INNOVATIVE BRINE TREATMENT STRATEGY BASED ON EDM AND VALUABLE COMPOUND RECOVERY

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Abstract

It is well known that desalination plants generate huge amount of brines which are discharged into the receiving environment and nowadays it is necessary to adopt new brine management strategies to minimize their potential negative impact. In this sense, LIFE+ Zelda project is proposed in order to demonstrate and disseminate the technical feasibility and economical sustainability of decreasing the overall environmental impact of desalination systems by adopting a new brine management strategy based on the use of electrodialysis metathesis (EDM) and valuable compound recovery processes with the final aim of reaching a zero liquid discharge process. The members of the project consortium are Abengoa Water (Spain), Fundació CTM Centre Tecnològic (Spain), Fujifilm (The Netherlands) and WssTP (EU).

Keywords: brine management; electrodialysis metathesis; zero liquid discharge

I. INTRODUCTION

Most current brine management strategies discharge brines into the environment and constitute one of the most important environmental impacts of desalination technologies, especially in those regions with high vulnerability to salinity gradients [1]. The Life+ ZELDA project (LIFE12 ENV/ES/000901), which started on July 2013, aims to demonstrate and disseminate the technical feasibility and economical sustainability of decreasing the overall environmental impact of desalination systems by adopting brine management strategies based on the use of electrodialysis metathesis (EDM) and valuable compound recovery processes with the final aim of reaching a zero liquid discharge (ZLD) process.

Differently from conventional electrodialysis, the EDM configuration is designed to separate the EDM concentrate in two waste streams of highly soluble salts: one contains sodium with anions and the other contains chloride with cations. This way, the sparingly soluble salts such as CaSO4, MgSO4 or CaCO3 are not produced in either of the two concentrate streams [2].

Once the brine has been treated with the EDM, the two generated concentrate streams will be treated by a compound recovery process in order to obtain valuable compounds and reach a ZLD desalination process [3-4].

The members of the project consortium include Fujifilm (The Netherlands), who has developed high performance ion-exchange membranes for the EDM process, Abengoa Water (Spain), responsible for the compound recovery process, the Water Supply and Sanitation Technology Platform (WssTP), which will be in charge of the dissemination activities and Fundació CTM Centre Tecnològic (Spain), who will be responsible for laboratory and modeling activities and will also perform the coordination tasks of the project. The multinational partnership gives to the Zelda project an important transnational approach and their different profiles and activities provide the necessary means to assure a good project development. This paper summarizes the results from the modeling and experimental validation of different scenarios regarding compound recovery in the ZLD stage for desalination brines.

II. MATERIAL AND METHODS

In order to reach the objectives of the Life+ ZELDA project, the two stages of the new brine management strategy will be tested and optimized at bench scale and also at pilot scale.
For the EDM stage, it has developed novel ion-exchange membranes specifically designed to increase the performance of the EDM process. The membranes will be firstly tested at bench scale using real brines from full scale desalination plants, and several operational conditions will be assessed in order to evaluate its performance and to establish the best operational conditions to properly design the pilot plant.
At the same time, several studies will be performed to evaluate which valuable compounds can be easily recovered from the EDM concentrates using chemical speciation software and also bench scale experimentation. Operational conditions such as feed composition and temperature, pH and residence time will be evaluated.
Using the results obtained in bench-scale experimentation, the two stages of the new brine management system will be carefully designed, constructed and coupled to obtain a reliable pilot plant to treat brines from seawater and brackish water desalination plant.
Finally, in order to demonstrate the environmental benefits of the new EDM-ZLD technology in the treatment of desalination brine, the constructed pilot plant will be installed and operated in two desalination plants, firstly in a seawater desalination plant, and then in inland brackish water desalination plant. Furthermore, the environmental benefits and the economic impact of the new process will be assessed by means of the life-cycle assessment and life-cycle costs analysis.

III. RESULTS

III.1 Compound recovery strategies for seawater desalination brines

Several precipitation routes have been proposed in order to evaluate different scenarios to select the most appropriate one for each case. The scenarios have been firstly studied theoretically by using chemical speciation software (Phreeqc), and then, once the best scenario has been identified, it has been evaluated experimentally at bench scale to validate the simulations. A typical seawater desalination brine composition is presented in Table 1.
Brine purification is one of the most important steps for brines valorization. The presence of different impurities in the generated brines can seriously hamper the correct process performance. The easiest way to purify the brines consists in selectively precipitate the different impurities by adding the suitable reagents. Figure 1 shows the different scenarios that have been defined for brine purification.

Table 1. Average brine composition of seawater desalination plant

Parameter	Units	Average value
TDS	mg/L	58150
Chloride	mg/L	30540
Sodium	mg/L	17140
Calcium	mg/L	961
Magnesium	mg/L	1880
Potassium	mg/L	545
Sulphate	mg/L	4450
Bicarbonate	mg/L	666
Nitrate	mg/L	14.9
Silice	mg/L	23.1
Boron	mg/L	4.83
Temperature	ºC	20.5
pH	u pH	7.49

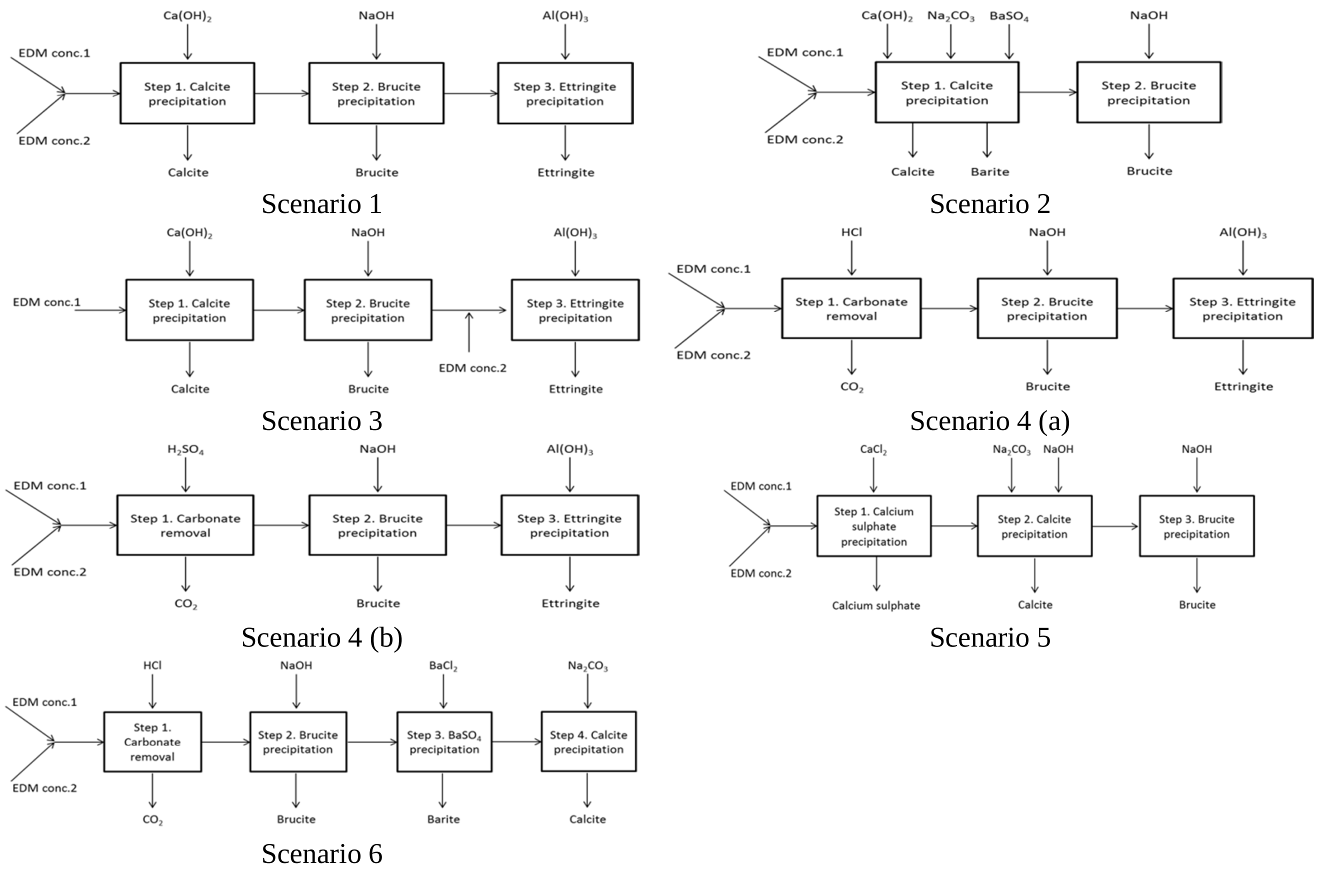

Figure 1. Routes to recover valuable compounds from seawater RO brine

III.2 Simulations using preliminary data

In order to evaluate the different precipitation routes, simulations using Phreeqc chemical speciation software have been performed. A first estimation of the two EDM concentrates composition has been predicted (Table 2) and used in order to check the best compound recovery strategy.

Table 2. First theoretical approach of EDM concentrates composition using seawater RO brine

Parameter	Units	EDM Conc.1	EDM Conc.2	Mix of the two currents
Sodium	mg/L	32800	43200	38000
Calcium	mg/L	3170	294	1730
Magnesium	mg/L	3320	140	1730
Potassium	mg/L	1330	131	730
Chloride	mg/L	66200	61200	63700
Sulphate	mg/L	209	8040	4120
Bicarbonate	mg/L	1120	1120	1120

The results obtained in the simulations for scenarios 1, 2, 4a, 4b, 5 and 6 have been compared. The following tables (3-5) show the composition of the final NaCl content, the amount of reagents needed and the compounds recovered in each case.

The analysis of the results reveals that the best option to recover valuable compounds from seawater desalination plants correspond to Scenario 6.

Table 3. Final concentrations obtained in the six different scenarios proposed for treating seawater brines

	units	Initial concentration	Scenario 1	Scenario 2	Scenario 4.a	Scenario 4.b	Scenario 5	Scenario 6
TIC	mg/L	38000	0.53	63.7	1.2	0.43	17.4	400
Ca^{2+}	mg/L	1730	0.23	9.92	260	11.7	37.4	0.35
C^{l-}	mg/L	1730	65540	64200	69110	68200	71680	94780
K^{+}	mg/L	730	784	701	785	776	784	773
Mg^{2+}	mg/L	63700	0.01	0.02	0.012	1.23e-02	0.082	0.64
Na^{+}	mg/L	4120	42680	41600	44560	45400	46660	62900
SO_4^{2-}	mg/L	1120	320	277	3.3	2260	783	915
pH		7.5	12	11.9	12	12	11.5	11

Table 4. Amounts of reagent used in each scenario proposed for treating seawater brines

	units	Scenario 1	Scenario 2	Scenario 4.a	Scenario 4.b	Scenario 5	Scenario 6
$Ca(OH)_2$	g/L	0.7	0.7				
HCl	mol/L			4.96e-4		4.96e-4	
H_2SO_4	mol/L				2.48e-4		
NaOH	g/L	6.9	6.16	6.12	6.12	6.12	7
$NaAlO_2$	g/L	3.89		4.05	2.13		
BaCl2	g/L		8.02			8.32	
Na_2CO_3	g/L		1.35			5.04	42.5
$CaCl_2$							42

Table 5. Amount of compound recovered in each scenario proposed for treating seawater brines

	units	Scenario 1	Scenario 2	Scenario 4.a	Scenario 4.b	Scenario 5	Scenario 6
Calcite	g/L	1.87	4.95			4.72	38.4
Brucite	g/L	4.5	4.05	3.98	3.98	3.98	4.1
Ettringite	g/L	16		20.2	9.5		
Barite	g/L		9			9.32	
Gypsum	g/L						0.80

III.2 Experimental validation of selected route

Selected route has been validated at laboratory scale using, first a synthetic solution and, later on, a real EDM effluent. The synthetic feed solution to perform the precipitation experiments at bench scale has been prepared considering the composition used in the simulations. Table shows the different ion concentrations of the feed solution obtained.

Table 6. Synthetic feed water composition for the bench scale experimentation

Parameter	Concentration (mg/L)
Sodium	38000
Calcium	1730
Magnesium	1730
Potassium	730
Chloride	63700
Sulphate	4120
Bicarbonate	1120

The route that has been validated is the one showed in Figure 2.

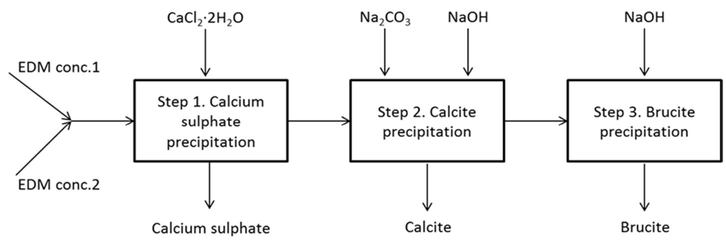

Figure 2. Diagram of the recovery route validated at bench scale

After each precipitation step, the solution containing the precipitated solid has been filtrated in order to separate the solid from the solution before starting the following stage. All the collected samples have been analyzed and the ion concentration obtained has been compared with the results obtained in the simulations (Table 7).

Table 7. Compositions after each precipitation step (seawater brine, synthetic sample)

	Units	End of 1st step (T)	End of 1st step (R)	End of 2nd step (T)	End of 2nd step (R)	End of 3rd step (T)	End of 3rd step (R)
Cl^-	mg/L	93900	81700	93100	76300	93040	78600
Na^+	mg/L	43500	33700	60700	49900	65500	69800
Ca^{2+}	mg/L	12600	14500	0.5	87.6	0.14	2.2
SO_4^{2-}	mg/L	1570	1960	1060	1470	1060	1410
Mg^{2+}	mg/L	1800	1630	1790	1180	1.5	1.1
TIC	mg/L	126	133	125	82	125	83
pH	upH	5.5	6.26	8.75	8.75	11	12.48

(T): theoretical, predicted in the simulations / (R): real, analyzed in the experiment samples

As it can be observed in the previous table, the results predicted in the simulations are quite similar than the ones obtained in the bench scale experiments. Just highlight that calcite does not precipitate entirely in the first step, so the calcium concentration decreases from the second to the third precipitation step.

On the other hand, it can also be observed that brucite precipitation starts in the second step, so it seems that it will not be easy to recover all the brucite in the last step of the process.
Real samples obtained have also been used to validate the precipitation route for seawater brines. The concentrate streams used were firstly characterized and with the obtained compositions the theoretical simulation of the scenario has been done in order to estimate the necessary amount of reagents. With the simulation results, the bench scale experimentation has been done.
The concentrate sample used was obtained from a set of experiments done using commercial monoselective membranes: ACS/CMS (Asahi Glass) with brine as the feed solution. Table 8 shows the initial composition of the brine together with the concentrate composition and the concentration factor (C.F) obtained for each ion.

Table 8. Feed water and concentrate stream compositions in Fujifilm experiment using ACS/CMS membranes

Parameter	Sewater brine (mg/L)	ED Concentrate at 250 A/m2 (mg/L)	C.F
Chloride	29718	104140	3.50
Nitrate	108	401	3.71
Sulphate	4182	1931	0.46
Sodium	15005	69310	4.62
Potassium	589	2464	4.18
Calcium	893	832	0.93
Magnesium	1667	1058	0.63
TIC	84	50.4	0.60

Using this concentrate composition, the simulation of the selected scenario for the seawater case has been done. As it can be observed in the previous table, the sulphate concentration in the concentrate stream is lower than < 4 g/L. Therefore, the first step of the precipitation route, which corresponds to the addition of $CaCl_2$ to reduce the sulphate concentration, will not be necessary.
Using the real sample and the previous amounts of reagents, the precipitation experiment has been done and the composition after each step has been determined.
Table 9 show the comparison of the real concentrations obtained with the ones estimated in the simulation.

Table 9. Compositions after each precipitation step (Almeria brine, ACS/CMS membranes)

Ion	Units	End of 1st step (T)	End of 1st step (R)	End of 2nd step (T)	End of 2nd step (R)
Sodium	mg/L	73000	80900	74000	76700
Chloride	mg/L	103000	96000	103000	97400
Sulphate	mg/L	2270	2078	2310	2030
Calcium	mg/L	0.4	44	0.2	1
Magnesium	mg/L	1050	881	0.01	9
TIC	mg/L	700	650	700	515
pH	upH	9.39	9.35	12.3	12.5

(T): theoretical, predicted in the simulations / (R): real, analyzed in the experiment samples

The conclusions after comparing the theoretical and the real compositions obtained, are quite similar than the ones observed for the synthetic sample (Table 8).
The results predicted in the simulations are similar than the real ones obtained in the bench scale experimentation. However, the calcite is not entirely precipitated in the first step, whereas brucite starts

its precipitation in the first step, making it difficult to completely separate the calcite and brucite precipitations.

IV. CONCLUSIONS

In the framework of the ZELDA project a compound recovery route for seawater desalination brines after EDM treatment have been selected and evaluated using modeling and simulation and validated at laboratory scale. The route includes calcium sulphate precipitation, followed by a calcite precipitation and finally brucite precipitation in order to obtain a high concentrated sodium chloride stream.
Results obtained from simulations are quite similar to those performed at laboratory scale showing that the proposed EDM-ZLD process is a feasible way to manage brines generated at seawater desalination plants.
Next steps in the ZELDA project will be to design and construct a prototype of the proposed process and test its performance in a real seawater desalination plant to further demonstrate the feasibility of the proposed process.

V. REFERENCES

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