which also provides the essential environment for proliferation of life. However, recent global climate changes are seemingly accelerating the unpredictability of secure water supply sources—even in developed countries—threatening society’s sustainable growth. Over one-third of the world’s population is exposed to water-stress situations. A value projected to grow to more than half of the world population in 2025. This global societal issue is now entangled together with many other problems, including environment sustainability, public health and energy security.

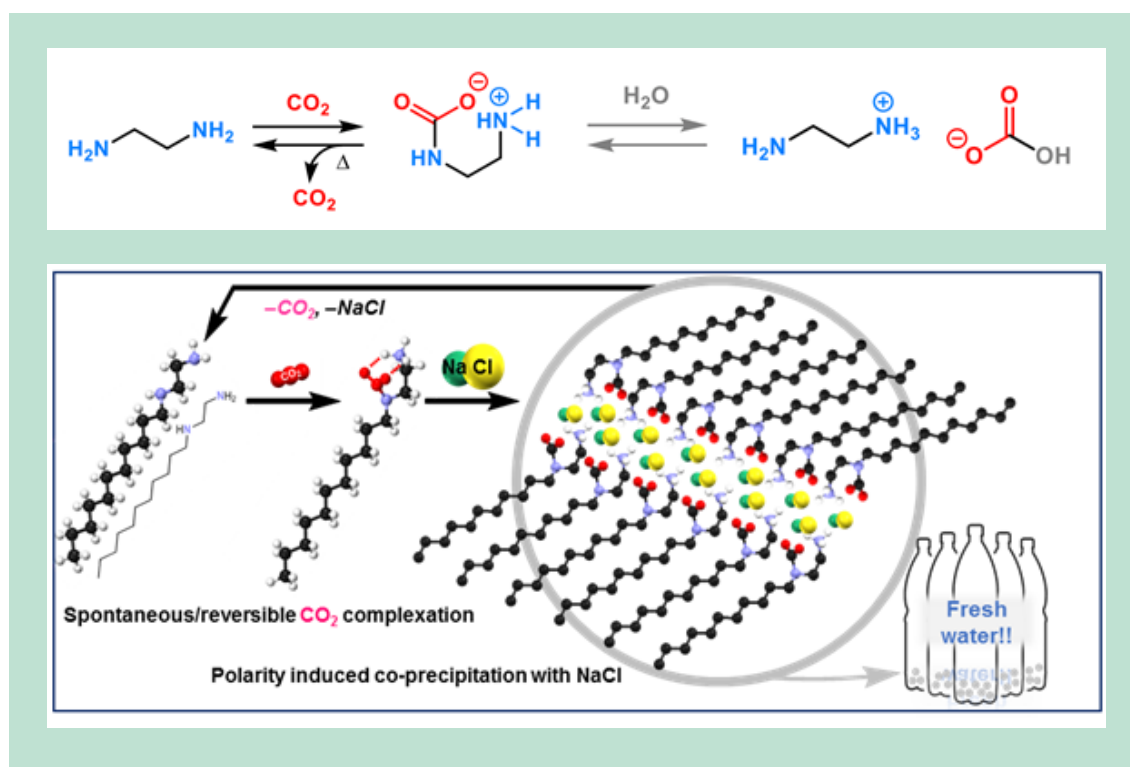
Desalination of sea water or brackish water is one of the permanent solutions for secured potable water supply. Although reverse osmosis implemented with membrane materials can provide efficient desalination process, more practical and energy-neutral process is yet to be developed. Herein, we demonstrated facile desalination catalyzed by carbon dioxide and promoted by CO<sub>2</sub>-responsive diamines, which can dynamically self-aggregate and co-precipitation with NaCl from aqueous media, completing desalination to 99.6% salinity reduction. Recent development in more unconventional desalination or potable water production heavily depend on solar energy (ACS Nano, DOI: 10.1021/acsnano.7b08196) with an aid of selective solid state material for water harvesting from air (H. Kim et al., Science, 10.1126/science.aam8743 (2017)).

The on-going industrial and research efforts addressing the issue of desalination are mainly focused on engineering aspects: developing more efficient reverse osmosis membranes and related interfaces, as a mean to reduce energy consumption. Compared to conventional thermal desalination plants, semi-permeable membranes are a great improvement. However, the energy consumption of the state-of-the-art systems (1.8 kWh/m<sup>3</sup>) is still considerably higher than the theoretical minimum energy of desalination for seawater at 35,000 parts per million salt and at a typical pure water recovery of 50 % (1.06 kWh/m<sup>3</sup>). This technology largely aims at rejecting ions on the boundary of a semipermeable membrane. Therefore, it requires high pressures, which is highly energy intensive, and is consequently mostly used in large-scale plants. The development of simpler, light-weighted desalination methods and materials is therefore highly desirable, to increase water availability for individuals under extreme conditions. In this context, it is quite surprising that (to the best of my knowledge) there are no significant research programs addressing the desalination processes while underlining fundamental science.

### Appendix 1.3 Background

Organic amines can reversibly complex with carbon dioxide, resulting in the thermally labile carbamate salt. This reaction is more prominent in the case of diamines, because of the intra-molecular stabilization effect provided by hydrogen bonding and ion-ion interactions (Figure A1.1).

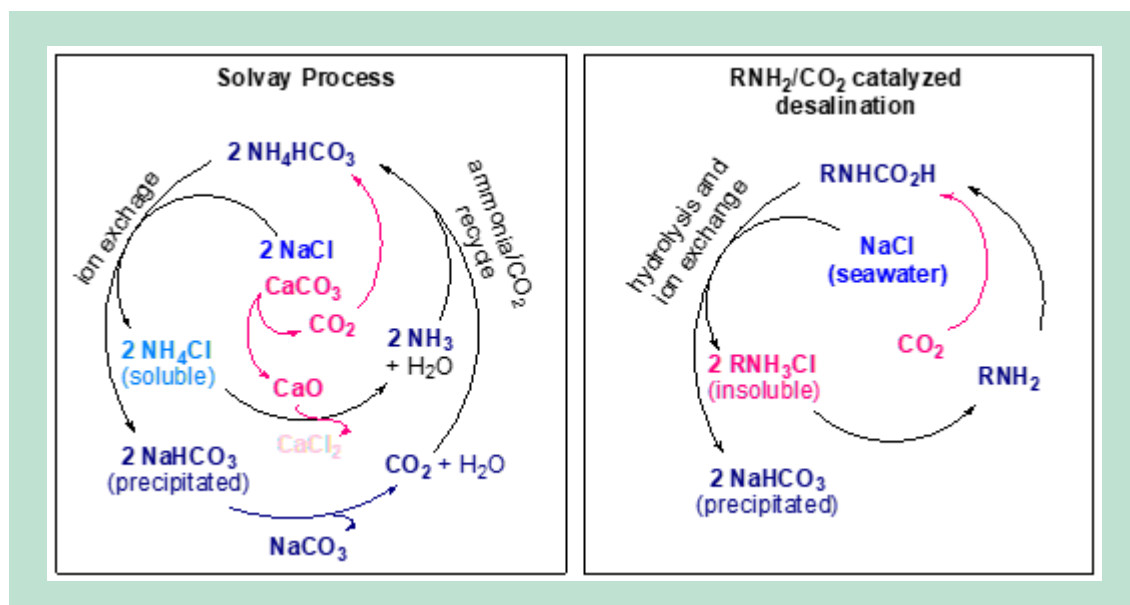
Under reduced pressure or higher temperature, the dissociation of CO<sub>2</sub> occurs spontaneously, and the parent diamines are regenerated. This reversible carbon dioxide capture process has been well studied and applied in many fields, namely in carbon capture processes (T. M. McDonald et al., Nature 2015, 519, 303). However, to the best of our knowledge, the polar diamine-CO<sub>2</sub> complex has not been utilized to capture polar species in aqueous phase. This might be rooted on in general high solubility of diamines and related compounds in water. For example, aqueous solution of aminoethanol has been the choice of amine-scrubbing for CO<sub>2</sub> capture, although the process suffers with the highly corrosive amine functional group and the energy penalty for regeneration due to the high heat capacity of water.



**FIGURE A1.1.** Reversible CO<sub>2</sub>-complexation of ethylene diamine and the concept of catalytic desalination using alkylated diamines and CO<sub>2</sub> induced self-aggregation.

A reported CO<sub>2</sub>-responsive autonomous aggregation (or precipitation) was powered by polarity alteration of the monomeric entity. The spontaneous self-assembly of nano-sized materials was demonstrated by decorating gold nanoparticles with diamines, upon which self-aggregate driven by the surface polarity changes of nano-particle by CO<sub>2</sub> exposure. Although CO<sub>2</sub> is one of the most problematic greenhouse gases, low toxicity of CO<sub>2</sub> and accessibility in chemical industry prompted us to provide a solution for desalination using the self-aggregating diamines utilizing carbon dioxide. Considering the polar nature of minerals in seawater, a CO<sub>2</sub>-responsive self-assembly should be able to induce co-precipitation or catalytic Solvay process with minerals, namely NaCl, in water. Solvay process has been utilized for producing sodium bicarbonate and sodium carbonate starting from ammonia, sea water and CO<sub>2</sub> in water, Figure A1.2. The lower solubility of sodium bicarbonate is the driving force to precipitate out the salt, however, the soluble ammonium chloride remains in the solution. In our desalination process,

the use of organic diamines will drive the process to generate insoluble ammonium chloride, which can complete the desalination by precipitating sodium bicarbonate. The insoluble ammonium chloride then can be recycled via base treatment, by removing HCl.



**FIGURE A1.2.** Comparison of Solvay process and amine- $\text{CO}_2$  catalyzed desalination.

This behaviour would be an energy-efficient process by using waste carbon dioxide, a greenhouse gas, whose excess is a major problem in itself. The organic  $\text{CO}_2$ -responsive materials—typically diamine derivatives—can be recycled by simple basification or reducing the pressure or using mild heat to release carbon dioxide and therefore generating organic amine/ $\text{NaCl}$  mixtures. Then this mixture can be processed for extraction to complete the catalytic cycle of desalination in terms of diamines and  $\text{CO}_2$ . To demonstrate the feasibility of the proposed catalytic desalination, we designed a simple experiment using a synthetically straightforward diamine.

#### Appendix 1.4 Design of desalination

The  $\text{CO}_2$ -mediated desalination using diamine will be conducted using general method as described below:

Alkyl-chain-modified diamine is treated with  $\text{CO}_2$  in saline water or seawater. Upon the spontaneous formation of carbamate or bicarbonate, or carbonate salt of ammonium cation, the  $\text{CO}_2$ -responsive unit is now activated to chelate  $\text{NaCl}$  (or salt). These ion-ion interactions can now trigger self-aggregation of the molecular unit by taking advantage of lone alkyl chain induced by Van der Waals forces. The outer sphere of the obtained high molecular weight molecular network is presumably hydrophobic therefore, exhibit low solubility in aqueous solutions. The spontaneous precipitation occurs within 60-120 seconds, where the separation can be performed to provide salinity-reduced water.

#### Appendix 1.5 Determination of salinity

Salinity was determined by measuring conductivity of the solution by employing electrode specialized for  $\text{NaCl}$  and other salt for water quality control (Figure 2). Background  $\text{CO}_2$  effect was measured to identify the conductivity difference in the presence of carbonate ions in deionized water and saline water in the absence of diamine additives. The observed conductivity changes were negligible (up to 60  $\mu\text{S}/\text{cm}$ , note that  $\text{NaCl}$  3.5 g/L corresponds to 6200  $\mu\text{S}/\text{cm}$ ). These experiments assured us that the effect of  $\text{CO}_2$  in salinity measurement will be only positive, therefore, the observed salinity reduction is not related to background  $\text{CO}_2$  introduction to the solution.

Benchtop NMR (Tveskaeg®) was employed to precisely determine concentrations of sodium cation and chloride ions in solution state. The measurement was conducted at room temperature with temperature compensation.

### **Appendix 1.6 Desalination by bubbling CO<sub>2</sub>**

As mentioned above, salinity was determined by measuring conductivity of the solution by employing electrode specialized for NaCl and other salt for water quality control. Pure CO<sub>2</sub> was introduced by syringe tubing or similar set-ups. The exothermic CO<sub>2</sub>-complexation generates fluctuation the CO<sub>2</sub>-absorption therefore, temperature control might be necessary. However, under operating reaction conditions, we employed reaction conditions without temperature control to show the easiness of the application of the invention in practical sense.

### **Appendix 1.7 Radical polymerization**

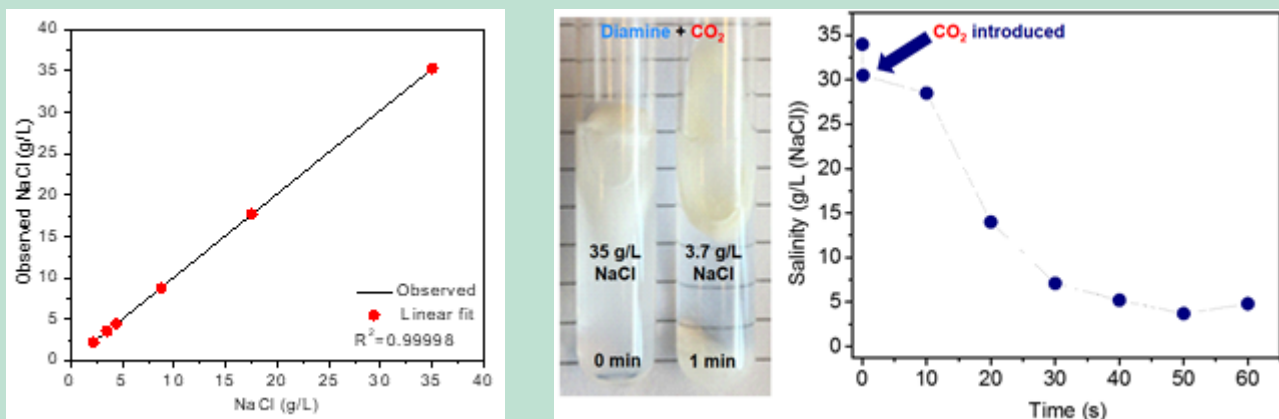
The stabilizer (t-butyl catechol) was removed from styrene and commercial 1,4-divinylbenzene by washing chemicals with excess of 1 per cent aqueous sodium hydroxide aqueous solution and twice with water. To a solution of water, acacia gum and sodium chloride, was added a styrene, 1,4-divinyl benzene, azobisisobutyronitrile, diamine and chlorobenzene. The reaction mixture was deoxygenated by purging with argon atmosphere for at least 30 min at room temperature. Then, the reaction vessel was heated to 110°C and stirred for 12 hours under N<sub>2</sub> atmosphere. After cooling to room temperature, the reaction mixture was filtered and washed with water. The polymeric residue was suspended in 300 mL of water and stirred for at least 1 hour and then filtered. The filtered residue was suspended in 400 mL of methanol and stirred for 1 hour and then filtered. After washing with adequate solvents, the polymer was dried overnight in vacuum to afford 6 g of diamine functionalized polymer as a white solid.

### **Appendix 1.8 Simplified synthesis of polymeric diamine**

To a solution of PEI (polyethyleneimine, random polymer) in THF, alkyl halide was added dropwise while keeping the reaction temperature to room temperature with water bath. The mixture was vigorously stirred for 18 h, and the reaction mixture was washed with organic solvents and water. The remaining gel-like polymers was then used without further purification.

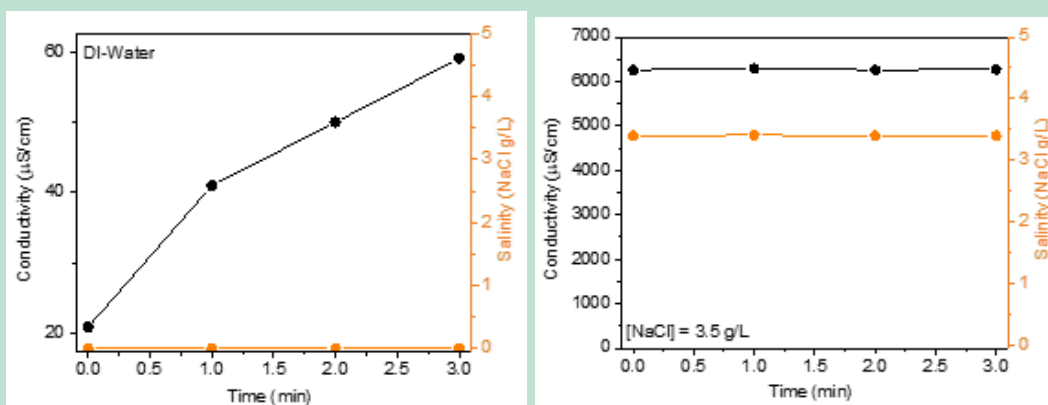
### **Appendix 1.9 Discussion**

We performed the desalination experiment using a model seawater solution (15 mL, NaCl 3.5 g/L, measured by a specialized salinity meter). A diamine (2 mL, 10 equivalents based on NaCl) was dispersed in the NaCl solution, and CO<sub>2</sub> was bubbled. Immediate precipitation was observed, while the temperature of the solution increased 2-3°C due to the exothermicity of the process. More importantly, the salinity of the model sea-water solution – estimated from conductivity measurement - dropped to 0.6 g/L—which implies a more than 85% NaCl reduction after 2 minutes. Furthermore, the test at the ‘real’ concentration of NaCl in aqueous solution (NaCl 35 g/L) showed also promising result, showing 90% reduction of salinity in 60 second, by introducing CO<sub>2</sub> ‘slowly’ while stirring the solution with magnetic stirrer – see Figure A1.3. These preliminary results highlight the importance of CO<sub>2</sub> concentration to the formation of aggregates, and more in-depth studies on kinetics and other experiments to quantitative CO<sub>2</sub>-diamine complexes will be followed.



**FIGURE A1.3.** Calibration curve of conductivity meter and salinity (Left). Diamine solution in saline water before CO<sub>2</sub> and after CO<sub>2</sub> introduction and recorded salinity of model sea water solution in the presence of diamine by function of time - blue arrow indicates when CO<sub>2</sub> is introduced (Right).

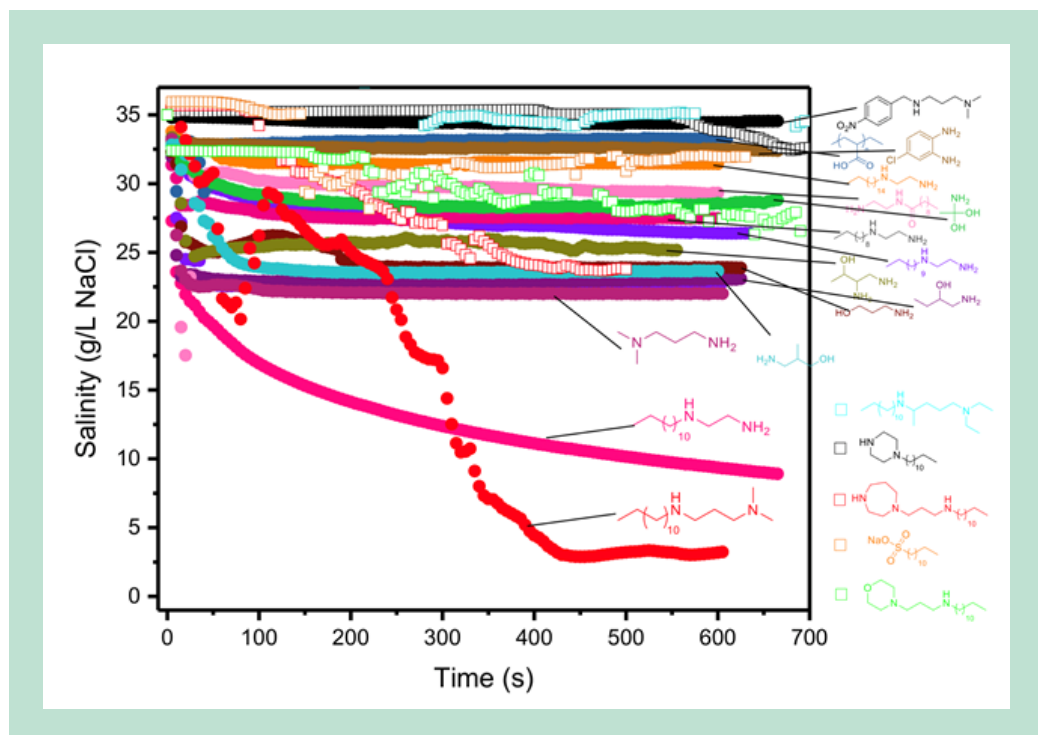
At this juncture, to rule out the effect of the applied CO<sub>2</sub> in the conductivity measurement and therefore salinity measurement, control experiments were performed in the absence of diamines under conditions with deionized water and saline water. The increase of conductivity was negligible (Figure A1.4). Although the solubility of CO<sub>2</sub> in water would change the conductivity of the solution by forming carbonic acid and (bi)carbonate, we concluded that the solubilized CO<sub>2</sub> and related ions would not affect our salinity measurement under our experimental conditions.



**FIGURE A1.4.** Control experiment of salinity/conductivity with CO<sub>2</sub> addition without amines with DI-water (Left) and with saline water (Right).

After identifying the performance of the diamine, we decided to reveal the structure-performance relationship of the diamine-mediated desalination process. We have tested more than 50 different nitrogen-based compounds including polymeric materials, see Figure A1.5. After this optimization, we concluded that diamine-based CO<sub>2</sub>-responsive materials were optimal for this process. Under “real”-conditions (35 g/L NaCl aq. solution), we achieved 89% reduction of NaCl within 60 seconds. And moreover, this NaCl-binding process was highly efficient such

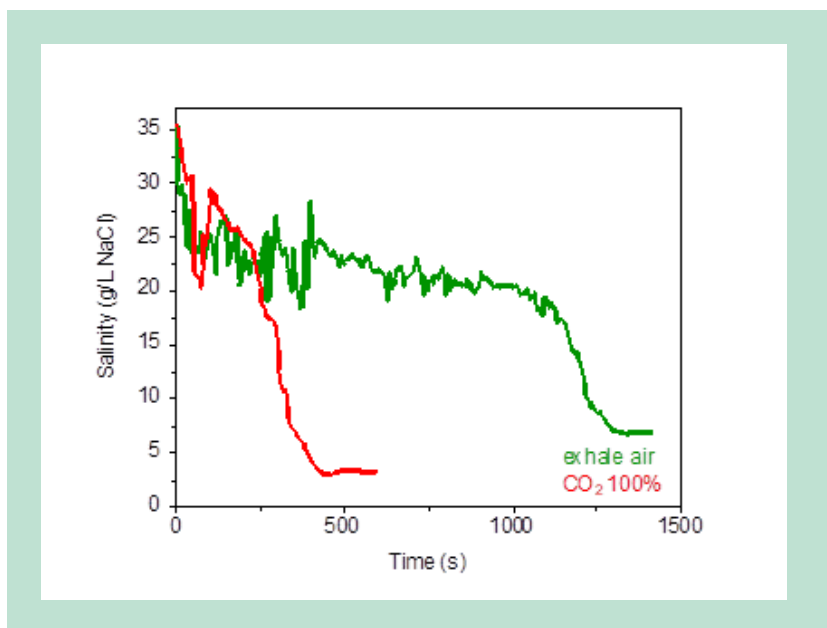
that the reduced salinity was maintained after long period of time (>12 hours), which is critical for further separation of the salt out of the aqueous system via ultra-filtration and other techniques which are under-development in our laboratory.



**FIGURE A1.5.** Salinity reduction capacity of various tested molecules – salinity calculated from conductivity measurement.

With the optimal diamine, we tested a different source of carbon dioxide – for example exhale air. A multiple balloon was prepared and was used instead of pure CO<sub>2</sub>. Exhale air contains approximately 10 times higher concentration (4000 ppm) than atmospheric air (400 ppm). Surprisingly, the desalination experiment showed similar trend compared to pure CO<sub>2</sub> although it requires longer time to reach the lowest salinity point after 1200 seconds, see Figure A1.6.



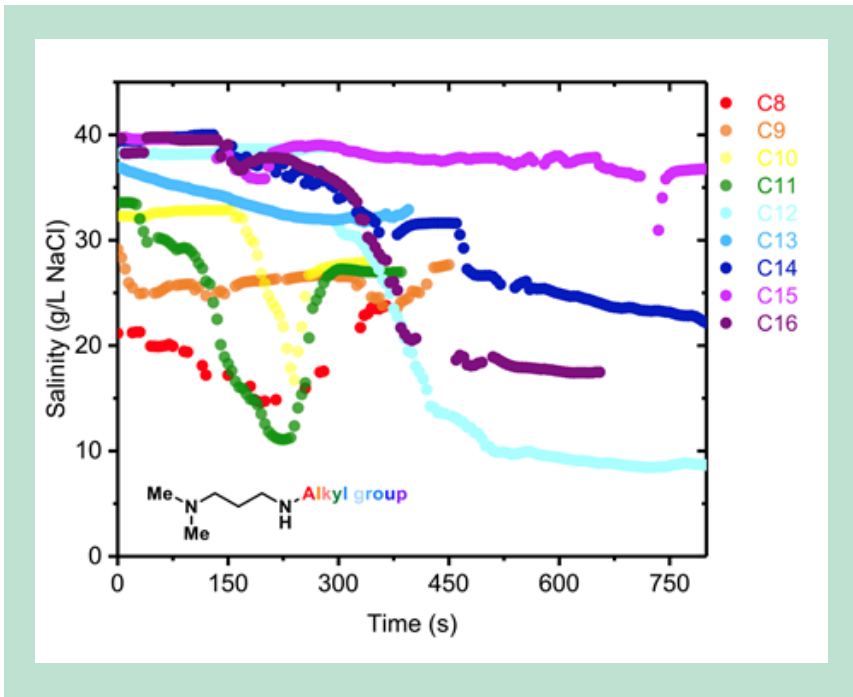


**FIGURE A1.6.** Effect on salinity (calculated from measurement of Conductivity) with n,n-dimethyl-1,3-n'-dodecyldiamine and exhale air (green) compared to pure CO<sub>2</sub>.

Although the chain length of the alkylated diamine plays a significant role in the effect on and the capacity of salinity reduction – measured as change in conductivity - we observed that three tested diamines in Figure A1.7 showed similar trend of conductivity reduction under otherwise identical conditions. It is evident that the chain length of C12 is optimal, while longer chain length is detrimental in terms of conductivity reduction performance (C13-C16). C8 and C9 groups were also tested, however, displayed lower conductivity reduction, which might be ascribed to the higher hydrophilicity. The control of ambivalent hydrophobic and hydrophilic nature seems critical to attain the desired desalination performance. Also, it would be plausible that the formation of (reverse) micelles can be manipulated by the chain length, therefore affecting the salinity reduction capacity.

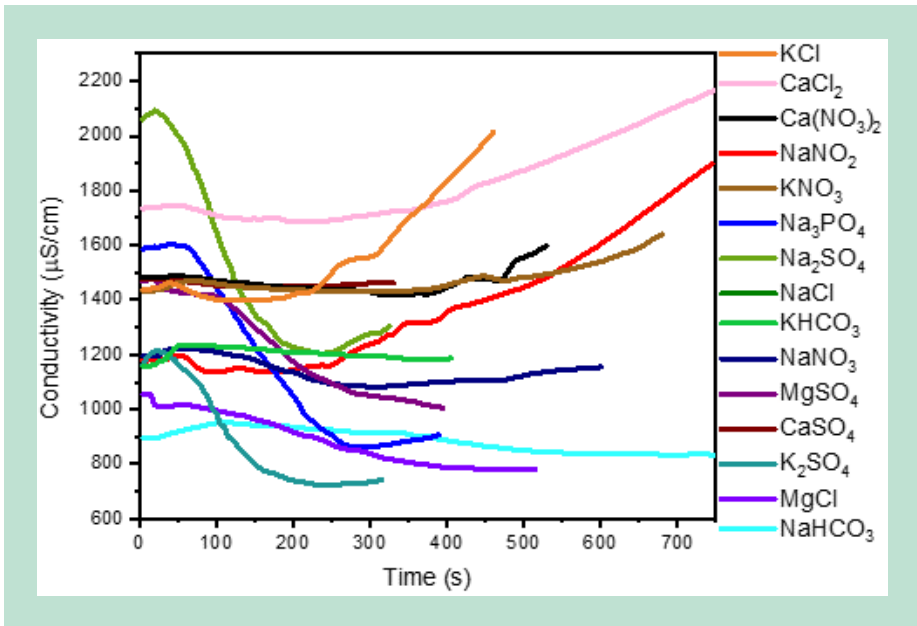
Additionally, the observed salinity was increased after certain time in the case of C10 and C11-decorated diamine, indicating the instability of NaCl/diamine or ammonium carbonate. The presence of adequate length of alkyl-chain showed superior stability of this state, indicated by the stable salinity over time (after 200 seconds), maintaining low salinity after stopping CO<sub>2</sub> supply. We presumed that during the CO<sub>2</sub> injections, diamine-CO<sub>2</sub> complexes form kinetically viable supramolecular complex, which were attempted to be analysed by DLS.

However, due to the complexity and reversibility of the system, no solid conclusion was deduced. This thermodynamically unstable, kinetically viable state can be further understood as far-from-equilibrium state, by consuming CO<sub>2</sub> as a molecular fuel, while forming carbonate and carbonic acid-diamine complexes. The presence of multiple ions will be critical to engineer the supramolecular structure.



**FIGURE A1.7.** The effect of aliphatic alkyl chains in salinity reduction performance based on conductivity measurement.

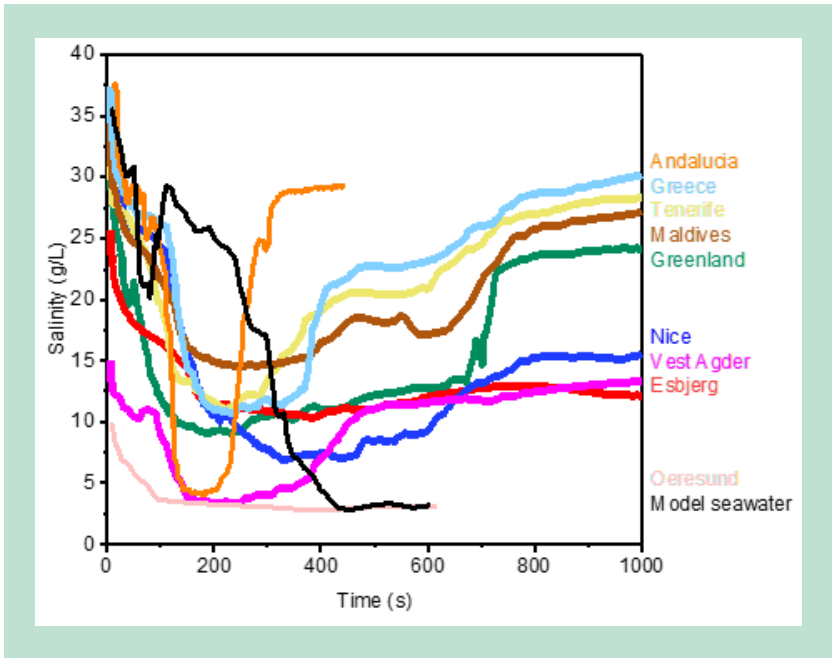
Considering that seawater is a complex mixture of salts, we tested various salts for our desalination process to explore the possibility of desalting process of individual salts. As summarized in Figure A1.8, various salt showed in general decrease of conductivity by introducing the diamine upon CO<sub>2</sub> injection at room temperature. Although it is difficult to rationalize the trend, various ion-containing aqueous solutions can in principle be applied for “desalt” process. Within 100-200 seconds, minimum conductivity was obtained which can be maintained in the case of for example, NaCl, Na<sub>3</sub>PO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, whereas fast reverse processes were observed with KCl, CaCl<sub>2</sub>, and NaNO<sub>2</sub>.



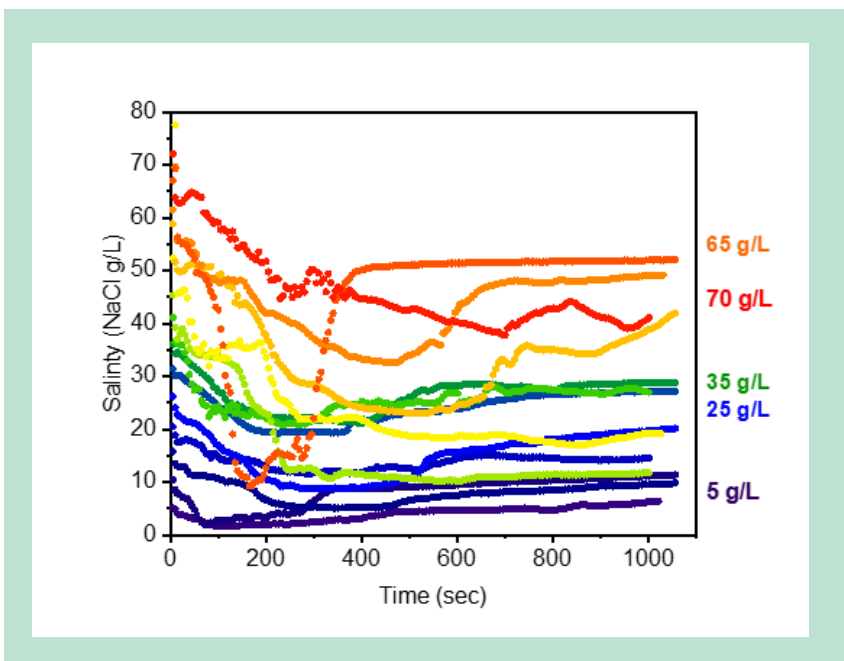
**FIGURE A1.8.** Conductivity reduction test using the optimized diamine and CO<sub>2</sub> with various ions.

In this regard, real seawater samples collected from many different places were tested (Figure A1.9). Regardless the source of the seawater sample, salinity reduction measured as conductivity reduction was observed while the minimum salinity and its remaining time period vary.

Figure A1.10 shows the reduction in salinity measured as conductivity reduction as a function of different start concentrations of salt.



**FIGURE A1.9.** Salinity reduction measured as conductivity reduction using seawater compared with model seawater (NaCl aqueous solution) as function of time after initiation of CO<sub>2</sub> introduction.



**FIGURE A1.10.** The effect of initial salt concentrations measured as conductivity reduction in diamine-mediated salinity reduction at room temperature.

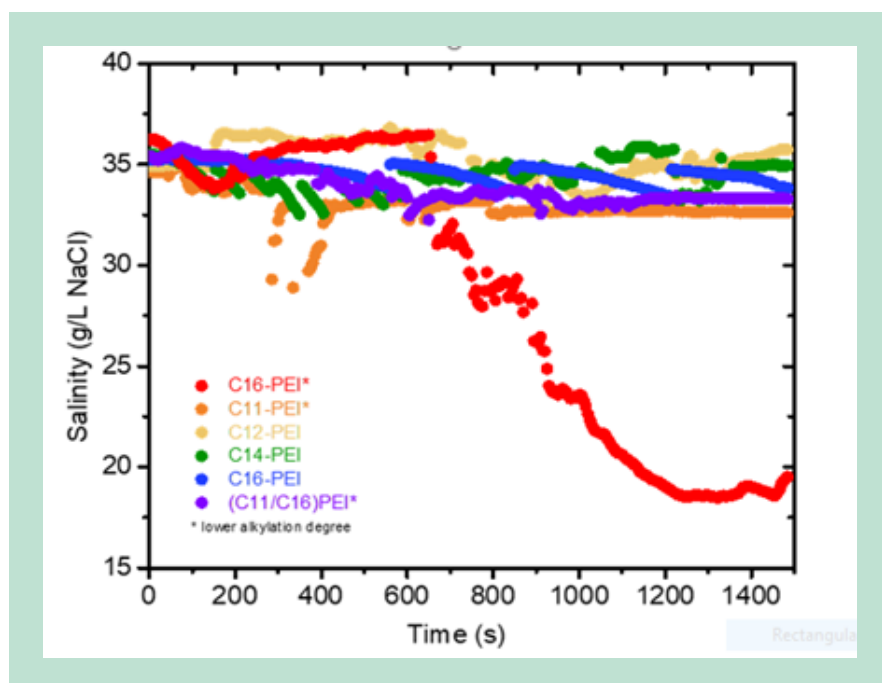
Further analysis of the chemical and physical changes of water samples after ultrafiltration would be necessary to investigate the process. To facilitate easy separation and regeneration

of the diamine polymers, these can be immobilized or supported on a polymeric material. In addition to enabling a more efficient recovery of the diamine, the use of polymeric diamines will also minimize risk of potential contamination of the produced water with excess diamine.

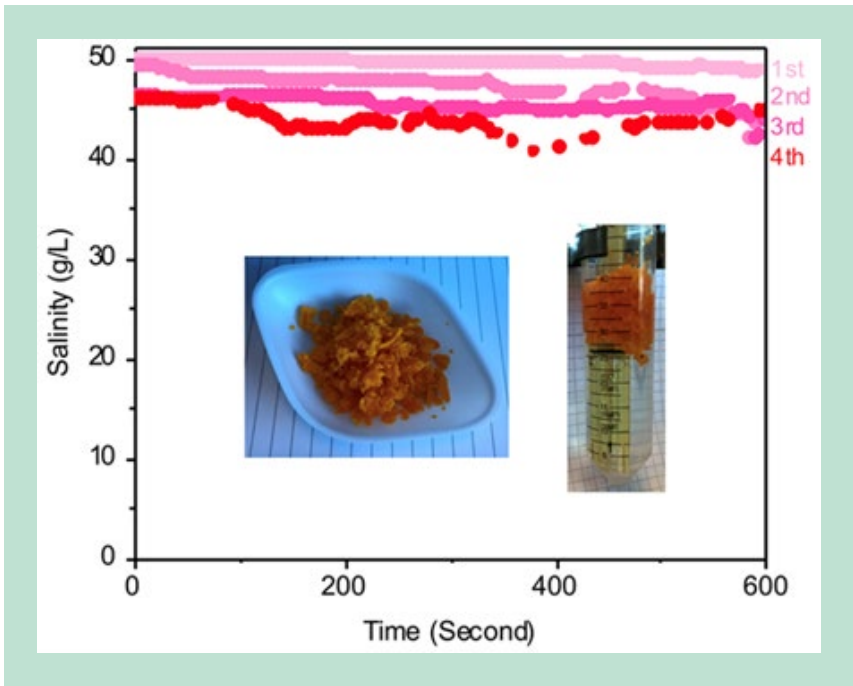
Polyethyleneimines (PEI) – amine-based polymers – have initially been chosen as the substrate and optimized by branch structure for optimal performance. The resulting polymer consists of repeating units of amine and is well known for applications in drug delivery, as detergents in water treatment and cosmetics, as well as in CO<sub>2</sub> capture. Chemical functionalization of PEI polymers is a fairly simple chemical process, and the Lee group showed that alkyl chain-modified PEI can be applied in the desalination process (Figure A1.11).

For example, C16-alkyl chain modified PEI presented superior desalination capacity compared to others. Moreover, the obtained polymer can in the initial lab-scale experiments be recycled more than 4 times. Accordingly, these polymeric diamines show promising recyclability and processability, resulting in up to 10% salinity reduction (from 50 to 45 g/L after 4 cycles) from high saline water by repeating the cycle with the same polymer (Figure A1.12). These results indicate the potential of the polymer-supported diamines for desalination and water purification with CO<sub>2</sub>, without any external energy sources for filtration or thermal distillation processes.

Based on these preliminary results, next steps are to improve the capacity and the efficiency of the salinity reduction – based on conductivity measurement - with immobilized diamines. In addition, the chosen diamines, both monomeric and polymeric will be evaluated for their toxicology profile to verify and compare the performance in desalination and in vivo and environmental effect.

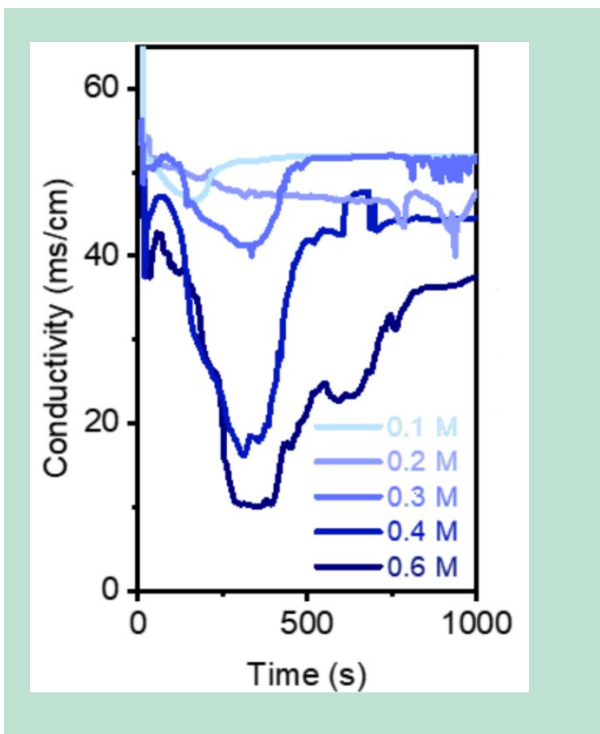


**FIGURE A1.11.** Salinity reduction based on conductivity measurement using PEI-based diamines.



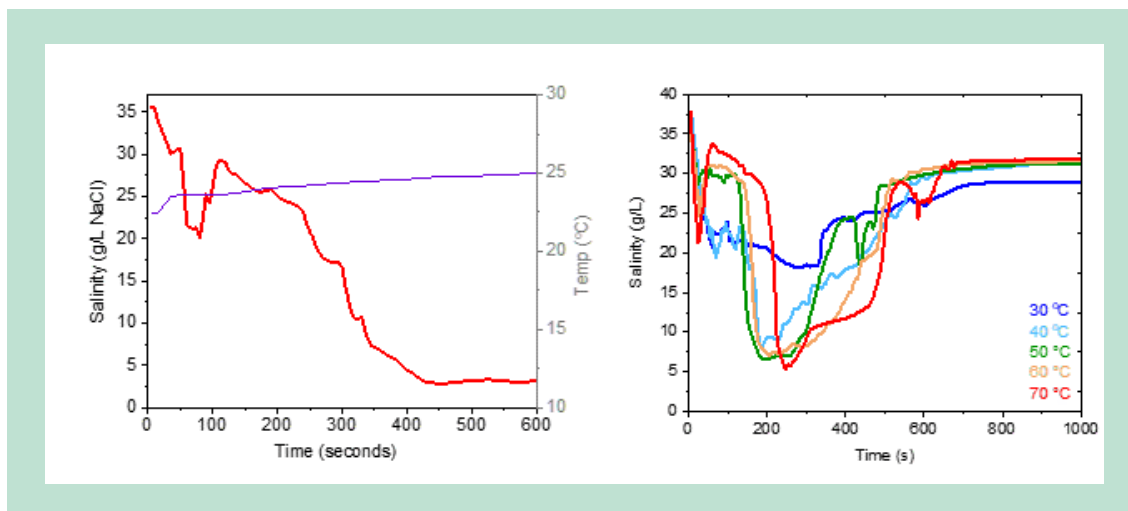
**FIGURE A1.12.** Results from lab-scale with 4 times recycling of C16-alkyl chain modified PEI.

To investigate the mechanism of the desalination, we conducted conductivity measurement at different concentrations of diamine, to determine the critical micelle concentration (CMC). Our attempts with DLS (dynamic light scattering) measurement were insufficient to draw any conclusion due to the low correlation prohibited acquiring reasonable data in terms of micelles and particle sizes and distribution. Therefore, we decided to use conductivity changes with respect to the amounts of diamines. By varying the concentration, we observed different behaviors of diamine and salinity reduction in 20 mL solution of NaCl, see Figure A1.13. Between 0.3M and 0.4M concentration of diamine, significant difference of conductivity was observed in the same period of time, indicating the presence of CMC.



**FIGURE A1.13.** Effect of concentrations of diamines on conductivity.

Variations with temperature and salts further confirmed that the aggregation process is affected by external temperatures – Figure A1.14. Further experimental work needs to be conducted to shed some light on the mechanism of the process.



**FIGURE A1.14.** In-situ measurement of process temperature (Left). Temperature effect on salinity reduction measured as conductivity reduction (Right).

It is postulated that the dehydration of (reverse)micelles is facilitated at higher temperatures therefore, more significant salinity reduction was induced at >40°C. Further analysis of diamine- CO<sub>2</sub> interactions was conducted by 1H and 13C NMR spectroscopy.

To verify the obtained results regarding desalination, <sup>23</sup>Na and <sup>35</sup>Cl NMR spectroscopy was employed to precisely determine the concentrations of sodium and chloride ions in the solution before and after the desalination process with monomeric diamines and polymeric diamine (PEI-C16). In this measurement we observed up to 12% chloride ion capture from the parent solution by using polymeric diamine and carbon dioxide – Table A1.1.

**TABLE A1.1.** Salinity reduction measured by benchtop <sup>23</sup>Na and <sup>35</sup>Cl NMR

Sample	sodium (mg/L)	chloride (mg/L)	Salinity (g/L)	remark
50 g/L NaCl	19670	30330	49,7	
After C12-diamine	21321	27454	45,0	- 10% chloride
35g/L NaCl	14657	19545	32,0	
After PEI-C16	14313	17200	28,2	- 12% chloride



## **Appendix 2. Experiment with testing of the chloride electrode**



## Experiment with testing of the Chloride electrode, 18.03.2021

During the experimental work with the immobilized diamines a significant number of experiments were conducted in which a chloride electrode was applied for characterization purposes. During these experiments the electrode was placed in a flow cell carrying column effluent. The chloride electrode was a HACH Intellical ISECL181 combination chloride ISE.

The objective was to validate the readings of chloride concentrations as measured by the electrode. The validation covered the chloride concentration range 0-10000 mg/L and relevant flow range of 5-40 ml/min.

The experimental set-up is shown at Figure A2.1. Five chloride standard solutions were prepared: 100 ppm, 500 ppm, 1000 ppm, 5000 ppm and 10000 ppm. The chloride probe was then calibrated with HACH Standards in a normal analysis set-up – a beaker with magnetic stirrer. Subsequently the probe signal was monitored for the 5 prepared chloride solutions in the beaker set-up. Finally, each of the prepared chloride solutions were fed to the flow chamber equipped with the chloride probe and the probe signal was monitored for four different flows: 5 mL/min, 10 mL/min, 20 mL/min and 40 mL/min. The results are shown in Table A2.1.

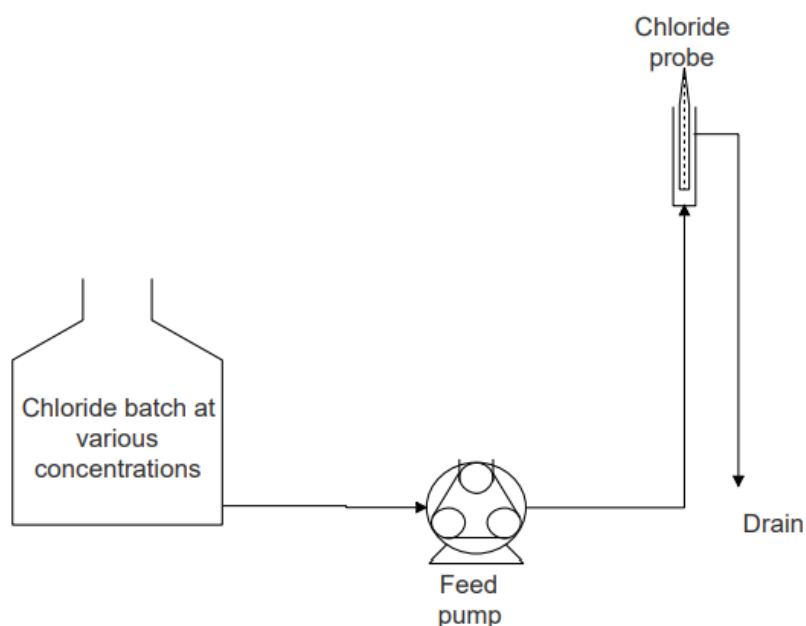


Figure A2.1 Experimental set-up for validation of the chloride probe in flow cell operation.

As can be seen from Table A2-1 the chloride electrode showed reliable results for all tested flow regimes – typically within 10% deviation from the expected concentrations. Thus, the chloride probe is accepted as well suited for documentation of hydraulic residence time distributions when using NaCl as a tracer.

Table A2.1 Experimental results from validation of the chloride probe in flow cell operation.

18.03.2021 Electrode testing											
		Standardized procedure		5 mL/min		10 mL/min		20 mL/min		40 mL/min	
NaCl in 1L [g]	Chloride [mg/L]	Chloride [mg/L]	[mV]	Chloride [mg/L]	[mV]	Chloride [mg/L]	[mV]	Chloride [mg/L]	[mV]	Chloride [mg/L]	[mV]
0	0	9,71	199,9	3,75	224,1	3,21	228	2,9	230,7	2,71	232,3
0,16	100	96,5	141,2	111	138	107	138,9	104	139,5	99	140,7
0,83	500	422	102,6	452	101,2	462	101	460	101	446	101,8
1,66	1000	903	83,8	991	81,9	991	81,9	983	82	976	82,2
8,26	5000	5115	40,1	5323	39,5	5269	39,4	5367	39	5402	38,9
16,49	10000	9838	23,2	1,04E+04	22,4	1,06E+04	22	1,08E+04	21,6	1,10E+04	20,8

# **Appendix 3. Experimental report on chloride removal and mass balance**

## Experiment 09.03.2021 with determination of Chloride sorption capacity for a CO<sub>2</sub> activated diamine coupled resin.

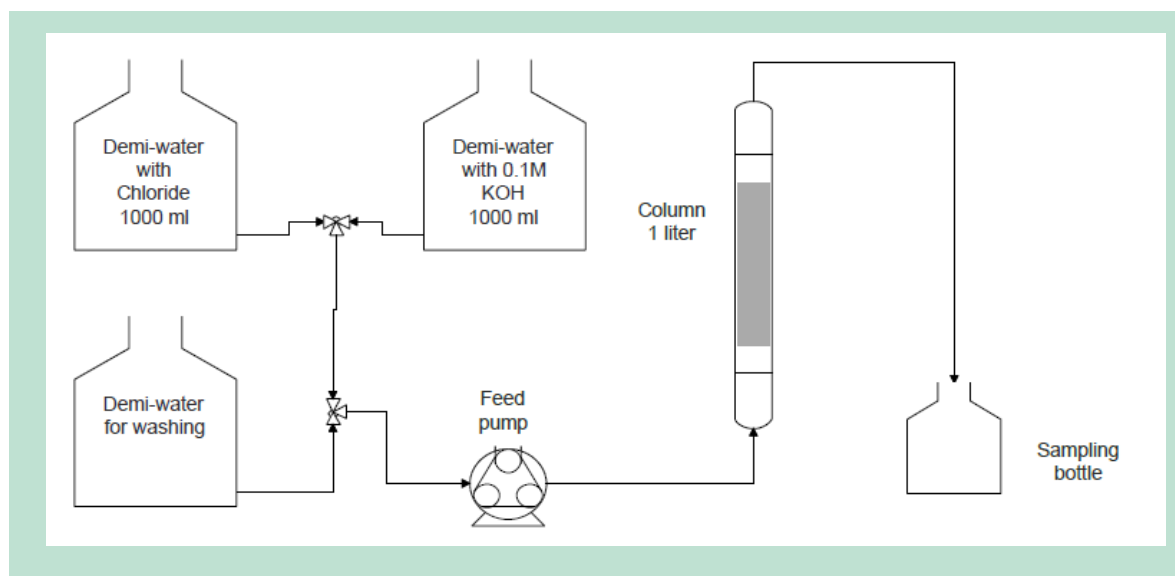
### Objective

The objective of the experiment was to investigate the Chloride sorption capacity of a CO<sub>2</sub> activated column with diamine coupled resin. The volume of the column is 1000 mL

### Procedure

The experiment was conducted on 09.03.2021.

The experimental set-up was as illustrated in Figure A3.1. The 1000 mL column was filled with diamine coupled resin – where diamine coupling had been prepared by MipSalus.



**Figure A3.1 Experimental set-up**

Initially the diamine coupled resin was activated with CO<sub>2</sub> by recycling of CO<sub>2</sub> saturated demineralized water. Recycling took place over 3 hours.

After CO<sub>2</sub> activation 1000 ml of a solution with approx. 3.0 g/L Cl in demineralized water was pumped through the column with the pump flow of 20 mL/min. Following this the input was switched to demineralized water.

Sampling of the column effluent was planned according to the retention time distribution for the applied flow and took place as follows:

- Sample A: Feed solution approx. 3.0 g/L Cl.
- Sample B: Effluent from the column for the period 0-20 min (approx. 400 ml)
- Sample C: Effluent from the column for the period 20-100 min (approx. 1600 ml)
- Sample D: Effluent from the column for the period 100-120 min (approx. 400 ml)

Subsequently the column was washed with 0.1 M KOH to eluate the ion exchanged Chloride and the following effluent samples were taken:

- Sample E: Effluent from the column for the period 0-20 min. (approx. 400 mL)
- Sample F: Effluent from the column for the period 20-100 min. (approx. 1600 mL)
- Sample G: Effluent from the column for the period 100-120 min. (approx. 400 mL)

Further, an experiment with testing of potential sorption of Sodium and Chloride in a column with resin which was not coupled with diamine was undertaken. This was done to make sure that observed sorption could be attributed to the diamine involved mechanism.

## Results

The samples were analyzed at KU and the results of the chemical analyses are shown in Table A3.1. The analysis of Chloride in the feed solution was found to be 2907 mg/L.

As can be seen from the data the sorption capacity of the column was 82% of the Chloride fed to the column at a concentration of 2.9 g/L, and from the balance between input and output can be seen that all Chloride was recovered through the KOH treatment – which made the balance fit nicely, close to 100%.

Thus, the sorption capacity of the ion exchange resin was determined to 2.3 g/L Chloride corresponding to approx. 0.066 eqv Cl/L bed volume.

**Table A3.1 Results from analyses of effluent from the column during the experiment.**

<b>1. Activation with re-cycling of CO<sub>2</sub> saturated demi-water through column</b>				
<b>2. Feed to column with 1000 ml 2,91 g Cl/L followed by feed with demi-water</b>				
Sample		Chloride conc (g/L)	Volume (ml)	Chloride mass (mg)
B	Sample 0-20 min before peak	0,14		
B	Sample 0-20 min before peak	0,07	400	43
C	Sample 20-100 min	0,32		
C	Sample 20-100 min	0,32	1600	511
D	Sample 100-120 min	0,07		
D	Sample 100-120 min	0,04	400	21
<b>3. Feed with 0,1 M KOH 20 ml/min</b>				
E	Sample 0-20 min before peak	0,04		
E	Sample 0-20 min before peak		400	14
F	Sample 20-100 min	1,45		
F	Sample 20-100 min	1,45	1600	2326
G	Sample 100-120 min	0,04		
G	Sample 100-120 min	0,04	400	14
Chloride mass passing the column				574
Chloride eluated				2354
<b>Chloride balance to compare with 2910 mg Cl input</b>				<b>2928</b>

Sodium in Sample C was determined at KU by NMR to 1.27 g Na/L. When calculating the Sodium mass in the sample volume of 1600 mL and comparing to the Sodium mass in the feed volume of 1000 mL this shows a very fine agreement. Thus, no Sodium was retained in the column when Cl was ion exchanged.

Selected samples were analyzed for inorganic Carbon at UAQ's lab to investigate the hypothesis of release of Bicarbonate in exchange of the Chloride removed. The selected samples were A, B, C, and D and the results are shown in Table A3.2.

The chemical analyses results show that significant inorganic Carbon (Bicarbonate) was released from the resin during sorption of Chloride – as also expected from the mechanistic hypothesis for the understanding of the process. The released inorganic Carbon as calculated from the sample volume of 1.6 L amounts to 0.094 eqv inorganic Carbon which is somewhat higher than expected from calculation of the ion exchanged Cl which amounts to 0.066 eqv Cl. However, it can be concluded that the experimental data supports the overall mechanistic hypothesis – and that more experimental work with resin with considerably higher capacity will

be better suited for more detailed investigation of the mechanism and evaluation of the commercial possibilities.

**Table A3.2 Results from analysis of inorganic Carbon**

Sample		IC [mg/L]
A	Feed	0.44
B	0-20 min	1.2
C	20-100 min	705
D	100-120 min	5.9

Finally, an experiment was undertaken with a column filled with resin without diamine. This was done to investigate if Chloride was removed by sorption to the resin matrix itself and not solely controlled by the coupled diamine. Previously, experiments with identification of retention time distributions had been performed during which any initial irreversible binding of Chloride to the resin might have taken place. Subsequently the column had been thoroughly washed with demineralized water.

The column had a volume of 150 mL and two experiments with pulse dosing of Chloride were undertaken at two different flows. The pulse dose consisted of 5 mL Chloride solution at a concentration of 80 g/L Cl – and the two flow regimes applied were 5 mL/min and 10 mL/min, respectively. A volume of 400 mL demineralized water was applied at both experiments. Effluent was collected and Na and Cl concentrations in the collected effluent volumes of 400 mL were determined at KU.

Table A3.3 shows the experimental results. As can be seen from the Table there is a very good recovery of Na as well as Cl in the effluent from the column with the tested resin without diamines. Recovery is found in the range of 102-111% - which is well within expected uncertainties. This goes for the 5 mL/min flow as well as the 10 mL/min flow.

**Table A3.3 Results from experiment with resin not coupled with diamine.**

	Na	Cl	Volume
<b>Input: 5 mL 80 g Cl/L</b>	<b>263 mg</b>	<b>400 mg</b>	
Out: 5 ml/min	711 mg/l	1071 mg/l	400 ml
Out: 10 ml/min	977 mg/l	1358 mg/l	300 ml
<b>Recovery: 5 ml/min</b>	<b>284 mg (108%)</b>	<b>428 mg (107%)</b>	
<b>Recovery: 10 ml/min</b>	<b>293 mg (111%)</b>	<b>407 mg (102%)</b>	

Thus, from these data it is safe to conclude that there is no sorption related to the resin itself – and that the sorption is related to the coupled diamine.

### Conclusions

The main conclusion is that the diamine coupled resin was able to capture Chloride by ion exchange. The Chloride capture efficiency for the applied experimental conditions was 82%. The capacity for Chloride capture was found to be 0.066 eqv Cl/L of bed volume.

The Chloride mass balance showed that all Chloride fed to the column was recovered as non-captured Chloride in the effluent or as Chloride recovered through KOH wash (ion exchange regeneration). Thus, the mass balance showed a fine agreement between input and output.

Sodium was not removed during the sorption experiment. Thus, no Sodium removal mechanism was observed.

Inorganic Carbon was released from the diamine coupled resin during the ion exchange with Chloride. Released inorganic Carbon during ion exchange was found to be 0.094 eqv/L bed volume which was somewhat higher than expected from the Chloride data. However, the data still confirm the important role of inorganic Carbon in the mechanism under investigation. The experiment with the column with resin which was not diamine coupled showed that no sorption of Sodium or Chloride took place.

# **Appendix 4. Experimental report on fluoride removal and mass balance**

## Experiment 13.04.2021 with determination of Fluoride sorption capacity for a CO<sub>2</sub> activated diamine coupled resin.

### Objective

The objective of the experiment was to establish preliminary assessment regarding the potential ability of the diamine coupled resin with respect to ion exchange of Fluoride.

In this first experiment with testing of the ability and capacity of the resin to capture Fluoride we have focused on a direct comparison with the capacity found for Chloride.

We have therefore used the same procedure and experimental set-up as applied for the experiment for determination of the capacity for Chloride removal.

### Experimental set-up

The experiment was conducted on 13/04/2021. Figure A4.1 shows the experimental set-up.

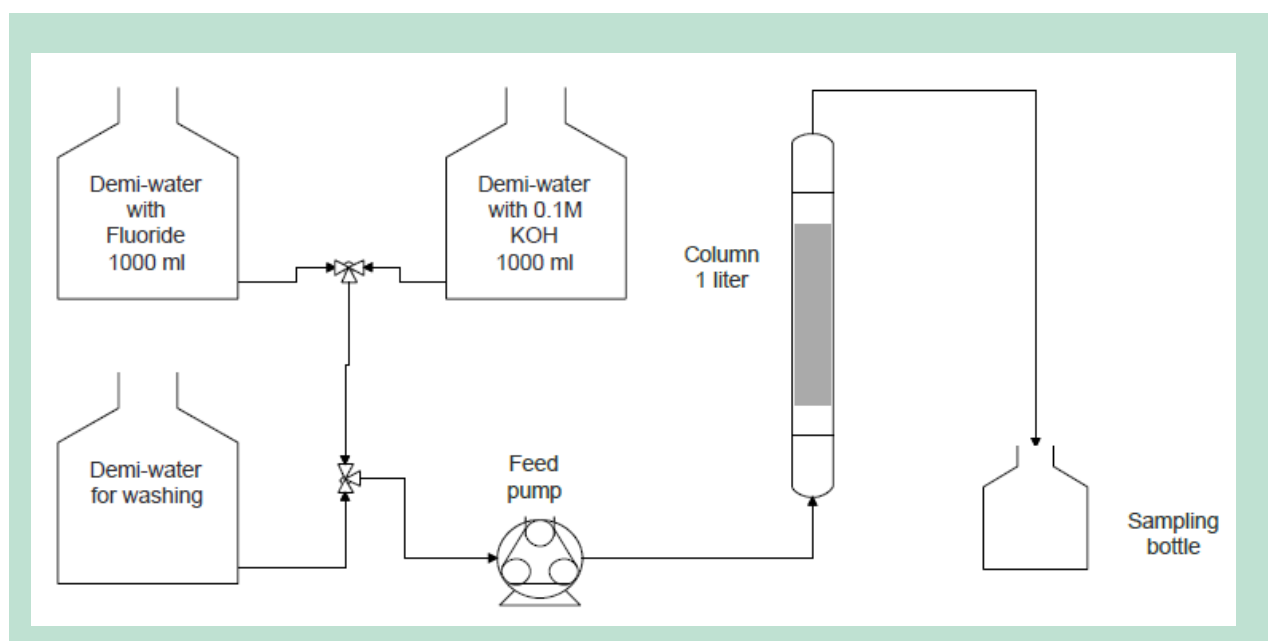


Figure A4.1 Experimental set-up for test with Fluoride sorption.

### Experimental procedure.

The experimental procedure was as follows:

- 1) The column/resin (1000 mL) was activated with CO<sub>2</sub> by recycling CO<sub>2</sub> saturated demineralized water (40 ml/min) to the column over a 1000 mL lab-cylinder with submerged diffusor – CO<sub>2</sub> flow through the cylinder was 700 mL/min for 2.5 hours.
- 2) A 2000 mL solution of NaF – 1.6 g Fluoride/L – was prepared (which is approx. the same eqv. conc as applied for the experiment with determination of the Chloride ion exchange capacity). 1000 mL of the solution was kept in sample bottle, F0.
- 3) After approx. 2.5 hours of CO<sub>2</sub> activation of the diamine in the column CO<sub>2</sub> activation was ended.
- 4) Dosing of the 1000 mL Fluoride solution was initiated. Flow was 20 mL/min. When all Fluoride solution was dosed, the flow was switched to demineralized water (same flow).
- 5) Column effluent was collected for the first 20 min in sample bottle F0-20 and sample volume was measured. Volume of F0-20 is 440 ml.
- 6) Column effluent was collected for the next 60 min in sample bottle F20-80 and sample volume was measured. Volume of F20-80 is 1320 ml.



- 7) Column effluent was collected for the next 20 min in sample bottle F80-100 and sample volume was measured. Volume of F80-100 is 440 ml.

After Fluoride dosing and wash with demi-water the column was washed with 1 liter 0.1M KOH through the following procedure:

- 1) 1 liter 0.1 M KOH was prepared.
- 2) The KOH was dosed to the column with the flow 20 mL/min). When all KOH was dosed pumping was switched to demi-water (same flow).
- 3) Column effluent was collected for the first 20 min in sample bottle KOHF0-20 and sample volume was measured. Volume of KOHF0-20 is 440 mL.
- 4) Column effluent was collected for the next 60 min in sample bottle KOHF20-80 and sample volume was measured. Volume of KOHF20-80 is 1290 mL.
- 5) Column effluent was collected for the next 20 min in sample bottle KOHF80-100 and sample volume was measured. Volume of KOHF80-100 is 440 mL.
- 6) Washing with demi-water was continued for 1 hour.

Feed sample (F0) and samples with Fluoride peaks F20-80 and KOHF20-80 were analyzed with AquaPorin's HACH meter (Type DR3900) using HACH reagents for determination of Fluoride.

### Results

From previous experiments with determination of residence time distributions as well as from experiment with chloride capacity determination, it is known that the samples taken at time 20-80 min into the loading with Fluoride as well as 20-80 min into the KOH wash phase will contain almost all Fluoride. These samples were analyzed for Fluoride.

Results are shown in Table A4.1. From the Table can be seen that 1460 mg Fluoride was fed to the column. The effluent Fluoride which was not captured in the column amounted to 552 mg while the captured Fluoride amounted to 988 mg.

The sum of the Fluoride detected in the effluent during loading and during the subsequent KOH wash amounted to 1540 mg – and when compared to the input Fluoride the balance shows recovery of 105% of the influent. Thus, all Fluoride could be accounted for in the mass balance.

As can be seen from the data, the removal of Fluoride under the test conditions amounted to 68% of the incoming Fluoride.

**Table A4.1** Data from the experiment with ion exchange of Fluoride.

Sample	Feed (F0)	F20-80	KOHF20-80
Sample dilution	1000	1000	1000
Analysis (mg/L)	1.46	0.418	0.766
Conc. F (mg/L)	1460	418	766
Volume (mL)	1000	1320	1290
Mass F (mg)	1460	552	988
Capacity eqv/L of bed volume			0.052
Inorg-C eqv/L of bed volume			0.040

From the data can be calculated that the observed capacity under the test conditions for the 1 liter column for ion exchange removal of Fluoride was 0.052 eqv F/L of bed volume. This is comparable with the capacity for Chloride capture, 0.066 eqv/L of bed volume.

The amount of inorganic Carbon in Sample F20-80 was analyzed with HACH analysis to give information regarding the hypothesis for the mechanism controlling the ion exchange. The inorganic Carbon released during ion exchange of 988 mg Fluoride was found to be corresponding to 0.040 eqv/L.

### **Conclusions**

The main conclusion is that the diamine coupled resin was able to capture Fluoride by ion exchange. The Fluoride capture efficiency for the applied experimental conditions was 68%.

The capacity for Fluoride capture was found to be 0.052 eqv F/L of bed volume which is comparable to the capacity found for Chloride, 0.066 eqv Cl/L bed volume.

The Fluoride mass balance showed that all Fluoride fed to the column was recovered as non-captured Fluoride in the effluent or as Fluoride recovered through KOH wash (ion exchange regeneration). Thus, the mass balance showed a fine agreement between input and output. Released inorganic Carbon during ion exchange of Fluoride was found to be 0.040 eqv/L bed volume to be compared to the Fluoride capacity of 0.052 eqv/L bed volume.

# **Appendix 5. Experimental report on nitrate removal and mass balance**

## Experiment 14.04.2021 with determination of Nitrate sorption capacity for a CO<sub>2</sub> activated diamine coupled resin.

### Objective

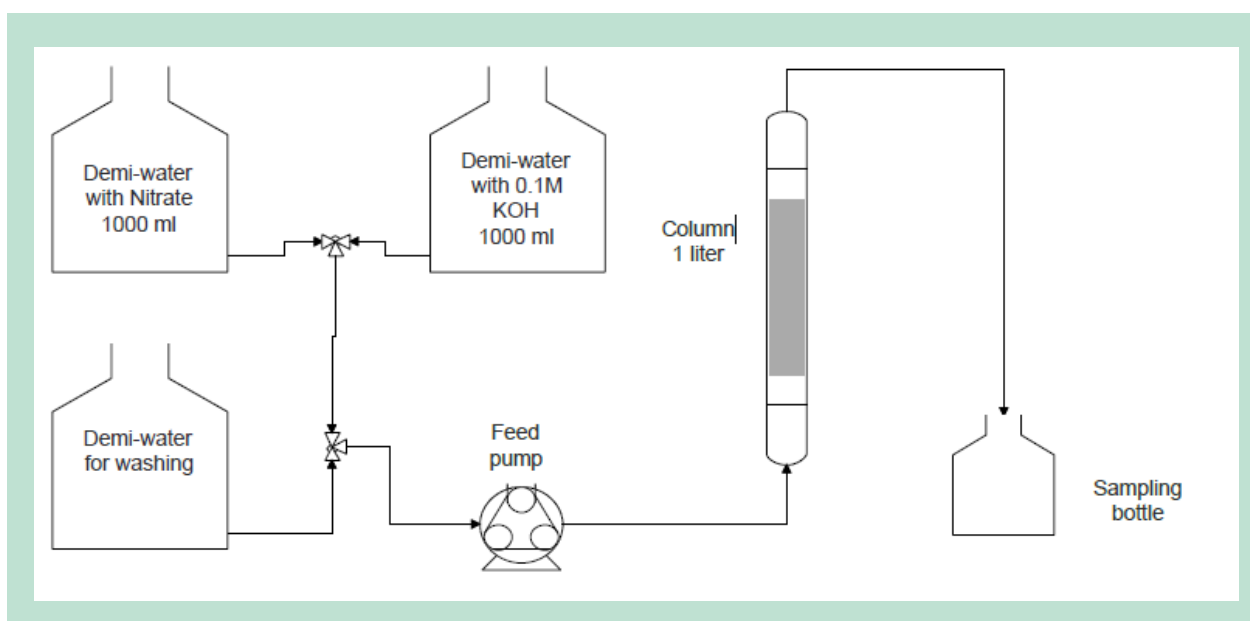
The objective of the experiment was to establish preliminary assessment regarding the potential ability of the diamine coupled resin with respect to ion exchange of Nitrate.

In this first experiment with testing of the ability and capacity of the resin to capture Nitrate we have focused on a direct comparison with the capacity found for Chloride.

We have therefore used the same procedure and experimental set-up as applied for the experiment for determination of the capacity for Chloride and Fluoride removal.

### Experimental set-up

The experiment was conducted on 14/04/2021. Figure A5.1 shows the experimental set-up.



**Figure A5.1** Experimental set-up for test with Nitrate sorption.

### Experimental procedure.

The experimental procedure was as follows:

- 8) The column/resin (1000 mL) was activated with CO<sub>2</sub> by recycling CO<sub>2</sub> saturated demineralized water (40 ml/min) to the column over a 1000 mL lab-cylinder with submerged diffusor – CO<sub>2</sub> flow through the cylinder was 700 mL/min for 2.5 hours.
- 9) A 2000 mL solution of NaNO<sub>3</sub> – 5,2 g Nitrate/L – was prepared (which is approx. the same eqv. conc as applied for the experiment with determination of the Chloride ion exchange capacity). 1000 mL of the solution was kept in sample bottle, NO3-0.
- 10) After approx. 2.5 hours of CO<sub>2</sub> activation of the diamine in the column CO<sub>2</sub> activation was ended.
- 11) Dosing of the 1000 mL Nitrate solution was initiated. Flow was 20 mL/min. When all Nitrate solution was dosed, the experimental plan was to switch to demineralized water (same flow). However, due to a misunderstanding the pump was running dry and injected air for 10-20 min before dosing of demineralized water was initiated.
- 12) Column effluent was collected for the first 20 min in sample bottle NO3-0-20 and sample volume was measured. Volume of NO3-0-20 is 440 ml.

- 13) Column effluent was collected for the next 60 min (excluding the 20 min of air dosing) in sample bottle NO3-20-80 and sample volume was measured. Volume of NO3-20-80 is 1320 ml.
- 14) Column effluent was collected for the next 20 min in sample bottle NO3-80-100 and sample volume was measured. Volume of NO3-80-100 is 440 ml.

After Nitrate dosing and wash with demi-water the column was washed with 1 liter 0.1M KOH through the following procedure:

- 7) 1 liter 0.1 M KOH was prepared.
- 8) The KOH was dosed to the column with the flow 20 mL/min). When all KOH was dosed pumping was switched to demi-water (same flow).
- 9) Column effluent was collected for the first 20 min in sample bottle KOHNO3-0-20 and sample volume was measured. Volume of KOHNO3-0-20 is 440 mL.
- 10) Column effluent was collected for the next 60 min in sample bottle KOHNO3-20-80 and sample volume was measured. Volume of KOHNO3-20-80 is 1290 mL.
- 11) Column effluent was collected for the next 20 min in sample bottle KOHNO3-80-100 and sample volume was measured. Volume of KOHNO3-80-100 is 440 mL.
- 12) Washing with demi-water was continued for 1 hour.

Feed sample (NO3-0) and samples with expected NO3 peaks NO3-20-80 and KOHNO3-20-80 were analyzed with AquaPorin's HACH meter (Type DR3900) using HACH reagents for determination of Nitrate. Further, analyses were undertaken on all other samples due to unexpected large deficit (missing Nitrate) when calculating the Nitrate balance between input and output.

### Results

From previous experiments with determination of residence time distributions as well as from experiments with Chloride and Fluoride capacity determinations, it was known that the samples taken at time 20-80 min into the loading with Nitrate as well as 20-80 min into the KOH wash phase expectedly would contain almost all Nitrate passing through the column. Results are shown in Table 1. From the Table can be seen that 5159 mg Nitrate was fed to the column while 3045 mg was found in the effluent during KOH wash. Thus, a large deficit is found between input Nitrate and output Nitrate. Due to this deficit in Nitrate balance the remaining samples were also analyzed. This, however, revealed almost no further effluent Nitrate to be added to the balance.

**Table A5.1** Data from the experiment with ion exchange of Nitrate.

Sample	Feed (NO3-0)	NO3-0-20	NO3-20-80	NO3-80-100	KOHNO3-0-20	KOHNO3-20-80	KOHNO3-80-100
Dilution	50	10	17	10	5	25	10
N (mg/L)	23,4	0	0	0	0	20,9	19,1
NO3 (mg/L)	5159	0	0	0	0	2314	85
Volume (mL)	1000	440	1290	440	440	1300	440
Mass NO3 (mg)	5159	0	0	0	0	3008	37
Capacity (Eqv/L)						0,049	
Inorg-C (Eqv/L)							

The mass of the Nitrate detected in the effluent during loading and during the subsequent KOH wash amounted to 3045 mg – and when compared to the mass of Nitrate dosed to the column the balance shows that 2114 mg of Nitrate is missing. The explanation for the missing Nitrate might be that this Nitrate was sorbed to the resin matrix. Further experimental work is needed to investigate this phenomenon.

From the data can be calculated that the observed capacity under the test conditions for the 1 liter column for ion exchange removal of Nitrate was 0.049 eqv NO<sub>3</sub>/L of bed volume. This is comparable with the capacity for Chloride capture, 0.066 eqv/L of bed volume and the value found for Fluoride, 0.052 eqv/L of bed volume.

The amount of inorganic Carbon in Sample NO<sub>3</sub>-20-80 was analyzed with HACH analysis to give information regarding the hypothesis for the mechanism controlling the ion exchange. The inorganic Carbon released during ion exchange of 3045 mg Nitrate was found to be corresponding to 0.091 eqv/L.

### **Conclusions**

The main conclusion is that the diamine coupled resin was able to capture Nitrate by ion exchange. The Nitrate capture efficiency - related to ion exchange - for the applied experimental conditions was 60%. The 60% was defined as the mass of Nitrate which was desorbed by wash with 0.1 M KOH.

The capacity was found to be 0.049 eqv/L of bed volume which is comparable to the capacity found for Chloride, 0.066 eqv/L bed volume and the capacity found for Fluoride, 0.052 eqv/L of bed volume.

Missing Nitrate in the mass balance amounted to the remaining 40%. This might be caused by non-specific sorption of nitrate in the resin matrix – a sorption which was not reversible through washing with demineralized water or with 0.1 M KOH.

Released inorganic Carbon during ion exchange of Nitrate was found to be 0.091 eqv/L bed volume to be compared to the Nitrate sorption capacity of 0.049 eqv/L bed volume.

## **Appendix 6. Safety data sheet for 3-(Dimethyl- amino)-1-propyl- amine**

**SIKKERHEDSDATABLAD**

I henhold til Forordning (EF) nr. 1907/2006

Udgave 8.1

Revisionsdato 01.04.2020

Trykdato 06.07.2020

**PUNKT 1: Identifikation af stoffet/blandingen og af selskabet/virksomheden****1.1 Produktidentifikatorer**

Produkt navn	:	3-(Dimethylamino)-1-propylamine
Produkt nummer	:	D145009
Mærke	:	Aldrich
Indeks-Nr.	:	612-061-00-6
REACH No.	:	Registreringsnummer er ikke tilgængelig for dette stof. Stoffet og anvendelse af stoffet er undtaget fra registrering, da der ikke kræves årlige registrering.
CAS-Nr.	:	109-55-7

**1.2 Relevante identificerede anvendelser for stoffet eller blandingen samt anvendelser, der frarådes**

Identificerede anvendelser	:	Laboratoriekemikalier, Produktion af stoffer
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**1.3 Nærmere oplysninger om leverandøren af sikkerhedsdatabladet**

Firma	:	Merck Life Science ApS Vandtårnsvej 62A, DK-2860 SØBORG, DENMARK
Telefon	:	+45 43 56 59-20
Fax	:	+45 43 56 59-05
E-mail adresse	:	TechnicalService@merckgroup.com

**1.4 Nødtelefon**

Nødtelefonnummer	:	+(45)-69918573 (CHEMTREC) Ved akut udrykning og livsfare - 112
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**PUNKT 2: Fareidentifikation****2.1 Klassificering af stoffet eller blandingen****Klassifikation i henhold til regulativ (EC) No 1272/2008**

Brandfarlige væsker (Kategori 3), H226  
Akut toksicitet, Oralt (Kategori 4), H302  
Akut toksicitet, Hud (Kategori 4), H312  
Hudætsning (Kategori 1B), H314  
Hudsensibilisering (Kategori 1), H317  
Specifik målorgantoksicitet - enkelt eksponering (Kategori 3), Åndedrætssystem, H335

For den fuldstændige tekst af faresætningerne nævnt i dette punkt, se punkt 16.



Signalord	Fare
Faresætning(er)	
H226	Brandfarlig væske og damp.
H302 + H312	Farlig ved indtagelse eller hudkontakt.
H314	Forårsager svære ætsninger af huden og øjenskader.
H317	Kan forårsage allergisk hudreaktion.
H335	Kan forårsage irritation af luftvejene.
Præventive sætning(er)	
P210	Holdes væk fra varme, varme overflader, gnister, åben ild og andre antændelseskilder. Rygning forbudt.
P303 + P361 + P353	VED KONTAKT MED HUDEN (eller håret): Alt tilsmudset tøj tages straks af. Skyl/brus huden med vand.
P304 + P340 + P310	VED INDÅNDING: Flyt personen til et sted med frisk luft og sørg for, at vejtrækningen lettes. Ring omgående til en GIFTINFORMATION/læge.
P305 + P351 + P338	VED KONTAKT MED ØJENENE: Skyl forsigtigt med vand i flere minutter. Fjern eventuelle kontaktlinser, hvis dette kan gøres let. Fortsæt skylning.
P333 + P313	Ved hudirritation eller udslet: Søg lægehjælp.
P403 + P235	Opbevares på et godt ventileret sted. Opbevares køligt.

Supplerende faresætninger ingen

### 2.3 Andre farer

Dette stof/blanding indeholder ingen komponenter, der anses for at være enten persistente, bioakkumulerende og toksiske (PBT) eller meget persistente og meget bioakkumulerende (vPvB) ved niveauer på 0,1% eller højere. Tårefremkalder.

## PUNKT 3: Sammensætning af/oplysning om indholdsstoffer

### 3.1 Stoffer

Synonymer	: N,N-Dimethyl-1,3-diaminopropane N,N-Dimethyl-1,3-propanediamine
Formel	: C <sub>5</sub> H <sub>14</sub> N <sub>2</sub>
Molekylvægt	: 102,18 g/mol
CAS-Nr.	: 109-55-7
EF-Nr.	: 203-680-9
Indeks-Nr.	: 612-061-00-6

Komponent	Klassificering	Koncentration
<b>3-Aminopropyldimethylamine</b>	Flam. Liq. 3; Acute Tox. 4; Skin Corr. 1B; Skin Sens. 1; STOT SE 3; H226, H302, H312, H314, H317, H335	<= 100 %

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#### **4.1 Beskrivelse af førstehjælpsforanstaltninger**

##### **Generelle anvisninger**

Søg læge. Vis dette sikkerhedsdatablad til vagtlægen.

##### **Hvis det indåndes**

Hvis indåndet, flyt tilskadedekomne til frisk luft. Hvis ingen vejtrækning, giv kunstigt åndedræt. Søg læge.

##### **I tilfælde af hudkontakt**

Fjern øjeblikkeligt forurenede tøj og sko. Vaskes af med sæbe og rigeligt vand. Søg læge.

##### **I tilfælde af øjenkontakt**

Skyl omhyggeligt med rigeligt vand i mindst 15 min. og søg læge.

##### **Ved indtagelse.**

Fremprovoker IKKE opkastning. Giv aldrig en bevidstløs person noget gennem munden. Skyl munden med vand. Søg læge.

#### **4.2 Vigtigste symptomer og virkninger, både akutte og forsinkede**

De vigtigste kendte symptomer og virkninger er beskrevet i mærkning (se afsnit 2,2) og / eller i § 11

#### **4.3 Angivelse af om øjeblikkelig lægehjælp og særlig behandling er nødvendig**

Ingen data tilgængelige

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### **PUNKT 5: Brandbekæmpelse**

#### **5.1 Slukningsmidler**

##### **Egnede slukningsmidler**

Brug vandspray, alkoholbestandigt skum, pulver eller kuldioxid.

#### **5.2 Særlige farer i forbindelse med stoffet eller blandingen**

Carbonoxider, Nitrogenoxider (NO<sub>x</sub>)

#### **5.3 Anvisninger for brandmandskab**

Benyt om nødvendigt luftforsynet åndedrætsværn ved brandbekæmpelse.

#### **5.4 Yderligere oplysninger**

Anvend vandtåge til at køle uåbnede beholdere.

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### **PUNKT 6: Forholdsregler over for udslip ved uheld**

#### **6.1 Personlige sikkerhedsforanstaltninger, personlige værnemidler og nødprocedurer**

Brug personligt beskyttelsesudstyr. Undgå indånding af dampe/tåge/gas. Sørg for tilstrækkelig ventilation. Fjern alle antændelseskilder. Evakuer personale til sikre områder. Vær opmærksom på ophobning af dampe der kan danne en eksplosiv koncentration. Dampe kan ophobes i lave områder. For personlig beskyttelse se punkt 8.

#### **6.2 Miljøbeskyttelsesforanstaltninger**

Sørg for at forhindre yderligere lækage eller udslip, hvis det er sikkerhedsmæssigt muligt. Produktet må ikke komme i kloak afløb. Udlledning til miljøet skal undgås.

### 6.3 Metoder og udstyr til inddæmning og oprensning

Opbevar og opsaml spild med en elektrisk beskyttet støvsuger eller ved våd-børstning og placer i affaldsbeholder i henhold til lokale regler (se punkt 13).

### 6.4 Henvisning til andre punkter

Bortskaffelse se punkt 13.

---

## PUNKT 7: Håndtering og opbevaring

### 7.1 Forholdsregler for sikker håndtering

Undgå kontakt med huden og øjnene. Undgå indånding af dampe eller tåger. Holdes væk fra antændelseskilder - Rygning forbudt. Tag forholdsregler for at forebygge opbygning af statisk elektricitet. For forholdsregler se afsnit 2,2.

### 7.2 Betingelser for sikker opbevaring, herunder eventuel uforenelighed

Opbevares køligt. Opbevar beholderen tæt lukket på et tørt og godt ventileret sted. Åbnede beholdere skal lukkes ophyggeligt efter brug og opbevares opretstående for at forebygge lækage.

Opbevar under inert gas.

### 7.3 Særlige anvendelser

Bortset fra de anvendelser, der er nævnt i afsnit 1,2 er der ingen andre specifikke anvendelser fastsat

---

## PUNKT 8: Eksponeringskontrol/personlige værnemidler

### 8.1 Kontrolparametre

#### Indholdsstoffer med grænseværdier

Indeholder ingen stoffer med grænseværdi for erhvervsmæssig eksponering.

### 8.2 Eksponeringskontrol

#### Egnede foranstaltninger til eksponeringskontrol

Skal håndteres i overensstemmelse med god erhvervshygiejne og sikkerhedsforanstaltninger. Vask hænder før pauser og ved arbejdstids ophør.

#### Personlige værnemidler

##### Beskyttelse af øjne / ansigt

Tætsluttende beskyttelsesbriller. Ansigtsskærm. Anvend sikkerhedsbriller testet og godkendt under NIOSH (US) eller EN 166 (EU) standarder.

##### Beskyttelse af hud

Håndteres med handsker. Handsker skal undersøges inden brug . Brug rigtig teknik til at tage handskene af (uden at røre handskens ydre overflade) for at undgå hudkontakt til dette produkt. Bortskaffelse af forurenede handsker efter brug skal ske i overensstemmelse med gældende lovgivning samt god laboratorie praksis. Vask og tør hænderne.

De valgte beskyttelseshandsker skal opfylde specifikationerne i EUs Forordning 2016/425 samt standarden EN 374, der er afledt deraf.

Fuldstændig kontakt

Materiale: Fluorineret gummi

minimumstykkelse: 0,7 mm

Gennemtrængningstid: 480 min

Materiale testet: Vitoject® (KCL 890 / Aldrich Z677698, Størrelse M)

Ved stænk

Materiale: Nitrilgummi

minimumstykkelse: 0,4 mm

Gennemtrængningstid: 54 min

Materiale testet: Camatril® (KCL 730 / Aldrich Z677442, Størrelse M)

Data kilde: KCL GmbH, D-36124 Eichenzell, Telefon +49 (0)6659 87300, e-mail sales@kcl.de, Test metode: EN374

Hvis det bruges i opløsning, eller blandes med andre stoffer og under forhold som afskiller sig fra EN 374, kontaktes leverandøren af de EC godkendte handsker.

Denne anbefaling er kun vejledende og skal vurderes af en hygiejne- og sikkerhedseksperter der er bekendt med den specifikke anvendelse hos vores kunder. Dette skal ikke fortolkes som en godkendelse til nogen specifikke anvendelses scenarier.

### **Kropsbeskyttelse**

Hel beskyttelsesdragt til beskyttelse mod kemikalier, Brandhæmmende, antistatisk beskyttelsesbeklædning., Typen af beskyttelsesudstyr skal vælges i henhold til koncentrationen og mængden af det farlige stof på det pågældende arbejdssted.

### **Åndedrætsværn**

Hvis risikovurdering viser at der skal bruges luftrensende respiratorer br (US) eller type ABEK (EN14387) respirator patron som back up. Hvis respir luft respirator. Brug udelukkende åndedrætsværn og komponenter testet og godkendt i henhold til passende lovgivning såsom NIOSH (USA) eller CEN (EU).

### **Kontrol af miljømæssig eksponering**

Sørg for at forhindre yderligere lækage eller udslip, hvis det er sikkerhedsmæssigt muligt. Produktet må ikke komme i kloak afløb. Udledning til miljøet skal undgås.

---

## **PUNKT 9: Fysiske og kemiske egenskaber**

### **9.1 Oplysninger om grundlæggende fysiske og kemiske egenskaber**

a) Udseende	Form: klar, væske Farve: farveløs
b) Lugt	som amin
c) Lugttærskel	Ingen data tilgængelige
d) pH-værdi	12,7 ved 100 g/l ved 20 °C
e) Smeltepunkt/frysepunkt	Smeltepunkt/frysepunkt: -69,99 °C - lit.
f) Begyndelseskogepunkt og kogepunktsinterval	133 °C - lit.
g) Flammepunkt	32 °C - lukket digel
h) Fordampningshastighed	Ingen data tilgængelige
i) Antændelighed (fast stof, luftart)	Ingen data tilgængelige
j) Øvre/nedre antændelses- eller eksplosionsgrænser	Højeste eksplosionsgrænse: 12,35 %(V) Laveste eksplosionsgrænse: 2,3 %(V)
k) Damptryk	5 mmHg ved 20 °C
l) Dampmassefylde	3,53 - (Luft = 1,0)
m) Relativ massefylde	0,812 g/cm <sup>3</sup> . ved 25 °C



n) Vandopløselighed	1.000 g/l ved 20 °C - opløselig
o) Fordelingskoefficient: n-oktanol/vand	log Pow: -0,4
p) Selvantændelsestemperatur	215 °C ved 1.013,25 HPa
q) Dekomponeringstemperatur	Ingen data tilgængelige
r) Viskositet	Ingen data tilgængelige
s) Eksplosive egenskaber	Ingen data tilgængelige
t) Oxiderende egenskaber	Ingen data tilgængelige

## 9.2 Anden sikkerhedsinformation

Relativ dampvægtfylde 3,53 - (Luft = 1,0)

---

## PUNKT 10: Stabilitet og reaktivitet

### 10.1 Reaktivitet

Ingen data tilgængelige

### 10.2 Kemisk stabilitet

Stabilt under de anbefalede opbevaringsforhold.

### 10.3 Risiko for farlige reaktioner

Ingen data tilgængelige

### 10.4 Forhold, der skal undgås

Varme, flammer og gnister.

### 10.5 Materialer, der skal undgås

Stærke oxidationsmidler, Kulsyre (CO<sub>2</sub>)

### 10.6 Farlige nedbrydningsprodukter

Farlige dekomponeringsprodukter dannet under brand. - Carbonoxider, Nitrogenoxider (NO<sub>x</sub>)

Andere farlige dekomponeringsprodukter - Ingen data tilgængelige  
I tilfælde af brand: se afsnit 5

---

## PUNKT 11: Toksikologiske oplysninger

### 11.1 Oplysninger om toksikologiske virkninger

#### Akut toksicitet

LD50 Oralt - Rotte - han og hun - 410 mg/kg  
(OECD test guideline 401)

LC50 Indånding - Rotte - 4 h - > 4 ppm

LD50 Hud - Rotte - 1.630,4 - 2.805,3 mg/kg  
(OECD test guideline 402)

#### Hudætsning/-irritation

Hud - Kanin

Resultat: Ætsende

#### Alvorlig øjenskade/øjenirritation

Øjne - Kanin

Resultat: Ætsende

(OECD test guideline 405)

### **Respiratorisk sensibilisering eller hudsensibilisering**

Maksimeringstest - Marsvin

Resultat: Kan give overfølsomhed ved kontakt med huden.

(OECD test guideline 406)

### **Kimcellemutagenicitet**

Ingen data tilgængelige

In vitro-test for genmutation i pattedyrceller

lymfomaceller fra mus

Resultat: negativ

OECD test guideline 474

Mus - han og hun - Knoglemarv

Resultat: negativ

### **Kræftfremkaldende egenskaber**

IARC: Ingen forbindelse i dette produkt tilstede i mængder større end eller lig 0,1 % er identificeret som sandsynlig, mulig eller bekræftet kræftfremkaldende stof overfor mennesker af IARC.

### **Reproduktionstoksicitet**

Ingen data tilgængelige

### **Specifik målorgantoksicitet - enkelt eksponering**

Indånding - Kan forårsage irritation af luftvejene. - Luftveje

### **Specifik målorgantoksicitet - gentagen eksponering**

Ingen data tilgængelige

### **Aspirationsfare**

Ingen data tilgængelige

### **Yderligere information**

Toksicitet ved gentagen dosering - Rotte - Oralt - No observed adverse effect level - 50 mg/kg - Lveste dosis, som medfører en skadevirkning - 250 mg/kg

RTECS: TX7525000

Materialet virker ekstremt ødelæggende på slimhinder, øvre luftveje, øjne og hud., Efter vores bedste overbevisning er de kemiske, fysiske og toksikologiske forhold ikke undersøgt tilstrækkeligt.

---

## **PUNKT 12: Miljøoplysninger**

### **12.1 Toksicitet**

Toksicitet overfor fisk Statisk test LC50 - *Leuciscus idus melanotus* - 122 mg/l - 96 h  
(OECD test guideline 203)

Toksicitet for dafnier og andre hvirvelløse vanddyr Statisk test EC50 - *Daphnia magna* (Stor dafnie) - 59,46 mg/l - 48 h

Toksicitet overfor alger EC50 - *Desmodesmus subspicatus* (grønalg) - 56,2 mg/l - 72 h

### **12.2 Persistens og nedbrydelighed**

Biologisk nedbrydelighed Resultat: 60 - 70 % - Let bionedbrydeligt.  
(OECD test guideline 301D)

### 12.3 Bioakkumuleringspotentiale

Ingen data tilgængelige

### 12.4 Mobilitet i jord

Ingen data tilgængelige

### 12.5 Resultater af PBT- og vPvB-vurdering

Dette stof/blanding indeholder ingen komponenter, der anses for at være enten persistente, bioakkumulerende og toksiske (PBT) eller meget persistente og meget bioakkumulerende (vPvB) ved niveauer på 0,1% eller højere.

### 12.6 Andre negative virkninger

Skadelig overfor vandlevende organismer.

Kan være skadelige for organismer, der lever i vand, på grund af påvirkning af pH.

Ingen data tilgængelige

Skadelig for vandlevende organismer, med langvarige virkninger.

---

## PUNKT 13: Bortskaffelse

### 13.1 Metoder til affaldsbehandling

#### Produkt

Brændes i en kemisk forbrændingsovn udstyret med efterbrændkamre og skrubber. Ekstra påpasselighed skal udvises, da materialet er meget brandfarligt. Overskud og ikke genanvendelige opløsninger bør leveres til et anerkendt bortskaffelsesfirma.

#### Forurenede emballage

Bortskaffes som ikke-forarbejdet produkt.

---

## PUNKT 14: Transportoplysninger

### 14.1 UN-nummer

ADR/RID: 2734

IMDG: 2734

IATA: 2734

### 14.2 UN-forsendelsesbetegnelse (UN proper shipping name)

ADR/RID: POLYAMINER, FLYDENDE, ÆTSENDE, BRANDFARLIGE, N.O.S. (3-Aminopropyldimethylamine)

IMDG: POLYAMINES, LIQUID, CORROSIVE, FLAMMABLE, N.O.S. (3-Aminopropyldimethylamine)

IATA: Polyamines, liquid, corrosive, flammable, n.o.s. (3-Aminopropyldimethylamine)

### 14.3 Transportfareklasse(r)

ADR/RID: 8 (3)

IMDG: 8 (3)

IATA: 8 (3)

### 14.4 Emballage gruppe

ADR/RID: II

IMDG: II

IATA: II

### 14.5 Miljøfarer

ADR/RID: nej

IMDG Marin forureningsfaktor (Marine pollutant): nej

IATA: nej

### 14.6 Særlige forsigtighedsregler for brugeren

Ingen data tilgængelige

---

## PUNKT 15: Oplysninger om regulering

### 15.1 Særlige bestemmelser/særlig lovgivning for stoffet eller blandingen med hensyn til sikkerhed, sundhed og miljø

Dette sikkerhedsdatablad overholder kravene i Forordning (EU) nr. 1907/2006.

## 15.2 Kemikaliesikkerhedsvurdering

For dette produkt udføres en kemikaliesikkerhedsvurdering .

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### PUNKT 16: Andre oplysninger

#### Fuldstændig tekst af faresætninger refereret til under punkt 2 og 3.

H226	Brandfarlig væske og damp.
H302	Farlig ved indtagelse.
H302 + H312	Farlig ved indtagelse eller hudkontakt.
H312	Farlig ved hudkontakt.
H314	Forårsager svære ætsninger af huden og øjenskader.
H317	Kan forårsage allergisk hudreaktion.
H335	Kan forårsage irritation af luftvejene.

#### Yderligere oplysninger

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### **Investigations of a possible novel desalination technology**

Basic research on a new potential desalination technology was conducted. The research was based on the observation that introduction of CO<sub>2</sub> to an aqueous solution of diamine and NaCl resulted in a rapid decrease in conductivity in the solution. Following upscaled experiments and analyses, the conclusion was, that the desalination technology process was in fact not a desalination process removing both cations and anions, rather it was an anion exchange process, where the CO<sub>2</sub> activated diamine was able to exchange the formed bicarbonate with chloride anions in solution.

It was decided, to investigate the possibility of immobilizing the diamine on an available epoxide functionalized resin, to produce an anion exchange resin that could be commercialized in the drinking water treatment market and the industrial water market. Experimental work showed that the activated immobilized diamine was able to exchange bicarbonate with chloride, fluoride, and nitrate. Results confirmed the hypothesis regarding the ion exchange mechanism; that target anions were removed from the feed solution through exchange with bicarbonate ions. All three tested anions are problematic anions for which a considerable global market exist.

So far, a limited dataset exists, and future investigations are fundamental in elucidating and determining the potential commercial viability and environmental sustainability of a technology based on the CowaTech resin concept. Due to limited resources, further development of the technology is discontinued under the auspices of CowaTech ApS.



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