European Twinning for research in Solar energy to (2) water (H2O) production and treatment technologies
GA Number: 101079305
European Research Executive Agency REA.C3

Sol2H2O

Funded by the European Union

Fast Track School #2

Introduction to Solar-driven Water production & Treatment technologies and brine treatment processes Beyond State of the Art

POZO IZQUIERDO, 25.-26.09.2024

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Sol2H2O

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Andrea Cipollina

MF-PFR for selective recovery of Mg and Ca from brines

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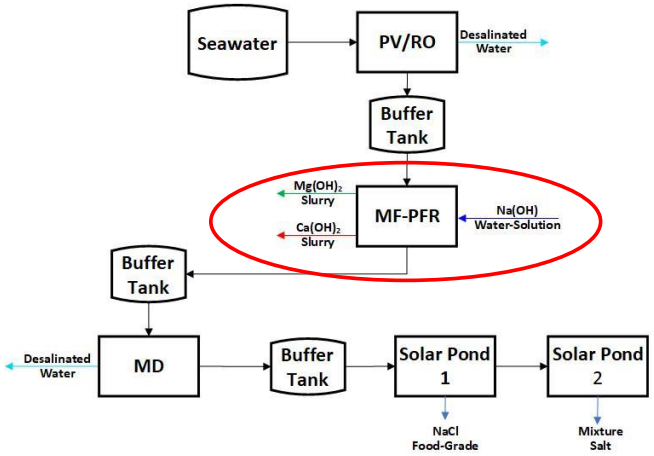
Minerals extraction in sustainable desalination

The SOL2H2O integrated process scheme:



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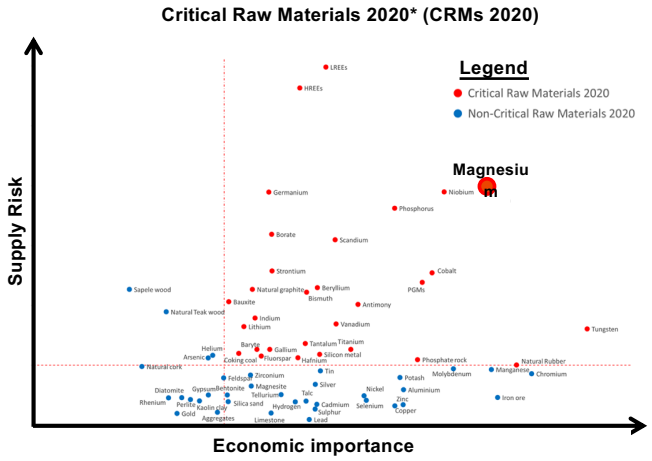
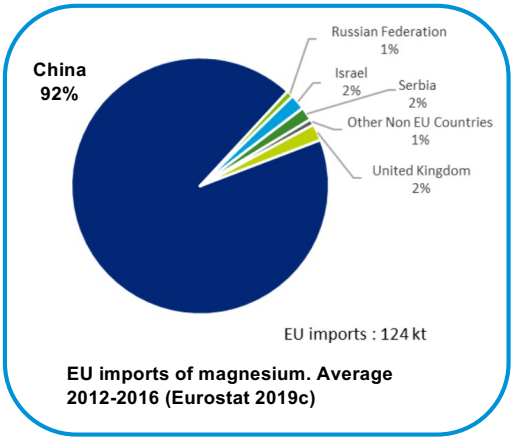
Critical $Mg(OH)_2$ supply





EU imports of magnesium. Average 2012-2016 (Eurostat 2019c)

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Development of a novel crystalliser: the MF-PFR

GOALS:

-ACHIEVE HIGH RECOVERY of Mg and Ca;

- GUARANTEE HIGH PURITY of $Mg(OH)_2$;

- TRIGGERING CRYSTALS GROWTH and

- CONTROL AGGREGATION/AGGLOMERATION

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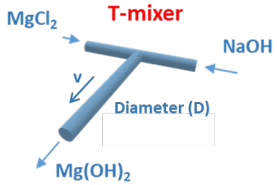
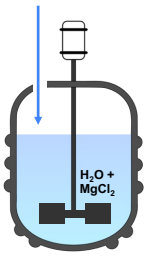
First steps towards Mg recovery from brines

Testing different reacting configurations &
Steps towards the scale-up



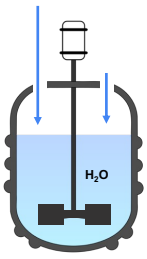
Ultra fast mixing
High supersaturation levels

Semi-batch



Fast mixing
Medium supersaturation levels

Double-feed Semi-batch



Fast mixing
Low supersaturation levels

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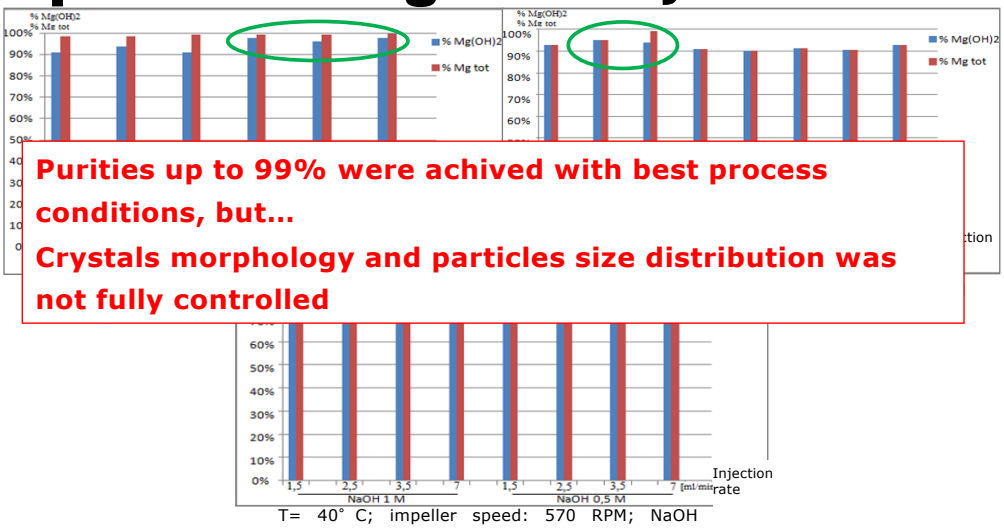
First steps towards Mg recovery from brines



Purities up to 99% were achived with best process conditions, but…

Crystals morphology and particles size distribution was not fully controlled

T= 40° C; impeller speed: 570 RPM; NaOH injection rate: 1,5-2,5-3,5-7 ml/min

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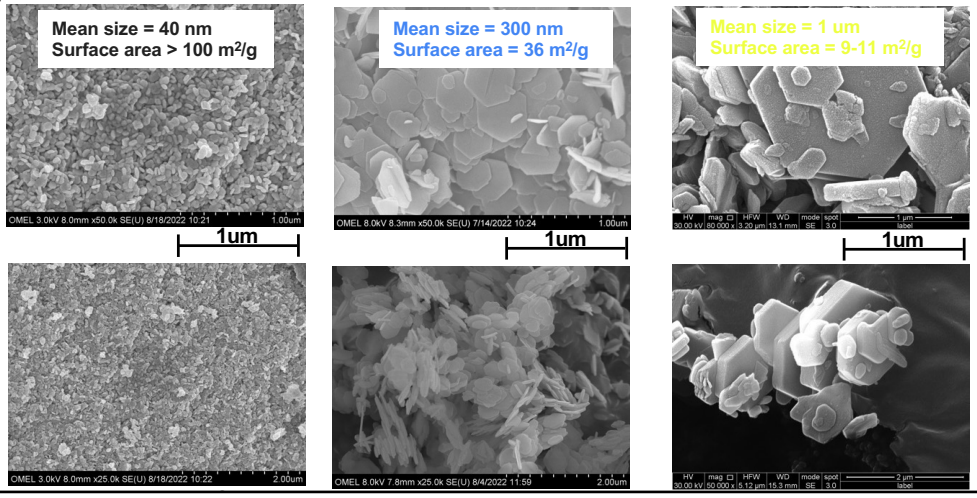
First steps towards Mg recovery from brines

How operating configurations affect size and morphology?

T-mixer product	Double-feed configuration	Commercial product Magnifin® H10
Mean size = 40 nm Surface area > 100 m²/g	Mean size = 300 nm Surface area = 36 m²/g	Mean size = 1 um Surface area = 9-11 m²/g



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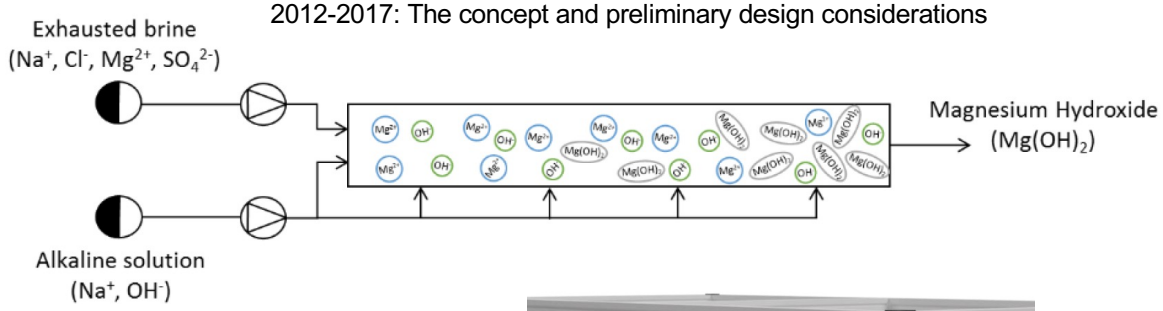
The idea of the multiple feed plug-flow

2012-2017: The concept and preliminary design considerations



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The idea of the multiple feed plug-flow

2017-2020: Design consolidation and patent application

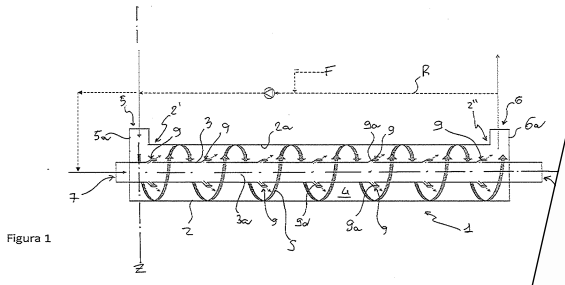
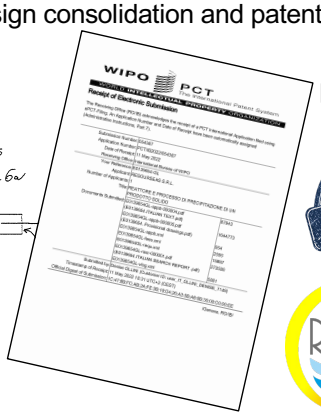


Figura 1



Italian Patent: Granted

(WORLD) PCT Patent: Under Examination

Academic Spin-off constituted in 2017

Bevacqua, M., Vassallo, F., Cipollina, A., Micale, G., Tamburini, A., Papapetrou, M., & Vicari, F. (2021). Reattore e processo di precipitazione di un prodotto solido (Patent No. Application IT 102021000012473).

Bevacqua, M., Vassallo, F., Cipollina, A., Micale, G., Tamburini, A., Papapetrou, M., & Vicari, F. (2022). Reactor and process for the precipitation of a solid product (PCT/IB2022/054367_PCT).

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Andrea Cipollina

MF-PFR implementation examples: past projects ZERO BRINE and WATER MINING

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 869467.

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R&D testing of the MF-PFR crystalliser

The ZERO BRINE project

Fig. 5. A picture of the novel proprietary crystallization reactor tested at the Brine Excellence Center laboratory of University of Palermo (a), then installed and operated at the premises of Plant One (Botlek, Rotterdam, NL) (b).

Vassallo, F., La Corte, D., Cancilla, N., Tamburini, A., Bevacqua, M., Cipollina, A., Micale, G., 2021. A pilot-plant for the selective recovery of magnesium and calcium from waste brines. Desalination 517, 115231. https://doi.org/10.1016/j.desal.2021.115231

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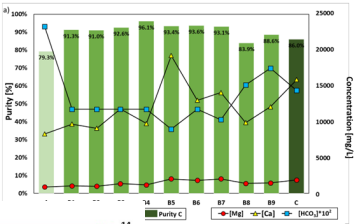
R&D testing of the MF-PFR crystalliser

The ZERO BRINE project

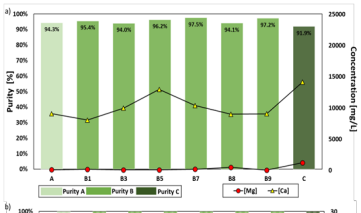
ZERO BRINE

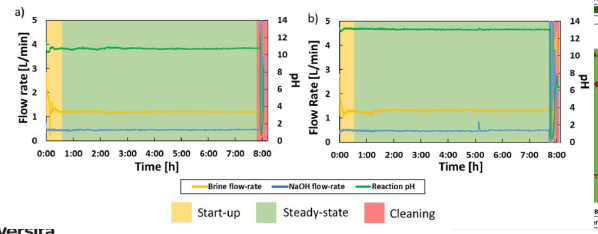
Brine nature: regeneration water for softening IX

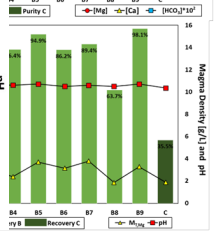
Magnesium precipitation

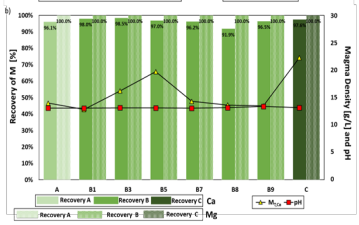


Calcium precipitation









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Vassallo, F., La Corte, D., Cancilla, N., Tamburini, A., Bevacqua, M., Cipollina, A., Micale, G., 2021. A pilot-plant for the selective recovery of magnesium and calcium from waste brines. Desalination 517, 115231. https://doi.org/10.1016/j.desal.2021.115231

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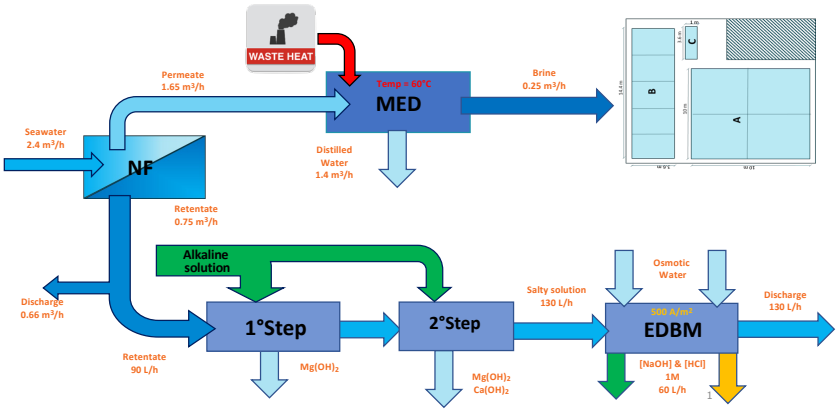
R&D testing of the MF-PFR crystalliser

The WATER MINING project

water mining
value for society



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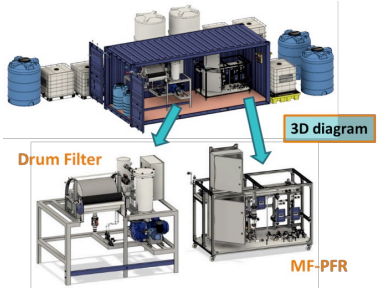
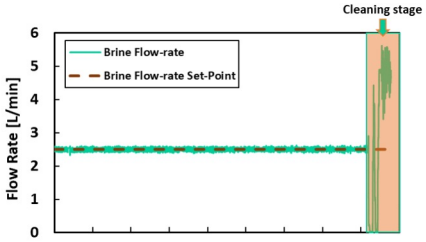
R&D testing of the MF-PFR crystalliser

The WATER MINING project



Working hours: 480
working days: 60



Mg recovery [%]	$Mg(OH)_2$ purity [%]	Removal (Mg/Ca) [%]	$Ca(OH)_2$ Purity [%]
97-99	95-99	95-99/90-98	50-91

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Sol2H2O

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MF-PFR implementation examples: ongoing activities to run beyond the State of the Art

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Sol2H2O

SEArcular MINE

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Andrea Cipollina

MF-PFR implementation scenario 1
The SEArcularMINE project

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 869467.

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R&D testing of the MF-PFR crystalliser

The SEArcularMINE project

SEArcular MINE

SEArcularMINE project

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R&D testing of the MF-PFR crystalliser

The SEArcularMINE project

SEArcularMINE project

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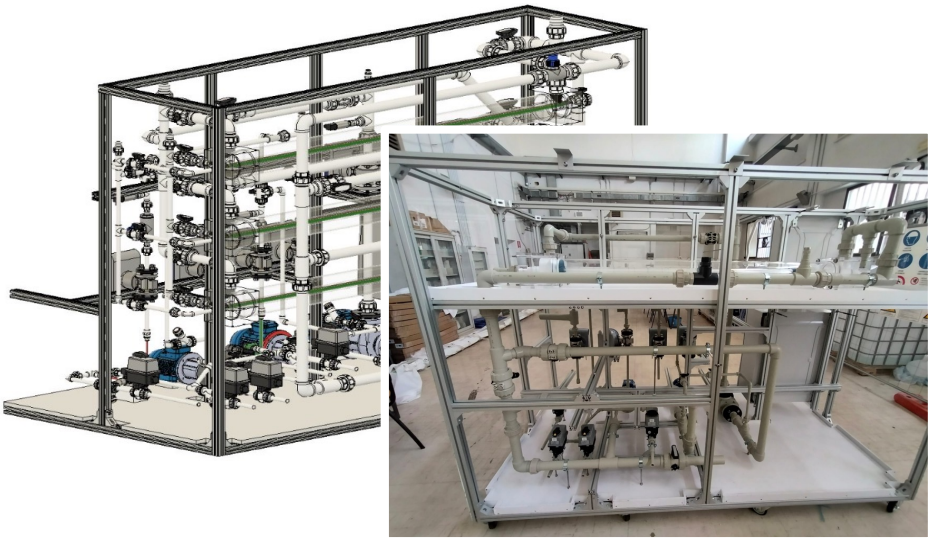

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R&D testing of the MF-PFR crystalliser

The SEArcularMINE project

SEArcularMINE project

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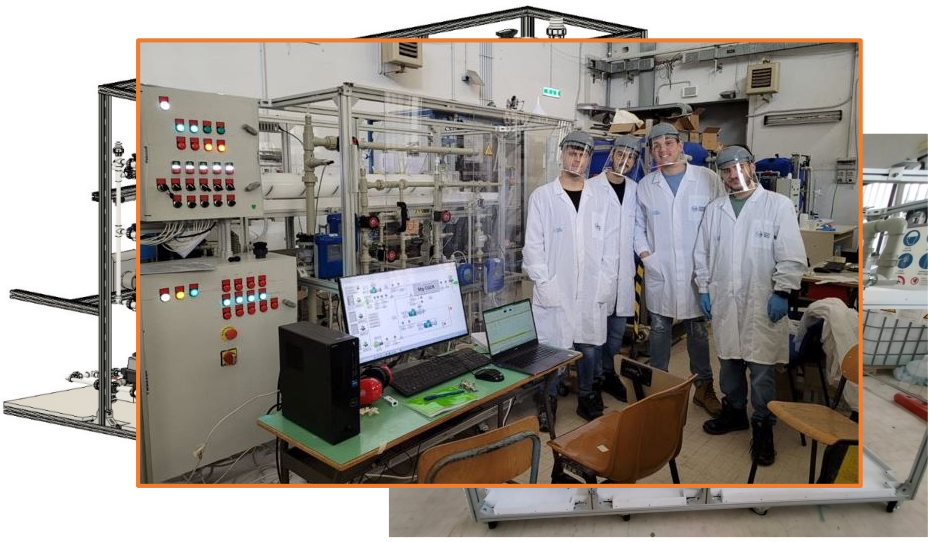

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Magnesium Hydroxide

Tests

Investigated parameters:
NaOH flowrate and pH variation (Test T)

	T1	T2	T3
NaOH Flow rate [L/h]	156	180	216
pH	10.3	11.5	12.7

$[Mg^{2+}]$=53.4 g/L
$[Ca^{2+}]$<LOQ

	M1	M2	M3
NaOH Flow rate [L/h]	75	89	105
pH	10.3	11.5	12.7

$[Mg^{2+}]$=24.3 g/L
$[Ca^{2+}]$<LOQ

SEArcularMINE project

Settling velocities, Filtration rate, SEM.

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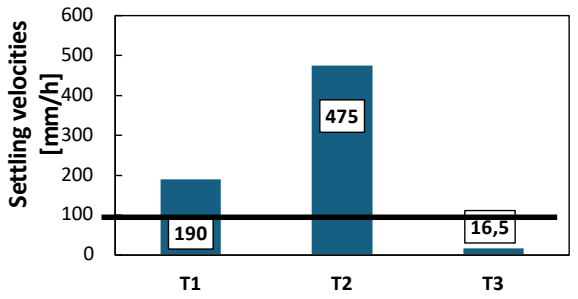
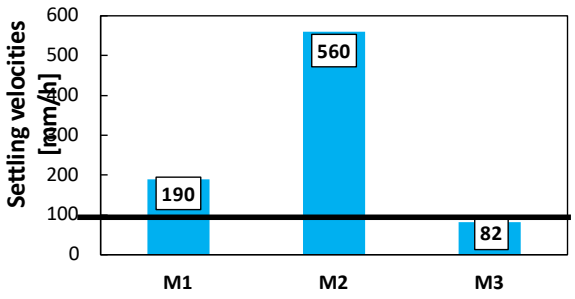
Magnesium Hydroxide

Analysis – Settling Velocities





SEArcularMINE project

Reference settling rate the literature [1].

[1] *M. Turek, W. Gnot, Precipitation of magnesium hydroxide from brine, Ind. Eng. Chem. Res. 34 (1) (1995) 244–250.* https://doi.org/10.1021/ie00040a025

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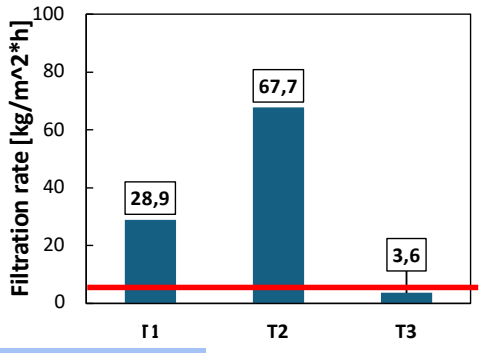
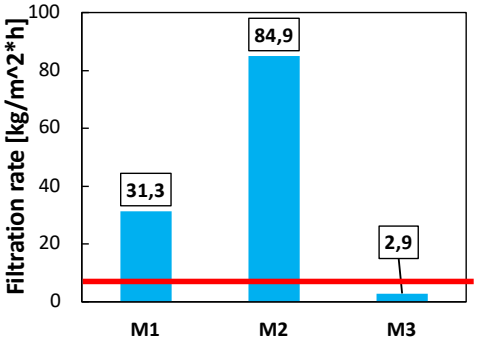
Magnesium Hydroxide

Analysis – Filtration rate





Reference filtration rate the literature [1].

[1] *M. Turek, W. Gnot, Precipitation of magnesium hydroxide from brine, Ind. Eng. Chem. Res. 34 (1) (1995) 244–250.* https://doi.org/10.1021/ie00040a025

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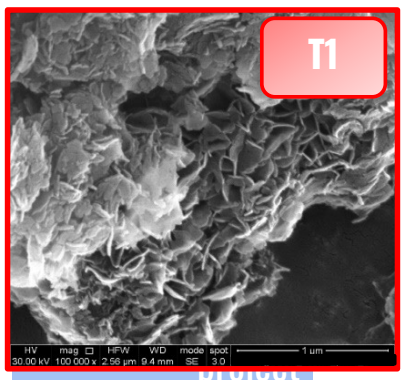
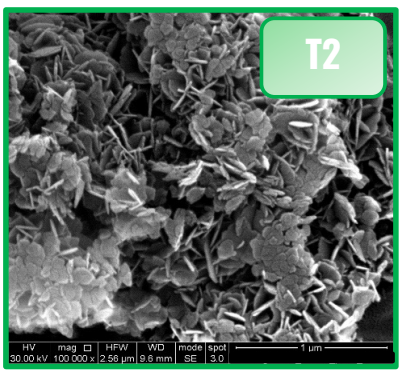
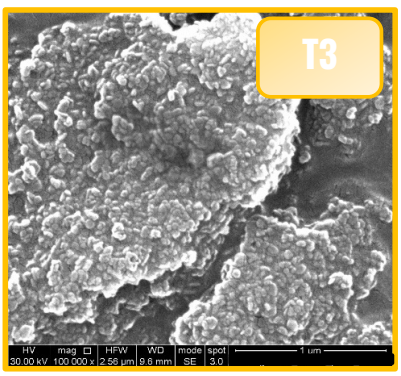
Magnesium Hydroxide

Analysis – SEM







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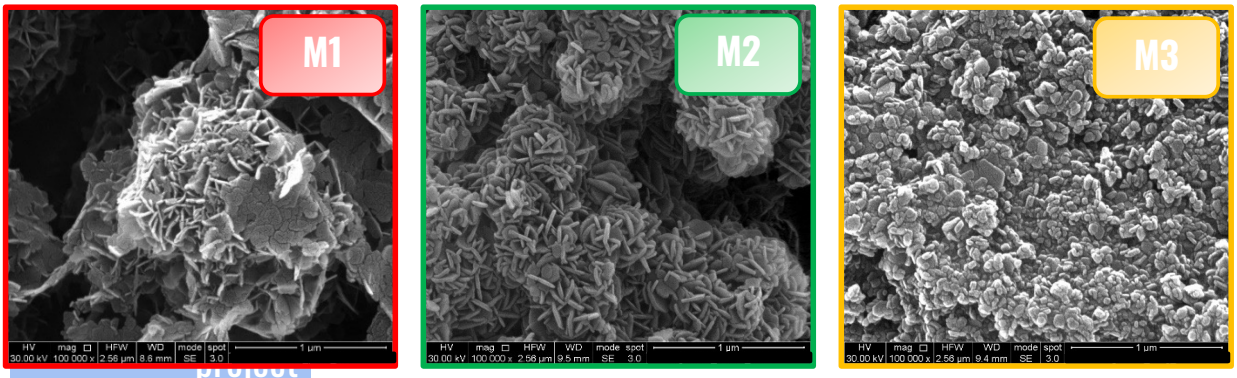
Magnesium Hydroxide

Analysis – SEM



project

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REwaise
Resilient Water Innovation for Smart Economy

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Andrea Cipollina

MF-PFR implementation scenario 2
The REWAISE project

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 869496.

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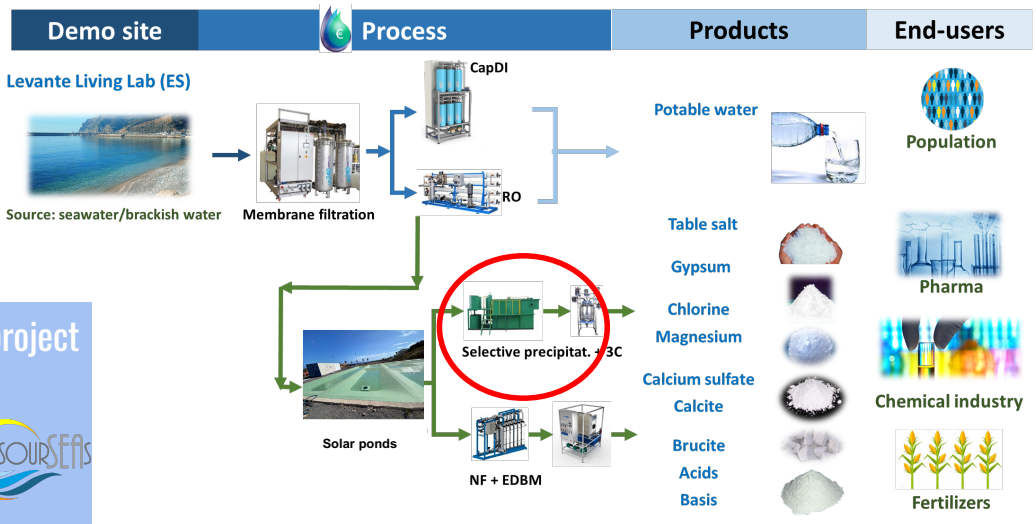
REwaise
Resilient Water Innovation for Smart Economy

Process description

A minimum liquid discharge (MLD) desalination for water recovery maximization and resources reclamation



Rewaise project

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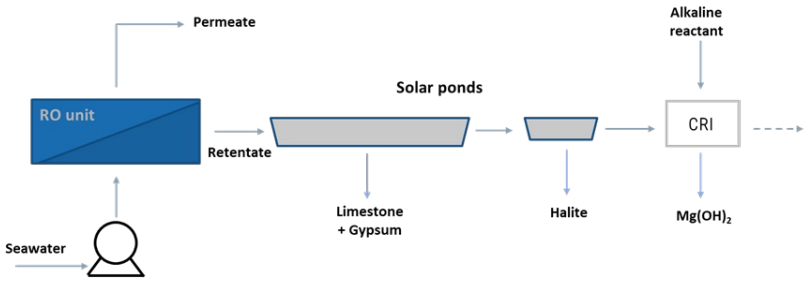
REwaise
Resilient Water Innovation for Smart Economy

Low energy desalination & minerals recovery

The aim of the activities is the recovery of valuable materials via:

- Saltponds
- Magnesium crystallizer



Rewaise project

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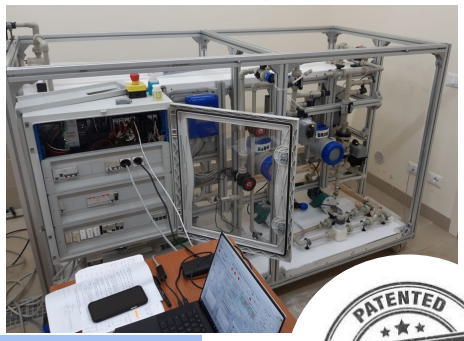
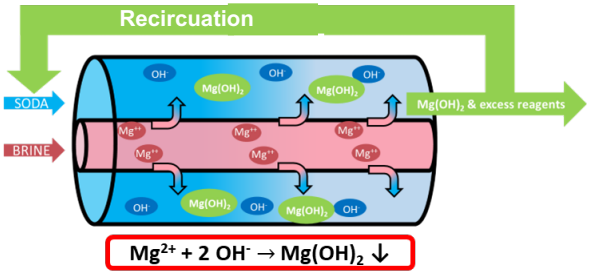
Magnesium reactor

Crystallization reactor design and construction





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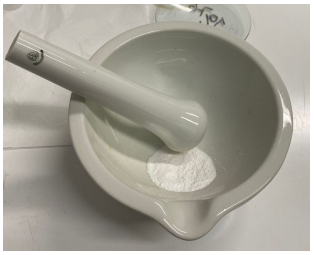

Magnesium Hydroxide

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Magnesium reactor

Crystallization reactor installation in Tenerife (Canary Islands, Spain)

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Magnesium reactor

REwaise Resilient Water Innovation for Smart Economy

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Tests

Test	RO Brine	NF Brine	RO Bittern	NF Bittern
Mg^{2+} [g/L]	2.25	3.43	26.5	48.5
Ca^{2+} [g/L]	1.20	1.15	0.13	0.07
Brine/Bitter Flow rate [L/h]	260	215	32	24
NaOH Flow rate [L/h]	121	128	213	213

Results – Sedimentation rate

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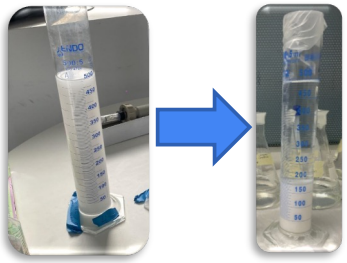

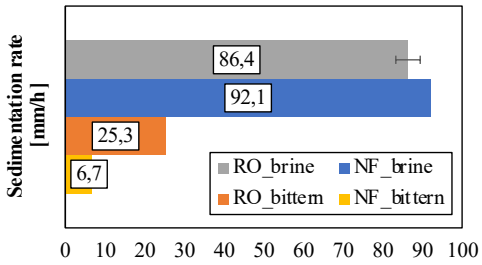

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Magnesium reactor

REwaise Resilient Water Innovation for Smart Economy

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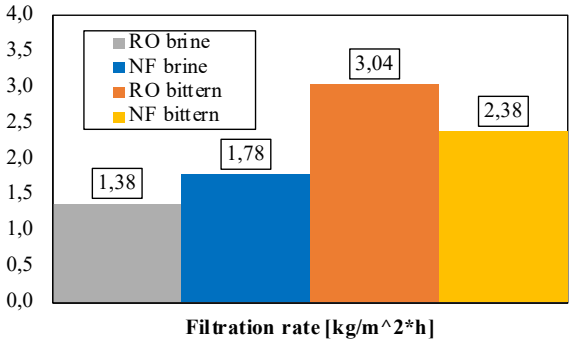

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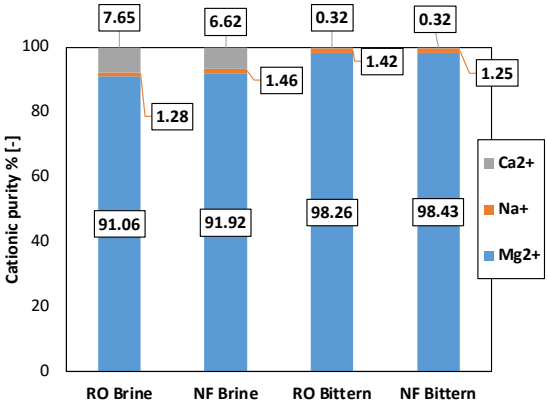
Results – Filtration rate

Results – Cationic purity



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Sol2H2O

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MF-PFR technology: Conclusions and perspectives

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Conclusions & perspectives (1/2)

- The recovery of Magnesium from seawater brines is technologically possible and economically sustainable;
- The use of conventional reactors allows the separation of $Mg(OH)_2$ up to high purity, but the control of granulometry can be problematic;
- The use of MFPFR technology allows a better control of the reaction conditions, moving towards better separability of slurry and more controlled morphology;
- Pilot scale activities carried our in different projects with different brine composition have successfully demonstrate the operability of this technology

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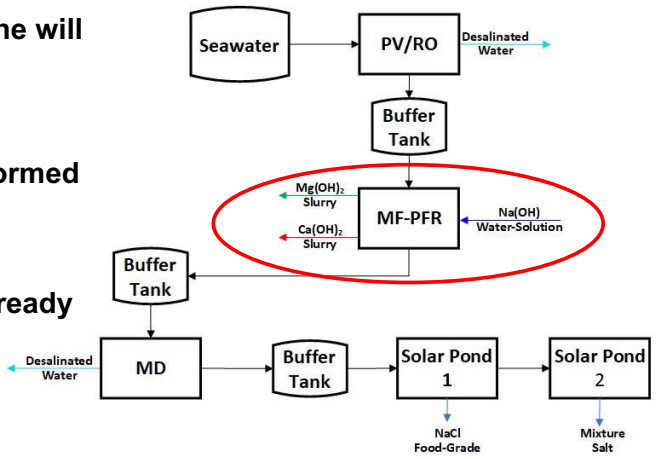
Conclusions & perspectives (2/2)

- A MFPFR pilot unit will be installed and operated within the SOL2H2O pilot facility;
- $Mg(OH)_2$ precipitation tests from RO brine will be performed to characterised the performance under these conditions;
- A second precipitation step will be performed to remove Ca in the form of $Ca(OH)_2$, assessing its efficiency;
- The obtained bivalent-free brine will be ready for further concentration and NaCl production in the artificial saltworks



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Thank you

For any question (after the Q&A session) feel free to send an email to: andrea.cipollina@unipa.it

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