Nutrient recovery from seawater brine - a circular economy approach for Bio-Based Fertilizers production

S. Katsiolis , J. Novakovic, I.A. Athanasoulia, M. Kyriazi, K. Moustakas, D. Malamis
National Technical University of Athens, School of Chemical Engineering,
Unit of Environmental Science Technology,
9 Iroon Polytechniou Str., Zographou Campus, GR-15780 Athens, Greece
(E-mail: spykatsiolis@mail.ntua.gr)

Spiridon A. Katsiolis
Contact details:
spykatsiolis@mail.ntua.gr

Introduction

- Water is one of the most important natural resources and a key to the survival of living organisms. Due to its importance, it needs to be managed in a sustainable way since it is an environmental, social and economic asset.
- A commonly method used to produce fresh water in the areas facing scarcity problem is seawater desalination by reverse-osmosis.
- This method produces 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.
- 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

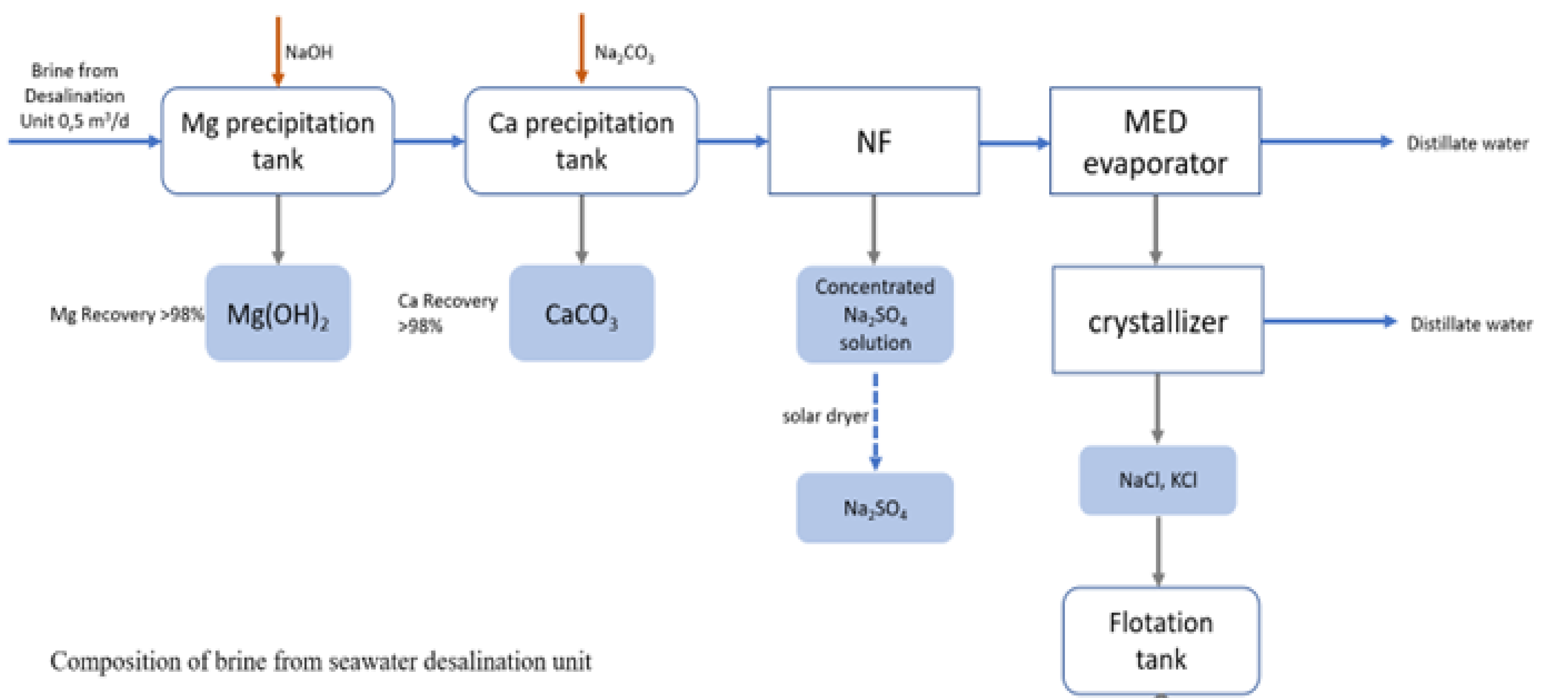
The aim of this study was to investigate the process parameters for the optimization of $Mg(OH)_2$, $CaCO_3$ and KCl recovery in terms of valorization of brine as a wastewater stream from the desalination plants. Potassium can be reused as a primary macronutrient, while Mg^{2+} and Ca^{2+} as micronutrients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

Materials & Methods

Samples were taken from a small desalination plant of a hotel in Sounio, south-east Athens, collected and stored at ambient conditions.

Analysis were performed according to Standard Methods (APHA).

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



	K	Na	Ca	Mg	Cl	SO_4^{2-}	HCO_3^-
mg/l	813	19674	1552	2736	35400	3820	238
	815	19521	1523	2739	37000	3840	238

Figure 1 Process flow diagram of the proposed seawater brine treatment

Methodology

1. Precipitation of the Mg^{2+} from seawater brine into $Mg(OH)_2$ after adding NaOH in the brine and stirring.
2. Na_2CO_3 was added in the brine after Mg^{2+} removal for $CaCO_3$ precipitation.
3. After pH conditioning, the brine (without Mg^{2+} and Ca^{2+}) can be led to NF unit for Na_2SO_4 separation from NaCl-KCl rich stream.
4. Monovalent salt stream is further concentrated by MED evaporator and crystallizer and KCl is separated from NaCl by flotation.
5. The KCl crystals were collected and washed with ethanol.

Factorial design

Recovery of Mg^{2+} and Ca^{2+} was designed through a 2^2 factorial experiment of two parameters (reactant's quantity and stirring time).
Experiments realized under various conditions and combinations of parameters. The parameters are presented at the table below accompanied by the equations that resulted from the analysis. The upper and lower level are defined based on the symmetry of stoichiometry.

$X_1 \rightarrow$ reactant quantity $X_2 \rightarrow$ stirring time $b_0, b_1, b_{12} \rightarrow$ importance factors
Equation 1: For $Mg(OH)_2$ recovery the important parameters are X_1 and the interaction of X_1 and X_2.
Equation 2: For $CaCO_3$, factorial design could not be applied because the extreme values where arithmetically close to the stoichiometric ones.

Factorial parameters			Factorial levels		
	unit		-1	0	+1
Reactant's quantity	g/ml	X_1	90 % of stoichiometry	stoichiometry	110% of stoichiometry
Stirring time	min	X_2	15	30	45

Table 2 Parameters and levels of the factorial design

$$Y = b_0 + b_1 {}^* X_1 + b_{12} {}^* X_1 X_2 = 1.549 - 0.156 {}^* X_1 - 0.098 {}^* X_1 X_2$$

Equation 1 First degree equation for Mg^{2+} recovery

$$Y = b_0 = 0.999$$

Equation 2 Zero degree equation for Ca^{2+} recovery

Results

- 99.7 % recovery of $Mg(OH)_2 \rightarrow$ 90 % of NaOH stoichiometric quantity and 45 min. stirring.
- 100% precipitation of $CaCO_3$ $\rightarrow$ stoichiometric quantity of Na_2CO_3 and 30min. stirring.
- XRD analysis (Fig. 2) shows the presence of Brucite and Magnesite and some $CaCO_3$ impurities in precipitated $Mg(OH)_2$.
- Figure 3 demonstrates Calcite – Portlandite precipitation
- Figure 4 presents XRD analysis of Sylvite (KCl) (with traces of Potassium sulfate) separated from NaCl
- Recovered KCl crystals are shown in Image 1.

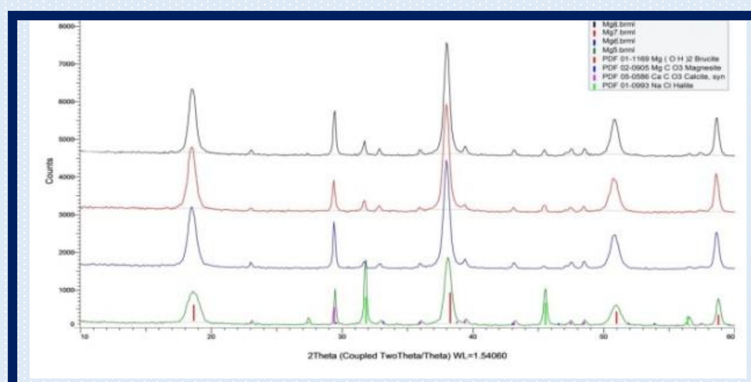


Figure 2. XRD analysis of precipitated **$Mg(OH)_2$**

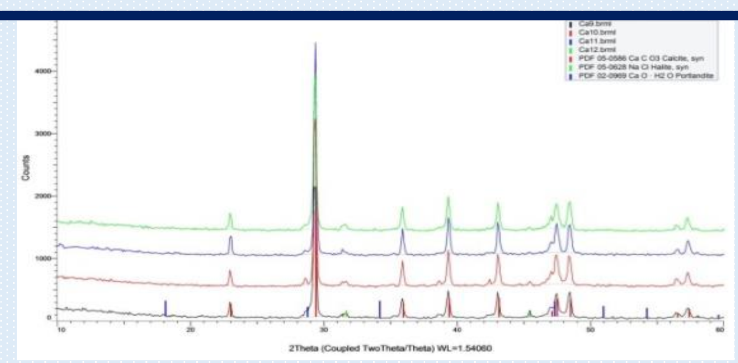


Figure 3. XRD analysis of precipitated CaCO3

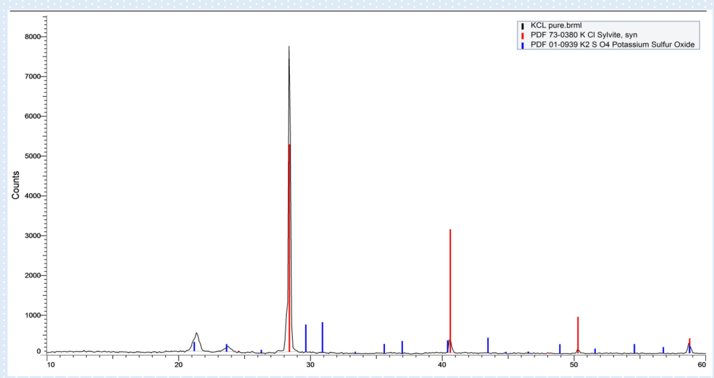


Figure 4. XRD analysis of separated **KCl**

$CaCO_3$

Image 1. KCl crystals

Conclusions

- The main contribution of this work is the acquisition of end-products that add high value in the existing desalination plants, thus the alignment with EU Circular Economy Package and sustainability in the agricultural sector.
- In addition, recovery of nutrients from brine reduces the CO_2 emissions in comparison with the conventional methods of nutrients production.
- This technology facilitates compliance with proposed regional/EU-27 regulations towards replacing the production of fossil-based fertilizers.
- The introduced SB technology framework outlines a sustainable, competitive Zero Liquid Discharge approach to completely convert SB into reclaimed water and salts of commerce.
- The results of this preliminary work justify for the feasibility of the process upscaling.

Acknowledgments
This work was funded by the WALNUT project (Horizon 2020, Project Number 101000752)

References
Le Dirach, J., Nisan, S., & Poletiko, C. (2005). Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems, Desalination , Saint Paul-lez-Durance, France.
Arash Shahmansouri, Joon Min, Liyan Jin, Christopher Bellona (2015), Feasibility of extracting valuable minerals from desalination concentrate: a comprehensive literature review, Journal of cleaner production, NY, USA.
T. Jeppesen, L. Shu, G. Keir, V. Jegatheesan, (2009), Metal recovery from reverse osmosis concentrate, Journal of cleaner production, Townsville, Australia