# Design of a Zero Liquid Discharge system for the recovery of $Mg(OH)_2$, $CaCO_3$ and KCl from seawater desalination brine to be used as Bio-Based Fertilizers

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## Introduction

- 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 specialized 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 practices in countries using large-scale desalination plants is to reject brine back to the sea, leading to degradation of local fauna and flora.
- Brine treatment can contribute to the minimization of the environmental footprint of desalination plants.
- This study summarizes preliminary investigations to achieve recovery of $Mg(OH)_2$, $CaCO_3$ and KCl, in contest of valuable micro and macro nutrients recoveries from desalination brine.

## Aim

The aim of this study was to investigate the process parameters for the optimization of $Mg(OH)_2$ , $CaCO_3$ and KCl recovery in terms of valorization of brine as a wastewater stream from the desalination plants. Potassium can be reused as a primary macronutrient, while $Mg^{2+}$ and $Ca^{2+}$ as micronutrients for the manufacturing of bio-based fertilizers.

## Materials & Methods

- Samples are taken from a desalination plant at south-east Athens.
- Lab-scale experiments were designed and conducted to treat 200 ml and 50 L samples of seawater RO desalination brine.
- Analyses were performed according to Standard Methods (APHA).
- The bench-scale experiments of the proposed seawater brine treatment methodology are described in Figure 1.

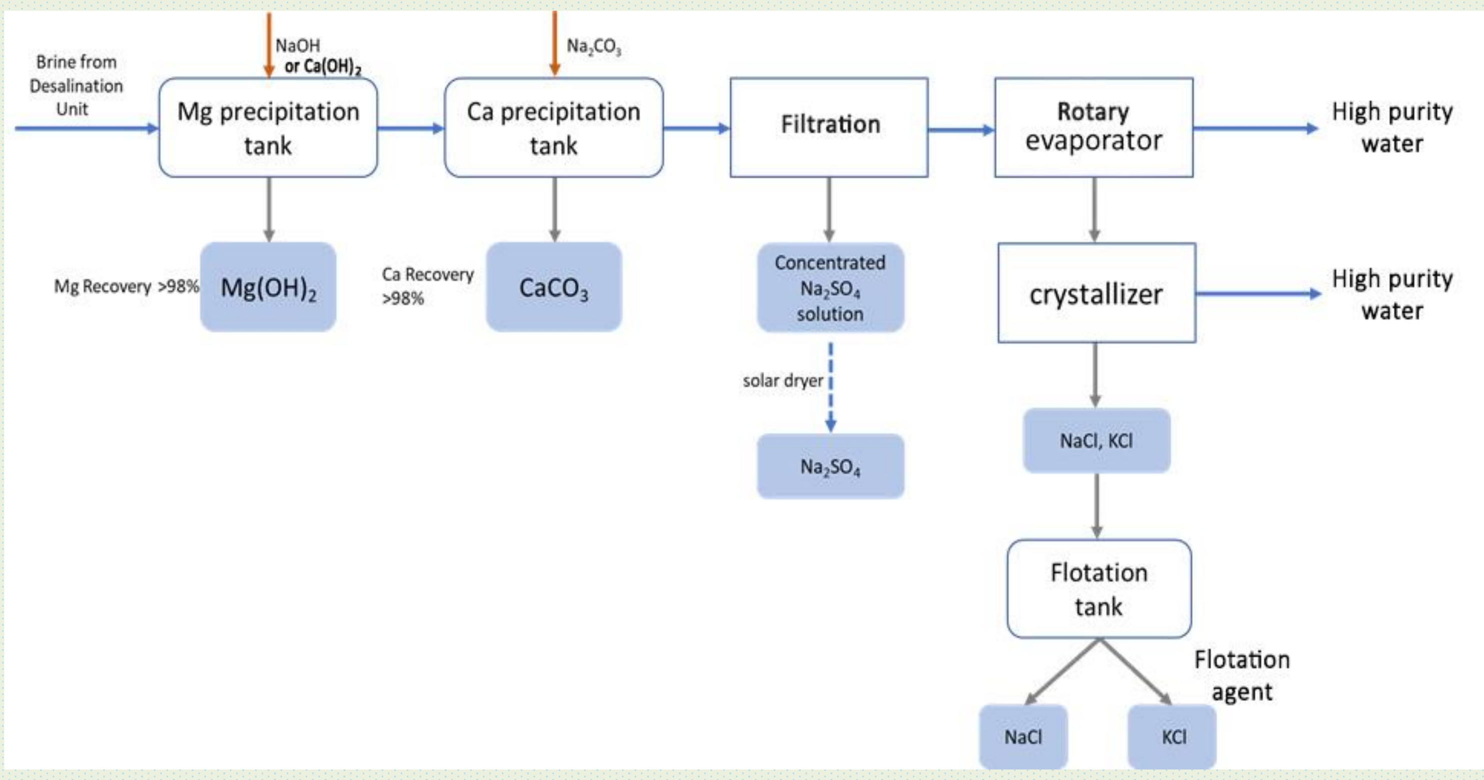



**Figure 1** Process flow diagram of the proposed seawater brine treatment

## Methodology

I. The first step of the brine treatment train is the precipitation of $Mg^{2+}$ in the form of $Mg(OH)_2$. The addition of NaOH and $Ca(OH)_2$ as reagents for $Mg^{2+}$ recovery is studied.
II. $Na_2CO_3$ is added to the brine after $Mg^{2+}$ removal for $CaCO_3$ precipitation.
III. After pH conditioning, the brine (without $Mg^{2+}$ and $Ca^{2+}$) will be led to filtration for $Na_2SO_4$ separation from NaCl - KCl rich stream.
IV. The monovalent salt stream is further concentrated by a rotary evaporator for the reclamation of high-purity water.
V. KCl is separated from the mixed salt of NaCl-KCl using a flotation technique.
VI. Sodium Dodecyl Sulfate and Hexadecyl Trimethyl Ammonium Bromide are used as flotation agents.

## Factorial design

For the recovery of $Mg^{2+}$ and $Ca^{2+}$ a $2^2$ factorial experiment was designed for statistical evaluation of the tests and results. The design parameters for assessment and optimization include mixing time and the quantity of reagent added, which are examined under various parameter values.
Below are presented the equations that resulted from the factorial experiments.

*Y = -2.228 + 0.102 * (NaOH (2M) addition) + 0.077 * (stirring time) – 0.003 * (NaOH (2M) addition) * (stirring time) (1)*

Equation 1 shows that when NaOH is used as a reagent for $Mg^{2+}$ recovery, its quantity is the most important factor. However, besides reagent's addition also stirring time is statistically important including its interaction with the reagent.

*Y = 0.295 + 0.47 * ($Ca(OH)_2$ addition) (2)*

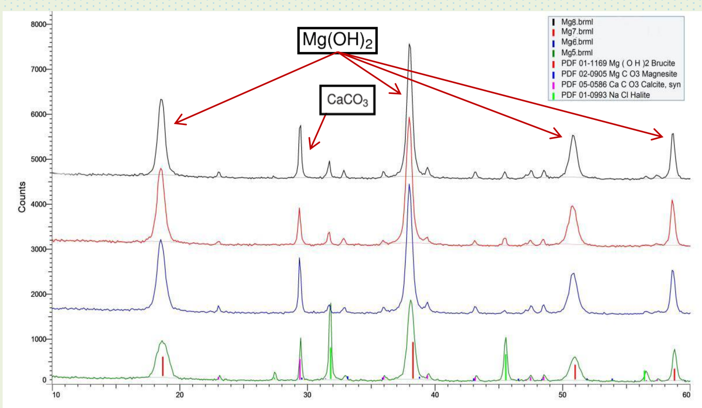
First degree equation (2) shows that the most important parameter for $Mg^{2+}$ recovery through $Ca(OH)_2$ addition is reagent's quantity, whereas reaction time is not considered as a factor that can affect the results.

*Y = 0.9372 + 0.0081 * ($Na_2CO_3$ addition) + 0.0002 * (stirring time) (3)*

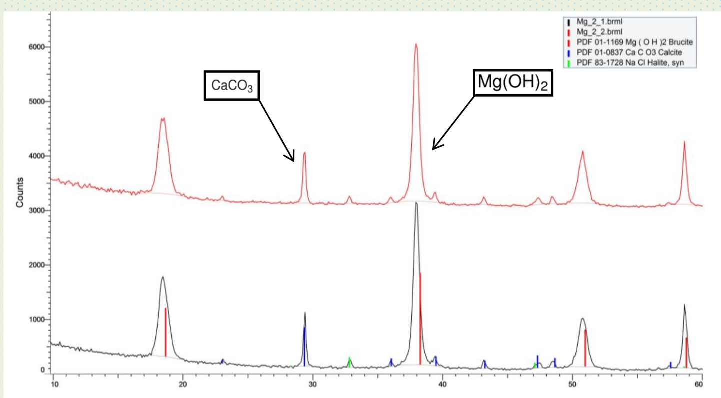
Equation (3) shows that $Ca^{2+}$ removal increases both with $Na_2CO_3$ addition and stirring time. However, reagent's addition has a greater effect on $Ca^{2+}$ removal because of its greater coefficient.

## Results

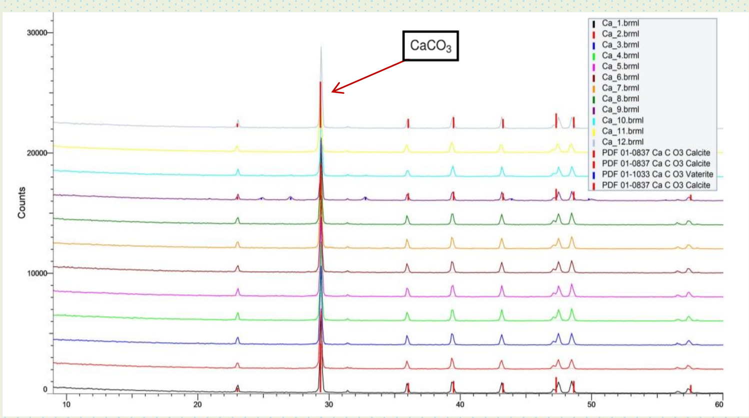
- Using sodium hydroxide (NaOH) as a reagent yields higher purity (~93%) for magnesium recovery salts when the stirring time of the mixture is longer (45 min).
- The purity of the recovered calcium carbonate ($CaCO_3$) salts remains unaffected by the conditions, with all trials exhibiting high performance (~99%).
- The important parameters for the recovery of potassium chloride (KCl), which affect the recovery ratio and salts' purity, are the type of flotation agent added its volume and the particle size of the recovered solid.
- Hexadecyl Trimethyl Ammonium Bromide showed better performance at an even smaller amount of 0.03% and reached a recovery of 90% with similar purity of 60% of recovered KCl.



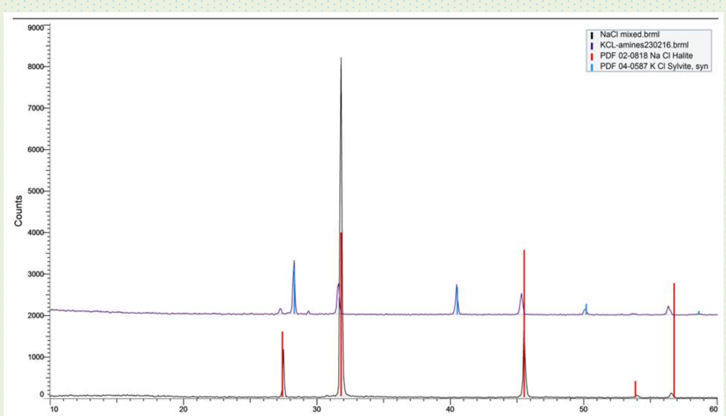

**Graph 1** XRD analysis of solid Mg(OH)2 using NaOH as reagent




**Graph 2** XRD analysis of solid $Mg(OH)_2$ using $Ca(OH)_2$ as reagent




**Graph 3:** XRD analysis of solid $CaCO_3$



**Graph 4** XRD analysis of recovered KCl using Hexadecyl Trimethyl Ammonium Bromide as flotation agent

## Conclusions

- The main achievement of this work is proof that macro and micronutrients can be recovered from the brine produced by an RO desalination plant.
- Recovered salts of $Mg(OH)_2$, $CaCO_3$ and KCl from this task are of such purity as to be used as nutrients for Bio-based Fertilizers.
- This work contributes to the definition of the main designing of the pilot system parameters and their values.
- The acquisition of end-products that add high value to the existing desalination plants, thus the alignment with the Circular Economy Package.
- This technology facilitates compliance with proposed regional/EU-27 regulations towards replacing the production of fossil-based fertilizers.

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