

# Investigation of Membrane Distillation Crystallization for Desalination Processes

DEPARTMENT OF PROCESS AND LIFE SCIENCE ENGINEERING | LUND UNIVERSITY

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May 2025

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Master in Membrane Engineering for Sustainable, MESD

Erasmus Mundus Joint Master

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# Preface

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## Popular Scientific Summary

This thesis explores a new method for cleaning salty water and extracting salts, called Membrane Distillation Crystallization (MDCr). This method not only purifies water but also recovers valuable salts, making it a sustainable solution to two global problems: water shortage and pollution from leftover saltwater (brine).

The process works by using a special membrane that allows only water vapor to pass through, separating it from the salty water. By heating the water, the vapor moves through the membrane, which only allows gas to pass through, and is cooled on the other side to form fresh, clean water. As the salty water becomes more concentrated, salt starts to form crystals. The research looks at how different factors, such as temperature, mixing, and the type of membrane, affect how well this process works in cleaning water and forming salt crystals.

The experiments tested different types of membranes, including flat sheets and hollow fibers, to see how they affected the rate at which water passed through and how well the salts formed crystals. The study found that increasing the temperature helped the process work faster, but scaling (salt buildup on the membrane) still created problems. Mixing the water helped to prevent the salt from settling at the bottom, but it did not improve the quality of the crystals or the speed of the water recovery as expected.

The research shows that controlling the temperature, choosing the right membrane, and using mixing are important factors to make this method more efficient. While scaling and other issues remain, using seed crystals to start the crystal formation and improving the materials used in the membranes might help to fix these problems in the future.

Overall, this thesis demonstrates that MDCr could be a valuable tool for desalinating water and reducing waste, making it a more environmentally friendly solution. However, more work is needed to improve the technology and make it suitable for large-scale use.



## Summary

Brine disposal remains one of the most significant environmental challenges associated with desalination, driving the need for sustainable technologies such as zero liquid discharge (ZLD) systems. Among emerging ZLD techniques, membrane distillation crystallization (MDCr) offers a promising approach by integrating water recovery with salt crystallization. In MDCr, a hydrophobic membrane separates water vapor from concentrated brine via a temperature-driven vapor pressure gradient, while the remaining solution reaches supersaturation, enabling salt crystallization.

This study investigated key operational parameters in MDCr, particularly the effect of bottom-section mixing and feed temperature. Experiments were conducted using a polytetrafluoroethylene (PTFE) flat sheet membrane and polyvinylidene fluoride (PVDF) hollow fiber membranes in a custom-built reactor divided into a warm distillation zone and a cooler crystallization zone. The influence of thermal gradients, membrane type, and mixing intensity on water flux and crystal formation was evaluated.

The tests with the flat sheet membrane demonstrated a permeate flux of 2.63 LMH and showed evidence of crystallization, though the limited surface area of the membrane resulted in lower feed concentration and slower crystallization.

The system was then tested using the hollow fiber membrane. The results showed that increasing the temperature gradient from around 20 °C to 30 °C significantly improved water flux, increasing it from 1.02 LMH to a stable range of 2.25–2.35 LMH (125%). This was due to the stronger driving force for vapor transport at higher temperature differences. However, after about 120 hours of continuous operation, scaling started to appear on the membrane surface. At a feed conductivity of 160 mS/cm, the flux dropped to 0.99 LMH, and visible needle-shaped salt crystals formed on the membrane and inner walls of the reactor.

In the mixing test, the membrane flux remained stable at an average of 2.1–2.2 LMH, with the temperature in the top section maintained in the beginning at approximately 52°C. However, an issue arose after about one day of operation when a leak was detected in membrane I, leading to a sharp increase in feed conductivity, indicating membrane damage. Afterwards, two replacement modules were tested, and membrane III was used to continue the test, but it exhibited a reduced flux (down to 1.7 LMH) and a quicker rise in permeate conductivity, indicating increased membrane wetting. Despite these issues, the introduction of mixing prevented the salt from settling at the bottom of the reactor, ensuring a more uniform distribution of the solutes and keeping the concentration gradient between the top and bottom sections of the reactor. Turbidity measurements confirmed initial crystal suspension, followed by settling and growth.

Tests without mixing produced larger, more elongated crystals with prominent needle-like structures, which were primarily composed of calcium (Ca) and sulfur (S), being sodium (Na) being more abundant in square-like crystals. In contrast, crystals formed during the mixing tests were smaller and more diverse in shape.

Overall, these findings highlight the potential of MDCr as a sustainable desalination technology, though challenges such as membrane scaling and wetting require further attention. Future work should focus on optimizing membrane materials and operational conditions to enhance long-term stability and scalability for industrial applications.

## Table of abbreviations

|               |                                              |
|---------------|----------------------------------------------|
| MD            | Membrane Distillation                        |
| MDCr          | Membrane Distillation Crystallization        |
| ZLD           | Zero Liquid Discharge                        |
| RO            | Reverse Osmosis                              |
| DCMD          | Direct Contact Membrane Distillation         |
| VMD           | Vacuum Membrane Distillation                 |
| AGMD          | Air Gap Membrane Distillation                |
| SGMD          | Sweep Gas Membrane Distillation              |
| OMD           | Osmotic Membrane Distillation                |
| PTFE          | Polytetrafluoroethylene                      |
| PVDF          | Polyvinylidene Fluoride                      |
| LMH           | Liters per square meter per hour             |
| VCF           | Volume Concentration Factor                  |
| SEM           | Scanning Electron Microscope                 |
| EDS           | Energy Dispersive X-ray Spectroscopy         |
| DI            | Deionized                                    |
| CP            | Concentration Polarization                   |
| TG            | Temperature Gradient                         |
| CG            | Concentration Gradient                       |
| ITAM          | Instalación de Desalinización de Agua de Mar |
| HF            | Hollow Fiber                                 |
| rpm           | Revolutions Per Minute                       |
| $\mu\text{m}$ | Micrometer                                   |
| mS/cm         | MilliSiemens per centimeter                  |

# Table Of Contents

|     |                                                 |    |
|-----|-------------------------------------------------|----|
| 1   | Introduction.....                               | 11 |
| 1.1 | Aim and limitations.....                        | 11 |
| 2   | Background.....                                 | 13 |
| 2.1 | Global Water Scarcity.....                      | 13 |
| 2.2 | Principles of Membrane Distillation.....        | 13 |
| 2.3 | Principles of Crystallization.....              | 14 |
| 2.4 | Integration of MD and Crystallization.....      | 16 |
| 2.5 | Key Parameters Influencing MDC Performance..... | 17 |
| 2.6 | Challenges in MDC and Research Trends.....      | 18 |
| 2.7 | Previous Research.....                          | 19 |
| 3   | Material and methods.....                       | 21 |
| 3.1 | Setup and Experimental Method.....              | 21 |
| 3.2 | Membrane.....                                   | 22 |
| 3.3 | Feed.....                                       | 23 |
| 3.4 | Crystal measurement.....                        | 23 |
| 4   | Results and discussion.....                     | 24 |
| 4.1 | Flat sheet membrane.....                        | 24 |
| 4.2 | Hollow Fiber Membrane.....                      | 25 |
| 4.3 | SEM analysis of Crystals.....                   | 41 |
| 5   | Conclusion.....                                 | 47 |
| 6   | Future work.....                                | 49 |
|     | References.....                                 | 50 |
| 7   | Appendix.....                                   | 52 |
| 7.1 | EDS Analysis.....                               | 52 |

# 1 Introduction

Water contamination from industrial waste and wastewater is a significant and growing concern, particularly as the global demand for water increases while freshwater supplies decrease. An important source of contamination is the discharge of brine produced during desalination processes and industrial wastewater, both of which often contain high concentrations of harmful salts and chemicals. Current treatment methods, such as reverse osmosis (RO) and various filtration techniques, have made progress in managing water quality. However, they often face challenges such as high energy consumption, inefficiency under certain conditions, and the generation of concentrated waste streams that still require disposal[1, 2].

As the demand for freshwater intensifies, there is a pressing need to adopt sustainable approaches that not only purify water but also recover valuable resources, such as salts, from wastewater. Zero liquid discharge (ZLD) methods have emerged as a promising solution for minimizing waste and ensuring that all water is reused or purified. Membrane distillation crystallization (MDCr) has shown potential in achieving these goals[3, 4].MDCr integrates membrane distillation (MD) with crystallization, enabling the simultaneous recovery of both clean water and valuable crystalline salts from brine and other concentrated solutions. In this process, water vapor is separated from the feed solution via a hydrophobic membrane, which is driven by a temperature difference between the feed and permeate sides. This process concentrates the remaining solution to a point of supersaturation, which then facilitates the crystallization of salts. By optimizing the operating conditions, such as temperature and flow rates, MDCr can improve the efficiency of both water recovery and salt production [4-6].

The advantages of MDCr include its ability to operate at lower temperatures compared to traditional distillation methods, and its potential to recover both pure water and high-purity salts such as sodium sulfate and lithium [3, 7, 8]. However, challenges such as membrane fouling, and scaling, as well as the need for precise control of supersaturation levels are still preventing its industrial-scale application. Recent advances in membrane technology, such as the incorporation of nanoparticles and nanocellulose, have shown promise in reducing membrane fouling and scaling and thus improving the long-term stability of the MDCr process[9, 10].

Thus, membrane distillation crystallization represents a significant advancement in water treatment and resource recovery. With ongoing research focused on optimizing the process conditions and membrane performance, MDCr could play a crucial role in addressing the global water crisis while contributing to a circular economy by recovering valuable minerals from wastewater [4, 11].

## 1.1 Aim and limitations

The aim of this project is to enhance the understanding of the process and optimize its operational parameters. Additionally, it aims to explore potential improvements through the incorporation of techniques such as mixing. The study investigates the effects of permeate flow rate, temperature, mixing, and seeding on process efficiency.

However, some limitations are inherent to this approach. Each successful test requires at least two weeks to complete, which imposes significant time constraints. Furthermore, controlling the temperature within the crystallization and distillation reactors is not entirely precise, as the system relies on a jacket for heating and cooling rather than a dedicated temperature control

device. Additionally, due to the formation of crystals on the walls and at the bottom of the setup, it is not feasible to collect and accurately measure their weight for comparison across different tests.

## 2 Background

### 2.1 Global Water Scarcity

The increasing global demand for clean water, driven by population growth and industrial development, has intensified freshwater scarcity in many regions. Despite covering 71% of the Earth's surface, only about 2.5% of the planet's water is freshwater, and an even smaller fraction (approximately 0.008%) is readily accessible as surface water [3]. The remainder is trapped in glaciers, ice caps, and deep groundwater reservoirs, making it largely unavailable for immediate use. As a result, desalination has emerged as a critical solution for meeting freshwater needs and preserving existing resources [3].

RO remains the dominant method for seawater desalination. However, one of its major drawbacks is the generation of highly concentrated brines, which are difficult to manage and cause environmental risks. The recovery efficiency in RO systems typically ranges from 30% to 50%, which means a significant volume of saline concentrate has to be disposed [8]. Disposal practices such as deep-well injection, surface water discharge, and land applications (which involve disposing of brine by spraying it onto salt-resistant vegetation or specially prepared soils that can absorb and slowly reduce the salinity of the water[12]) can severely disrupt ecosystems by increasing salinity levels and introducing harmful substances into the environment[6].

To mitigate these challenges, ZLD technologies have gained significant attention. ZLD systems aim to eliminate wastewater discharge by recovering almost all the water from saline streams, leaving only solid residues behind[6]. Among the most promising ZLD strategies is MDCr, which is a hybrid process that combines MD and crystallization. MD uses hydrophobic membranes to selectively transport water vapor across a temperature-induced vapor pressure gradient, enabling efficient separation of pure water from saline or contaminated streams. The remaining concentrated solution is then crystallized to recover valuable salts and/or minimize waste[6].

### 2.2 Principles of Membrane Distillation

MD is a thermally driven separation process in which only volatile components of a liquid feed are allowed to pass through a hydrophobic, microporous membrane in the form of vapor. This transport occurs due to a difference in vapor pressure created by a temperature gradient across the membrane, typically established between a heated feed and a cooler permeate stream. The hydrophobic properties of the membrane ensure that non-volatile solutes are retained, leading to effective separation and concentration of the feed solution[1, 3, 8].

One of the key features of MD is its ability to treat high-salinity streams that are challenging for pressure-driven membrane processes. Unlike RO, MD is not significantly affected by feed salinity because the driving force is thermal rather than osmotic or pressure-based. As a result, MD can operate at relatively low hydraulic pressures and moderate temperatures, offering a simpler setup with potentially lower mechanical energy requirements[8].

There are several configurations of MD that are useful for different operational conditions and needs (Figure 2.1):

- Direct Contact Membrane Distillation (DCMD), s. Figure 2.1(a): Both the hot feed and cold permeate are in direct contact with opposite sides of the membrane. Although this setup is the

most studied due to its simplicity, it suffers from higher conductive heat losses, making it less energy-efficient[8].

- Vacuum Membrane Distillation (VMD), s. Figure 2.1 (b): A vacuum is applied on the permeate side to enhance the vapor flux. This configuration provides higher driving forces and water fluxes, but is more susceptible to membrane fouling and wetting[1, 8].

- Air Gap Membrane Distillation (AGMD), s. Figure 2.1 (c): A layer of stagnant air separates the membrane from the condensation surface, reducing conductive heat loss. It is regarded as one of the most energy-efficient configurations and is favorable for industrial-scale applications[8].

- Sweep Gas Membrane Distillation (SGMD), s. Figure 2.1 (d): An inert gas flows along the permeate side to carry vapor to an external condenser. While it reduces heat loss, the need for an additional condenser can complicate the system design[1, 8].

- Osmotic Membrane Distillation (OMD): This configuration utilizes a concentration gradient between the feed and draw solutions to drive mass transfer, enhancing performance in certain crystallization applications[1].

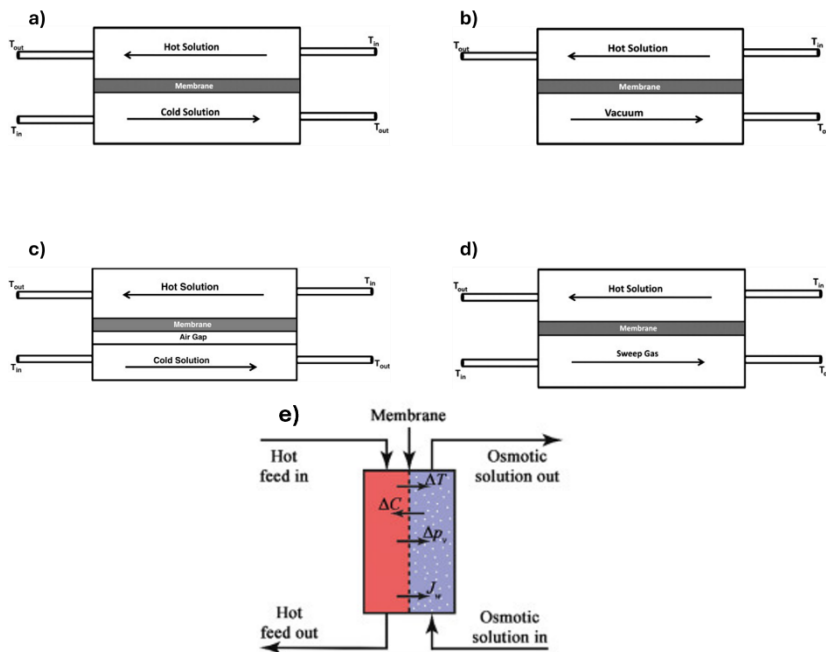


Figure 2.1. Different MD configurations[13] a)Direct Contact Membrane Distillation b)Vacuum Membrane Distillation c)Air Gap Membrane Distillation d)Sweep Gas Membrane Distillation. (Figure used with permission from Alkhudhiri, A., Darwish, N., & Hilal, N. (2012). Membrane distillation: A comprehensive review. *Desalination*, 287, 2–18. © 2011 Elsevier B.V. Licensed under a RightsLink/CCC license.) e) Osmotic Membrane Distillation (used with permission from Elsevier under RightsLink License Number 5327651467219, granted on May 26, 2025. Source: "Module 5: Membrane Distillation" as published in *Comprehensive Membrane Science and Engineering*, Elsevier, 2023)[14]

MD presents several advantages, especially in integrated processes like MDCr. These include the ability to handle highly concentrated solutions, achieve high solute rejection, operate at low temperatures using waste heat, and support controlled supersaturation conditions favorable for

crystallization[1]. Despite its benefits, MD is not without limitations. Major challenges include temperature polarization, where heat loss at the membrane interface reduces the effective driving force, and membrane scaling, in which salts precipitate on the membrane surface or within its pores, leading to reduced flux and potential pore wetting[1, 8].

## 2.3 Principles of Crystallization

Crystallization is a fundamental unit operation used for purification and separation in various industrial applications, particularly in the pharmaceutical, petrochemical, food, and chemical sectors. It operates on the basis of inducing supersaturation in a solution, which is the primary driving force for the formation and separation of crystals from a liquid phase [8]. Supersaturation can be achieved through different methods, including cooling, solvent evaporation, or anti-solvent addition. Each of these approaches influences the solubility of the solute, thereby enabling crystallization to proceed [1].

From a thermodynamic perspective, the solubility curve (Figure 2.2) defines the conditions under which a solution becomes saturated. Once this curve is crossed, further changes in parameters such as temperature or concentration can lead the system into the metastable or unstable zones. These zones are crucial for nucleation and crystal growth. Specifically, the metastable zone allows for crystal growth (especially when seed crystals are introduced), whereas the unstable zone is necessary for spontaneous nucleation to occur. No crystallization happens in the stable zone, where the solution is undersaturated [1, 8].

The kinetics of crystallization are defined by two core mechanisms: nucleation and growth. Nucleation refers to the initial formation of small, stable crystalline clusters, whereas growth describes the enlargement of these nuclei into larger crystals. In conventional crystallization systems, these processes typically occur simultaneously. However, in membrane-based systems such as MDCr, it is possible to separate them. The membrane surface can act as a nucleation site, promoting heterogeneous nucleation. Once formed, the crystals may detach and move into the bulk solution, where the conditions are more favorable for crystal growth due to lower levels of supersaturation [1].

Control over the level of supersaturation plays a significant role in determining crystal attributes such as size, shape, purity, and polymorphic form. Adjusting parameters like solution temperature, concentration gradients, and the presence of seeding agents allows precise tuning of nucleation rates and growth dynamics. This control is particularly critical in industrial settings where reproducibility and product quality are essential. Limitations in conventional systems include challenges in achieving consistent supersaturation levels, energy efficiency, and uniformity in crystal characteristics [8].

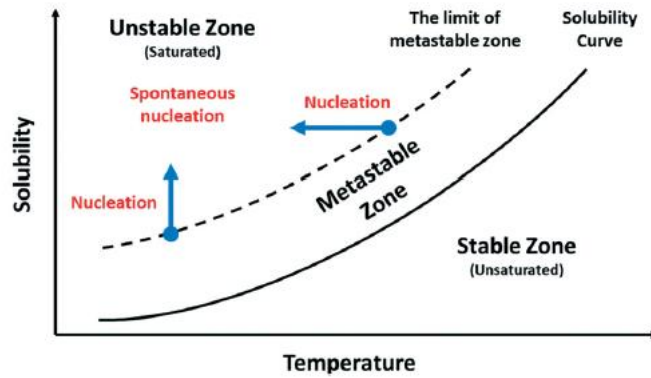


Figure 2.2. Solubility Curve[8](Used with permission of the Royal Society of Chemistry, from "Membrane distillation crystallization for brine mining and zero liquid discharge: opportunities, challenges, and recent progress," *Environmental Science: Water Research & Technology*, 5(7), 1202-1221, 2015. Copyright 2015, permission conveyed through Copyright Clearance Center, Inc.)

## 2.4 Integration of MD and Crystallization

As discussed, MDCr is a hybrid process that merges membrane distillation with crystallization, enabling simultaneous water purification and solute recovery. In this integrated setup, membrane distillation removes water vapor from a concentrated feed solution through a hydrophobic membrane, gradually increasing the solute concentration. As the solution becomes saturated and then supersaturated, crystallization is induced, leading to the formation and recovery of solid crystals. This system addresses the challenge of treating high-salinity waste streams by enhancing both water recovery and resource reclamation without requiring additional post-treatment steps[8, 15]

MDCr can continuously extract water vapor, promote and sustain supersaturation in the solution, which is an essential condition for crystal nucleation and growth. Membrane distillation not only serves as a separation barrier but also facilitates controlled crystallization by providing a consistent driving force through vapor pressure gradients[8, 15].

One strength of this process is the ability to recover both clean water and valuable crystal products in a single integrated system. Furthermore, compared to traditional evaporation-based crystallization, MDCr requires less energy to trigger solute precipitation, making it more energy-efficient and potentially more cost-effective [8, 15].

Another key benefit lies in its improved control over crystallization. Since water is continuously removed through the membrane, the concentration of solutes in the solution can be gradually increased to reach the desired point for crystal formation. This steady build-up allows for more precise control over when and how crystallization occurs, helping to produce crystals with more uniform size and shape. The membrane surface itself also promotes nucleation, accelerating the crystallization process and shortening the time needed for crystals to begin formation. From an environmental perspective, MDCr significantly reduces the volume of brine or liquid waste by recovering both water and solid materials. This makes it especially attractive for ZLD strategies[8, 15].

## 2.5 Key Parameters Influencing MDCr Performance

The performance of MDCr systems is influenced by several interconnected factors, including temperature gradient, flow conditions, concentration polarization, and the properties of the membrane itself (Table 2.1).

Temperature plays a major role in MDCr efficiency. As the feed temperature increases, vapor pressure rises exponentially, which directly boosts the permeate flux. However, higher temperatures can also lower salt rejection. A well-managed temperature difference between the top (MD zone) and the bottom (crystallization zone) is essential, as it is also crucial for controlling solubility and managing where crystallization happens. When effective crystallization occurs in the bottom zone, it helps to reduce unwanted scaling at the membrane surface by pulling solute away from the top region, due to the temperature-driven solute movement[8, 16]. Feed flow rate and mixing conditions are also important. Short residence times and high mixing speeds tend to produce smaller, more uniform crystals and support stable operation[16].

Concentration polarization (CP) is one of the key challenges in MDCr. It occurs when a layer of concentrated solute builds up near the membrane surface, creating local supersaturation. This can lead to crystal formation directly on the membrane, which clogs pores and reduces permeate flux. CP becomes more significant at higher feed concentrations and in systems with poor mixing. It often goes together with temperature polarization, and together they can severely impact performance[8, 16].

The membrane itself is a critical component in MDCr. Since it is in direct contact with highly concentrated and often crystallizing solutions, the material needs to be chemically stable, hydrophobic, and resistant to fouling/scaling. Commonly used membrane materials include PVDF, PTFE, PP, and PVC, with superhydrophobic membranes being especially effective due to their ability to resist wetting and fouling [16].

High surface porosity can increase the chances of crystals forming directly on the membrane. As vapor evaporates near the pore openings, it adsorbs heat from the surrounding area, lowers the local film temperature, and promotes further precipitation. Ideally, MDCr membranes should have low thermal conductivity, well-defined pore sizes, and good surface properties to minimize these issues [16]. Ultimately, the combination of temperature control, flow dynamics, and membrane design determines how well an MDCr system performs. When these factors are well-managed, it is possible to reduce fouling/scaling, maintain high water recovery, and improve the quality of the recovered crystals[8, 16].

*Table 2.1. Effect of different parameters on MDCr Performance*

| Parameter            | Effect on MDCr Performance                                                                        | Notes                                                                                | Ref  |
|----------------------|---------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------|
| Solute Concentration | High concentration enhances crystallization but increases scaling and concentration polarization. | Close to saturation, scaling is likely on the membrane surface, lowering water flux. | [3]  |
| Membrane Properties  | Key to mass transfer and heterogeneous nucleation; influence flux and fouling resistance.         | High porosity, hydrophobicity, and chemical stability are critical.                  | [15] |
| Flow Rate            | Enhanced flow near the membrane reduces polarization and improves flux and heat transfer.         | Turbulent flow lowers resistance and boosts mass                                     | [15] |

|                           |                                                                                                                |                                                                                                                                                                                              |      |
|---------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
|                           |                                                                                                                | transfer; very high rates reduce crystal size.                                                                                                                                               |      |
| Membrane Type             | Material impacts flux and fouling; ceramic membranes offer better stability than polymers in harsh conditions. | Hydrophobic coatings and structured membranes help improve performance.                                                                                                                      | [3]  |
| Temperature Gradient      | Drives mass transfer and enhances crystallization efficiency.                                                  | Hot MD zone and cooler crystallization zone promote continuous salt transport and prevent scaling.                                                                                           | [3]  |
| Feed Solution Composition | Determines solubility behavior and crystallization dynamics.                                                   | Multicomponent systems may exhibit competitive solute behavior, influencing nucleation pathways and selectivity.                                                                             | [5]  |
| Seeding                   | Reduces induction time and controls crystal size distribution.                                                 | Initiates crystallization in the metastable zone, enhancing crystal purity and lowering nucleation energy barriers.                                                                          | [8]  |
| Crystallizer Mixing       | Enhances mass and heat transfer, promoting uniform supersaturation and preventing agglomeration.               | Adequate mixing reduces local saturation spikes and promotes homogeneous nucleation throughout the crystallizer volume. Gentle stirring supports growth; prevents agglomeration and settling | [15] |

## 2.6 Challenges in MDCr and Research Trends

MDCr faces some challenges that currently limits its wide industrial application. The main issues include membrane wetting, membrane fouling and scaling, energy inefficiency, crystal product quality, and difficulties related to scaling up the process [2]. Among these issues, membrane wetting occurs when the feed solution gradually penetrates the membrane pores due to changes in membrane hydrophobicity during operation, leading to a reduction in the efficiency and stability of MDCr. Traditional methods for detecting membrane wetting, like measuring permeate conductivity, are useful but insufficient to fully address the problem[17].

Membrane fouling and scaling are also critical challenges. Scaling occurs when crystals form on the membrane surface, increasing temperature and concentration polarization, which can damage the membrane and shorten its lifespan[3]. Moreover, crystallization directly on the membrane surface leads to further fouling, negatively affecting overall MDCr performance[8].

Despite these challenges, recent research has made significant progress toward overcoming them. Innovative membrane modifications, such as adding silica nanoparticles or applying

surface fluorination coatings, have improved membrane hydrophobicity, increased flux, and enhanced resistance to fouling[5]. Practical approaches like induced crystallization using seeding and heating have also effectively controlled gypsum scaling and membrane wetting [17].

Future research directions for MDCr focus on developing advanced membrane materials with better durability and anti-wetting properties, optimizing process conditions for improved energy efficiency, engineering crystals to achieve desired shapes and purity, and effectively scaling up the process for industrial use [2]. Additionally, moving MDCr research from laboratory experiments to pilot-scale studies is essential to practically validate solutions and address theoretical and operational challenges, facilitating sustainable and economically feasible industrial applications[1].

## 2.7 Previous Research

Extensive research efforts have focused on exploring MDCr under various experimental conditions, aiming to optimize performance, reduce operational challenges, and enhance practical applicability.

You et al [10]. conducted experiments using VMDC to recover water and ammonium salts ( $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$ ) from high-salinity solutions. Their batch mode study revealed critical points for membrane fouling and distinguished between reversible fouling (for  $(\text{NH}_4)_2\text{SO}_4$ ) and irreversible fouling (for  $\text{NH}_4\text{Cl}$ ). Notably, they achieved recovery of  $125.7 \text{ kg/m}^3$  of  $\text{NH}_4\text{Cl}$  and  $58.4 \text{ kg/m}^3$  of  $(\text{NH}_4)_2\text{SO}_4$  crystals.

Choi et al [4]. introduced a novel fractional-submerged membrane distillation crystallizer (F-SMDC) for the treatment of high-salinity brine, particularly from seawater reverse osmosis (SWRO) processes. The system integrates membrane distillation and crystallization in a single submerged reactor using both a temperature gradient (TG) and concentration gradient (CG). By maintaining a high temperature and low concentration at the top portion of the reactor, and the reverse conditions at the bottom, the F-SMDC facilitates simultaneous water recovery and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) crystal production. Compared to conventional submerged membrane distillation crystallization (SMDC), F-SMDC achieved a higher volume concentration factor (VCF) of 3.5 (vs. 2.9 in SMDC) and enabled the generation of  $\text{Na}_2\text{SO}_4$  crystals with a narrow size distribution.

Choi et al[18]. expanded on their previous work by examining how the presence of various inorganic and organic compounds influences the performance of F-SMDC, specifically its ability to maintain CG and TG within the reactor. Using different salts like,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{MgSO}_4$ ,  $\text{NaCl}$ , and  $\text{NH}_4\text{Cl}$ , the study found that molecular weight and cation electronegativity strongly affect CG stability. For example, high molecular weight salts like  $\text{KCl}$  achieved a CG ratio up to 1.83 and initiated crystallization earlier (VCF 2.4) than expected, while lower weight salts such as  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  exhibited poor CG formation (ratios between 0.94 and 1.46).  $\text{Na}_2\text{SO}_4$  showed superior performance with only 12.56% flux decline, compared to 55.93% for  $\text{MgSO}_4$ , attributed to  $\text{Na}^+$ 's lower electronegativity. The study also found that inorganic CG formation could drive organic compounds (e.g., humic acid, alginate, bovine serum albumin) downward, reducing membrane fouling risk. Specifically, hydrophobic organic compounds and low molecular weight organics showed higher CG ratios and increased accumulation at the bottom portion, suggesting the F-SMDC process can simultaneously enhance water recovery, salt crystallization, and organic foulant mitigation.

Tan et al[9]. explored the enhancement of PVDF membranes for MDCr by the incorporation of  $\text{TiO}_2$  nanoparticles and nanocellulose. The study focused on structural modifications that improved membrane hydrophobicity, porosity, and permeability. Notably, silane modification following the addition of  $\text{TiO}_2$  and nanocellulose helped to recover hydrophobicity losses due to hydrophilic fillers. The modified membranes achieved a high salt rejection rate ( $>97\%$ ) and demonstrated improved flux and resistance to fouling during MDCr operation. The presence of nanocellulose contributed to larger pore size and higher porosity, optimizing water vapor transport and enabling effective crystallization without significant membrane fouling.

Zhang et al [19]. implemented a MDCr system for ZLD treatment of aniline wastewater. The use of hydrophobic PVDF membranes under VMD achieved high fluxes of up to 20 LMH and salt rejection of over 99% at  $60^\circ\text{C}$  and 500 mL/min flow rate. The study combined membrane technology with Fenton oxidation pretreatment, which effectively removed aniline compounds and enabled the recovery of pure water and salt crystals. The work demonstrated the feasibility of using MDCr in an industrial wastewater context, where it achieved high recovery efficiency and produced regular cubic salt crystals, validating its application in achieving ZLD.

Flatscher et al[6]. developed a novel seeded near-zero liquid discharge membrane crystallization system to treat hypersaline brines using MDCr. Their study incorporated synthetic mono-salt (290 g/L NaCl), multi-salt (255 g/L NaCl + 255 g/L  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), and real highway wastewater to evaluate the technology's performance. The mini-plant used a polypropylene tubular membrane and a classifier-based crystal separation unit. In the mono-salt test, a constant permeate flux of  $\sim 2.5\text{--}2.9 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  was maintained with 93% water recovery and 79% salt recovery. In the multi-salt experiment, the permeate flux reached  $1.76 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  with 89% water recovery and 60% salt recovery. For real wastewater, increasing the feed temperature from  $61^\circ\text{C}$  to  $70^\circ\text{C}$  boosted flux from 1.1 to a peak of  $4.7 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , and 99% water recovery was achieved. Notably, the use of seed crystals significantly reduced membrane scaling and ensured long-term stability. Crystals from the real wastewater were smaller ( $d_{50} = 95 \mu\text{m}$ ) compared to synthetic feed.

Ouda et al[20]. conducted a comprehensive investigation into the mechanisms that govern nucleation and crystal growth in MDCr, with particular emphasis on supersaturation rate control. By introducing a Nývlt-like equation, the authors demonstrated how operational parameters, including membrane area, temperature difference, and crystallizer volume, can be independently tuned to influence nucleation kinetics and metastable zone width. Their findings highlight that increasing supersaturation rate significantly reduces induction time and favors homogeneous nucleation in the bulk phase, thereby mitigating membrane scaling. Specifically, higher membrane area at constant flux maintained the same nucleation order across systems, suggesting MDCr scalability.

## 3 Material and methods

### 3.1 Setup and Experimental Method

The reactor (Figure 3.1) consists of two main sections. The top part is kept warm using a jacket and an isolating layer. This part is where distillation happens, and it is separated from the lower part using a cone to further improve the temperature gradient. The bottom part, where crystallization mainly happens, is kept cold using a jacket.



*Figure 3.1. a) Setup including the reactor, pumps, scale, conductivity meter, heater, and cooler b) Hollow fiber membrane hanging from the top section of the reactor*

When a hollow fiber membrane is used, the membrane hangs in the top part (Figure 3.1.b). Conversely, when a flat sheet membrane is used, feed from the top section of the reactor is pumped (HygiaFlex, HF-BT600N) to the external membrane setup and is sent back to the reactor after passing through the membrane. The permeate enters a cold bath in the cooler before being pumped into the beaker by a HygiaFlex HF-BT600N peristaltic pump. The permeate beaker is kept on a scale (PCE-BSH10000) to record the flux throughout the experiment. The conductivity of permeate in this beaker is measured regularly using a conductivity meter (sensION MM374). Additional feed during the process is added through the valve at the top of the setup, which is connected to the feed container. The feed drops down in the setup due to gravity and the rate was controlled using the valves. Samples from the reactor are taken regularly to measure conductivity (sensION MM374) and turbidity (HACH, TL 2300). A mixer was used to add agitation at the bottom of the reactor. Figure 3.2 shows a schematic design of the process. As illustrated in the figure, the reactor is divided into top and bottom sections by a funnel, which enhances both the concentration and temperature gradients within the system.

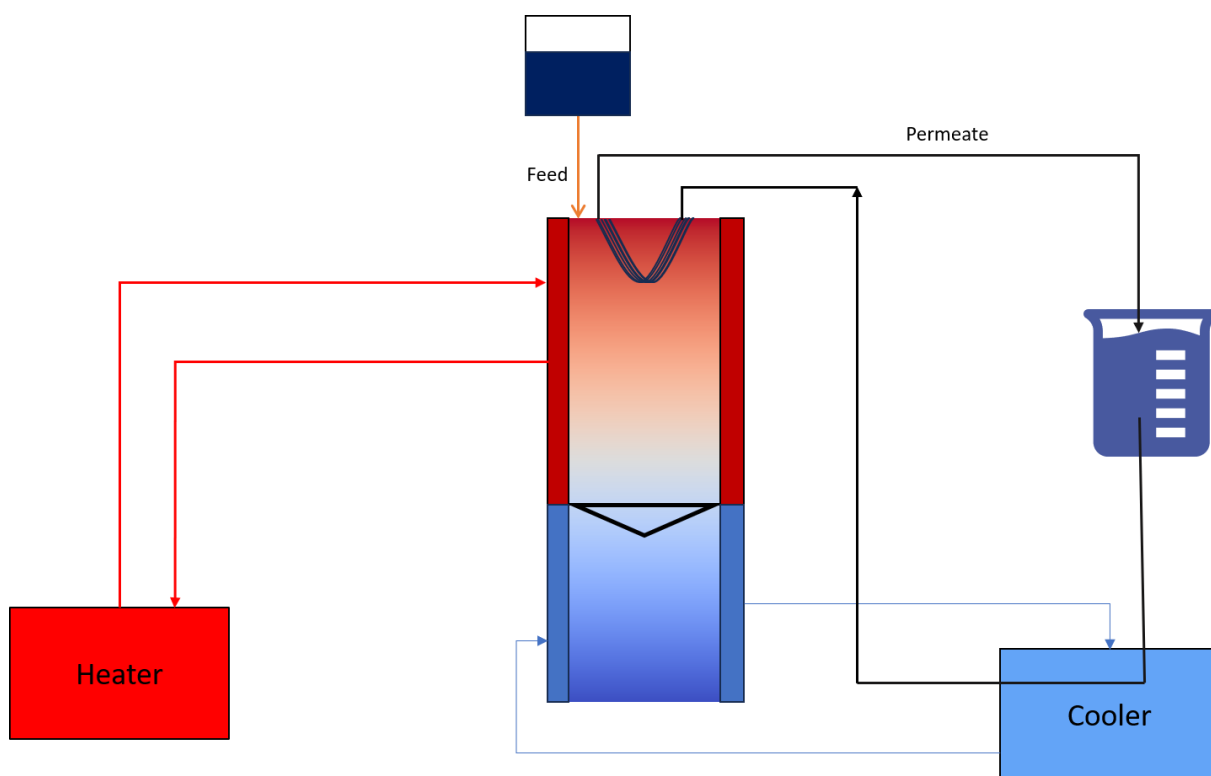


*Figure 3.2 Schematic design of the process*

The heating system circulates water through a jacket surrounding the top section, maintaining a temperature of up to 90 °C in the jacket. In contrast, a cooling system regulates the temperature in the bottom section, using a similar circulation set-up. The cooler is also utilized to reduce the temperature of the permeate. Permeate in the beaker is directly routed to the cooler, where it is cooled before entering the membrane.

### **3.2 Membrane**

A hollow-fiber polyvinylidene fluoride (PVDF) membrane (Econity) module was used (Figure 3.3). This membrane has a nominal pore size of 0.1  $\mu\text{m}$ , with outer and inner diameters of 1.2 mm and 0.7 mm, and a wall thickness of 250  $\mu\text{m}$ . The module had an effective membrane area of 176  $\text{cm}^2$  and comprised of 20 fibers, each 0.2 m long, potted at both ends. When scaling was observed, the membrane was washed and kept in DI water for at least 24 hours. In the tests with an external membrane, a polytetrafluoroethylene (PTFE) flat sheet membrane with a surface area of 16  $\text{cm}^2$ , a pore of 0.2  $\mu\text{m}$ , and a thickness of 70  $\mu\text{m}$  was also used.



*Figure 3.3. A hollow-fiber PVDF membrane*

### **3.3 Feed**

Brine from the Instalación de Desalinización de Agua de Mar (ITAM) seawater desalination plant in Barcelona was used for the tests, with an initial conductivity of 90-100 mS/cm, and it was added to the system at room temperature.

### **3.4 Crystal measurement**

The crystals were collected and filtered using a vacuum filter using a nylon membrane filter with a pore size of 0.2  $\mu\text{m}$ , if needed. Afterwards, their morphology was investigated using a Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray Spectroscopy (EDS) detector for elemental analysis.

## 4 Results and discussion

### 4.1 Flat sheet membrane

In this experiment, a flat sheet membrane with a surface area of 16 cm<sup>2</sup> was externally integrated into the system (Figure 4.1).

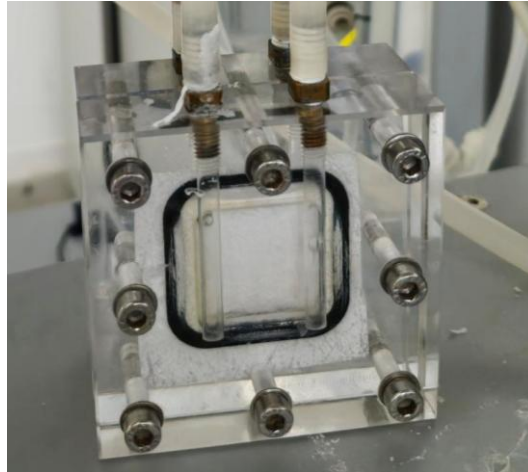


Figure 4.1. Flat Sheet Membrane

The membrane was operated continuously for 150 hours. During this period, the feed conductivity increased from 107 to 109 mS/cm. The average permeate flux was measured at 2.63 LMH, and a total of 650.8 g of permeate was collected. The temperature at the top section of the reactor was maintained between 48–52 °C, while the permeate temperature ranged from 17.3–17.9 °C, resulting in a temperature gradient of approximately 20–25 °C. Figures 4.2 illustrate the influence of temperature on flux at two different time intervals of the experiment.

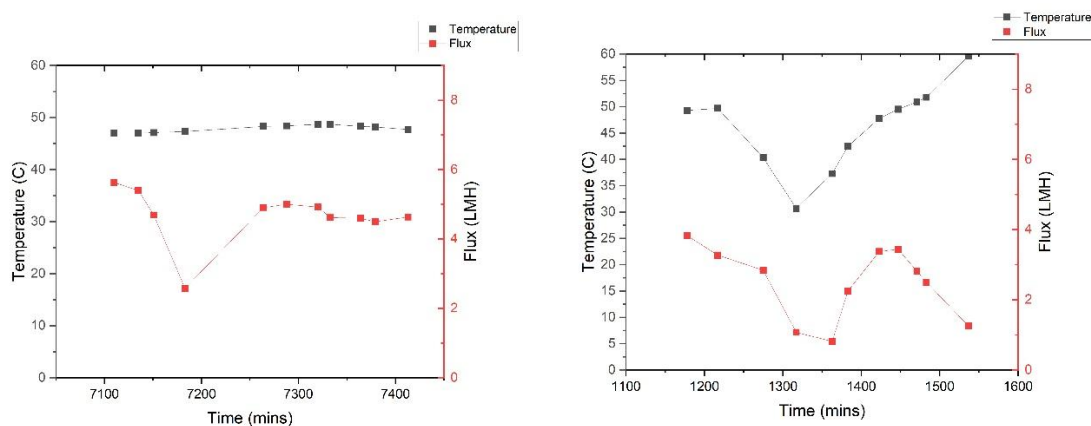


Figure 4.2. Influence of temperature on flux in flat-sheet membrane test

A clear correlation between the top section temperature and flux was observed, with both following similar trends. Nevertheless, the deviations from this pattern recorded at approximately 1450 and 7150 minutes, were attributed to system leaks that were subsequently identified and resolved. Although the membrane demonstrated relatively high flux, its limited surface area prevented sufficient concentration of the feed, which lowered the crystallization. Therefore, it

was necessary to use a larger membrane surface area in the following tests. Despite the relatively low conductivity within the system, evidences of crystallization were observed toward the end of the operation. The crystals primarily appeared as thin surface layers. Samples of these crystal deposits were collected (Figure 4.3) for further analysis using SEM.

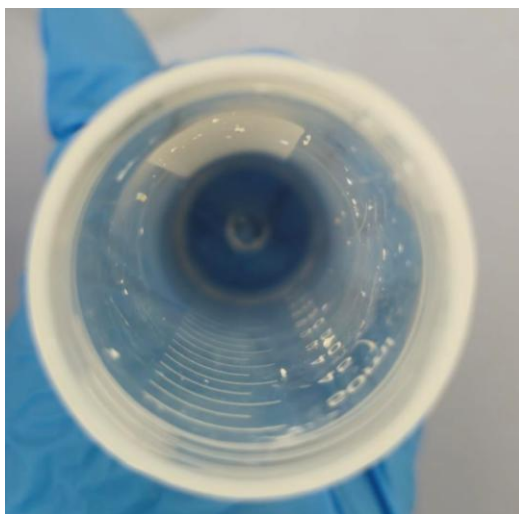


*Figure 4.3. Crystal deposits in the flat sheet membrane tests*

## **4.2 Hollow fiber membrane**

In this stage, a PVDF hollow fiber membrane with a surface area of 176 cm<sup>2</sup> was employed to enhance the efficiency of feed concentration and to promote crystallization.

### **4.2.1 Test without mixing**

#### ***Low-temperature operation***

In this setup, the temperature at the top of the reactor was maintained between 39–40 °C, while the permeate temperature ranged from 18.7–19.9 °C. This resulted in a temperature gradient of approximately 19–21.5 °C between the feed and permeate. Due to the relatively low operational temperature, the observed flux was limited to 1.02 LMH at a feed conductivity of 95 mS/cm. Figure 4.4 illustrates the relationship between flux and temperature during the experiment. As seen in the figure, both temperature and flux remained relatively constant, indicating that the system reached steady state condition.

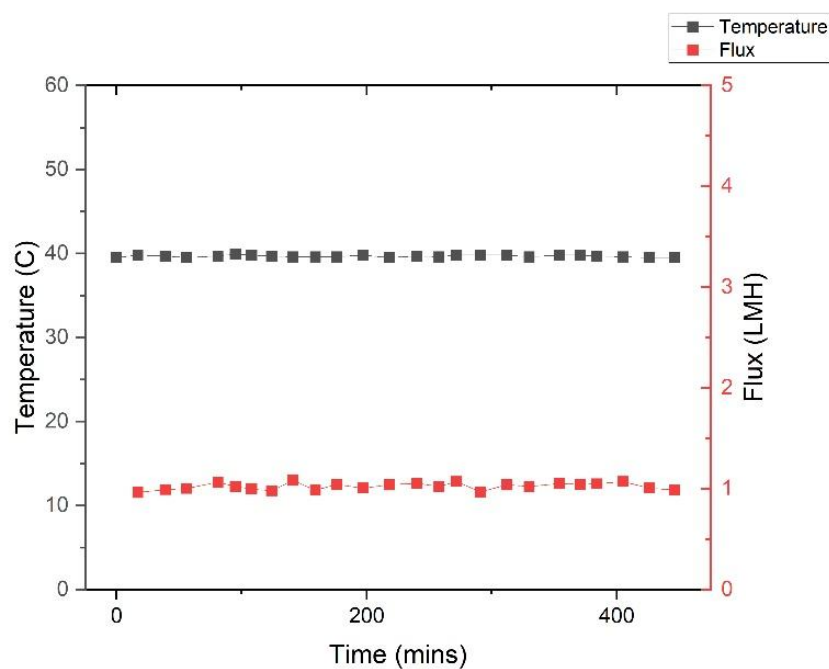


Figure 4.4. Flux at the low temperature run

The permeate was extracted at a pumping rate of 85 rpm, corresponding to an approximate flow rate of 0.3 L/min. Figure 4.5 presents the permeate conductivity profile during operation at a feed conductivity of 95–100 mS/cm. As depicted, permeate conductivity exhibited a slight but steady increase over time. Despite this trend, the membrane maintained a high rejection rate, consistently exceeding 99.98%.

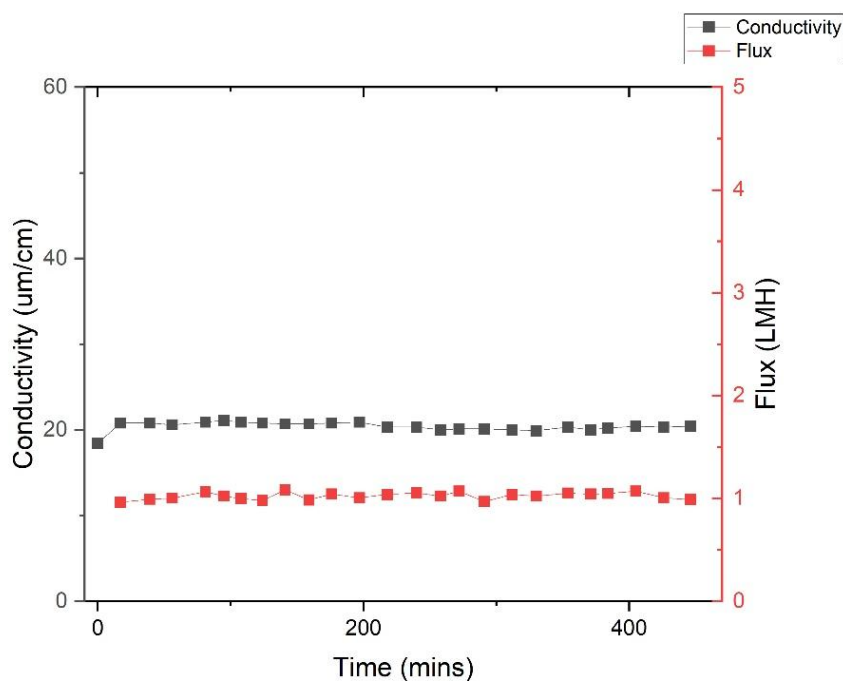


Figure 4.5. Permeate conductivity profile during the low temperature run at a feed conductivity of 95–100 mS/cm

### High-temperature operation

Due to the low flux and limited top temperature observed in the initial setup, modifications were made to the heating system. As a result, the top temperature could be stabilized at approximately 52 °C, while the permeate temperature remained at 21 °C. This led to a notable increase in the temperature gradient, which is an important driving force in this process. In comparison to the earlier low-temperature test, where the temperature difference was approximately 20 °C, the high-temperature setup achieved a temperature gradient of nearly 30 °C.

This enhancement in thermal driving force resulted in a significant increase in permeate flux, rising by approximately 125% from 1.02 LMH to a range of 2.25–2.35 LMH. Figure 4.6 illustrates the correlation between flux and temperature throughout the experiment. As shown, the flux remained relatively constant over time, indicating the establishment of steady state operating conditions.

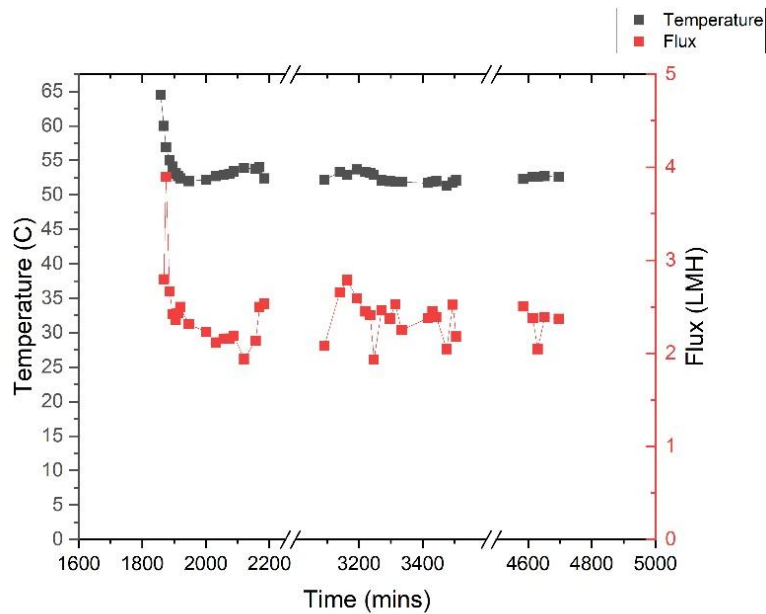


Figure 4.6. Flux and temperature at the high temperature run

### Scaling

After nearly 122 hours of operation, a noticeable accumulation of crystals appeared on the membrane surface, which was defined as scaling. This membrane scaling adversely affected system performance as the crystals formed on the surface blocked the pores and acted as a barrier for the vapor to move through. The permeate flux declined to 0.99 LMH, approximately 57% lower than its previous stable value. At this stage, the feed conductivity had risen to 160 mS/cm, indicating a substantial solute concentration. Figure 4.7 provides visual evidence of the scaling, showing needle-like crystal structures deposited on the membrane. CP could be a reason that contributed to the scaling, as it creates local supersaturation[8]. It might be possible to reduce this effect by adding a form of turbulence close to the membrane surface to minimize the possibility of scaling or delay it.

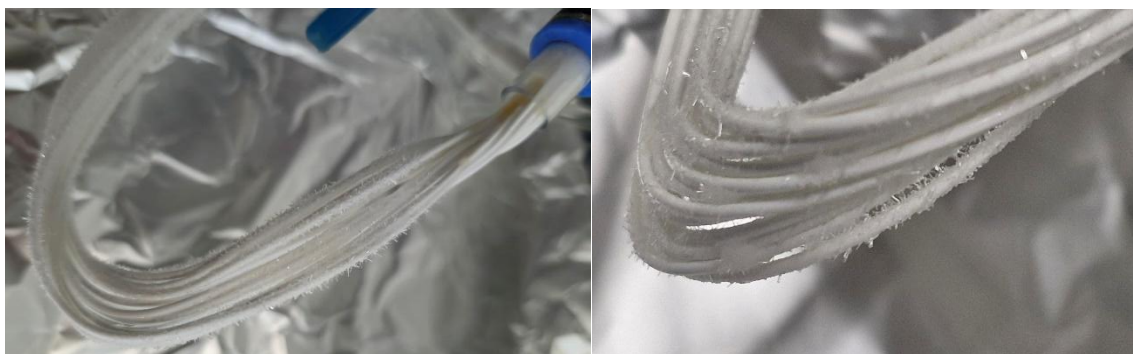


Figure 4.7. Membrane scaling

### **Washing after scaling**

To prevent damage to the membrane, the operation was stopped upon the observation of scaling. The membrane was subsequently washed and immersed in deionized (DI) water for 24 hours. After cleaning, the process was resumed, and the system operated at a feed conductivity of approximately 165–170 mS/cm. The average flux during this period was 2.1–2.2 LMH, indicating less than a 10% reduction compared to the pre-scaling flux measured at feed conductivities below 160 mS/cm.

The experiment was stopped at a feed conductivity of approximately 170 mS/cm following renewed evidence of scaling and a decrease in flux (1.8 LMH), at which point the membrane was cleaned once more. Figure 4.8. displays the flux and temperature profiles over time until the point of second scaling.

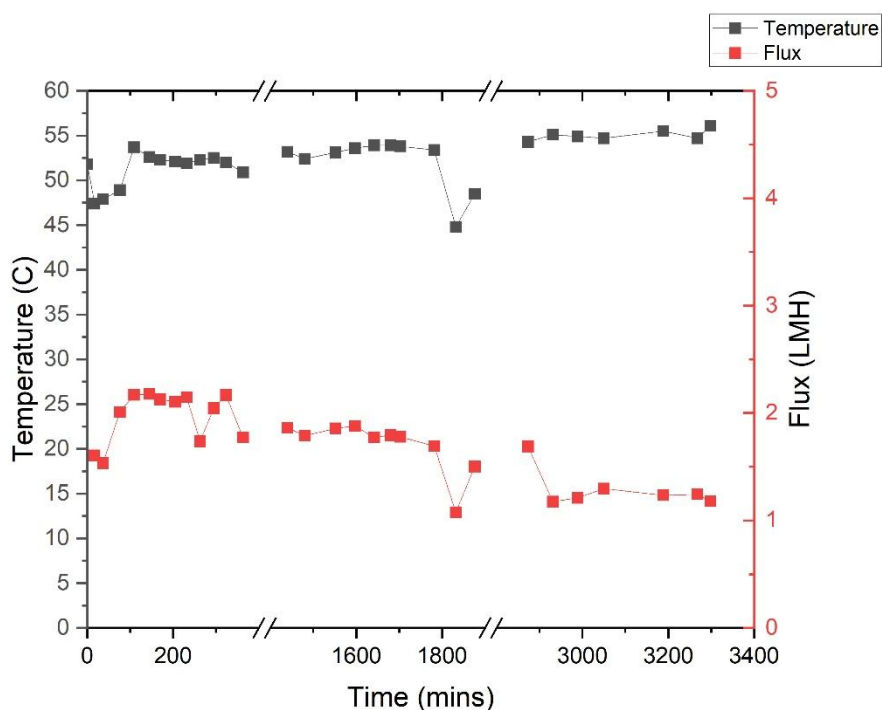


Figure 4.8. Flux and temperature profiles to the point of second scaling

### ***Parallel membranes***

To increase the effective membrane surface area, a second membrane with identical specifications was introduced into the system. The two membranes were connected in parallel. Table 4.1 summarizes the results of this experiment. Contrary to expectations, the total permeate flux did not increase proportionally. In fact, the observed flux was less than 50% of the typical value recorded when using a single membrane.

*Table 4.1. Results of Parallel Membranes*

| <b>Test</b> | <b>Pumping Speed</b> | <b>Top Temperature</b> | <b>Permeate Temperature</b> | <b>Flux (LMH)</b> | <b>Feed Conductivity</b> |
|-------------|----------------------|------------------------|-----------------------------|-------------------|--------------------------|
| Parallel 1  | 85 rpm, ~ 0.3 l/min  | ~51°C                  | ~22°C                       | 0.48              | ~170-175 ms/cm           |
| Parallel 2  | 160 rpm ~ 0.6 l/min  | ~50°C                  | ~20°C                       | 0.32              | ~170-175 ms/cm           |

This unexpected outcome may be attributed to a greater temperature drop in the upper region of the reactor, particularly near the membrane surfaces. The increased volume of low-temperature permeate circulating in this section could have led to localized cooling, which may not be precisely detected by the system's temperature sensors. Additionally, the close arrangement of the membranes within a limited reactor volume may have reduced the exposure of certain membrane areas to the feed solution, further reducing flux. Based on these observations, it was concluded that using a single membrane is more effective in the current configuration, and subsequent experiments were carried out accordingly.

### ***Results overview***

The experiment was concluded after 184 hours of continuous operation, producing a total of 5.74 L of permeate. Initially the was running at low temperature, it was continued at high temperature, where scaling occurred. The use of two membranes in parallel was also investigated in this test. During this period, the feed conductivity increased from 94.6 mS/cm to 175 mS/cm. The membrane maintained a rejection rate above 99% throughout the run. A summary of the experiment is provided in Table 4.2.

During the MDCr operation, the volume concentration factor (VCF) can be used to relate the amount of water extracted and feed added to the system. VCF is the ratio of the initial volume of the feed to the final volume of the concentrate after recovery of water[4]. The VCF used in this study was based on the volume of the reactor and the amount of fresh water produced. The total volume of feed solution in the MDCr reactor was kept at almost a fixed volume (2500 mL) to ensure continuous feeding of feed solution at the same ratio of produced fresh water. In this context, the VCF value was calculated as:

$$VCF = \frac{V_{reactor} + V_{total,permeate}}{V_{reactor}} \quad (\text{Eq 4.1})$$

As mentioned above, in this test, 5.74 L of permeate was produced, which corresponds to a VCF of 3.3.

Table 4.2. Results' summary of the test without mixing

| Test          | Pumping Speed      | Top Temperature | Permeate Temperature | Flux (LMH) | Feed Conductivity | VCF  |
|---------------|--------------------|-----------------|----------------------|------------|-------------------|------|
| Low temp      | 85 rpm, ~0.3 l/min | ~39-40°C        | ~18.7-19.9°C         | 1.02       | ~95 ms/cm         | 1.17 |
| High temp     | 85 rpm, ~0.3 l/min | ~52°C           | ~21°C                | 2.25-2.35  | ~100-130 ms/cm    | 2.31 |
| Scaling       | 85 rpm, ~0.3 l/min | ~52°C           | ~21°C                | 1.8        | ~160 ms/cm        | 2.6  |
| After scaling | 85 rpm, ~0.3 l/min | ~52°C           | ~21°C                | 2.1-2.2    | ~165-170 ms/cm    | 3.26 |
| Parallel 1    | 85 rpm, ~0.3 l/min | ~51°C           | ~22°C                | 0.48       | ~170-175 ms/cm    | 3.28 |
| Parallel 2    | 160 rpm ~0.6 l/min | ~50°C           | ~20°C                | 0.32       | ~170-175 ms/cm    | 3.3  |

Figure 4.9 illustrates the variation in feed conductivity over time. During the first 30 hours of operation, the increase in conductivity was relatively slow. This can be attributed to the system operating at lower temperatures during this period, with flux recorded at 1.02 LMH. when the system was subsequently operated at higher temperatures (as discussed earlier), the flux increased to above 2.2 LMH, resulting in a faster permeate extraction rate. Consequently, the feed conductivity increased at a faster rate during this phase.

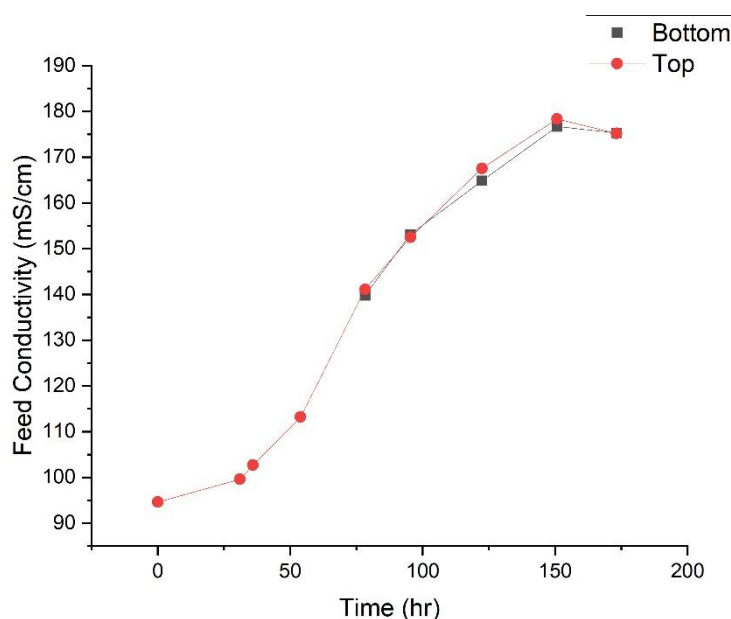


Figure 4.9. Feed conductivity over time at the top and bottom of the setup

Notably, the data presented in Figure 4.9. shows that the conductivity gradient, which relates to the concentration gradient, between the top and bottom sections of the reactor remained minimal, which was unexpected. One possible explanation is the rapid settling of salt particles,

leading to the formation of a thin sediment layer at the bottom of the lowest section. This phenomenon will be further addressed in subsequent sections.

Figure 4.10 illustrates the evolution of permeate conductivity over time at feed conductivities of approximately 100, 160, and 170 mS/cm. From the data, it can be seen that the rejection rate consistently remained above 98.5%. Additionally, the intervals with limited data over a few hours can be attributed to the operation occurring during nighttime, when data recording was not possible.

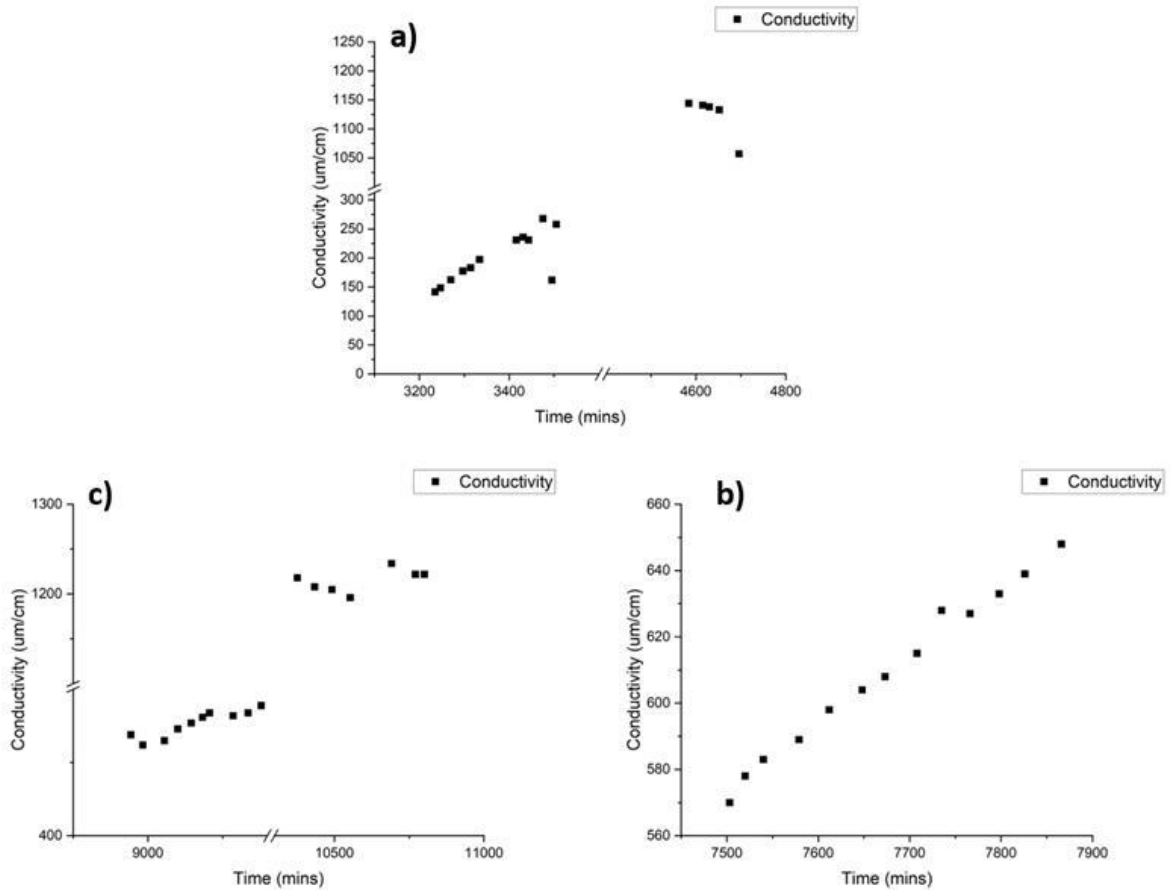


Figure 4.10. Permeate conductivity over time at feed conductivities of approximately a) 100, b) 160, and c) 170 mS/cm

Various crystal morphologies were identified following the experiment. As shown in Figure 4.11.a, a powder-like layer of salt formed at the bottom of the lowest reactor section. These deposits, along with the surrounding feed, were collected and filtered through a nylon membrane filter. Upon drying, needle-like crystal structures were observed (Figure 4.11.b).



*Figure 4.11. Crystallization at the bottom of the reactor: a) crystals after filtration, b) crystals at the bottom of the setup*

Crystallization on the inner walls of the reactor, particularly in the midsection and funnel, was more pronounced than at the base. This possibility could be due to the fact that the connection areas between the walls, funnel, and temperature sensors could provide a good area for crystals to stick to when nucleation happens, while being in contact with high salinity brine that moves down in the system. Aggregates of needle-shaped crystals were clearly visible to the naked eye, as shown in Figure 4.12.



*Figure 4.12. Crystallization on the inner walls of the reactor*

Similar crystalline deposits were also noted on the funnel separating the middle and bottom sections. All crystal samples were collected (Figure 4.13) for further analysis via SEM.



Figure 4.13. Crystal samples collected for analysis

#### 4.2.2 Test with mixing

##### *Membrane I*

The mixing test was initiated with membrane I, which had also been used in the test without mixing. During its operation, it exhibited similar flux and rejection characteristics as observed in the earlier tests. However, after approximately one day of operation, a leak was detected in the membrane, necessitating its replacement with membrane II. The likely cause of the leak was the prolonged usage of membrane I. The leakage occurred near the membrane potting, which, as indicated in previous assessments, was the most vulnerable part of the membrane. This weakness can be attributed to the inherent challenges of achieving perfect potting for hydrophobic membranes. Figure 4.14 below shows the flux and temperature changes during the test with membrane I. As seen, the flux remained consistent with the results from previous tests using the same membrane, with an average flux of 2.26 LMH.

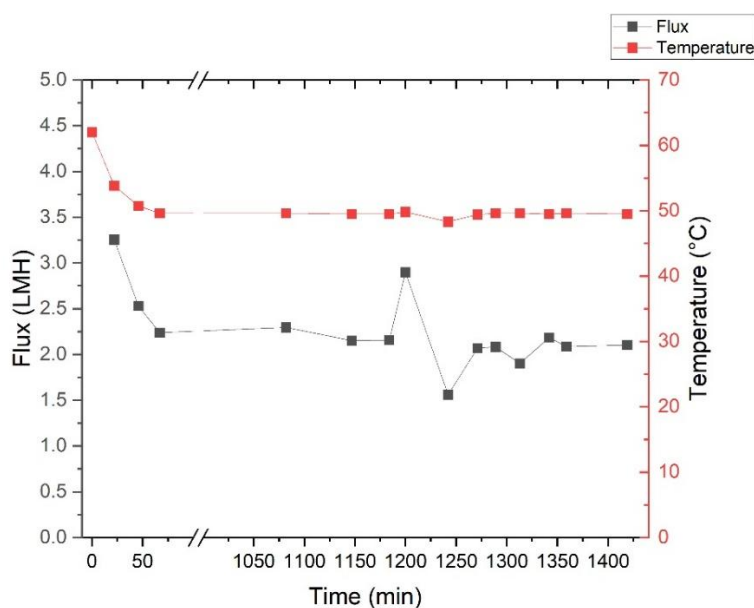


Figure 4.14. Flux and temperature changes in the mixing test using membrane I

Figure 4.15. illustrates the conductivity changes over time during this test. When compared to conductivity data from earlier tests (Figures 4.10. and 4.15.), it is evident that the conductivity increased more rapidly, indicating higher wetting and leakage, which suggests that the membrane's integrity was weakening over time.

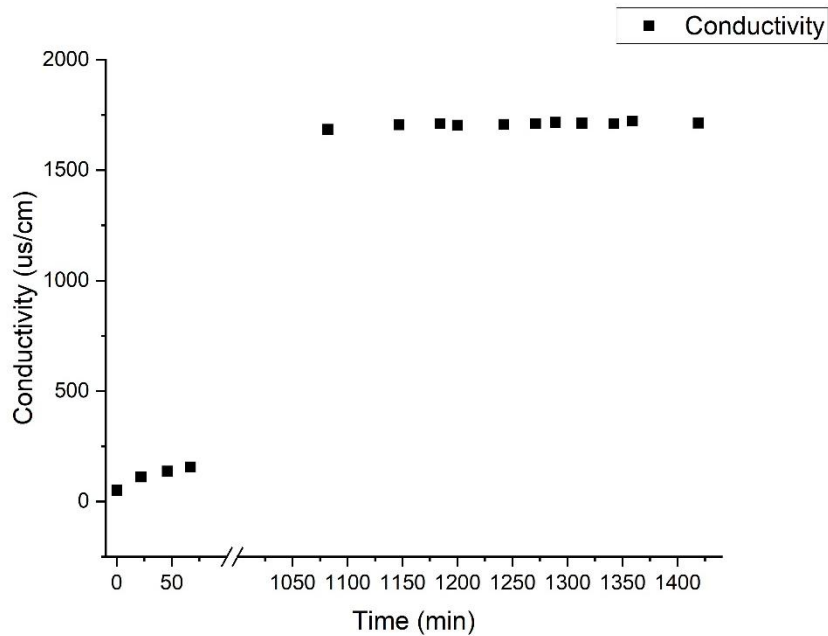


*Figure 4.15. Conductivity changes in the test with mixing using membrane I*

After noticing a rapid increase in conductivity, the operation was paused, and the membrane was inspected. It was found that one of the membrane fibers had broken, as shown in Figure 4.16.a. Silicone hot glue was used to seal the leak, but it became clear that this type of adhesive did not stick well to the membrane surface (Figure 4.16.b), and the leak continued. This could be due to the membrane's natural hydrophobicity. As a result, the membrane was replaced. While other adhesives might have worked, exploring those options was not practical due to time limitations, and replacing the membrane seemed to be the more effective solution.

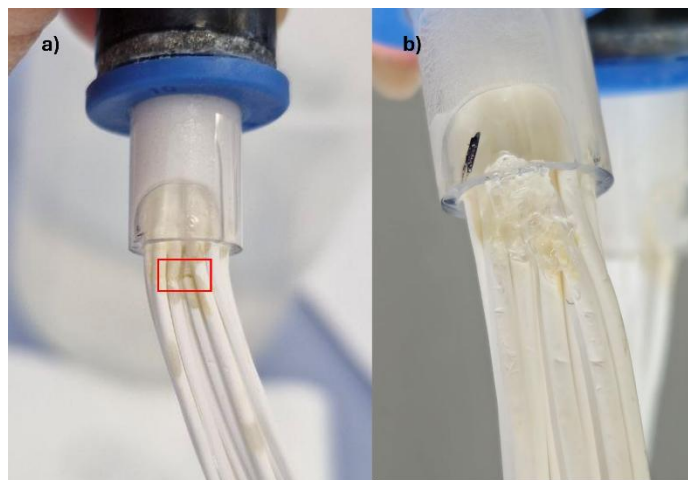


*Figure 4.16. membrane I breakage and repair attempt*

### ***Membrane II***

Membrane II was tested for the continuation of the test, but it showed leakage from the transparent potting area (as shown in Figure 4.17). This type of leakage is difficult to repair with glue or by blocking a single fiber, as it depends on the quality of the membrane's potting. As a result, it was necessary to replace the membrane with a different one.

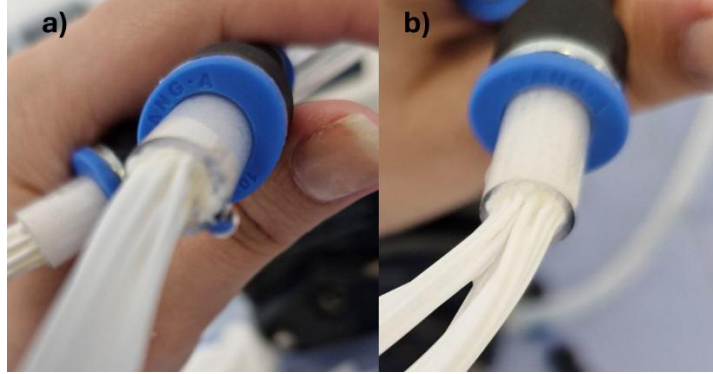


*Figure 4.17 membrane II's leak*

### ***Membrane III***

Membrane III was used to continuing the operation. This membrane did not show any visible leakage or breakage. However, as will be discussed in detail in the following sections, it exhibited a significantly lower flux and a faster increase in permeate conductivity compared to membrane I. These observations suggest that membrane III exhibited increased wetting and was generally less robust compared to membrane. Despite this, it was still possible to proceed with the test using membrane III.

Figure 4.18. shows how flux and temperature change over time before scaling occurred. Similar to previous tests, flux was directly related to temperature, with any changes in temperature having a significant impact on flux.

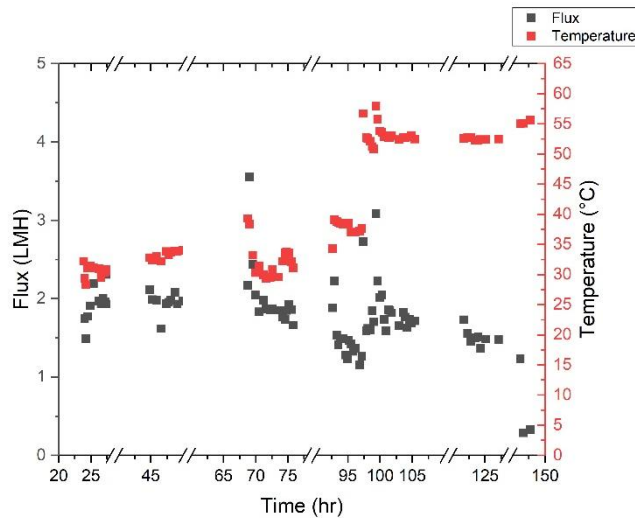


*Figure 4.18. Flux and temperature change over time before scaling, test with mixing using membrane III*

It was also evident that, as feed conductivity increased over time, flux gradually decreased. For feed conductivities between 100 and 115 mS/cm and 140 to 160 mS/cm, the average flux was 2.1 and 1.7 LMH, respectively. This represents a decrease of more than 25% compared to the flux observed under the same conditions with membrane I. Additionally, the figure shows that when scaling occurred, the flux drops further to 0.3 LMH, which was more than 80% lower than the average flux before scaling. This scaling was observed at a feed conductivity of 160 mS/c. At this point, the experiment was paused, and the membrane was stored in deionized (DI) water for two days over the weekend to remove the crystals that had formed on the membrane surface.

Figure 4.19 shows how conductivity changed over time in this test. As observed, conductivity increased more than expected, rising from less than 500  $\mu\text{S}/\text{cm}$  to over 2000  $\mu\text{S}/\text{cm}$  in just one day, which was not ideal. This sharp increase indicates that the rejection rate dropped to as low as 98% at several points, suggesting that membrane III had a higher wetting potential compared to membrane II. After 8863 minutes (147.7 hours), when the run was paused due to scaling, a noticeable jump in conductivity occurred, further indicating that scaling also affected the membrane's wetting potential.

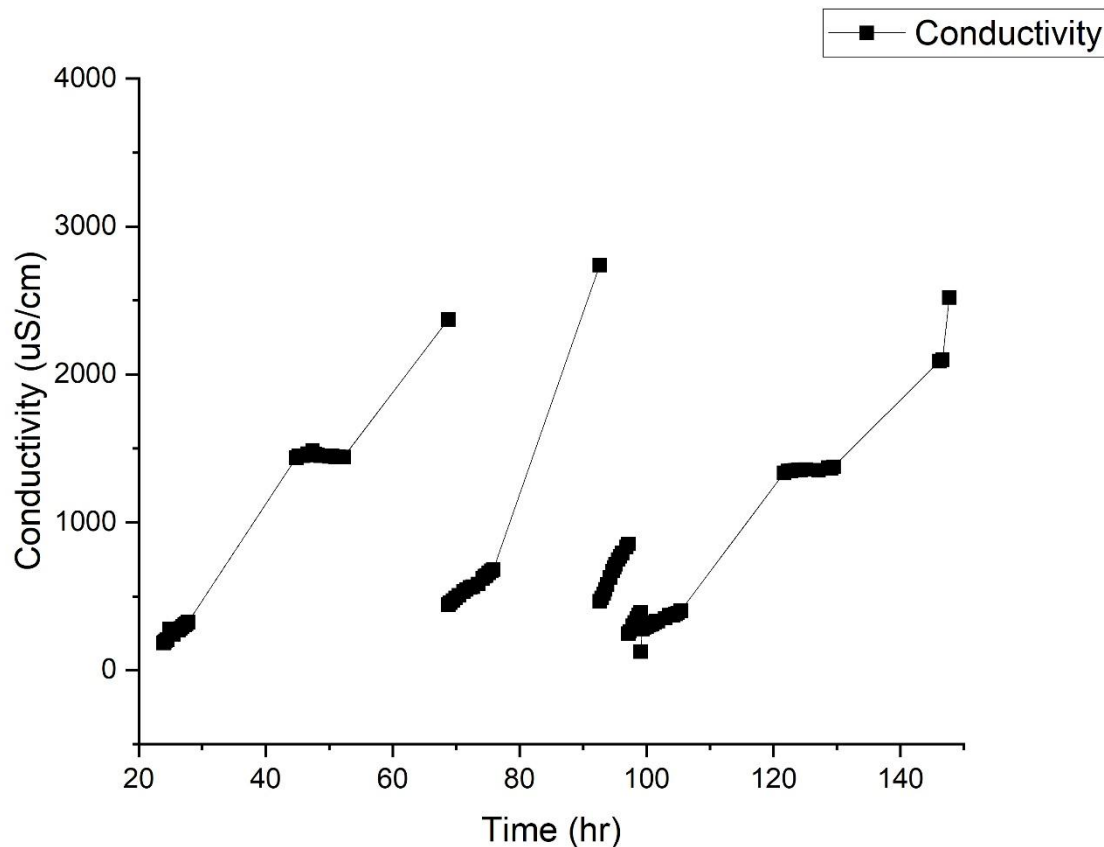


*Figure 4.19. Conductivity changes in the test with mixing using membrane III*

After washing the membrane and keeping it in DI water over the weekend, the test was restarted, and an average flux of 1.25 LMH was measured, which represents a more than 25% decrease compared to the flux observed before scaling. This significant decrease was unexpected and suggests that scaling may have caused some permanent damage to the membrane. However, it

is possible that with an extended washing period or the use of warm water, could have restored some more flux. In comparison to membrane I, membrane III appeared to be more prone to damage from scaling. Figure 4.20. illustrates the changes in flux after scaling occurred. As shown, after approximately one day of operation, the flux decreased to below 0.3 LMH, prompting the termination of the run.

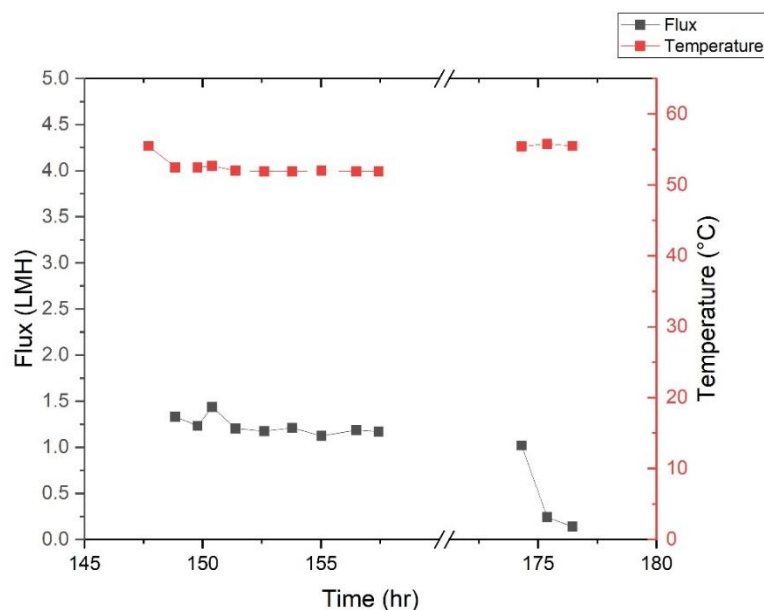


Figure 4.20. Flux changes after scaling

Figure 4.21 shows the changes in conductivity during this time.

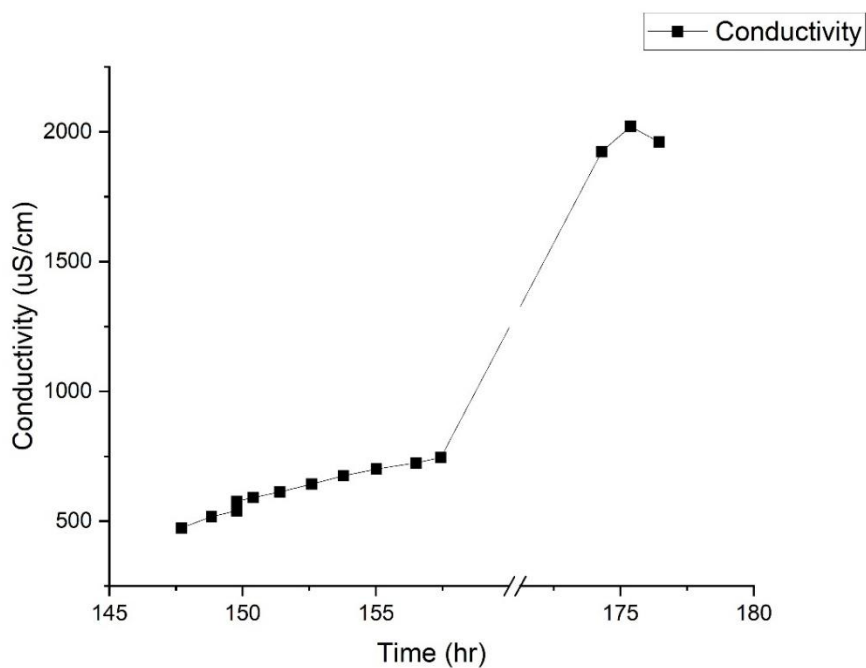


Figure 4.21. conductivity changes after scaling

During this test, feed conductivity at both the top and bottom sections, as well as turbidity, were measured continuously. Figure 4.22. shows the feed conductivity over time. A noticeable difference can be observed compared to the similar figure from the test without mixing (Figure 4.9). In this figure, a clear gradient is seen between the top and bottom conductivities, with the bottom section consistently showing higher conductivity. In the no-mixing test, salts began to settle rapidly, sometimes without proper crystallization (as shown in Figure 4.11.b), which resulted in lower conductivity in the bottom feed and reduced the gradient. However, with mixing in place, this settling phenomenon was prevented, allowing for a concentration gradient to persist between the top and bottom feeds. This test resulted in the extraction of 5.3 liters of permeate, which corresponds to a VCF of 3.1.

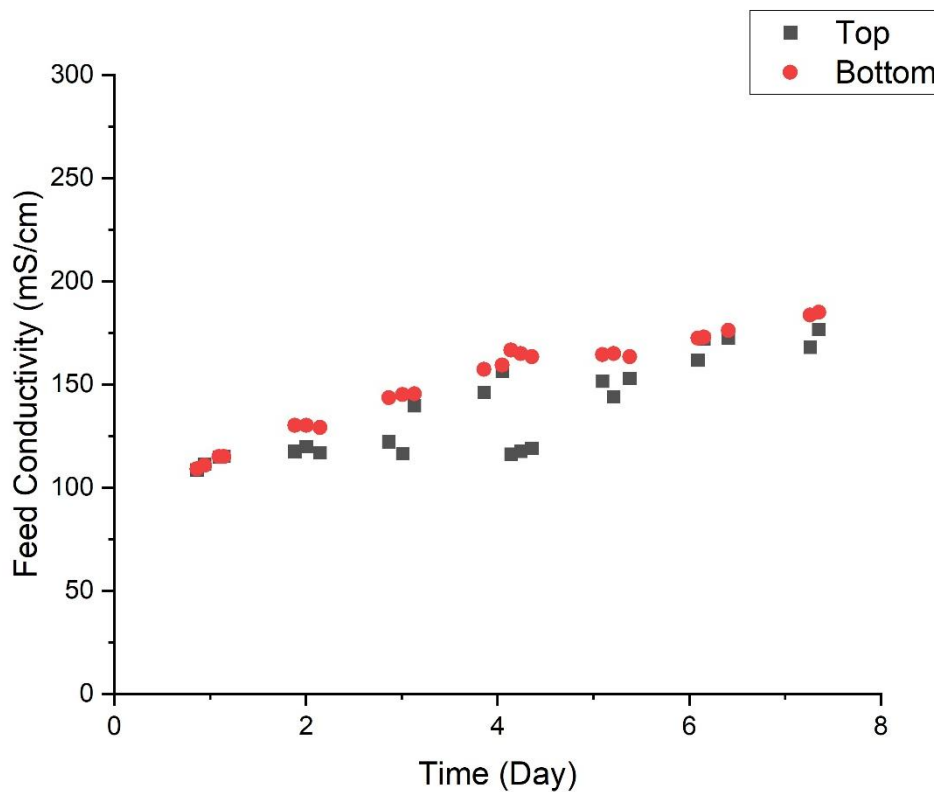


*Figure 4.22 Feed conductivity over time in the test with mixing*

After around four days of operation, a decrease in the top feed conductivity was observed, which requires some clarification. This drop occurred when some pipes were changed, and membrane III was reinstalled and tested. During this process, there was some permeate leakage into the feed, which caused a decrease in conductivity at the top section.

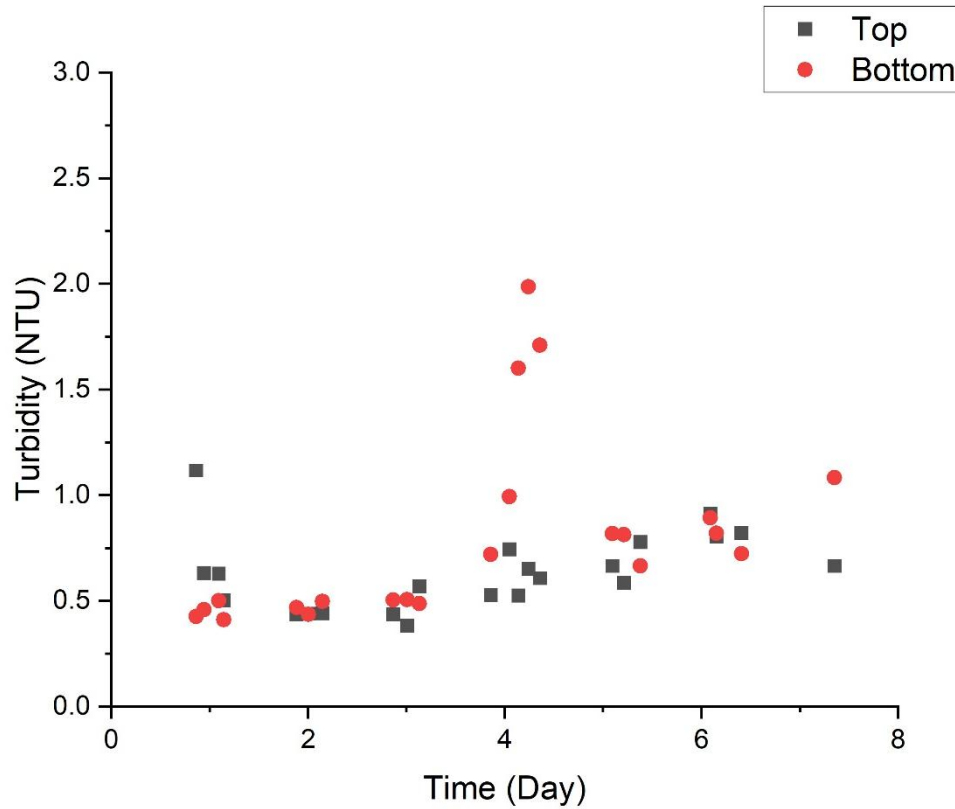


*Figure 4.23. Turbidity measurements at the top and bottom sections over time in the test with mixing*

Similarly, Figure 4.23. shows turbidity measurements at the top and bottom sections over time. Initially, both sections show similar and low turbidity levels, with no significant gradient. However, as the experiment progressed, the difference in turbidity increased, with the bottom turbidity reaching approximately four times that of the top. This suggests that nucleation was occurring within the system. Afterward, turbidity began to decrease, indicating that the test was now in the growing phase, with the formed crystals growing in size and settling either at the bottom or on the walls of the bottom section. Figure 4.24 clearly demonstrates this, with visible crystals growing on the sides of the bottom section and on the temperature sensor.

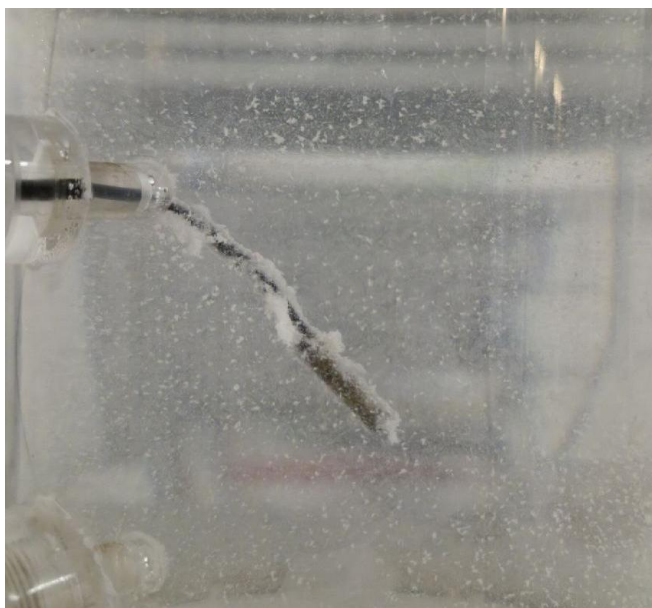


*Figure 4.24. Crystals growing on the sides of the bottom section and on the temperature sensor*

After the run was terminated, the feed tank was emptied, and crystals were observed. These crystals appeared to be different from those observed in the test without mixing. As mentioned earlier, the crystals from the no-mixing test had a needle-like structure. However, the crystals from the test with mixing mostly resembled a snow-like appearance. Figure 4.25. a shows the crystals that formed on the temperature sensor and the sides of the bottom section. Unlike the previous test, these crystals did not display a needle-like structure and were smaller and rounder.

Figure 4.25.b illustrates the crystals that formed on the funnel. Small needle-like structures were observed only at the edges of the funnel, where the water flow was more stationary. Figure 4.25.c shows the crystals that formed at the bottom of the reactor. A thick layer of salts had accumulated at the bottom, which was unexpected, as mixing was intended to prevent settling. However, it was possible that mixing could have prevented this settling at higher speeds.

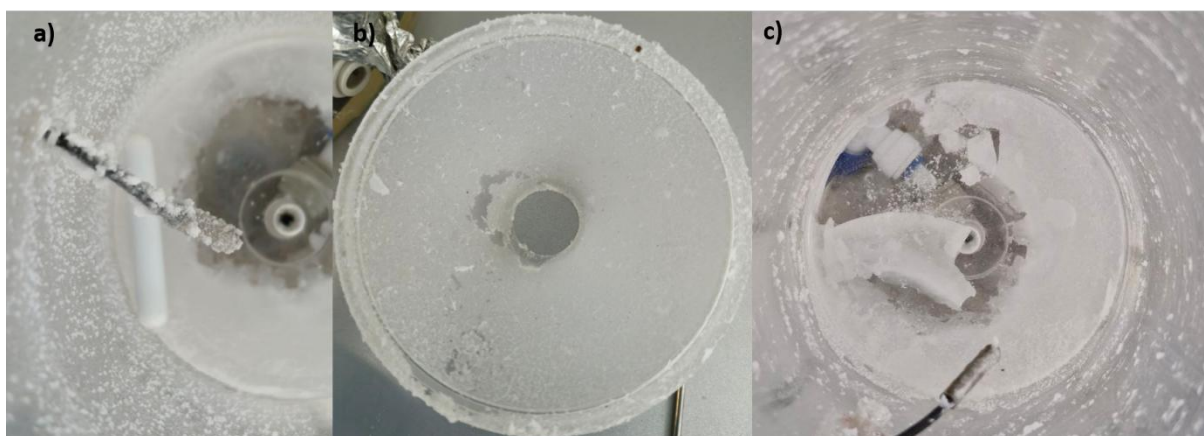


*Figure 4.25. Crystals formed in different sections of the reactor a) on the temperature sensor and the sides of the bottom section b) on the funnel c) at the bottom*

### 4.3 SEM analysis of Crystals

The SEM analysis provided details about two sets of samples: one set with mixing and the other without. Each set consisted of three samples, taken from various parts of the reactor. The results of these tests highlight the differences in the morphology and elemental composition of the crystals formed under different mixing conditions. Detailed results of EDS can be found in the appendix.

For the first set, where mixing was used, samples from the side walls of the reactor showed the presence of elongated crystals as well as agglomerates. The samples were slightly wet, but this did not cause problems in the examination. At 30x magnification, the conglomerated crystals appeared, while at 100x, elongated crystals could be clearly observed. Further analysis at 200x revealed that the agglomerates were composed of smaller crystals that had accumulated together. The sizes of the crystals were measured (Figure 4.26), with the conglomerates being 1.783 mm by 1.690 mm, elongated crystals measuring 847.4  $\mu\text{m}$  by 85.47  $\mu\text{m}$ , and agglomerates at 111.7  $\mu\text{m}$  by 247  $\mu\text{m}$ .

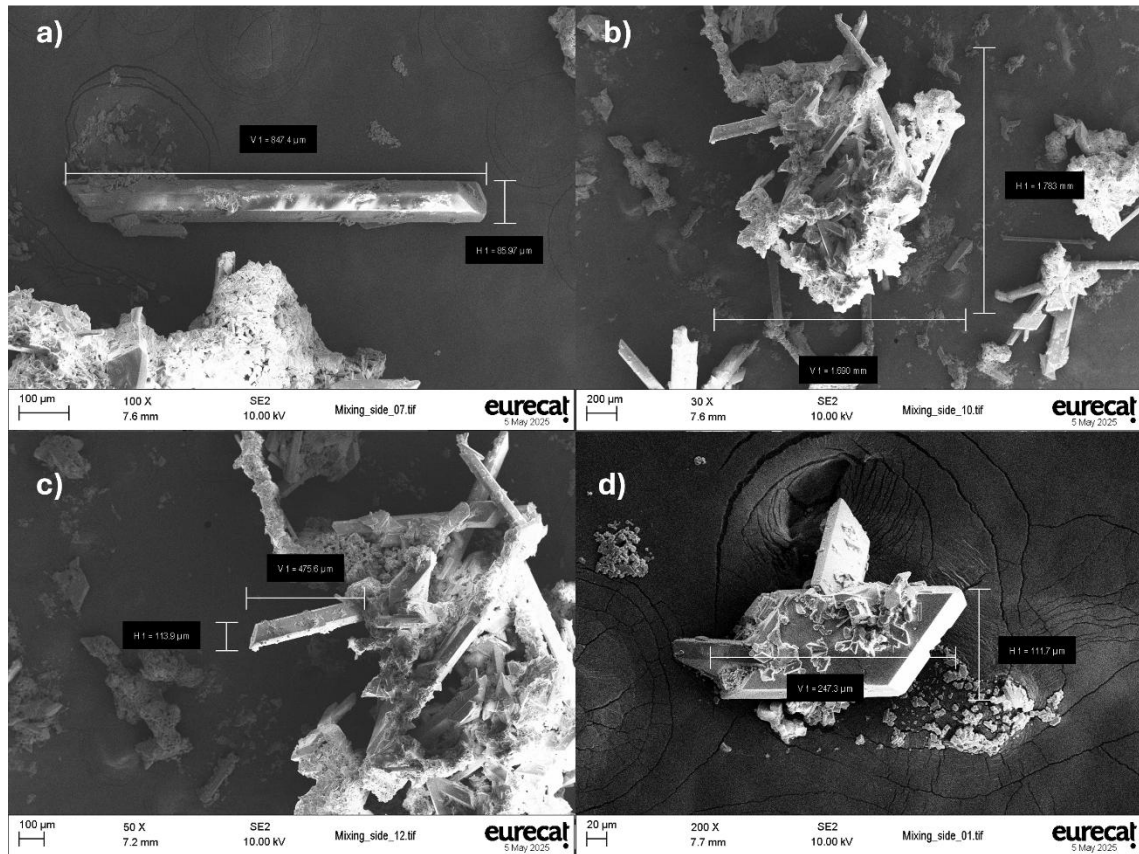


Figure 4.26. SEM analysis on crystals from the side walls of the reactor in the test done with mixing a) an elongated crystal measuring 847.4  $\mu\text{m}$  by 85.47  $\mu\text{m}$  at 100X b) a conglomerates crystal measuring 1.783 mm by 1.690 mm at 30X c) a needle-like part of a conglomerates crystals measuring at 475.6  $\mu\text{m}$  by 113.9  $\mu\text{m}$  d) an agglomerates crystal measuring 111.7  $\mu\text{m}$  by 247  $\mu\text{m}$  at 200X

The Energy Dispersive Spectroscopy (EDS) analysis was done to examine the presence of several elements in the samples, including Ca, S, Cl, Na, Mg, Sb, Rb, Se, Co, Ga, As, and Cs. The EDS analysis was conducted on one elongated crystal and one agglomerated crystal (on a spot

where a needle-like structure was observed). The results showed that in both cases, Ca was significantly more abundant than Na, and Mg was not present in significant amounts.

Samples taken from the bottom of the reactor during the mixing test revealed a different set of characteristics. These samples contained square-shaped crystals (Figure 4.27.c) that had formed a layer at the bottom of the reactor, alongside some elongated crystals. Despite the expectation that mixing would prevent this from happening, a consistent layer of crystals was still observed, which may be due to the mixing speed. The sample was also slightly wet, which can be observed in Figure 4.27. a and d. The crystals were examined at 30x magnification for the accumulated crystals and at 100x for the elongated ones. The EDS analysis was done on an agglomerated crystal, parts of an elongated crystal (Figure 4.27.d), and a square crystal. The results indicated that Na was more prevalent in the square crystals, while Ca and S were more present in the elongated crystals. In the agglomerated crystals, Ca and Na were present in similar amounts. Mg was not detected in significant amounts in these crystals.

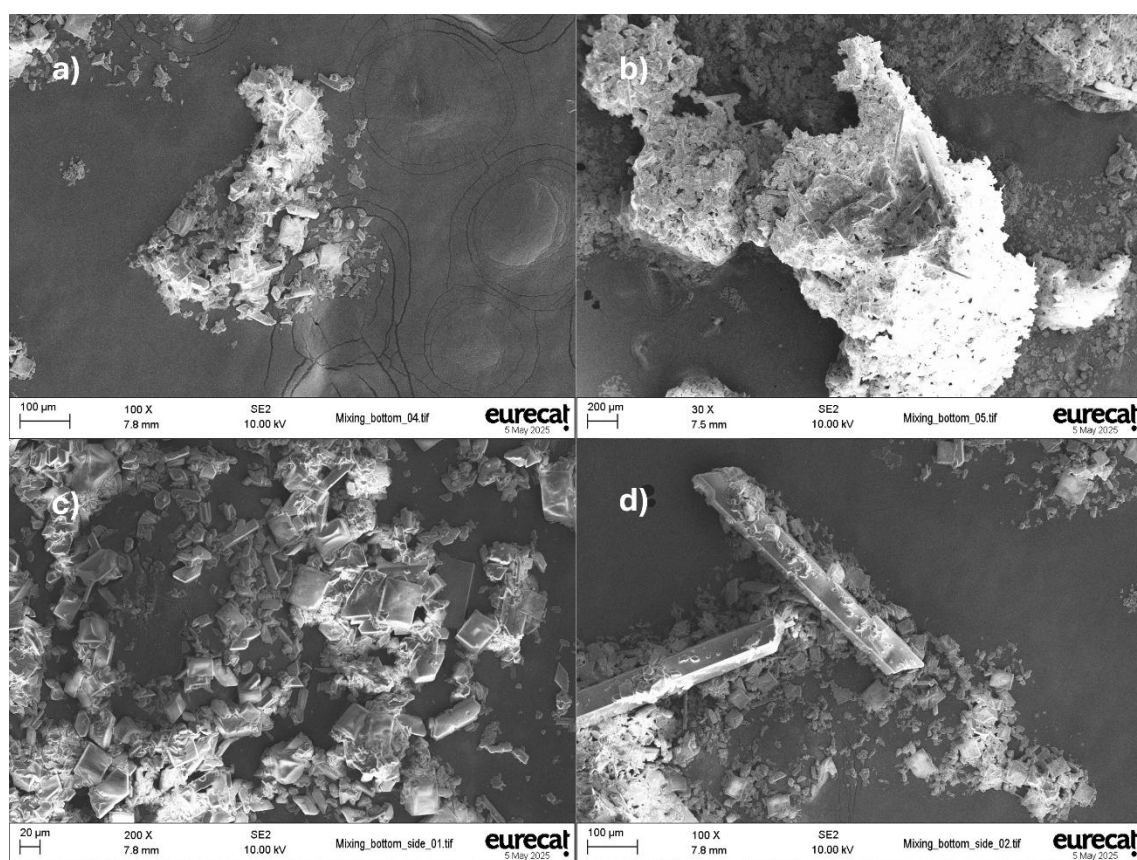


*Figure 4.27. SEM analysis on crystals from the bottom of the reactor in the test done with mixing: a) overview of the sample at 100X, b) accumulated crystals at 30X, c) overview of square-shaped crystals at 200X, d) needle-like crystals with small, squared crystals at 100X*

The samples from the mixing funnel were characterized by the presence of very small crystals, which could be best observed at magnifications of 200x to 300x (Figure 4.28). The crystals were mostly accumulated together, and the elongated crystals were observed in clusters. The size of the elongated crystals was measured at 153.5 μm by 16.19 μm, and they appeared to be mostly composed of S and Ca. Na-based crystals were not observed in significant amounts.

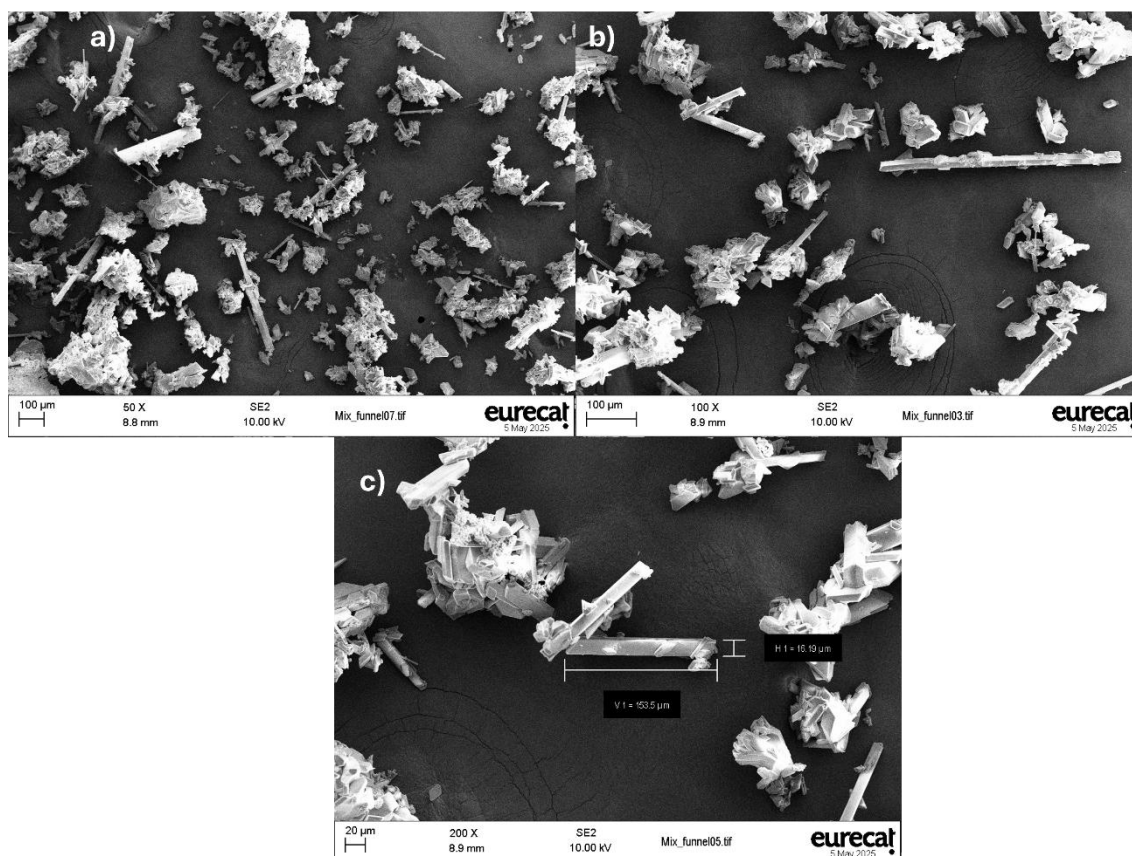


*Figure 4.28. SEM analysis on crystals from the funnel in the reactor in the test done with mixing: a) overview of the sample at 50X, b) overview of the sample at 100X, c) an elongated crystal which was measured at 153.5  $\mu\text{m}$  by 16.19  $\mu\text{m}$*

In the second set of samples, which were taken from the test without mixing, the samples from the side walls of the reactor showed elongated crystals that were longer than those in the mixing tests (Figure 4.29). These crystals, observed at 30x magnification, measured 2.185 mm by 282.8  $\mu\text{m}$ , and no agglomerates were apparent. The elongated crystals were topped with small square crystals, likely NaCl, and the larger crystals were predominantly Ca-based, containing higher levels of S. The EDS analysis of these crystals showed that Ca and S were more prevalent in the elongated crystals, while the Na-based crystals, which were smaller, had lower amounts of S. No significant presence of Mg was observed.

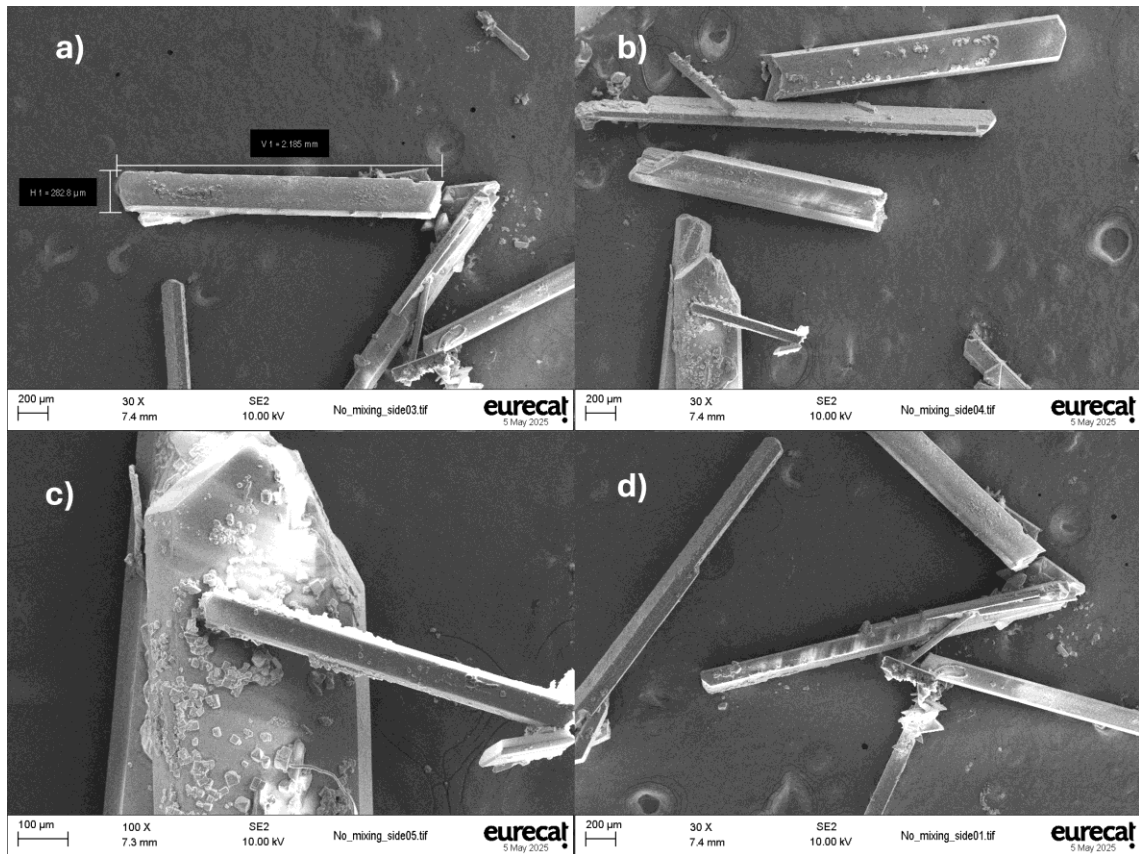


*Figure 4.29. SEM analysis on crystals from the side of the reactor in the test done without mixing: a) an elongated crystal measured 2.185 mm by 282.8  $\mu\text{m}$ , b) elongated crystals at 30X, c) small square-shaped crystals on top of it at 50X, d) elongated crystals with small, square-shaped crystals around them at 30X*

Samples taken from the funnel in the no-mixing test contained larger elongated crystals and some conglomerates (Figure 4.30). These crystals measured 2.046 mm by 183.4  $\mu\text{m}$  and were similar in size to the ones from the side walls of the reactor in the previous test. The EDS analysis revealed that these crystals were primarily composed of Ca, S, Cl, and Na, with no other major elements detected. Square crystals were found on top of the elongated ones, and as with the samples from the mixing test, Na was more prevalent in the square crystals, while Ca and S were more abundant in the elongated crystals, similar to the samples taken from the sides of the reactor in this test.

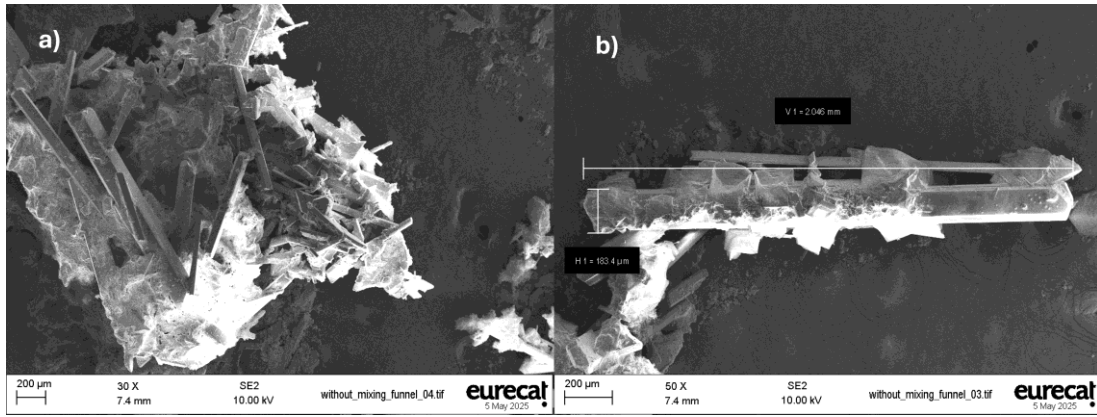


Figure 4.30. SEM analysis on crystals from the funnel in the reactor in the test done without mixing: a) a conglomerated crystal at 30X, b) an elongated crystal measuring 2.046 mm by 183.4  $\mu\text{m}$  at 50X

Finally, samples taken from the bottom of the reactor in the no-mixing test showed more accumulated crystals compared to the elongated ones (Figure 4.31). These crystals were smaller than those from other parts of the reactor, measuring 463.3  $\mu\text{m}$  by 27.35  $\mu\text{m}$ . The majority of these crystals were elongated or needle-like, and Ca was the dominant element in these crystals. Square-shaped crystals were less common, though one accumulated crystal without a needle-like structure was found and exhibited a high amount of Na.

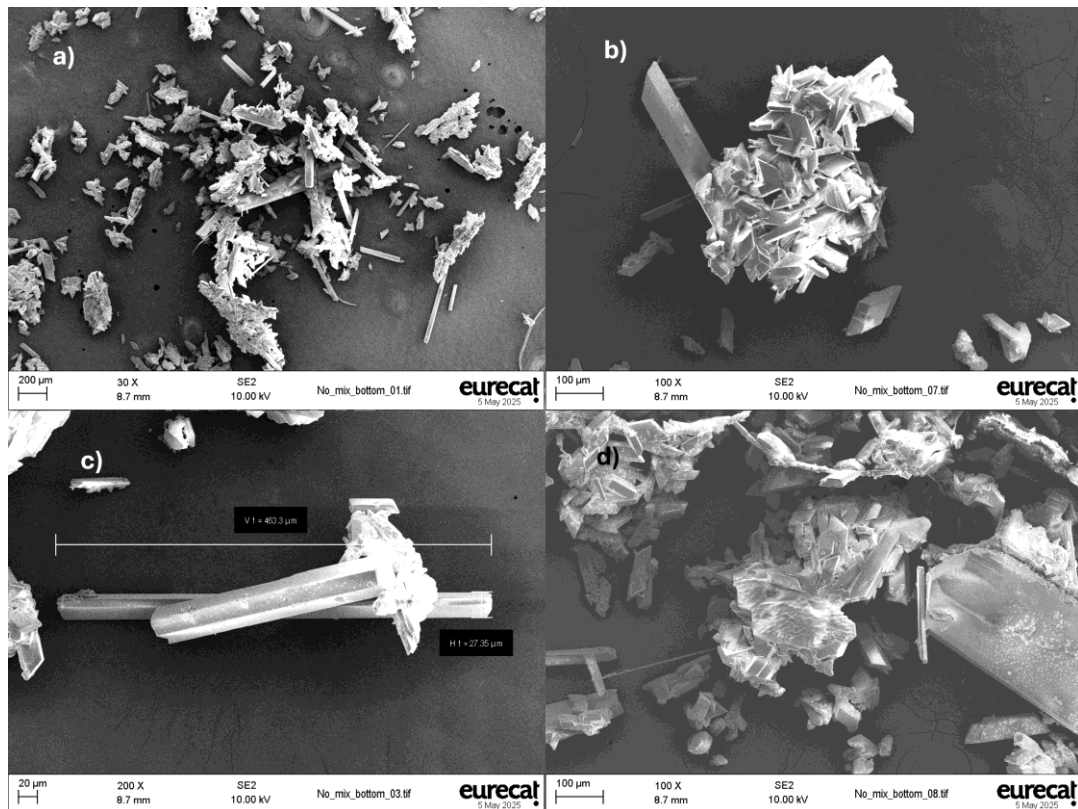


Figure 4.31. SEM analysis on crystals from the bottom of the reactor in the test done without mixing: a) overview of the crystals at 30X, b) an accumulated crystal at 100X, c) an elongated crystal measuring 463.3  $\mu\text{m}$  by 27.35  $\mu\text{m}$  at 200X, d) an accumulated crystal with a high amount of Na

Hence, the tests with mixing resulted in more diverse crystal shapes, with elongated crystals, agglomerates, and square crystals present in varying amounts depending on the location in the reactor. The EDS analysis consistently showed that Ca was the most abundant element in the elongated crystals, while Na was more present in the square-shaped crystals. On the other hand, the tests without mixing resulted in larger, elongated crystals with less agglomeration. These crystals were also primarily composed of Ca and S, with Na present in smaller amounts. A summary of these results is shown in Table 4.3. The needle-like structure for Ca-based salts and cuboidal for Na-based salts are primarily governed by differences in their crystallographic structures and nucleation behaviors, which have been observed in other works[21-24]. Ca salts such as calcium sulfate and calcium carbonate typically form anisotropic, elongated crystals due to their lower symmetry lattice systems and directional crystal growth [24]. In contrast, Na salts like sodium chloride tend to form isotropic, cubic, or prismatic crystals owing to their high-symmetry face-centered cubic structure, which promotes uniform growth in all directions[22].

*Table 4.3. Summary of SEM analysis*

| <b>Test Condition</b>   | <b>Crystal Morphology</b>                                     | <b>Dominant Elements</b>                  |
|-------------------------|---------------------------------------------------------------|-------------------------------------------|
| Without Mixing - Bottom | Needle-like and elongated; accumulated crystals               | Ca dominant; some Na in square crystals   |
| Without Mixing - Funnel | Large elongated crystals and conglomerates                    | Ca, S in elongated; Na in square crystals |
| Without Mixing - Walls  | Elongated needle-like crystals, topped with small square ones | Ca, S in elongated; Na in square crystals |
| With Mixing - Bottom    | Square crystals and some elongated, snow-like appearance      | Na in square; Ca, S in elongated          |
| With Mixing - Funnel    | Very small, clustered, elongated crystals                     | Ca, S                                     |
| With Mixing - Walls     | Elongated, conglomerates, and agglomerates                    | Ca > Na                                   |

As discussed in the previous sections, the crystals formed on the membrane exhibited needle-like structures, indicating that they are likely Ca-based, which were causing membrane scaling in these experiments. This observation aligns with findings from previous studies. For instance, Ali et al. demonstrated that crystal morphology significantly influences downstream processing: cubic Na-based crystals allowed cleaner recovery and resulted in less fouling, whereas calcium precipitates increased system maintenance due to their scaling tendency[25]. Similarly, Zhang et al. reported that sodium sulfate outperformed calcium sulfate in recovery efficiency, attributing this to the compact cubic form of sodium crystals, which facilitated sedimentation and filtration. In contrast, Ca salts tended to form dendritic structures and adhere to the membrane surfaces[26]. Pramanik et al. also noted that uniform cubic NaCl crystals were easily collected, while Ca-based crystals often necessitated pre-treatment or chelation to mitigate fouling[27]. This is support by, Yadav et al. observing that Na salts were removed more efficiently from brine, with lower energy consumption and higher crystallization yield, further reinforcing the preference for Na-based recovery approaches[28].

The differences between the two test sets highlight the effects of mixing on crystal formation and the distribution of elements in the reactor. The size and shape of the crystals, as well as their elemental composition, varied depending on the presence or absence of mixing, with the mixing tests leading to more diverse crystal structures.

## 5 Conclusion

This thesis explored the integration of Membrane Distillation Crystallization (MDCr) for desalination, focusing primarily on hollow fiber membranes and their performance under different operational conditions. The study assessed the effects of temperature gradients and mixing conditions on system efficiency, permeate flux, and crystallization outcomes. The flat sheet membrane, though useful for initial tests, had limited surface area which slowed feed concentration and crystallization. Therefore, the hollow fiber membrane was chosen for further experiments to improve these processes.

The results from the hollow fiber membrane experiments revealed significant differences in system performance depending on temperature and mixing conditions. In the initial tests without mixing, the system operated at lower temperatures (39–40°C), resulting in a permeate flux of 1.02 LMH and a steady state at approximately 95 mS/cm feed conductivity. As the system was operated at higher temperatures (52°C), the temperature gradient between the feed and permeate increased to about 30°C, which significantly increased the flux to 2.25–2.35 LMH. This improvement was a direct result of enhanced thermal driving force. However, with the increase in feed conductivity, scaling became evident after approximately 122 hours of operation, leading to a decrease in flux (0.99 LMH). This scaling issue was resolved temporarily by washing the membrane, although the flux did not fully recover. Despite these challenges, the system demonstrated a high rejection rate of salts (based on conductivity), consistently exceeding 99%.

When mixing was introduced, the flux initially had an average of 2.1–2.2 LMH, with the temperature maintained around 52°C. In the test with mixing, the experiment initially used membrane I, which exhibited similar flux and rejection characteristics as prior tests. However, after a day, a leak was detected, and the membrane was replaced with membrane II. Unfortunately, membrane II also showed leakage, and it was replaced with membrane III. While membrane III did not show visible leaks, it demonstrated a lower flux (1.7–2.1 LMH) and faster increase in permeate conductivity, indicating potential membrane wetting. The introduction of mixing successfully prevented the settling of salt particles at the bottom of the reactor, maintaining a more consistent concentration gradient between the top and bottom sections. This resulted in a more dispersed and less concentrated formation of crystals. The crystals formed during mixing were smaller and more diverse in shape compared to the non-mixing tests. However, despite the mixing, a thick layer of salt still accumulated at the bottom.

Crystal analysis using SEM-EDS revealed notable differences between the crystals formed under mixing and non-mixing conditions. In the mixing tests, the crystals were predominantly smaller and more scattered throughout the reactor, including elongated crystals, agglomerates, and some square-shaped crystals. However, the crystals formed in the non-mixing tests were larger, primarily elongated, with distinct needle-like structures. It was observed that elongated crystals were dominated by Ca, with Na being more abundant in the square crystals observed at the bottom of the reactor.

In conclusion, the tests conducted with the hollow fiber membrane under varying conditions demonstrated the significant impact of temperature and mixing on MDCr performance. Mixing helped to prevent the accumulation of salt particles at the bottom but did not improve crystal quality or flux substantially. The non-mixing tests resulted in more uniform, elongated crystals, while the mixing tests produced smaller, more scattered crystals. The findings from the

experiments demonstrated that MDCr is a promising process for desalination and resource recovery, but it faces challenges related to membrane material stability, scaling, membrane fouling, and flux decline under certain conditions. The results highlighted the importance of optimizing operational parameters, such as temperature gradients and membrane configurations, to improve system performance.

## 6 Future work

To address the scaling problem in MDCr, further investment in enhancing membrane materials is essential. Improving membrane performance by developing more resistant, fouling-resistant, and thermally stable materials could significantly reduce scaling and prolong membrane life cycle. Additionally, improving the hydrophobicity and porosity of membranes could help to mitigate crystallization on their surfaces.

A promising approach to reduce scaling is implementing a slow mixing strategy at the top of the reactor or employing a low-speed recirculation in the top section of the system. This approach could help to detach crystals that form on the membrane, thereby preventing or reducing scaling. The detachment of these crystals could also have the added benefit of serving as nuclei for further crystallization in the reactor, which might enhance overall system efficiency.

Seeding is another potential solution for improving the MDCr process. By introducing seed crystals, the crystallization process can be initiated at lower concentrations, effectively replacing spontaneous nucleation. This technique could improve crystal formation and size distribution, as well as reduce energy consumption associated with achieving supersaturation. However, it is crucial to optimize the seeding concentration and mixing rate. The goal is to prevent the seeds from settling too quickly while ensuring that the mixing does not significantly diminish the concentration and temperature gradients within the system, which are critical for efficient crystallization.

Future work should focus on determining the optimal seeding concentration and identifying the ideal mixing conditions that balance crystal growth, concentration maintenance, and temperature control. Additionally, further investigations are required to better understand how mixing rates and seed concentration influence both crystal size distribution and membrane fouling, ultimately improving the scalability and industrial application of MDCr systems.

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## 7 Appendix

### 7.1 EDS Analysis

#### 7.1.1 Samples from tests without mixing

##### *Sample from the bottom*

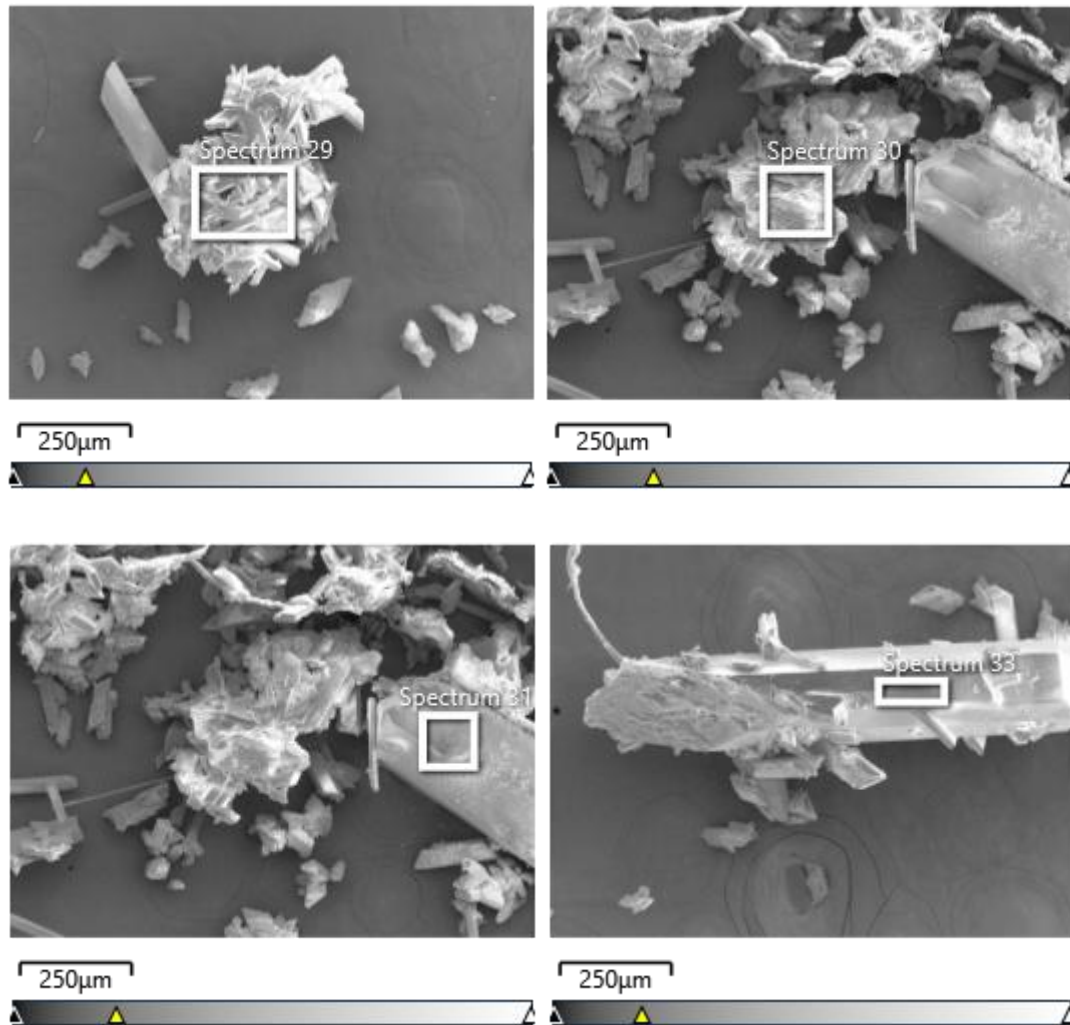


Figure 7.1. EDS Analysis, Samples from tests without mixing from the bottom

Table 7.1. EDS Analysis, Samples from tests without mixing from the bottom

| Spectrum Label | Spectrum 29 | Spectrum 30 | Spectrum 31 | Spectrum 33 |
|----------------|-------------|-------------|-------------|-------------|
| O              | 59.36       | 10.58       | 45.44       | 57.71       |
| Na             | 0.59        | 35.8        | 0.99        | 0           |

|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| Mg    | 0.1   | 0.2   | 0.27  | 0.05  |
| S     | 16.85 | 2.1   | 20.35 | 18.76 |
| Cl    | 0.97  | 48.09 | 1.64  | 0.61  |
| K     | 0.18  | 0     | 0     | 0.17  |
| Ca    | 21.95 | 3.23  | 30.33 | 22.7  |
| Zn    |       |       | 0.98  |       |
| Total | 100   | 100   | 100   | 100   |

*Samples from the sides of the reactor*

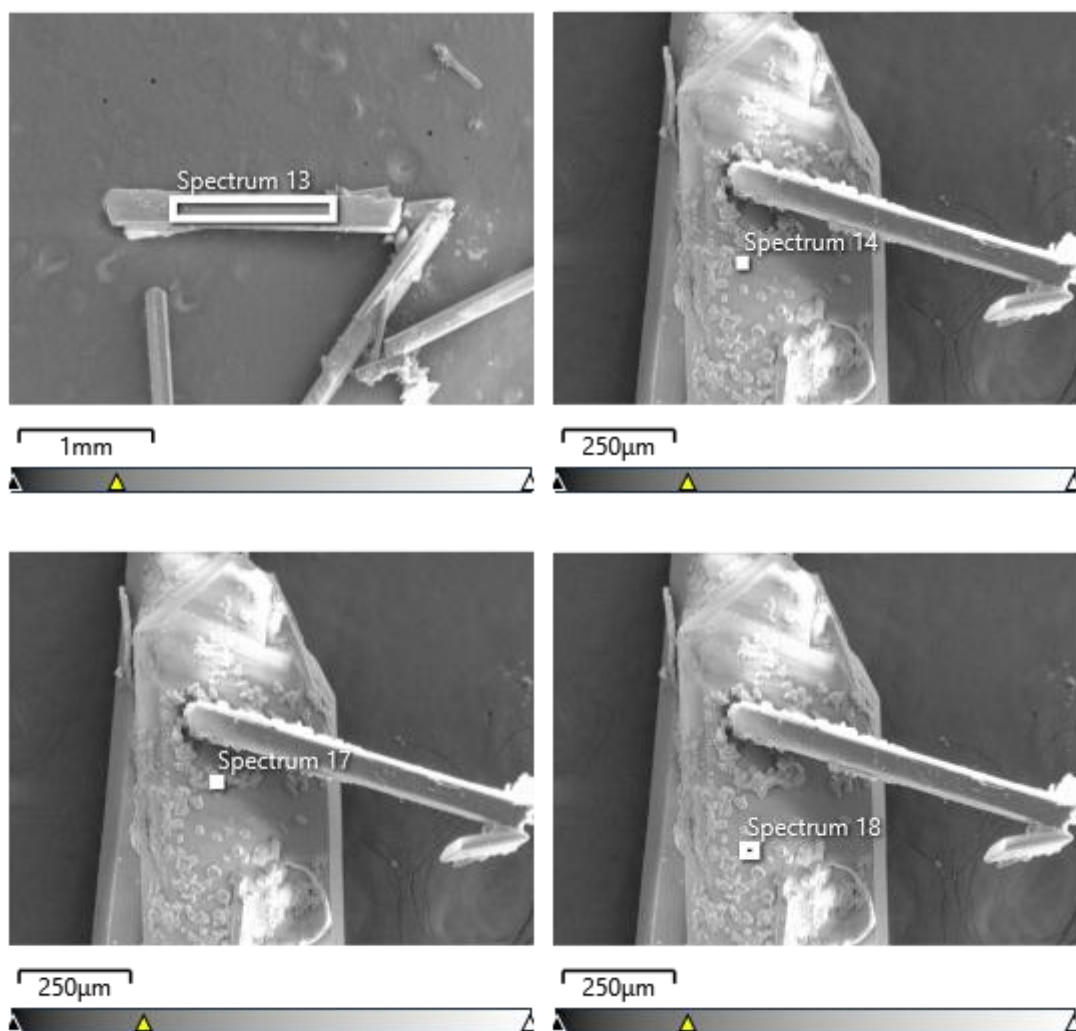


*Figure 7.2. EDS Analysis, Samples from tests without mixing from the sides of reactor*

*Table 7.2 EDS Analysis, Samples from tests without mixing from the sides of reactor*

| <b>Spectrum Label</b> | <b>Spectrum 13</b> | <b>Spectrum 14</b> | <b>Spectrum 17</b> | <b>Spectrum 18</b> |
|-----------------------|--------------------|--------------------|--------------------|--------------------|
| O                     | 53.26              | 8.83               | 32.1               | 62.17              |
| Na                    | 6.6                | 35.99              | 20.23              | 0.52               |
| Mg                    | 0.83               | 0.95               | 4.26               | 0.66               |
| S                     | 13.42              | 1.32               | 3.66               | 17.38              |
| Cl                    | 9.7                | 51.87              | 31.66              | 1.27               |
| K                     | 0                  | 1.05               | 1.95               | 0.49               |
| Ca                    | 16.19              |                    | 6.13               | 17.52              |
| Total                 | 100                | 100                | 100                | 100                |

*Samples from the funnel*

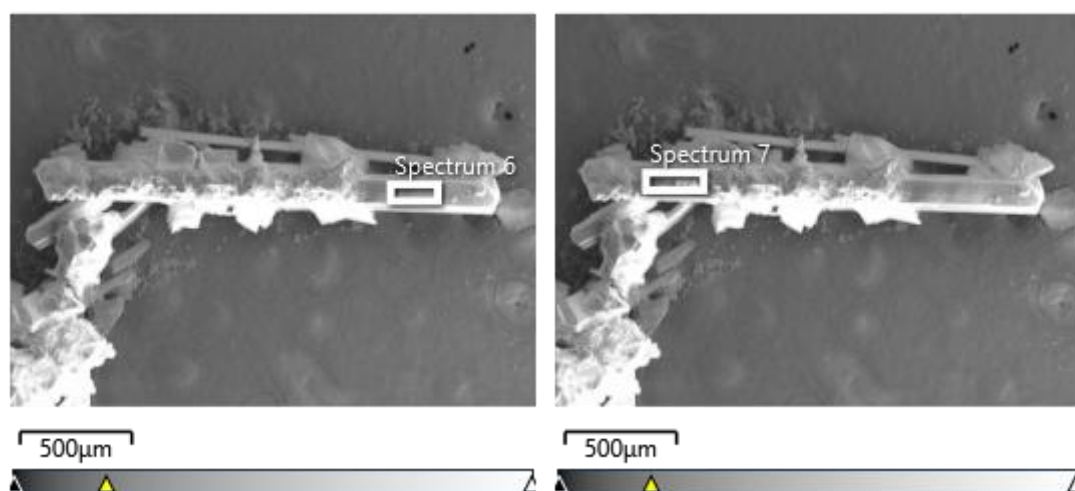


*Figure 7.3. EDS Analysis, Samples from tests without mixing from the funnel*

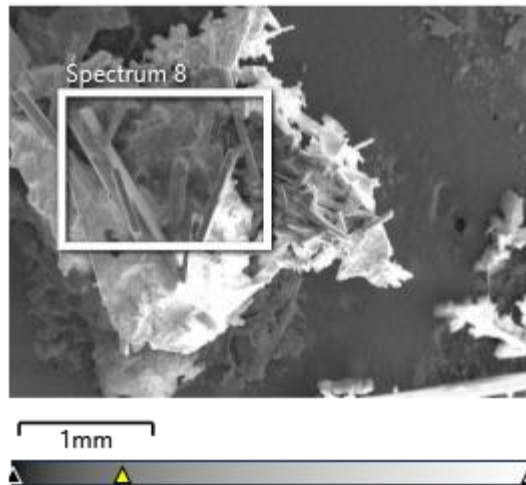


*Figure 7.4. EDS Analysis, Samples from tests without mixing from the funnel*

*Table 7.3. EDS Analysis, Samples from tests without mixing from the funnel*

| <b>Spectrum Label</b> | <b>Spectrum 6</b> | <b>Spectrum 7</b> | <b>Spectrum 8</b> |
|-----------------------|-------------------|-------------------|-------------------|
| O                     | 61.54             | 32.27             | 46.64             |
| Na                    |                   | 14.94             | 9.58              |
| Mg                    |                   | 7.68              |                   |
| P                     |                   | 0                 |                   |
| S                     | 18.37             | 4.9               | 10.75             |
| Cl                    |                   | 31.73             | 18.48             |
| K                     |                   | 1.22              |                   |
| Ca                    | 20.09             | 5.94              | 14.55             |
| Co                    |                   | 1.3               |                   |
| Cs                    |                   | 0                 |                   |
| Total                 | 100               | 100               | 100               |

### **7.1.2 Samples from tests without mixing**

#### ***Sample from the bottom***

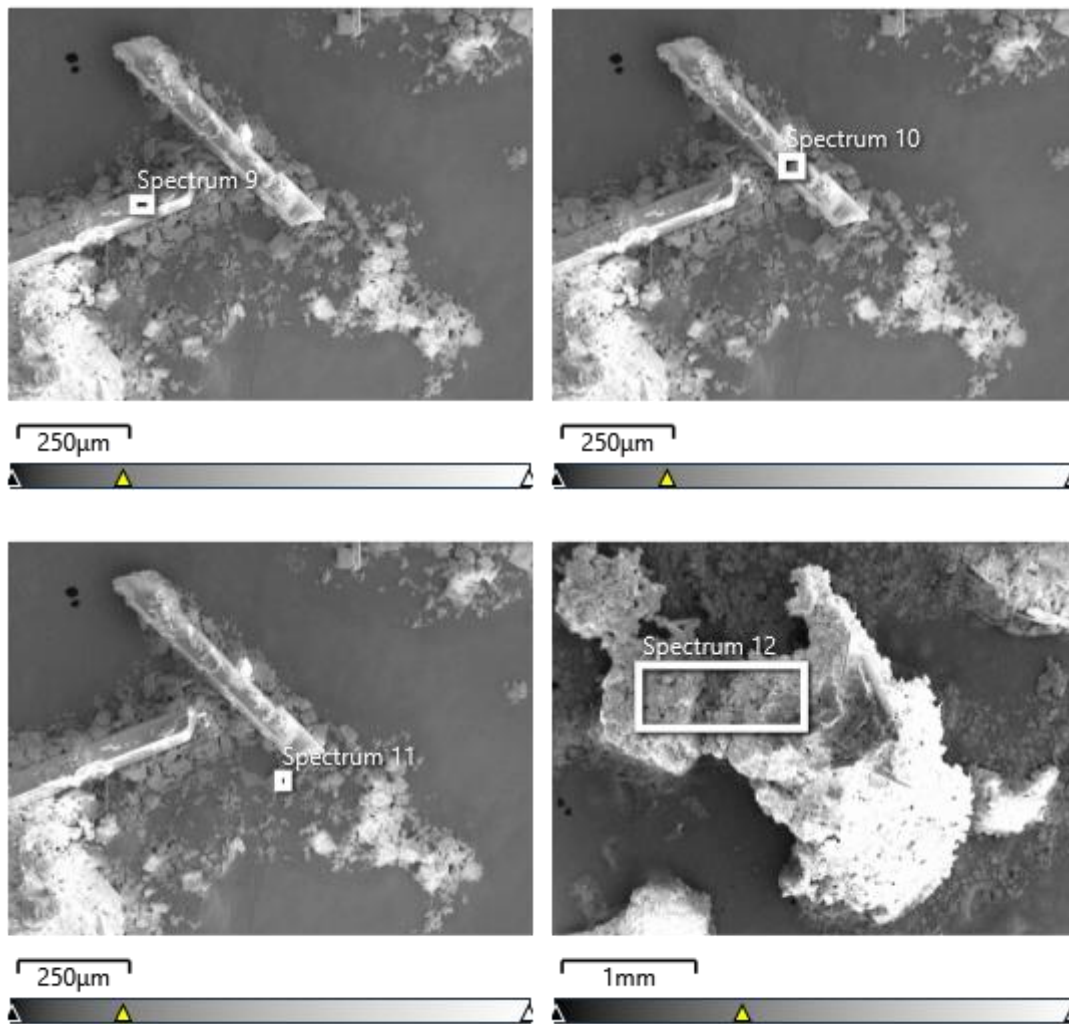


Figure 7.5. EDS Analysis, Samples from tests with mixing from the bottom

Table 7.4. EDS Analysis, Samples from tests with mixing from the bottom

| <b>Spectrum Label</b> | <b>Spectrum 9</b> | <b>Spectrum 10</b> | <b>Spectrum 11</b> | <b>Spectrum 12</b> |
|-----------------------|-------------------|--------------------|--------------------|--------------------|
| O                     | 57.24             | 59.43              |                    | 40.21              |
| Na                    | 0.47              | 1.65               | 38.48              | 14.49              |
| Mg                    | 0.44              | 0.45               |                    | 1.3                |
| S                     | 18.78             | 16.49              |                    | 11.16              |
| Cl                    | 2.46              | 3.24               | 59.93              | 18.86              |
| Ca                    | 20.61             | 18.74              | 1.59               | 13.98              |
| Total                 | 100               | 100                | 100                | 100                |

***Sample from the sides of the reactor***

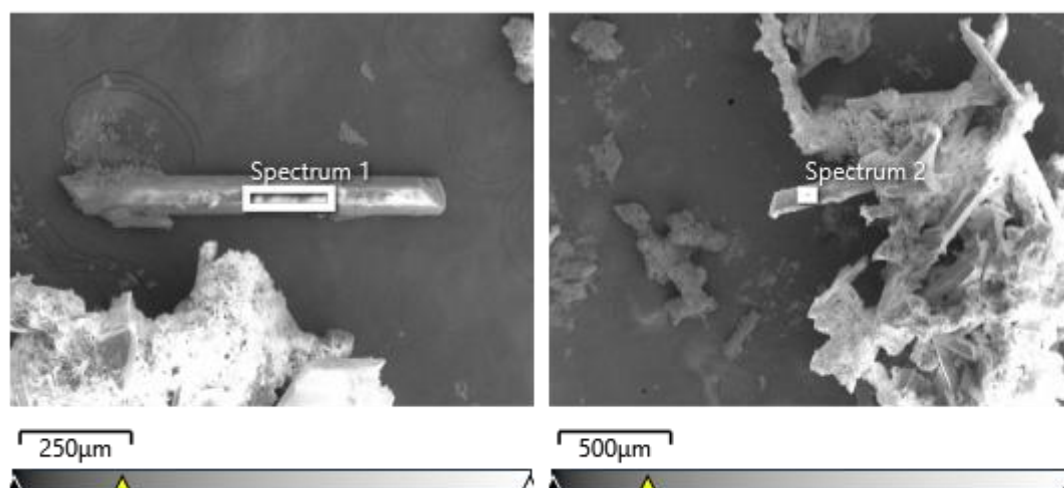


***Figure 7.6. EDS Analysis, Samples from tests with mixing from the sides of the reactor***

***Table 7.5 EDS Analysis, Samples from tests with mixing from the sides of the reactor***

| <b>Spectrum Label</b> | <b>Spectrum 1</b> | <b>Spectrum 2</b> |
|-----------------------|-------------------|-------------------|
| O                     | 58.2              | 68.5              |
| Na                    | 2.73              | 0.72              |
| Mg                    | 0.89              | 0.73              |
| S                     | 16.47             | 13.78             |
| Cl                    | 4.02              |                   |
| Ca                    | 17.19             | 11.53             |
| Co                    | 0                 | 1.36              |
| Ga                    | 0                 | 0                 |
| As                    | 0                 | 0                 |
| Se                    | 0.02              | 0.2               |
| Rb                    | 0.06              | 0.11              |
| Sb                    | 0.42              | 2.14              |
| Cs                    | 0                 | 0.94              |
| Total                 | 100               | 100               |

*Samples taken from the funnel*

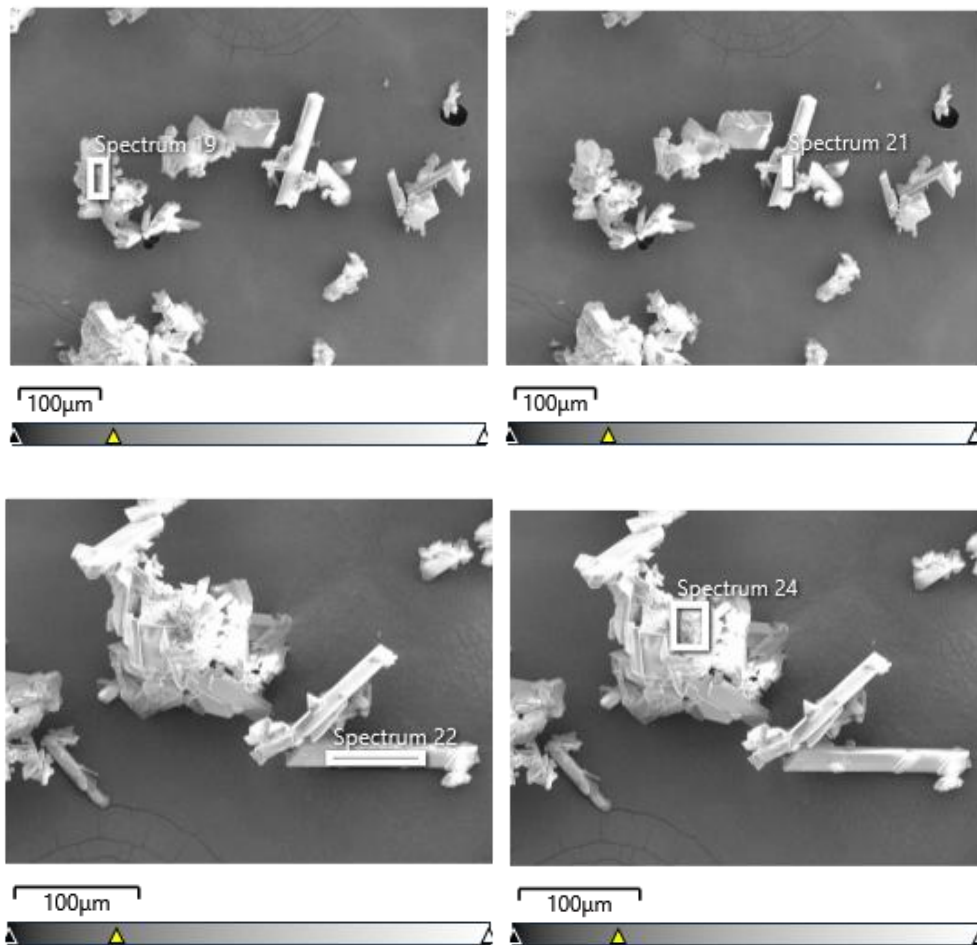


*Figure 7.7. EDS Analysis, Samples from tests with mixing from the funnel*

*Table 7.6. EDS Analysis, Samples from tests with mixing from the funnel*

| Spectrum Label | Spectrum 19 | Spectrum 21 | Spectrum 22 | Spectrum 24 |
|----------------|-------------|-------------|-------------|-------------|
| O              | 57.75       | 64.19       | 62.58       | 49.68       |
| Na             | 0.08        | 0           | 0.11        | 0.4         |
| Mg             | 0.61        | 0.34        | 0.36        | 2.96        |
| S              | 17.44       | 16.48       | 16.6        | 8.34        |
| Cl             | 1.09        | 0.54        | 0.69        | 9.77        |
| K              | 0.16        | 0           | 0.56        | 0           |
| Ca             | 22.87       | 18.44       | 19.11       | 28.85       |
| Total          | 100         | 100         | 100         | 100         |