

WALNUT

D2.6 - Report on Nanofiltration and selective crystallisation processes

WP2, T2.5 Nanofiltration and selective crystallisation processes

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List of abbreviations

Table 1: Abbreviations list

Abbreviation	
RO	Reverse Osmosis
AAS	Atomic Absorption Spectroscopy
XRD	Multiple Effect Distillation
NF	X-Ray Diffraction
MED	Nanofiltration
ZLD	Zero Liquid Discharge
BBF	Bio-Based Fertilisers
WAVE	Water Application Value Engine



Executive Summary

WalNUT deliverable D2.6 describes the work performed in the framework of Task 2.5. It is the predecessor of the design of a pilot system for the treatment of the waste stream produced from a RO desalination plant. The main targets are the recovery of high purity water and salts/minerals. These salts/minerals are economically prime important seawater-based micro and macronutrients to be valorised in/as Bio-based fertilisers. In the first part of the process, the salts will be recovered by precipitation as $\text{Mg}(\text{OH})_2$ and CaCO_3 after the addition of NaOH or $\text{Ca}(\text{OH})_2$ and Na_2CO_3 . Then, the divalent SO_4^{2-} will be separated from the brine using nanofiltration (NF). Next part of the process will target the NaCl - KCl salts and water recovery. Through water evaporation, a mixed salt of NaCl and KCl will be recovered. This concentrated brine will be further concentrated by applying thermal crystallisation. In the final stage, KCl will be separated from the mixed salt by flotation. The experiments are analysed and organised through a 2^2 factorial design in order to make a statistical evaluation of the tests and results. The parameters examined are reagents quantity and stirring time in order to optimize the purity and quantity of the recovered salts that will be obtained as marketable ingredients of Biobased Fertilisers (BBFs).

The objective of the proposed brine processing train is to optimize salts' removal ([Mg²⁺ recovery](#) in the form of magnesium hydroxide, [Ca²⁺ recovery](#) in the form of calcium carbonate and potassium chloride ([KCl recovery](#))) and to reclaim high purity water. The pillars of the processes are the yield of the recovery and the purity of the recovered micronutrients for their valorisation in/as Bio-based fertilisers.

The work in Task 2.5 is summarised in the following points:

- Lab-scale experiments were designed and performed for the treatment of 200 mL and 50 L seawater RO desalination brine.
- Three brine samples were collected from a RO desalination plant, during three different sampling campaigns, along with a seawater sample used for reference purposes (Table 3-1).
- The first step in the proposed brine processing train is brine [characterisation](#) in order to examine its main anions' and cations' concentration and to investigate any external parameters ([fluctuation in brine composition](#)).
- Next step is the recovery of Mg^{2+} , Ca^{2+} and K^+ in the form of $\text{Mg}(\text{OH})_2$, CaCO_3 and KCl respectively.
- Third step is the integration of brine treatment train according to a developed [factorial experimental design](#) in order to statistically evaluate the tests and results.
- The design parameters for their assessment and optimisation are the mixing time and the quantity of the reagent added; both are settled and examined under various parameter values.
- The investigated [experimental parameters](#) are the type of additives and addition rate (Table 3-3) as well as the [method](#) of addition, in terms of recovery efficiency, sedimentation speed (Figure 3-3) and precipitation density (Table 3-2)
- Analysis of the main physicochemical characteristics is performed targeting their [purity](#), [morphology](#) and particle size (Table 4-8).
- A [Simulation](#) of the nanofiltration process for the treatment of 1 m³ brine using the 'Water Application Value Engine' (WAVE) software is performed (the separation efficiency was set as the main optimisation parameter).

The results that derive from the performed work in Task 2.5 are summarised in the following points:

- As resulted from the factorial design, for the $\text{Mg}(\text{OH})_2$ recovery, reagent's addition is the most important parameter on salts precipitation phase.
- Regarding the [purity](#) of the recovered salts, by using NaOH as a reagent, the purity of magnesium is higher (~ 93%) when the stirring time of the mixture is longer (45 min). On the contrary, when $\text{Ca}(\text{OH})_2$ is used, recovered salts purity is higher (~86%) when the mixing time is shorter. As for the recovered CaCO_3 salts their purity is not affected by the conditions, therefore all trials offer high performance (~99%).



- No metals that may influence the fertilisers' performance and/or soil health are identified with Atomic Absorbance Spectroscopy.
- The important parameters for [KCl recovery](#) that affect the recovery ratio and salts' purity are the kind of flotation agent added, its volume and the particle size of the recovered solid. For this task two different flotation agents are used; Sodium Dodecyl Sulfate and Hexadecyl Trimethyl Ammonium Bromide. The former tends to be more selective towards the NaCl crystals besides the ones of KCl, while the latter shows higher selectivity towards KCl removal. Moreover, the amount of each flotation agent added together with the salts granulation range affect the recovered ratio of KCl salts and their purity.
- After scaling-up the initial lab-scale experiments (200 mL of brine) to treat 50 L of brine, the recovered salts were shipped to UNITO for the preliminary certification of their suitability for fertilisation purposes.
- The quantity and purity of recovered salts verify the factorial design in both the 200 mL and 50 L-scale experiments.
- The resulting effluent streams after the [NF simulation](#) are used for the optimisation of the downstream processes and the design of the Pilot plant 4.
- Aiming at the highest efficiency of $\text{Mg}(\text{OH})_2$, CaCO_3 , KCl, and NaCl recovery all energy aspects of the multi-evaporation and crystallisation steps in WalNUT D2.8 will be integrated with the detailed experimental design to be validated in WalNUT D3.5.

To sum up, recovered salts of $\text{Mg}(\text{OH})_2$, CaCO_3 and KCl from this task are of such purity so as to be used as nutrients for Bio-based Fertilisers.

Keywords: brine, potassium chloride, biofertilisers, nutrients, water scarcity, desalination, reverse osmosis, flotation



1. Introduction

1.3 Purpose and scope

Desalination of seawater is widely used to produce high purity water to deal with water scarcity throughout Europe and the other continents. It is carried out in specialised plants using different techniques. The principal method for high purity water production is reverse-osmosis (RO). The application of this method results in fresh water and brine; a hypersaline by-product considered waste with high concentration of minerals and metals.

Current practice in countries using large-scale desalination plants is to reject brine back to the sea, leading to the degradation of local fauna and flora. However, further processing of brine could result in the recovery of economically prime important materials such as magnesium, calcium, and potassium salts and high purity water. Brine treatment can contribute to the minimisation of the environmental footprint of desalination plant (Ogunbiyi, et al., 2021).

Given its limited geological sources, Mg^{2+} has been qualified as a Critical Raw Material by the European Union Commission ((Blengini et al., 2020). Thus, its recovery from brine could be an alternative source. Another salt with increasing consumption rate is KCl. It is estimated that under current consumption, world stocks of KCl will last until 2111 (United States Geological Survey, 2018). KCl is another salt that can be recovered from seawater desalination brine, as mentioned in the previous paragraph.

The work in this Task is the predecessor of the design of a pilot system for the treatment of the waste stream produced from a RO desalination plant. The main targets are the recovery of high purity water and salts/minerals. This salts/minerals are economically prime important nutrient resource based micro and macro nutrients to be valorised in /as Bio-based fertilisers. In the first part of the process, the salts will be recovered by precipitation as $Mg(OH)_2$ and $CaCO_3$ after the addition of NaOH or $Ca(OH)_2$ and Na_2CO_3 . Then, the divalent SO_4^{2-} will be separated from the brine using nanofiltration (NF). The next part of the process will target the NaCl-KCl salts and water recovery. Through water evaporation, a mixed salt of NaCl and KCl will be recovered. This concentrated brine will be further concentrated by applying thermal crystallisation. In the final stage, KCl will be separated from the mixed salt by flotation. The experiments are analysed and organised through a 2^2 factorial design in order to make a statistical evaluation of the tests and results. The parameters examined are reagents quantity and stirring time in order to optimize the purity and quantity of the recovered salts that will be obtained as marketable ingredients of Biobased Fertilisers (BBFs).



1.4 Contribution of partners

Table 2 shows an abstract of the contributions of WalNUT partners.

Table 2: Contribution of partners

Partner	Contribution
NTUA	Concept development and laboratory scale test for $\text{Mg}(\text{OH})_2$, CaCO_3 (liming materials) and KCl (inorganic fertiliser) recovery from seawater desalination brine.

1.5 Relation to other activities in the project

This deliverable gathers information of the brine treatment lab-scale technology in order to define the scale-up conditions as a first step to carry out the design, construction and operation of pilot plant 4. Thus, this deliverable is mainly related with Work Package 3 as well as Work Package 5 in which the environmental analysis is being carried out as shown in Table 3.

Table 3: Relation to other activities in the project

Task	Description
Task 3.5	Design, construction, installation and operation of the Pilot plant 4
Task 4.4	Field validation of agronomic performance in quadruplicate-randomised block design utilisation
Task 5.3	Environmental life cycle assessment of nutrient-recovery systems
Task 5.4	Life cycle costing and socioeconomic issues of NR and BBF systems
Task 5.5	Techno-environmental-socioeconomic assessment (for decision support)
Task 7.3	Exploitation plan



2. State of art

2.3 Water desalination challenges

Brine is a waste effluent generated by numerous industrial sectors; refineries, mines, metallurgy, water, chemical and food industry. Discharge of brine after dilution with fresh water to urban sewage, into artificial lagoons or into the soil is not sustainable because it provokes soil and underground water sources degradation (Kathijotes, 2013). Brine rejection poses as a serious environmental threat due to its high salinity and presence of chemicals.

2.4 Brine management

Brine management focuses on a series of treatments that aim to reduce the volumetric flow rate of the brine to be discharged. By reducing the volumetric flow, salt concentration increases and it becomes easier to precipitate the dissolved salts and other compounds. As a result, the effluent turns into a less hazardous material and salt extraction from the brine becomes more attractive. The available volume minimisation technologies, applicable on brine streams, include Reverse Osmosis (RO) and Nanofiltration (NF), membrane technologies, membrane distillation/evaporation, forward osmosis, vacuum membrane distillation, electrodialysis, Multiple Effect Distillation (MED), mechanical vapour compression, etc. Water treatment processes also aim to maximise the recovery of high purity reclaimed water and minimize waste. The ultimate target for any volume minimisation process is to achieve Zero Liquid Discharge (ZLD). Nowadays, most brine treatment trains are founded on a ZLD basis. This is an engineering approach to waste water treatment in which all water is recovered as high purity reclaimed water and contaminants are reduced to solid waste. In the case of brine, a ZLD practice results in two different outputs: value-added solids (salts and other chemicals) and high purity reclaimed water. As the waste water concentration increases, so do the salinity and the concentration of organics and contaminants, resulting in an increase in the effort and cost of handling and recovery itself as well as the cost for reagents and scaling compounds.

Targeting ZLD practices in seawater desalination facilities provides a number of benefits:

- Lower waste volumes that decrease the cost associated with waste management
- Reduction of transportation costs associated with off-site waste water disposal and impact of their emissions of greenhouse gases and community road incident risk
- Improvement of environmental performance and regulatory risk profile for future permitting allowance
- Some processes have the potential to recover valuable resources
- Additional water recovery.

In Europe and North America, the drive towards ZLD has been pushed by high costs of waste water disposal at inland facilities. These costs arise either from regulations that restrict disposal options or factors that influence the costs of disposal technologies. Another important reason to consider ZLD is the potential for recovering all available resources that are present in waste water.

The aim of this task is brine processing according to ZLD technology principles in order to achieve optimal recovery of salts – (i.e. magnesium hydroxide, calcium carbonate and potassium chloride) for the use as bio-based fertilising products. Through this scope, the supply chain of nutrients from brine is redesigned using innovative solutions and contributing to the circular economy and sustainability of the agricultural sector in the EU. Factorial experiments under various conditions are carried out to optimize the purity and quantity of the recovered salts which potentially can be used as ingredients of Bio-based Fertilisers (BBFs). The novelty of the process can be found in the combination of the technologies used such as precipitation, NF, low-



temperature evaporation, crystallisation, and flotation with an attempt to minimise energy consumption and ensure the feasibility and viability of the process.



3. Material and methods

3.3 Set-up

The bench-scale experiments of the proposed seawater brine treatment are described in Figure 3-1.

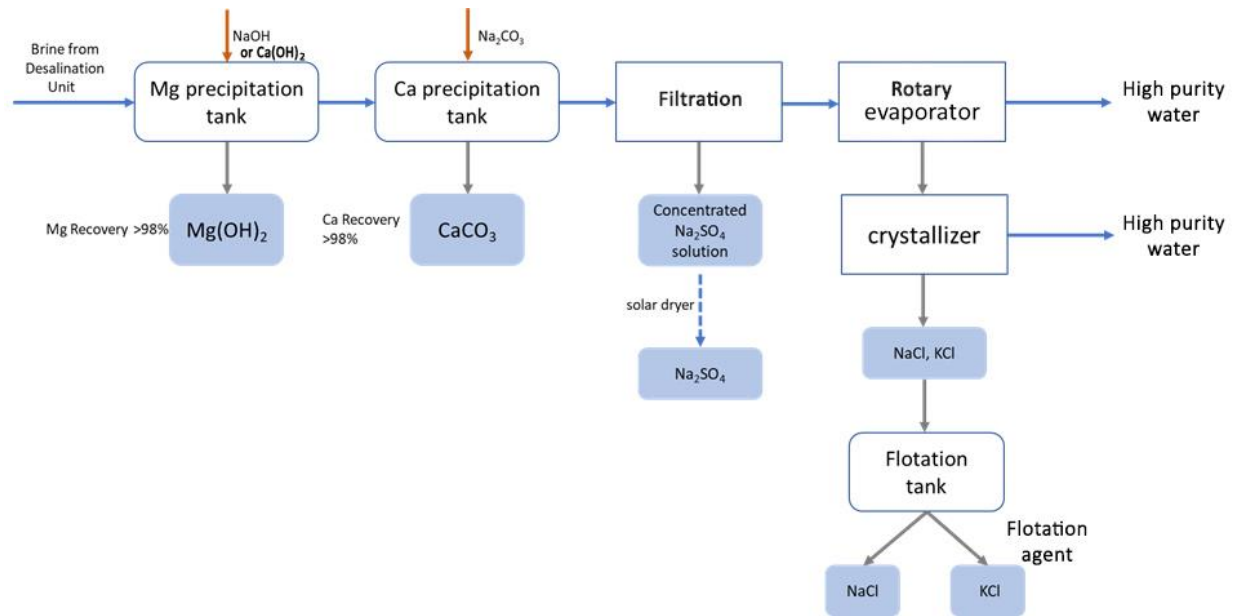


Figure 3-1: Process flow diagram of the proposed seawater brine treatment

The first step of the brine treatment train is the precipitation of Mg^{2+} in the form of $\text{Mg}(\text{OH})_2$. The addition of two reagents NaOH and $\text{Ca}(\text{OH})_2$ for Mg^{2+} recovery is studied. Two series of experiments are carried out under different values of stirring time and quantity of reagent to recover the best combination regarding the highest quantity and purity of Mg^{2+} recovery. Na_2CO_3 is added to the brine after Mg^{2+} removal for CaCO_3 precipitation. As in the former experiments series, stirring time and quantity of the reagent are the two parameters examined to achieve maximum recovery of CaCO_3 . After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) will be led to NF unit for Na_2SO_4 separation from NaCl - KCl rich stream. Monovalent salt stream is further concentrated by a rotary evaporator for the reclamation of high purity water. Then, KCl is separated from the mixed salt of NaCl - KCl using a flotation technique. Sodium Dodecyl Sulfate and Hexadecyl Trimethyl Ammonium Bromide are used as flotation agents. The efficiency of each floating agent is examined in terms of KCl recovery and purity.



3.4 Feedstock characterisation

Table 3-1 shows the concentration of main anions and cations contained in seawater and in brine treated during this project.

Table 3-1: Ions concentration in seawater and brine

Ions	Concentration in brine (mg/L) 1 st try – NaOH (2M) reagent	Concentration in brine (mg/L) 2 st try - Ca(OH) ₂ reagent	Concentration in brine (mg/L)-upscale	Concentration in seawater (mg/L)
K ⁺	813	874	906	480
Na ⁺	19674	17781	18230	8026
Ca ²⁺	776	740	760	450
Mg ²⁺	2736	2225	2200	1314
Cl ⁻	35400	44000	43800	27000
SO ₄ ²⁻	3820	5700	4730	4400
HCO ₃ ⁻	238	107	221	140
PO ₄ ³⁻	0.08	0.42	0.23	-
NO ₃ ⁻	0.01	1.1	0.8	-
TDS	6.85 g/100 mL	7.43 g/100 mL	7.48 g/100 mL	3.45 g/100 mL
Electrical Conductivity	64.2 mS/cm ²	74.1 mS/cm ²	73.2 mS/cm ²	50.0 mS/ cm ²
pH	7.77	7.7	7.8	7.5-8.4

3.5 Experimental procedure

3.5.1 Mg²⁺ Removal

For the Mg²⁺ removal, samples of 200 mL characterised brine are used. Chemical precipitation of Mg²⁺ is realised by using two different reagents. The first one is NaOH (2M) solution and the second one is solid Ca(OH)₂. Firstly, in every experimental series, the reagent is added under magnetic stirring. Different quantities of the reagent and different reaction times are examined. Sedimentation curves for magnesium hydroxide precipitation are also examined between 0-24 h. After the reaction, solid Mg(OH)₂ is separated through centrifugation (10min, 3500rpm) and then the liquid samples are collected. Liquid brine samples are diluted with nitric acid 1.5% and then are analysed through AAS method to measure the final concentration of Mg²⁺ and calculate its removal percentage (%). Solid is washed out with deionised water, then collected in a crucible and left at 105 °C until dry (Figure 3-2). Finally, the dry solid is weighted, ground and analysed through XRD method to determine its composition.



Figure 3-2: Recovered solid Mg(OH)₂



3.5.2 Effect of pouring vs spraying NaOH (2M) on sedimentation speed

Different ways of reagent addition are tested in order to achieve faster precipitation of produced $\text{Mg}(\text{OH})_2$. Besides pouring NaOH (2M) into brine, an alternative way of addition is the spray method. In this case, the sedimentation of produced salts is faster (Figure 3-3). Figure 3-4 shows two volumetric tubes with the same quantity of brine and NaOH (2M) that are left static in order to separate the liquid from the solid. It is observed that after 2.5 hours the left tube, where NaOH (2M) is added through spray method the separation of solids from liquids is faster resulting in a more dense precipitate (Table 3-2).

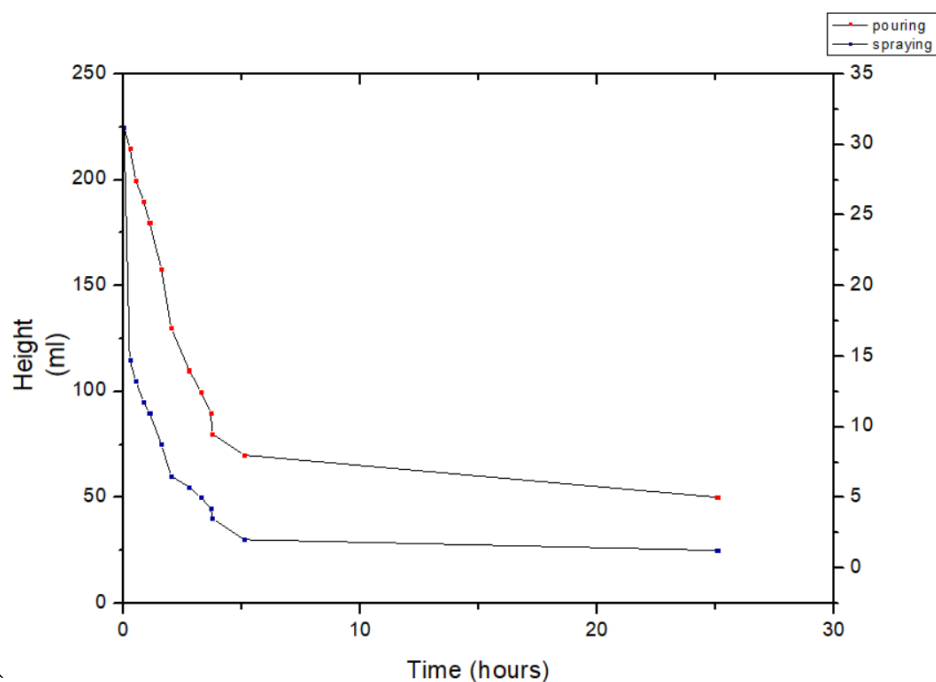


Figure 3-3: $\text{Mg}(\text{OH})_2$ slurry separation (24h) through spraying and pouring NaOH (2M).



Figure 3-4: Addition of NaOH (2M) by spraying (left) - without spraying (right)

Table 3-2: Precipitate density of $\text{Mg}(\text{OH})_2$ slurry (24h)

Ions	Precipitate density of $\text{Mg}(\text{OH})_2$ slurry (24h)
Pouring method	~30 g/l
Spraying method	~50 g/l

3.5.3 Ca²⁺ Removal

Solid sodium carbonate (Na₂CO₃) is added to brine samples without Mg²⁺ and the mixture is stirred. As a product of the reaction, a new solid is produced, CaCO₃ (Figure 3-5), which is separated from the liquid solution through centrifugation (10min, 3500rpm). The liquid solution is filtered and then diluted with nitric acid 1.5% to be analysed using AAS method. Through this analysis the concentration of Ca²⁺ is measured and the percentage (%) of Ca²⁺ removal is calculated. Solid CaCO₃ is washout out with deionised water. Finally, it is left at 105° C to dry and is analysed through XRD method.



Figure 3-5: Recovered solid CaCO₃

After pH conditioning, the brine (without Mg²⁺ and Ca²⁺) is led to a rotary evaporator for water and salt recovery. Recovered salt is led to flotation for the separation of KCl from NaCl.

3.6 Factorial Experimental Design

Recovery of Mg²⁺ and Ca²⁺ is designed through a 2² factorial experiment of two parameters (reagent's quantity and stirring time). Experiments are realised under various conditions and combinations of the upper and lower levels of the parameters. The experiments with the conditions that refer to level 0 were repeated 4 times for statistical evaluation. The parameters selected are quantity of the reagent and different reaction times; a series of experiments are carried out under different conditions and combinations of the two parameters. X₁ refers to reagent's quantity and X₂ to stirring time. Stoichiometric quantity of the reagent is used as centre of the factorial design and based on the symmetry are defined the upper and lower extreme values of the levels. Specifically, at the upper level (+1) 110% of reagent's quantity is added with a stirring time of 45 min while at the lower (-1), 90% of the stoichiometric quantity is added with 15 min stirring time (Table 3-3).

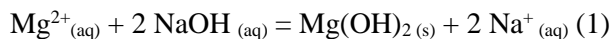
Table 3-3: Parameters and levels of the factorial design

Factorial parameters			Factorial levels		
	unit		-1	0	1
Reagent's quantity	g/mL	X ₁	90% of stoichiometry	stoichiometry	110% of stoichiometry
Stirring time	min	X ₂	15	30	45



3.6.1 Factorial design for the recovery of Mg^{2+} from brine using NaOH (2M) as reagent

Experiments for the recovery of Mg^{2+} , using NaOH (2M) as reagent are based on the chemical reaction (1):



The initial sample is 200 mL brine with 2.74g/L concentration in magnesium. Based on the above reaction, the stoichiometric quantity of NaOH (2M) for the precipitation of magnesium is 22.5 mL; mixing time for this level is settled at 30'. Conducting all possible combinations of the levels of the two parameters (Table 3-4), resulted in 12 experiments in total. For the upper and lower level, 4 trials take place with two replicates for each level. As for the centre, 4 replicates are realised for statistical validation.

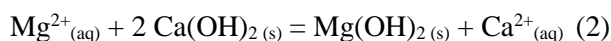
Table 3-4: Factorial design for Mg^{2+} recovery from brine using NaOH (2M) as reagent

Experiments A/A	Quantity NaOH (2M) (mL)	Mixing time (min)
1	20.25	15
2	20.25	15
3	24.75	45
4	24.75	45
5	20.25	45
6	20.25	45
7	24.75	15
8	24.75	15
9	22.5	30
10	22.5	30
11	22.5	30
12	22.5	30



3.6.2 Factorial design for the recovery of Mg^{2+} from brine using $Ca(OH)_2$ as reagent

Experiments for the recovery of Mg^{2+} , using $Ca(OH)_2$ as reagent are based on the chemical reaction (2):



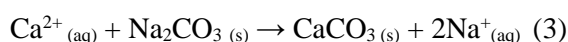
Similarly to the latter process, 200 mL of brine sample are used and based on the stoichiometry of the reaction, the quantity of $Ca(OH)_2$ for the $Mg(OH)_2$ precipitation is 1.356g under 30 min stirring time; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (Table 3-5), resulted in 12 experiments.

Table 3-5: Factorial design for Mg^{2+} recovery from brine using $Ca(OH)_2$ as reagent

Experiments A/A	Quantity $Ca(OH)_2$ (g)	Mixing time (min)
1	1.220	15
2	1.220	15
3	1.492	45
4	1.492	45
5	1.220	45
6	1.220	45
7	1.492	15
8	1.492	15
9	1.356	30
10	1.356	30
11	1.356	30
12	1.356	30

3.6.3 Factorial design for the recovery of Ca^{2+} from brine

Experiments for the recovery of Ca^{2+} , using Na_2CO_3 as reagent are based on the chemical reaction (3):



Using 200 mL of brine sample and based on the stoichiometry of the reaction (3), the quantity for the $CaCO_3$ precipitation is 0.48g Na_2CO_3 by stirring the mixture for 30'; these values are considered the center of the experimental design. Conducting all possible combinations of the levels of the two parameters (Table 3-6), resulted in 12 experiments.

Table 3-6: Factorial design for Ca^{2+} recovery from brine

Experiments A/A	Quantity Na_2CO_3 (g)	Mixing time (min)
1	0.43	15
2	0.43	15



3	0.53	45
4	0.53	45
5	0.43	45
6	0.43	45
7	0.53	15
8	0.53	15
9	0.48	30
10	0.48	30
11	0.48	30
12	0.48	30

3.7 KCl recovery from brine

After magnesium and calcium removal and pH conditioning from 10.5 to 7, the resulting brine is forwarded to a rotary evaporator for concentration and then to the oven for salt crystallisation. KCl is more soluble at high temperatures than NaCl, so every 2 min, brine is separated from the crystallised salt. The separated brine is expected to be more enriched in KCl, upon full evaporation. Three types of salt resulted and are named A, B and C; C is expected to be the most KCl-rich, while A is the least KCl-rich fraction. Mixed (NaCl-KCl) salt is led to a flotation cell for the separation of KCl from NaCl. For this purpose, a saturated solution of KCl and NaCl is prepared by dissolving 342 g KCl and 514 g NaCl in 2 L of deionised water. In every flotation trial, 10 g of the mixed salts are added into 40 mL of the saturated solution and then Sodium Dodecyl Sulfate 1% is used as flotation agent. The mixture is stirred for 10 min and air is provided through a pipe to create froth; KCl crystals are attached on bubbles and then are collected. Finally, crystals are left to dry. A quantity of salts is diluted with nitric acid 1.5% for further qualitative analysis through AAS method. XRD analysis is performed for each kind of salt, to study their composition qualitatively. The results obtained are given in Figure 3-6 to Figure 3-8.

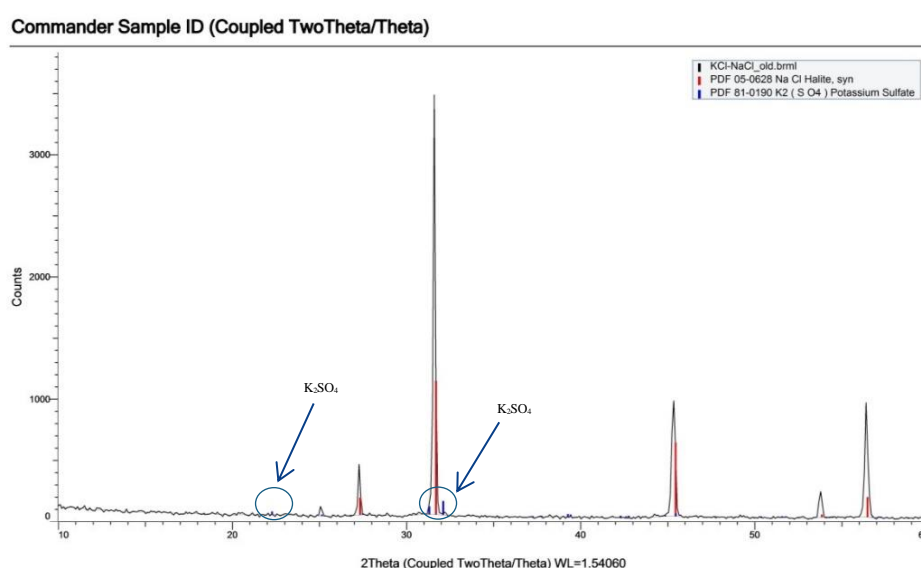


Figure 3-6: Mixed salt A XRD analysis



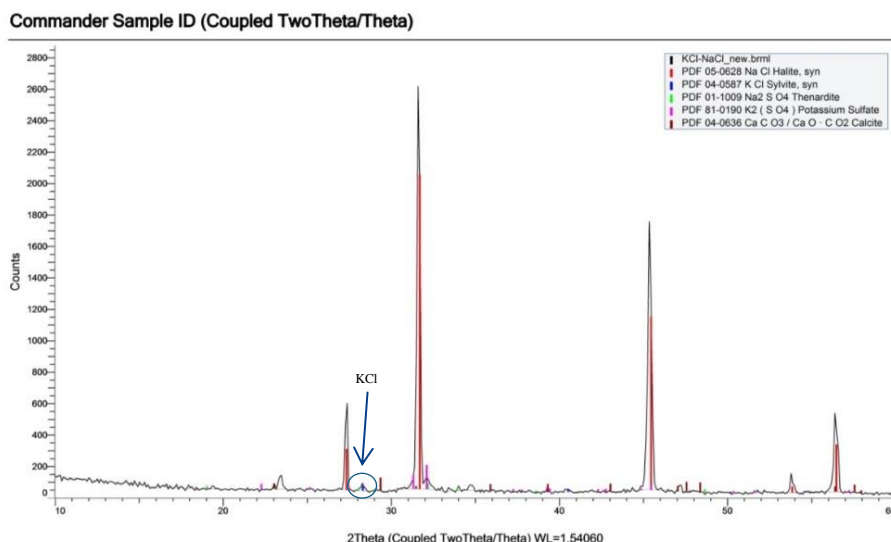


Figure 3-7: Mixed salt B XRD analysis

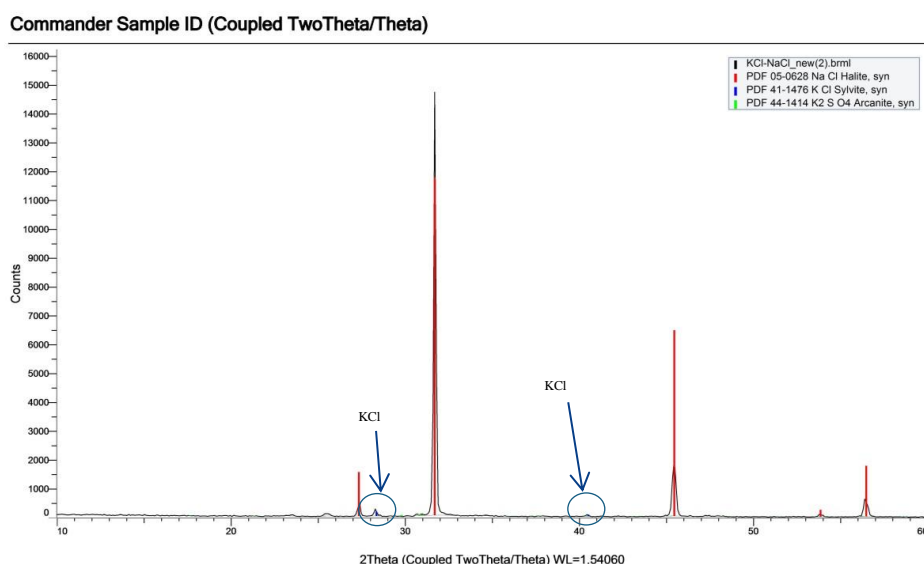


Figure 3-8: Mixed salt C XRD analysis

Peaks corresponding to NaCl in the form of halite (red peaks) are visible in all three plots. In Figure 3-6, which corresponds to salt A, some smaller peaks appear which are probably due to K_2SO_4 presence, while no peaks corresponding to KCl are found, due to the very low concentration of KCl in salt A. However, in Figure 3-7 and in Figure 3-8 (mixed salt B and C) a small peak (blue in color) is visible due to the presence of KCl (sylvite). Other peaks probably correspond to the compounds K_2SO_4 , Na_2SO_4 and $CaCO_3$. To achieve a quantitative estimate of the composition of mixed salt, the analytical AAS is used (Table 3-7).

Table 3-7: Mixed salt analysis using AAS

K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)
0.034	1.724	0.208	0.012	0.028



The concentration measured for potassium corresponds to 1.63 % KCl in salt B. There are also small concentrations of Mg^{2+} and Ca^{2+} which are probably not completely removed in the previous stages of the experiment. A total of 195 g of salt is collected where 52 g is salt A (less rich in K), 100 g salt B and 43 g salt C (richest in K). For the recovery of potassium by flotation method, 17 experiments are carried out where 10 g of salt are used for each one. The effect of the flotation agent addition is mainly studied keeping the amount of saturated KCl – NaCl solution constant; 40 mL are used in every experiment. In addition, tests are performed on how flotation time, mass of added salt and granulometry of the salt affect the recovered amount of KCl and its purity. Table 3-8 shows the conditions for each experiment and the recovered mass of solid.

Table 3-8: Conditions of the flotation experiments and the recovered solid mass

Experiments	Pretreatment time (min)	Flotation time (min)	Concentrated solution volume (mL)	Added salt (g)	Floating agent volume (mL)	Granulometry (μm)	Recovered solid (mg)
A1	5	5	40	10	5	-	360
A2	5	5	40	10	5	-	150
A3	5	5	40	10	2.5	-	200
A4	5	5	40	10	2.5	-	80
A5	5	5	40	10	1	-	70
B1	5	5	40	10	1	-	110
B2	5	5	40	10	5	-	180
B3	5	5	40	10	0.5	-	140
B4	5	5	40	10	0.5	-	80
B5	5	5	40	10	1	<180	60
B6	5	5	40	10	1	<180	60
B7	5	5	40	10	1	>180 & <1000	80
B8	5	5	40	10	1	>180 & <1000	100
C1	5	5	40	10	0.5	-	180
C2	5	5	40	10	0.5	-	130
C3	5	5	40	10	1	-	70
C4	5	5	40	10	1	-	100

As resulted from Table 3-8, recovered KCl quantity ranges from 60 mg to 200 mg with one single experiment providing 360 mg solid. According to the table, increasing the volume of the added flotation agent increases the recovered solid (Figure 3-9) as more froth is collected.





Figure 3-9: Recovered KCl crystals



4. Results and discussion

4.1 Results from the factorial design

4.1.1 Mg^{2+} recovery with NaOH (2M) addition

According to Table 4-1, the maximum Mg^{2+} removal and minimum Ca^{2+} removal have occurred on experiments 5 and 6. In these cases, 90% of reagent's stoichiometric quantity is mixed with brine sample for 45 min.

Table 4-1: $\text{Mg}(\text{OH})_2$ recovery through brine reaction with NaOH (2M)

N/N	Experiments A/A	Quantity NaOH (2M) (mL)	Mixing time (min)	% Mg^{2+} removal	% Ca^{2+} removal	$\text{Mg}^{2+}/\text{Ca}^{2+}$	Recovered $\text{Mg}(\text{OH})_2$ mass (g)
N1	1	20.25	15	86.50	67.20	1.49	0.76
	2	20.25	15	86.7	59.10	1.69	0.87
N2	3	24.75	45	99.00	82.30	1.22	0.90
	4	24.75	45	99.90	70.80	1.41	1.10
N3	5	20.25	45	89.90	48.80	2.05	0.60
	6	20.25	45	89.70	53.60	1.89	1.07
N4	7	24.75	15	98.80	69.20	1.43	0.97
	8	24.75	15	100.00	65.90	1.52	0.83
Centre							
Centre	9	22.25	30	92.00	54.60	1.68	0.84
	10	22.25	30	96.50	49.70	1.74	0.93
	11	22.25	30	95.50	50.50	1.79	0.85
	12	22.25	30	94.70	51.20	1.75	0.87
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0	100.00	1.276



Figure 4-1 shows that experiments with maximum amount of reagent and maximum stirring time (N2) result in largest amount of salts recovery.

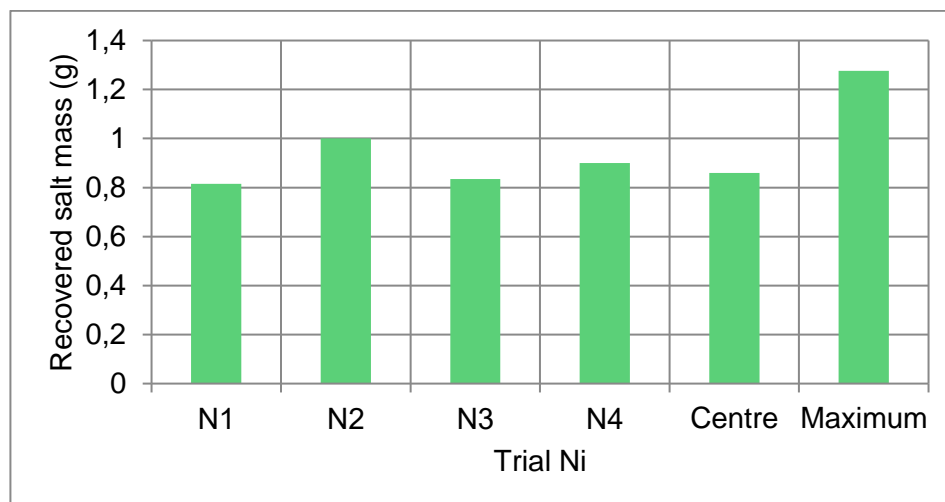


Figure 4-1: Mass of recovered Mg(OH)₂ for every trial

Table 4-2: Mg(OH)₂ recovery through brine reaction with NaOH (2M)

A/A	Quantity of NaOH (2M) (mL)	Stirring time (min)
N1	20.25	15
N2	24.75	45
N3	20.25	45
N4	24.75	15
Centre	22.25	30
Maximum	Stoichiometry	

After processing the factorial experimental results [(Alder,P et al., 1975), (Cochran W.G. et al, 1957)], the following model is developed, correlating the Mg(OH)₂ recovery from brine (Y, %) with the selected controlling parameters:

$$Y = -2.228 + 0.102 * (\text{NaOH (2M) addition}) + 0.077 * (\text{stirring time}) - 0.003 * (\text{NaOH (2M) addition}) * (\text{stirring time}) \quad (4)$$

Equation 4 shows that all parameters are statistically important including their interaction. Furthermore, both mathematical models proved to be adequate according to the Fisher criterion [(Allen, T.T, 2007) (Seidenfeld, T, 1992) (Pacheco-Torgal, F., 2013) (Selvamuthu, D., 2018), (Cox, D.R., 2000)].



4.1.2 Mg^{2+} recovery with $\text{Ca}(\text{OH})_2$ addition

According to Table 4-3, maximum Mg removal has occurred with higher reagent dosage.

Table 4-3: $\text{Mg}(\text{OH})_2$ recovery through brine reaction with $\text{Ca}(\text{OH})_2$

N/N	Experiments A/A	Quantity $\text{Ca}(\text{OH})_2$ (g)	Mixing time (min)	%Mg removal	Recovered $\text{Mg}(\text{OH})_2$ mass (g)
N1	1	1.220	15	86.88	0.936
	2	1.220	15	87.46	0.881
N2	3	1.492	45	99.98	1.652
	4	1.492	45	99.62	1.716
N3	5	1.220	45	86.91	1.145
	6	1.220	45	86.64	1.195
N4	7	1.492	15	99.98	1.030
	8	1.492	15	99.18	0.940
Centre					
Centre	9	1.356	30	94.39	1.390
	10	1.356	30	94.48	1.444
	11	1.356	30	95.30	1.368
	12	1.356	30	96.67	1.240
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	1.067

Figure 4-2 shows that experiments of N₂ trials provide the highest amount of salts recovery.

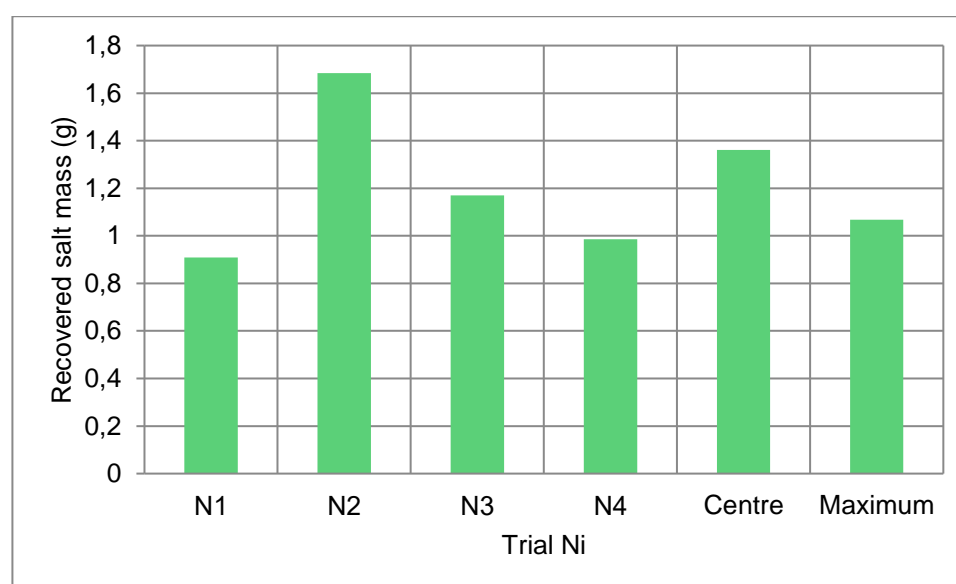


Figure 4-2: Mass of recovered CaCO_3 for every trial

First degree equation 5 shows that the most important parameter for Mg^{2+} recovery through $\text{Ca}(\text{OH})_2$ addition is reagent's quantity, whereas reaction time is not considered as a factor that can affect the results.

$$Y = 0.295 + 0.47 * (\text{Ca}(\text{OH})_2 \text{ addition}) \quad (5)$$



4.1.3 Ca^{2+} recovery with Na_2CO_3 addition

Table 4-4 shows that all different experiments result in an average class rate of 99% CaCO_3 recovery.

Table 4-4: CaCO_3 recovery through brine reaction with Na_2CO_3

N/N	Experiments A/A	Quantity Na_2CO_3 (g)	Mixing time (min)	%Ca removal	Recovered CaCO_3 mass (g)
N1	1	0.432	15	97.00	0.33
	2	0.432	15	98.00	0.35
N2	3	0.528	45	99.00	0.39
	4	0.528	45	98.00	0.34
N3	5	0.432	45	99.00	0.37
	6	0.432	45	99.00	0.38
N4	7	0.528	15	99.00	0.33
	8	0.528	15	99.00	0.37
Centre					
Centre	9	0.48	30	98.00	0.32
	10	0.48	30	99.00	0.35
	11	0.48	30	98.00	0.33
	12	0.48	30	99.00	0.37
	13	Maximum Mg^{2+} removal based on stoichiometry		100.00	0.45

Equation (6) shows that Ca^{2+} removal increases both with Na_2CO_3 addition and stirring time. However, reagent's addition has a greater effect on Ca^{2+} removal because of its greater coefficient.

$$Y = 0.9372 + 0.0081 * (\text{Na}_2\text{CO}_3 \text{ addition}) + 0.0002 * (\text{stirring time}) \quad (6)$$

4.1.4 Nanofiltration simulation model

According to the experimental process flow diagram (Figure 3-1) the brine after Mg^{2+} and Ca^{2+} removal will enter the NF unit. The occupation of the NF unit is necessary for the removal of SO_4^{2-} ions from the seawater desalination brine. Regarding the NF process unit the separation efficiency was set as the main optimisation parameter. Since in task 2.5, only small volumes of brine (200 mL and 50 L) were treated during the lab-scale experiments, it was not possible to implement NF step. Thus, it was decided to run a simulation model for the treatment of 0,5 m³/day of brine (Raw Feed composition is presented in Table 4-5) using the Water Application Value Engine (WAVE) software.

Table 4-5: Concentrations of brine ions and TDS before and after NF process

	Raw Feed (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
K	912.6	1,588	729.8
Na	21,974	37,701	17,718
Mg	11.6	30.57	6.46
Ca	17.4	45.98	9.66
SO_4^{2-}	3,416	15,046	271.3
TDS	58,688	103,304	46,616



After many runs with different types of NF membranes the most appropriate for Pilot Plant 4 seems to be the membrane NF270-2540 in terms of SO_4^{2-} removal. This membrane seems to be more appropriate (large pore diameter: 270 μm) because the stream is very dense and would create fouling and scaling issues. The removal efficiency results in the brine salts & TDS removal percentages are described in Table 4-6. The simulation was performed under $\text{pH}=7$. For this type of membrane and aforementioned conditions no special comments were derived from the wave simulation model regarding fouling or scaling issues.

Table 4-6: NF % removal of brine ions & TDS

	% removal of major ions
K	20
Na	19
Mg	44
Ca	44
SO_4^{2-}	92
TDS	21

To conclude, the simulation of the NF process using membrane NF270-2540 implied a 92% removal (Table 4-6) of SO_4^{2-} from the brine inlet. The resulting effluent streams will be used for the optimisation of the downstream processes.

4.2 Purity control

4.2.1 XRD purity control of recovered $\text{Mg}(\text{OH})_2$ salts using NaOH (2M) as reagent

Collected salt, is grinded and subjected to XRD analysis to examine its crystal structure and confirm the presence of magnesium and calcium. Analysis is performed in 12 different tests.

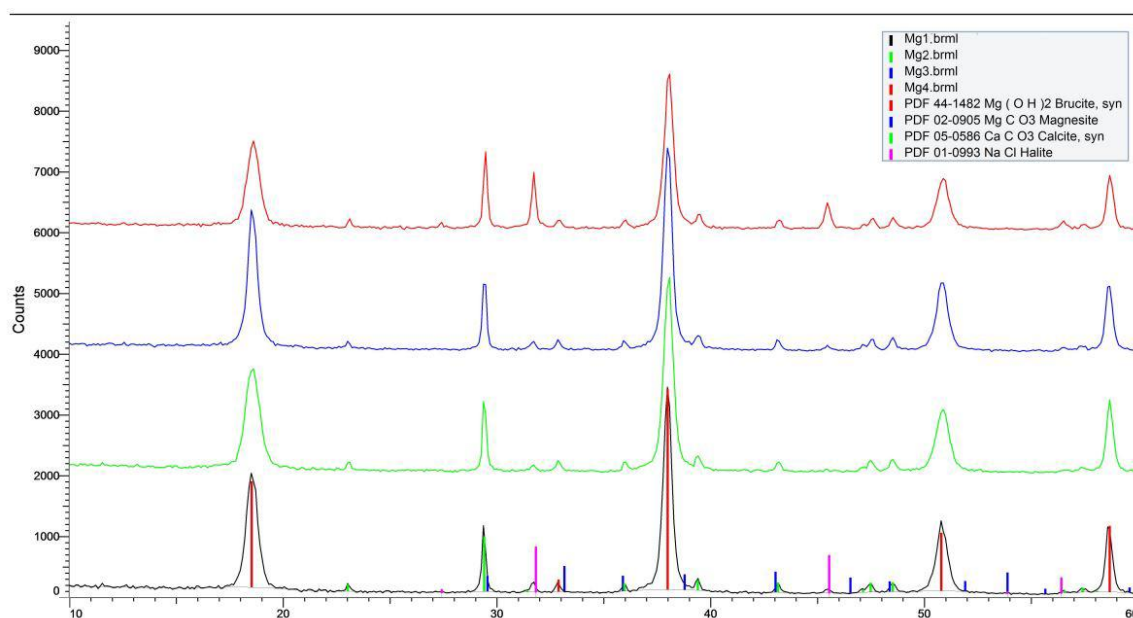


Figure 4-3: Crystal structure analysis of salts from tests 1-4

In tests 1-4 (Figure 4-3), the composition of salts is similar and magnesium appears in the form of Brucite ($\text{Mg}(\text{OH})_2$ red peaks) and Magnesite (MgCO_3 blue peaks); presence of calcium come in the form of Calcite (CaCO_3 green peaks) while chloride is in the form of Halite (NaCl pink peaks).

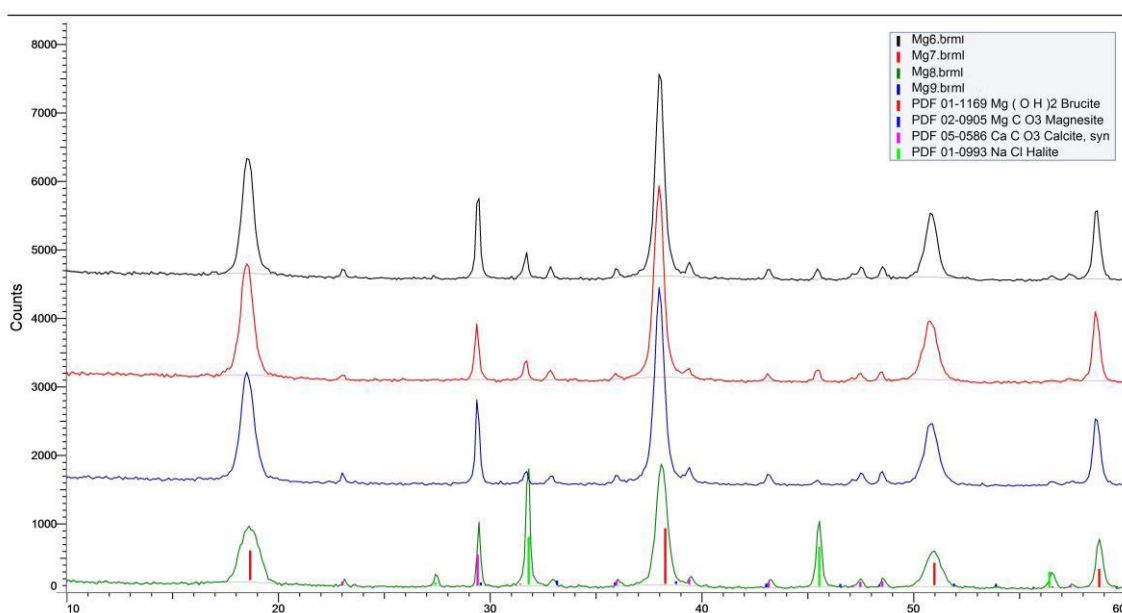


Figure 4-4: Crystal structure analysis of salts from tests 5 to 8

Crystal structure of salts in tests 5 to 9 (Figure 4-4) looks almost identical to tests 1-4 (Figure 4-3). Similarly, in these trials magnesium is revealed in the form of Brucite ($\text{Mg}(\text{OH})_2$ red peaks) and Magnesite (MgCO_3 blue peaks), calcium is in the form of Calcite (CaCO_3 red peaks) and sodium chloride in the form of Alite (NaCl green peaks).

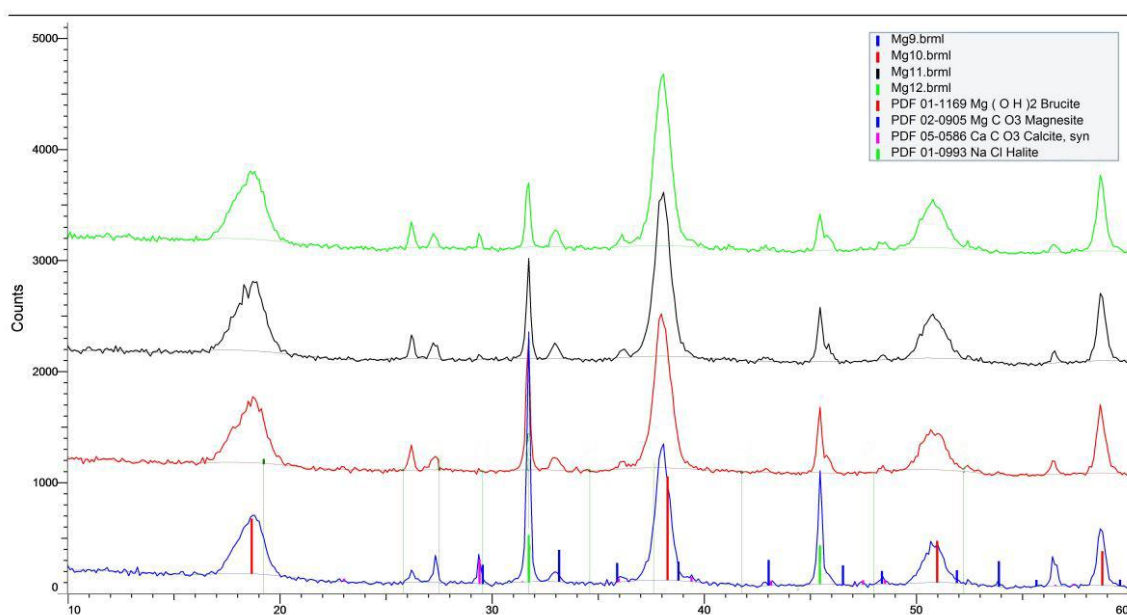


Figure 4-5: Crystal structure analysis of salts from tests 9 to 12

Trials 9 to 12 (Figure 4-5) are similar to previous tests in terms of crystal structure. All tests confirm that recovered salts consist of magnesium and calcium as well as sodium chloride.



4.2.2 AAS purity control of recovered $\text{Mg}(\text{OH})_2$ recovered salts using NaOH (2M) as reagent

Purity control of $\text{Mg}(\text{OH})_2$ solids with AAS method is realised by using a sample from each pair of identical conditions. For the analysis, 200 mg of each recovered salt is dissolved in nitric acid 1.5% solution and diluted. The concentration of elements K^+ , Na^+ , Ca^{2+} and Mg^{2+} is measured in mg/L and the results are listed in Table 4-7

Table 4-7: Atomic absorption results for solid $\text{Mg}(\text{OH})_2$

Stoichiometric quantity/Mixing Time	K^+ (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
90/15	0.9026	4.5022	6.425	54.4708
110/45	0.0923	3.9239	4.175	52.8292
90/45	0.0333	3.3587	4.925	53.6292
110/15	0.0167	13.8978	4.625	34.3542
100/30	0.1577	2.2913	7.125	56.1

Above data show that Mg is in highest concentration in all samples. Based on these value, the purity of $\text{Mg}(\text{OH})_2$ is calculated. The results are presented in Table 4-8.

Table 4-8: Percentage purity of solids in $\text{Mg}(\text{OH})_2$

Stoichiometric quantity/Mixing Time	% Purity in $\text{Mg}(\text{OH})_2$
90/15	88%
110/45	93%
90/45	92%
110/15	85%
100/30	89%

The highest purity of the recovered $\text{Mg}(\text{OH})_2$ is observed in experiments with higher mixing times for both tested reagent dosages. Shorter mixing time results in higher amounts of coprecipitated CaCO_3 which seems to be the main impurity in solid $\text{Mg}(\text{OH})_2$.

4.2.3 XRD purity control of $\text{Mg}(\text{OH})_2$ salts using $\text{Ca}(\text{OH})_2$ as reagent

Figure 4-6 demonstrates the XRD analysis of recovered solids from experimental runs 1 and 2. Black refers to trial 1 and red to trial 2. Production of solids 1 and 2 is realised under same conditions (90/15); 15 min reaction time and 0.9 * stoichiometric amount of reagent $\text{Ca}(\text{OH})_2$.



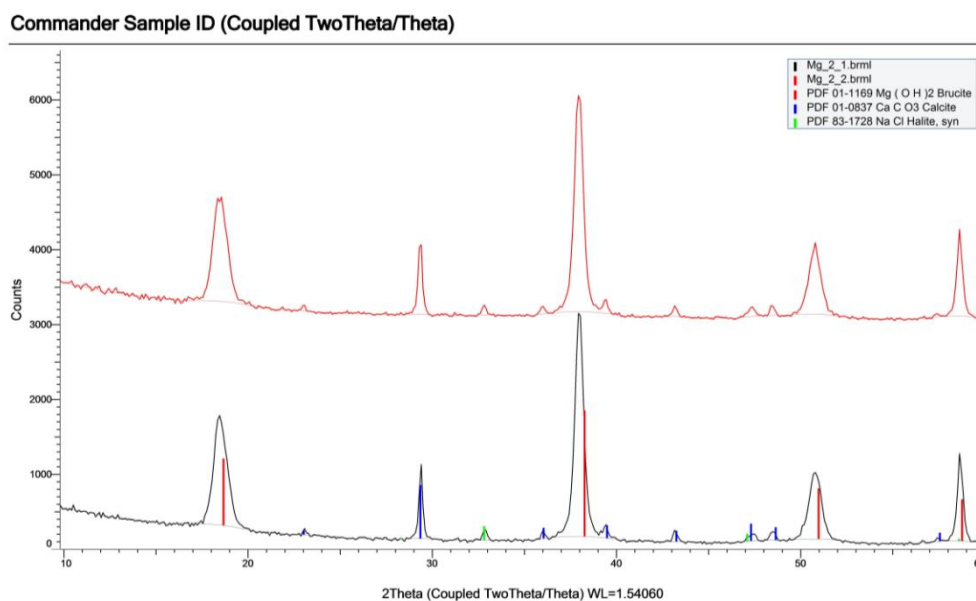


Figure 4-6: Crystal structure analysis of solid $\text{Mg}(\text{OH})_2$ for tests 1 & 2

These two figures are identical identifying the presence of $\text{Mg}(\text{OH})_2$ as brucite by a high intensity peak and lower intensity peaks corresponding to CaCO_3 and NaCl .

Figure 4-7 shows the analysis for trials 3 and 4. Black colour refers to trial 3 and red to trial 4. Tests are realised under same conditions (110/45); 45 min stirring time and 1.1 * stoichiometric amount of reagent.

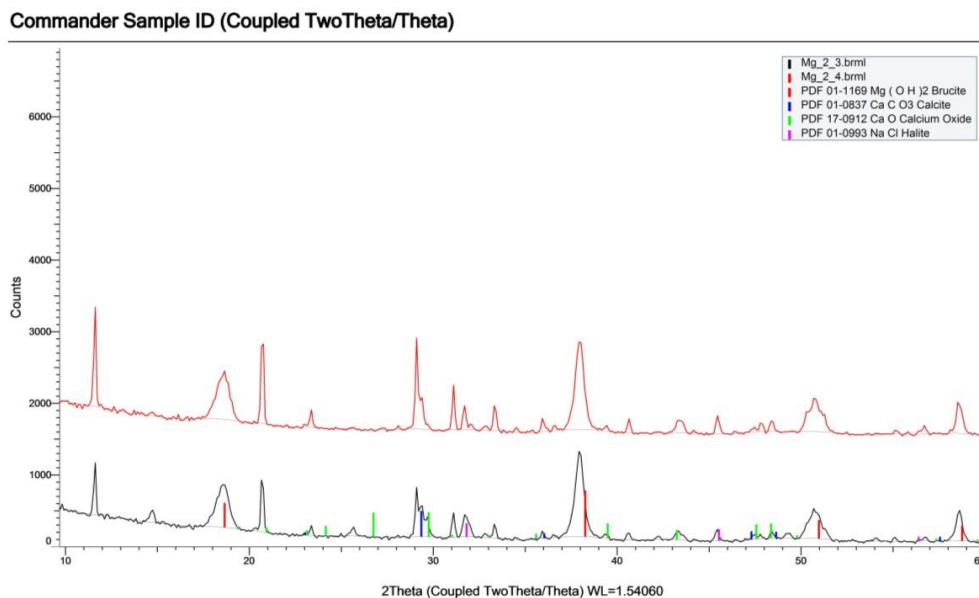


Figure 4-7: Crystal structure analysis of solid $\text{Mg}(\text{OH})_2$ for tests 3 & 4

Peaks corresponding to $\text{Mg}(\text{OH})_2$ are shown in red, CaCO_3 in blue and NaCl in green. There are also impurities which are probably CaO and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).



Figure 4-8 shows the XRD analysis of recovered salts from trials 5 and 6 under same conditions; 45 minutes stirring time and 0.9 * stoichiometric quantity of the reagent. Beside $\text{Mg}(\text{OH})_2$ there are also peaks of CaCO_3 , NaCl , gypsum, CaSO_4 , CaO .

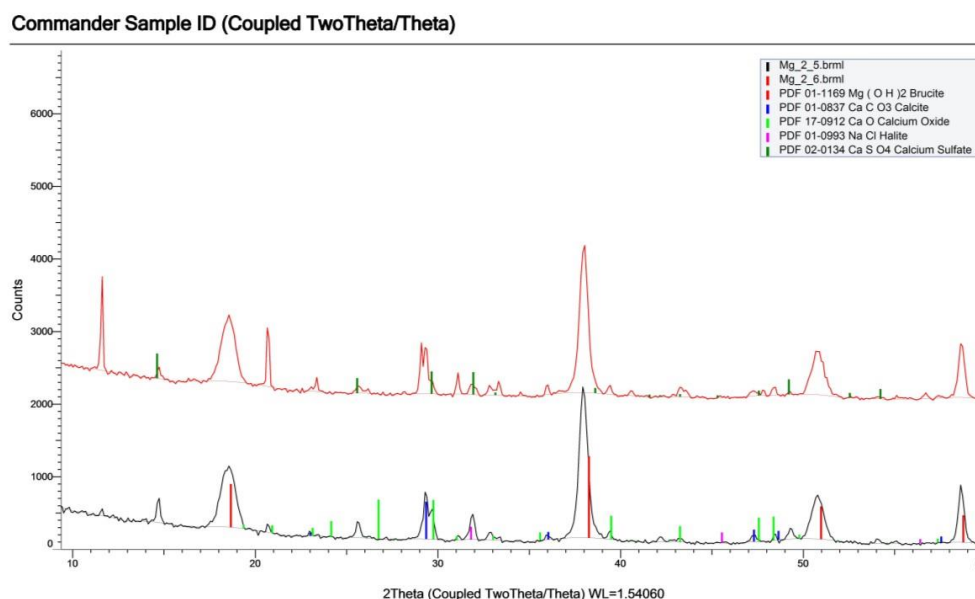


Figure 4-8: Crystal structure analysis of solid $\text{Mg}(\text{OH})_2$ for tests 5 & 6

Next, Figure 4-9 refers to recovered salts from 7 and 8 trials where stirring time is 15 min and the amount of reagent $\text{Ca}(\text{OH})_2$ is 1.1 x stoichiometric.

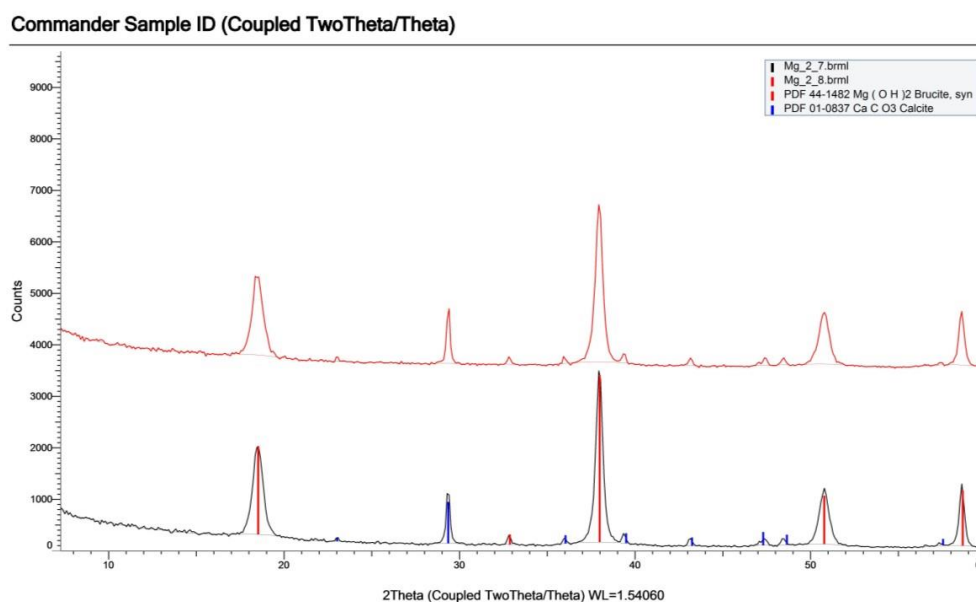


Figure 4-9: Crystal structure analysis of solid $\text{Mg}(\text{OH})_2$ for tests 7 & 8

Tests 7 and 8 are quite similar while no peaks of NaCl are detected comparing to previous analysis.



Finally, Figure 4-10 shows the XRD analysis of the four experimental tests (centre), where stirring time is 30 min and Ca(OH)_2 amount is the stoichiometric one. Results for the four trials of the centre are similar.

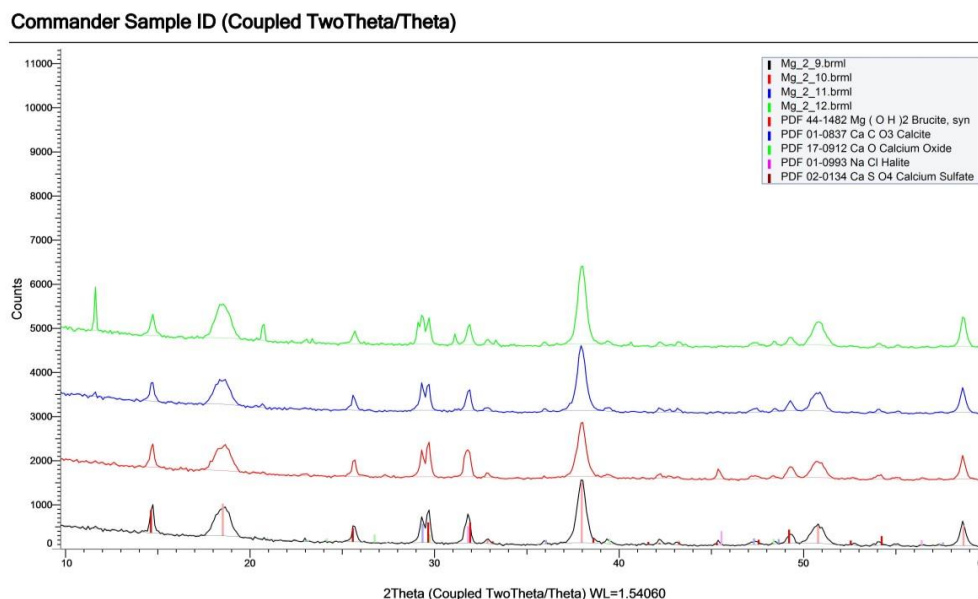


Figure 4-10: Crystal structure analysis of solid Mg(OH)_2 for tests 9, 10, 11, 12

A first estimation from above diagrams, is that solids from experiments (90/15) and (110/15), with shorter mixing time, contain fewer impurities and are expected to have greater purity. This fact is confirmed by AAS analysis (Table 4-9).

Table 4-9: Atomic absorption results for solid Mg(OH)_2 using Ca(OH)_2 as reagent

Stoichiometric quantity/Mixing Time	K^+ (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
90/15	0.0085	0.0143	0.455	1.7432
110/45	0.0009	0.0578	1.234	1.5700
90/45	0.0013	0.0055	0.971	1.8671
110/15	0.0001	0.0001	0.529	1.7858
100/30	0.0020	0.0475	1.298	2.0006

AAS analysis shows that Mg^{2+} is the dominant component in all samples. There is also a significant amount of Ca^{2+} , which is expected since CaCO_3 is detected through XRD analysis in all solids, as well as other Ca^{2+} compounds such as gypsum, CaO and CaSO_4 . In addition, Na^+ is present in small concentrations while K^+ as expected has a negligible concentration. Based on Figure 4-10, the purity of Mg(OH)_2 is calculated as a percentage of its mass (Table 4-10).



Table 4-10: Purity of solids in $\text{Mg}(\text{OH})_2$ using $\text{Ca}(\text{OH})_2$ as reagent

Stoichiometric quantity/Mixing Time	Solid $\text{Mg}(\text{OH})_2$ purity, %
90/15	86
110/45	67
90/45	76
110/15	85
100/30	71

The highest values of purity 86% and 85% (Table 4-10) were obtained when mixing time was shorter (15 min). These results comply with the responding XRD patterns accompanying these experiments (Figure 4-10).



4.2.4 XRD purity control of recovered CaCO_3 salts

XRD analyses for all solids (12 in total) are placed on a common diagram as they show excellent similarity (Figure 4-11).

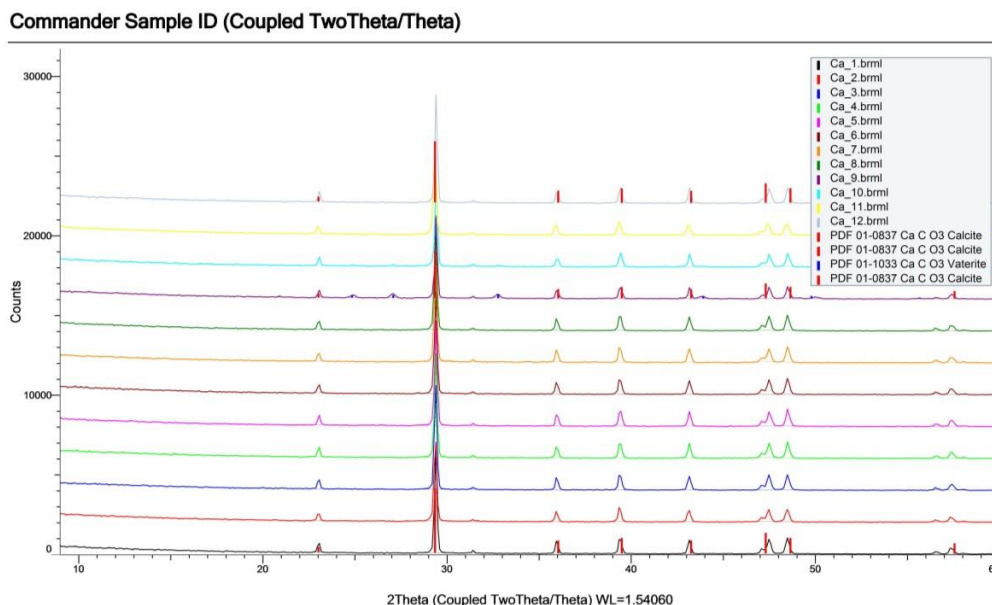


Figure 4-11: XRD analysis for CaCO_3 salts (1-12 trials)

Common peaks correspond to CaCO_3 as calcite (appear in red) in almost all 12, with the exception of sample 9 where it occurs as vaterite. More intense is the high sharp peak that appears near 29.5° . The absence of other peaks means that the samples are of high purity in CaCO_3 , while some very low peaks that appear are probably due to a small amount of NaCl . AAS purity control of recovered $\text{CaCO}_3(\text{s})$.

The purity of CaCO_3 solids has been assessed through Atomic Absorption Analysis. The concentration of elements K^+ , Na^+ , Ca^{2+} and Mg^{2+} in mg/L is measured and the results are given in Table 4-11.

Table 4-11: Atomic absorption results for solid CaCO_3

Stoichiometric quantity/Mixing Time	K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)
90/15	0.0026	0.1024	6.759	0.0001
110/45	0.0001	0.0382	6.239	0.0001
90/45	0.0009	0.0520	6.779	0.0001
110/15	0.0001	0.0752	7.327	0.0001
100/30	0.0045	0.0908	6.858	0.0001

In Table 4-11, it is shown that Ca^{2+} is at a concentration of 7 g/L, higher than rest of the elements measured. Mg^{2+} that is already removed has zero concentration; K^+ is also negligible, while there is a small amount of Na^+ .



From the measured Ca^{2+} concentration values, CaCO_3 purity is calculated as a percentage of its mass. Results are shown in Table 4-12.

Table 4-12: Atomic absorption results for solid CaCO_3

Stoichiometric quantity/Mixing Time	Solid CaCO_3 purity
90/15	~99%
110/45	~99%
90/45	~99%
110/15	~99%
100/30	~99%

Recovered salts are pure CaCO_3 . Therefore, a high recovery of Ca^{2+} from brine is achieved, with simultaneous production of high purity CaCO_3 .

4.2.5 XRD purity control KCl

XRD analyses of the recovered KCl salts from 17 flotation experiments are performed. The representative diffractograms are presented in Figure 4-12, 13 where XRD analysis of the initial mixed salt is compared to each recovered KCl.

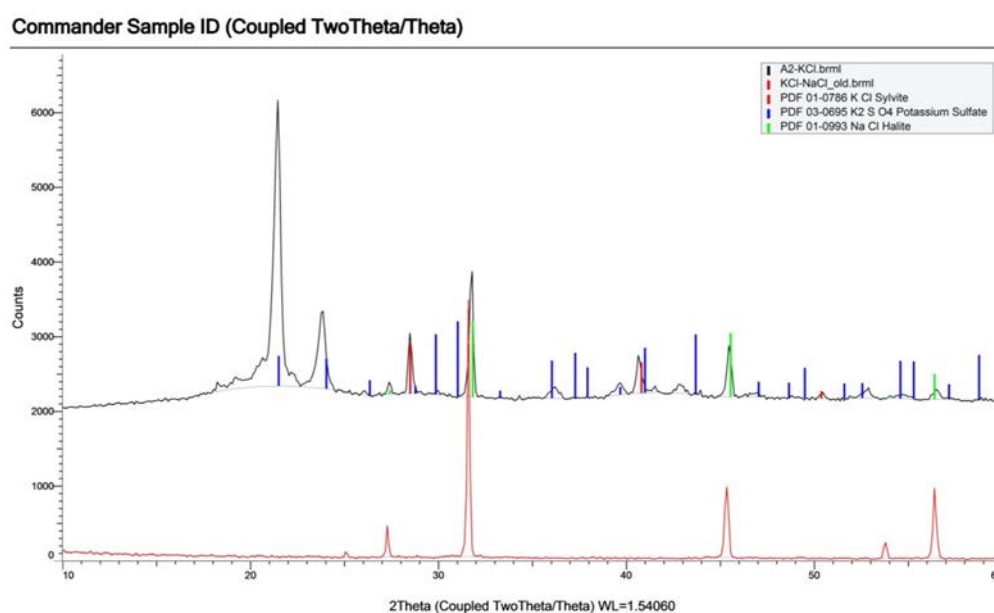


Figure 4-12: XRD analysis of recovered KCl using sodium dodecyl sulfate as flotation agent

When Sodium dodecyl sulfate is used as flotation agent there is presence of potassium sulfate which is raised up to the surface and inevitably collected (Figure 4-12).

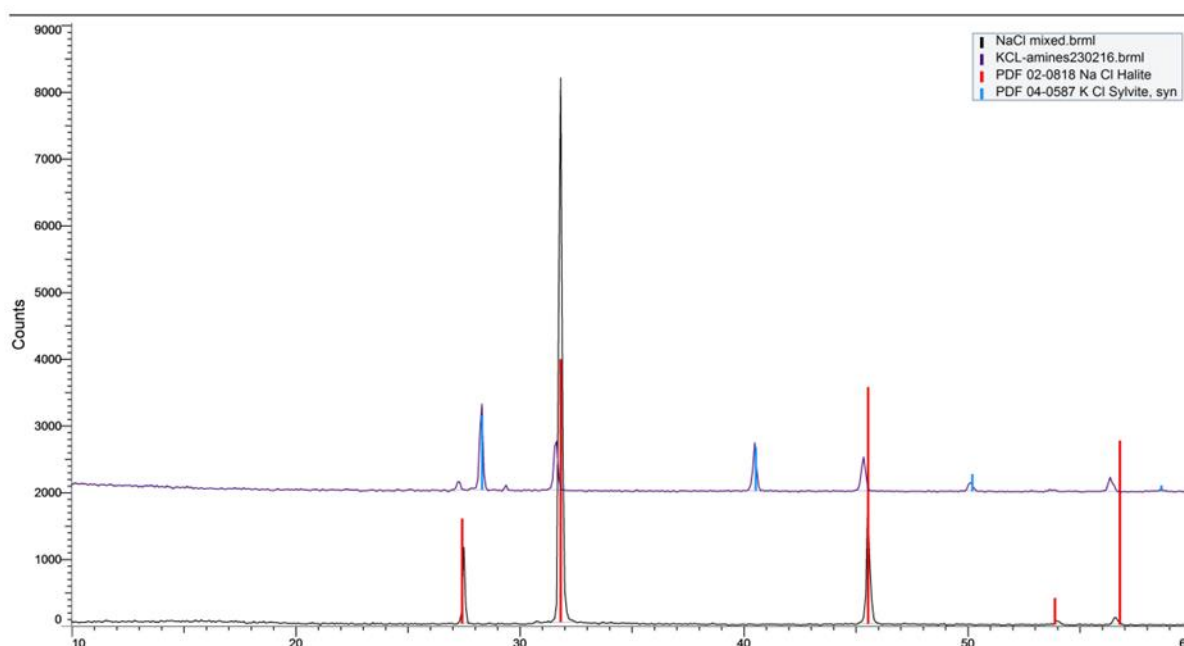


Figure 4-13: XRD analysis of recovered KCl using Hexadecyl Trimethyl Ammonium Bromide as flotation agent

It seems that Hexadecyl Trimethyl Ammonium Bromide shows high selectivity of KCl removal (Figure 4-13).

4.2.6 AAS purity control of recovered KCl crystals

The amount of solids collected are dissolved in 1.5% nitric acid liquid solution to measure the concentration of K^+ , Na^+ , Ca^{2+} and Mg^{2+} elements through the atomic absorption method. Table 4-13 shows the mass of solids collected and the concentration of the elements in mg/L.

Table 4-13: Atomic absorption measurements for solid KCl samples

Experiments A/A	Mass of recovered salt (mg)	K^+ (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
A1	70	0.0916	0.8189	0.246	0.0001
A2	21	1.0518	0.8835	0.082	0.0001
A3	57	0.2271	6.1648	0.064	0.0037
A4	6	3.6812	4.9705	0.070	0.0001
A5	2	0.6078	2.2300	0.040	0.0001
B1	27	0.3902	3.9352	0.019	0.0001
B2	27	0.6783	2.8157	0.023	0.0001
B3	27	0.3975	3.7197	0.016	0.0001
B4	18	0.1997	2.7130	0.015	0.0001
B5	1.5	0.5851	0.4081	0.065	0.0849
B6	1	0.6794	0.3846	0.031	0.0001



B7	10	11.9952	5.4080	0.232	0.0171
B8	0.5	0.3977	0.2931	0.023	0.0031
C1	59.5	0.8669	7.7236	0.013	0.0001
C2	7.5	4.9855	7.0533	0.089	0.0025
C3	1	0.9090	0.8953	0.081	0.0001
C4	6	2.8082	6.1888	0.086	0.0029
D1	0.7	0.4364	0.2742	0.032	0.0028

From Table 4-13 presence of K^+ is confirmed. In most measurements, Na^+ concentration appears high, but some of this may be due to floating agent (Sodium dodecyl sulfate, $C_{12}H_{25}SO_4Na$). There is also a small amount of Ca^{2+} , probably in the form of gypsum ($CaSO_4 \cdot 2H_2O$) and $CaSO_4$. Concentration of Mg^{2+} is low in all samples. Then, based on the K^+ concentration and the mass of each solid (Table 4-13), their % purity in KCl is calculated. Results are shown in Table 4-14.



Table 4-14: Calculation of KCl salts purity

Experiments A/A	Floating agent % vs mixed salt treated	Granulometry (μm)	% Salt recovery	% Purity
A1*	0.50	-	221	6.3
A2*	0.50	-	92	23.9
A3*	0.25	-	123	1.9
A4*	0.25	-	49	28.8
A5*	0.10	-	43	14.5
B1*	0.10	-	67	6.9
B2*	0.50	-	110	11.9
B3*	0.05	-	86	7.1
B4*	0.05	-	49	5.3
B5*	0.10	<180	37	19.3
B6*	0.10	<180	37	31.0
B7*	0.10	180 -1000	49	57.3
B8*	0.10	180 -1000	61	40.0
C1*	0.05	-	110	7.0
C2*	0.05	-	80	31.9
C3*	0.10	-	43	44.0
C4*	0.10	-	61	22.3
D1**	0.03		90	60

*Sodium dodecyl sulfate

**Hexadecyl Trimethyl Ammonium Bromide

By using higher amount of Sodium Dodecyl Sulfate, high recovery is achieved even more than 100% which means that apart from KCl, also NaCl crystals are raised up to the surface through froth. When lower amount of Sodium Dodecyl Sulfate is used, there is lower recovery ratio but some experiments resulted with better purity; high purity is achieved when 0.10% of the flotation agent vs mixed salt is used with a 180-1000 μm granulometry range (B7 experiment).

Apart from Sodium Dodecyl Sulfate, another flotation agent is tested (Hexadecyl Trimethyl Ammonium Bromide) with an even smaller amount of 0.03% and the preliminary results show that a 90% recovery of salt can be achieved with a purity of 60% in KCl.



5. Next steps

The design of the Pilot plant 4, with a capacity of 500 L/day, (Figure 5-1) (WalNUT D2.8), derives from the different scenarios that are evaluated in the previous sections of the lab-scale (200 mL, 50 L brine) experiments. The final design of Pilot plant 4 was derived from the results of the lab-scale experiments described in the previous paragraphs. In detail, the recovery of Mg and Ca will be done through precipitation of $\text{Mg}(\text{OH})_2$ and CaCO_3 with the addition of NaOH and Na_2CO_3 respectively as described in [Section 3.5](#). Following Calcium and Magnesium removal brine analyses show that except of Na and Cl ions brine contains SO_4^{2-} anions. To remove the sulphates mainly with the form of Na_2SO_4 the addition of a nanofiltration system is decided ([Section 4.1.4](#)). After the removal of divalent ions the brine contains mainly Na, Cl and K ions.

For the recovery of NaCl, KCl and desalinated water the permeate of the NF system it is decided to be concentrated more. For this reason, the brine using an MED evaporator and crystalliser. From these two systems high purity water as well as a mixed salt of NaCl and KCl will be recovered. The most appropriate way to separate KCl from NaCl at this stage as the lab-scale experiments show is to use a flotation cell with a flotation agent ([Section 3.7](#)). The main operational parameters of all the above systems are identified in the results section.

The preliminary design and PID of the reactors prototype at pilot scale will be developed accordingly to the above results. The main compartments of the pilot has been ordered and it is expected that it will be integrated and installed in Lavrion Technological and Cultural Park in the next months.

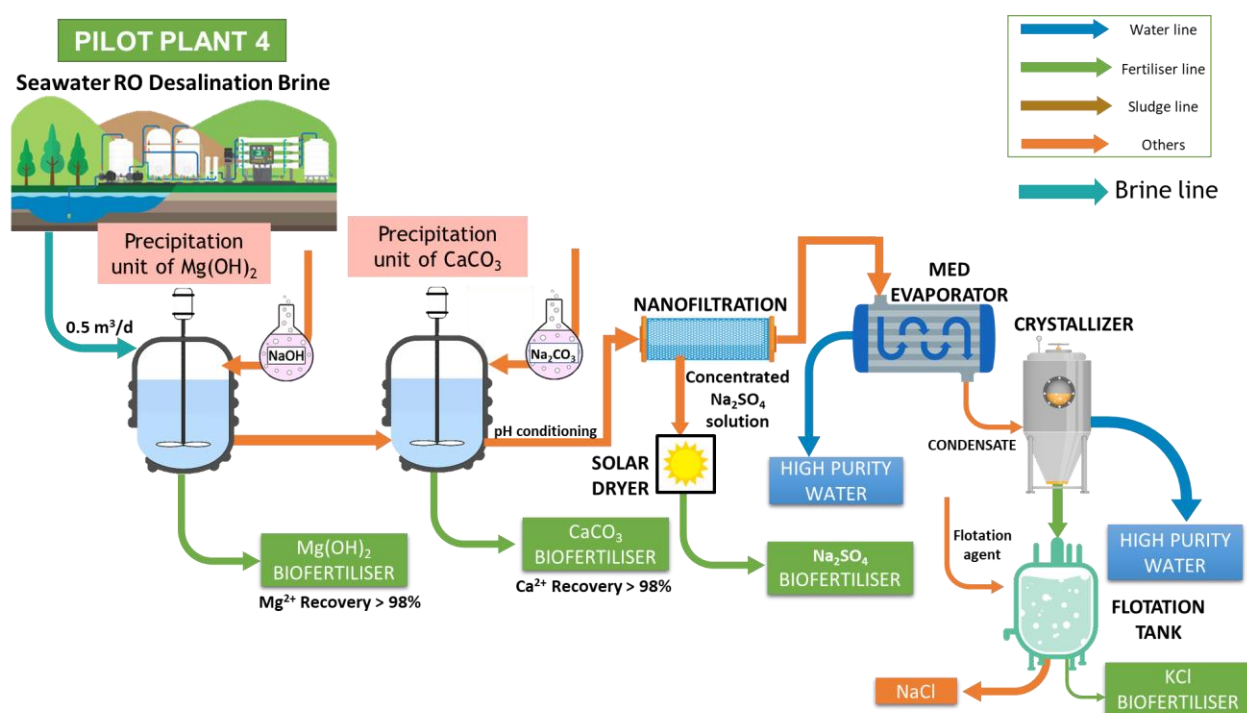


Figure 5-1. Process flow diagram of the proposed seawater brine treatment. The pilot unit is designed (D2.8) to treat 0.5 m³/d of the waste stream in a semi-automatic mode and will be controlled by an advanced programmable logic controller (PLC).



6. Conclusions

The main achievement of this work is the proof that macro and micronutrients can be recovered from the brine produced by an RO desalination plant. Furthermore, this work contributes to the definition of the main designing of the pilot system parameters and their values.

To achieve the recovery of water and salts from RO desalination brine next steps should be followed:

- $\text{Mg}(\text{OH})_2$ recovery (by precipitation)
- CaCO_3 recovery (by precipitation)
- Separation of the divalent SO_4^{2-} from the brine (by nanofiltration).
- Brine concentration (by water evaporation)
- Recovery of a mixed salt of NaCl and KCl
- Separation of KCl from the mixed NaCl-KCl salt (by flotation).

The acquisition of end-products that add high value in the existing desalination plants, thus the alignment with the Circular Economy Package. A sustainable brine treatment leads to avoidance of its disposal in the sea and decreases its impact on the environment and aquatic life. Also recovery of nutrients from brine reduces the CO_2 emissions in comparison with the conventional methods of nutrients production. Moreover, this technology facilitates compliance with proposed regional/EU-27 regulations towards replacing the production of fossil-based fertilisers.



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