UNIVERSITÀ DEGLI STUDI DI PALERMO
Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica (DICGIM)

REAPower

Magnesium recovery from concentrated brines

Andrea Cipollina

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Desalination for the Environment, Clean Water and Energy
Cyprus, 11th-15th May 2014

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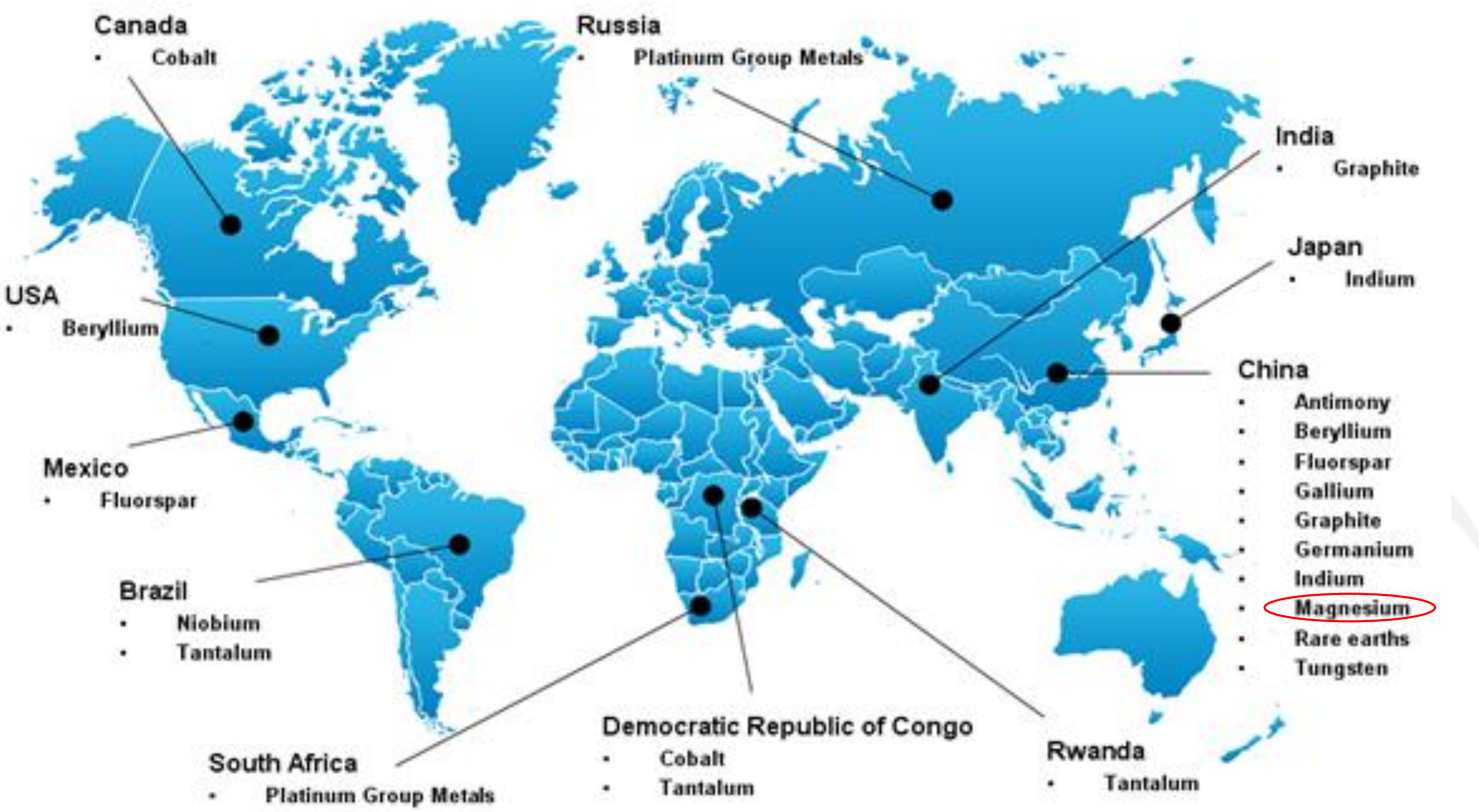
Production concentration of critical raw mineral materials



http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm,

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World production capacity of Magnesium compounds (MgO equivalent)

Country	Mg source	Produced MgO equivalent
China	Magnesite	4,18 mln tons/year
Russia	Magnesite	2,55 mln tons/year
USA	Magnesite and Sea Water	526 000 tons/year
Turkey	Magnesite	484000 tons/year
"	"	"
"	"	"
Italy	Magnesite	25 000 tons/year
Total	Magnesite and Sea Water	11,4 mln tons/year

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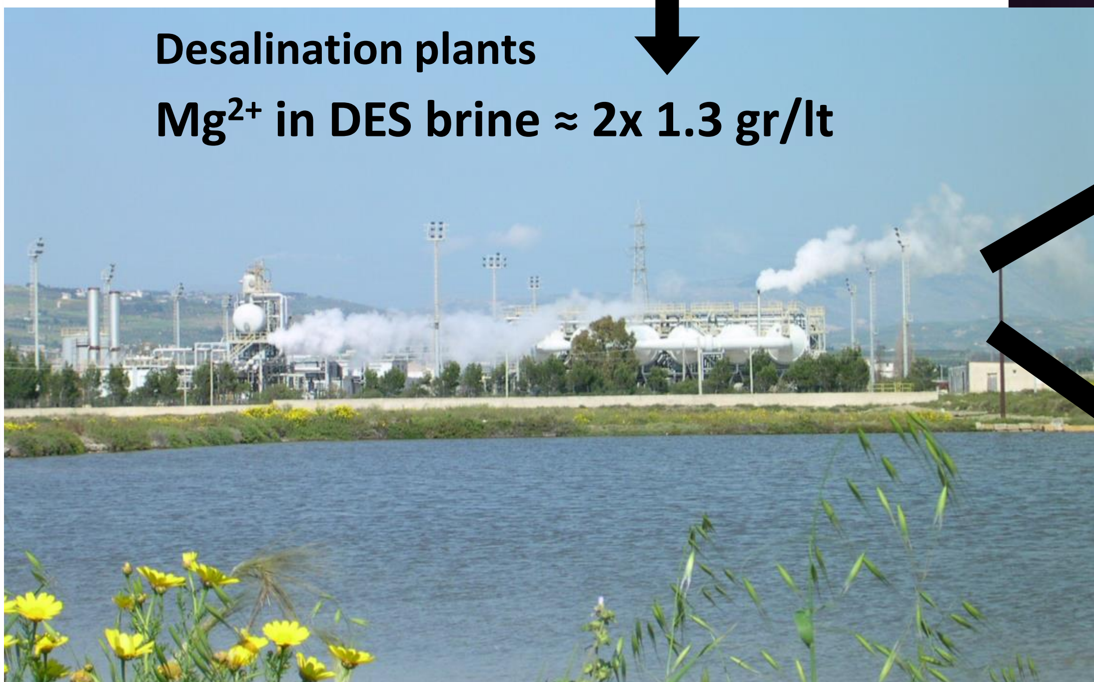
Possible sources Mg in concentrated brines

Mg^{2+} in SW ≈ 1.3 gr/lt

Mining industry



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Saltworks for the production of sea-salt

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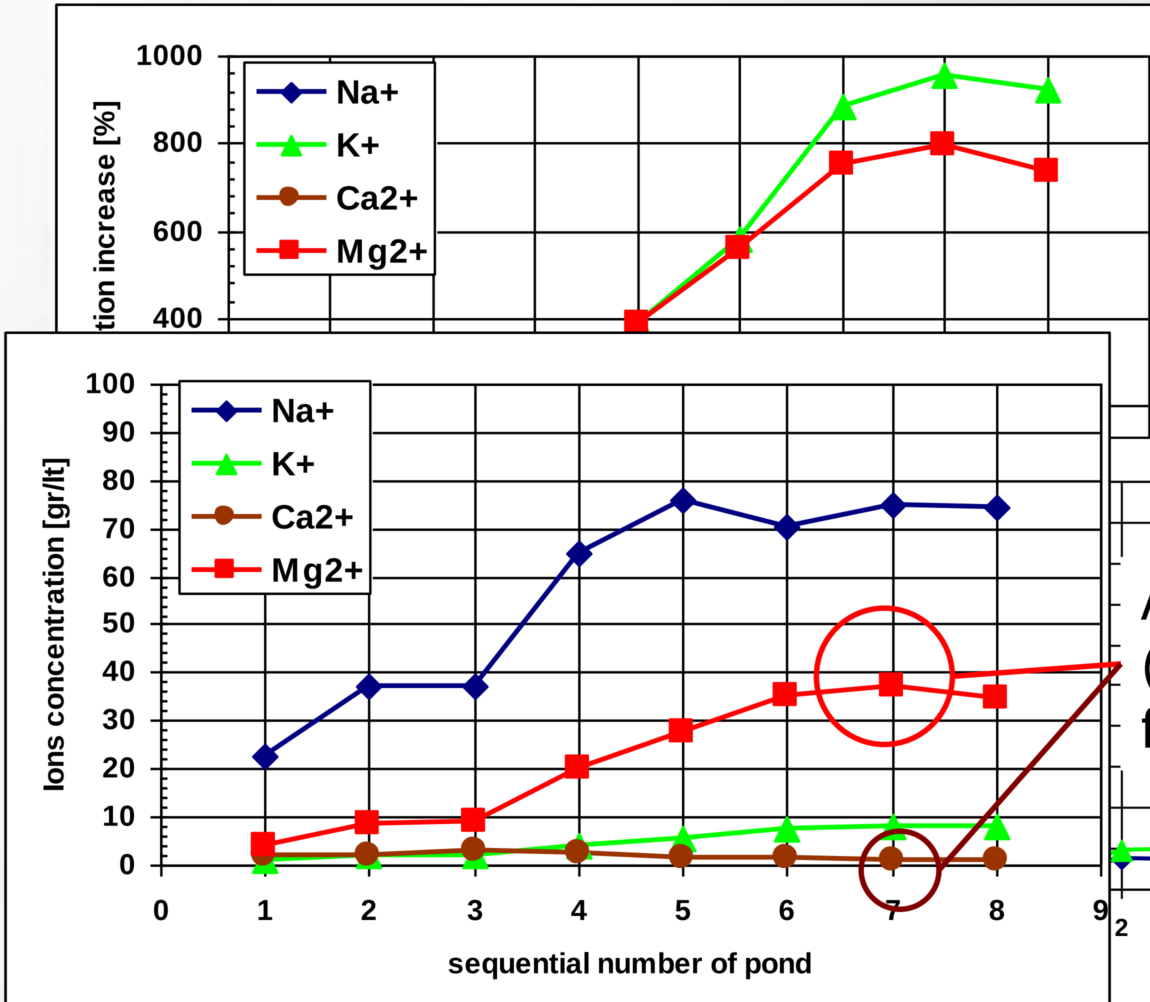
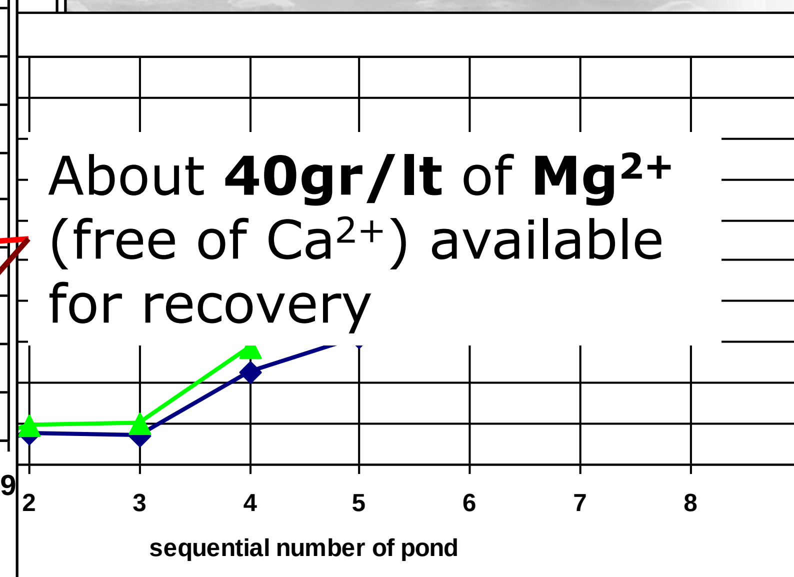
Potentials of exploitation of brines from saltworks

Ions concentration % increment along the basins of an experimental saltworks in Trapani (Sicily, Italy)





About **40gr/lt** of $\mathbf{Mg^{2+}}$ (free of Ca^{2+}) available for recovery

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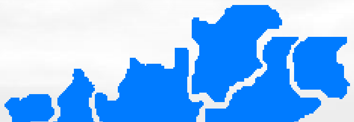
Potentials of exploitation of brines from saltworks



Italian sea-salt production facilities

A total potential of about **3,000,000 tons/year of MgO** extracted from saltworks brines can be estimated for the whole Mediterranean basin

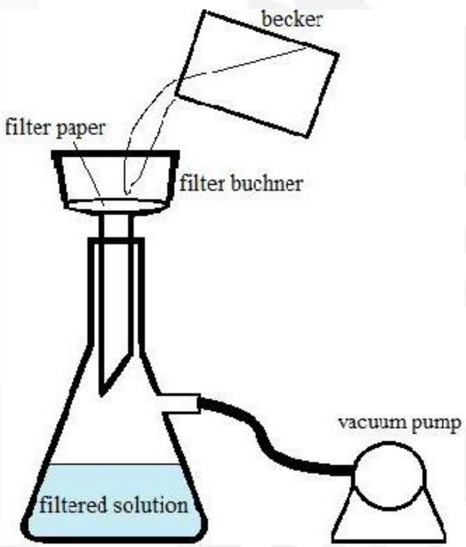
Conceptual steps for the **Reactive Crystallisation**

NaOH solution injection

Brine (Na^+; Mg^{2+}; Cl^-; SO_4^-; …)

$$MgCl_2 + MgSO_4 + 4NaOH \rightarrow 2Mg(OH)_2 + 2NaCl + Na_2SO_4$$

blending



$Mg(OH)_2$ precipitation and vacuum filtration

Crystals and exhausted solutions to the analytic analysis

Precipitate

Filtered solution

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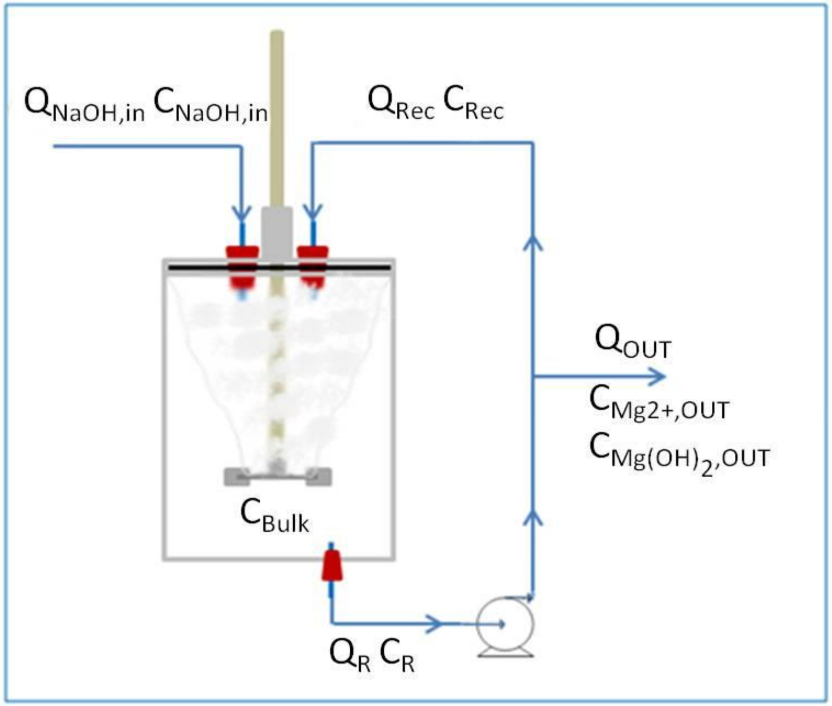
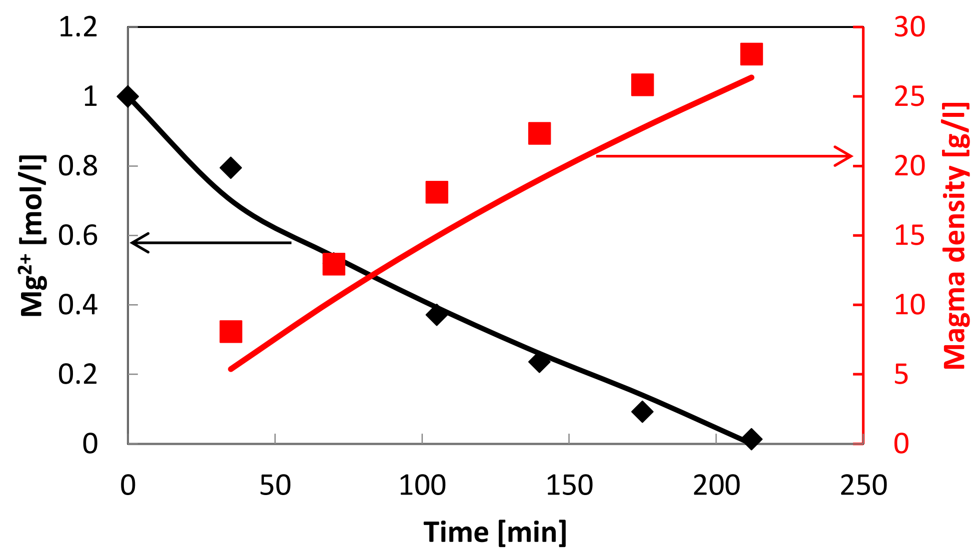
SEMI-BATCH REACTOR



Mass balance equations
(assuming instantaneous reaction):

$$0 - Q_{out} C_{Mg^{2+},out} - Q_{NaOH,in} C_{NaOH} = V \frac{dC_{Mg2+}}{dt} \qquad (1)$$

$$0 - Q_{out} C_{Mg(OH)_2} + Q_{NaOH,in} \frac{C_{NaOH}}{2} = V \frac{dC_{Mg(OH)_2}}{dt} \qquad (2)$$



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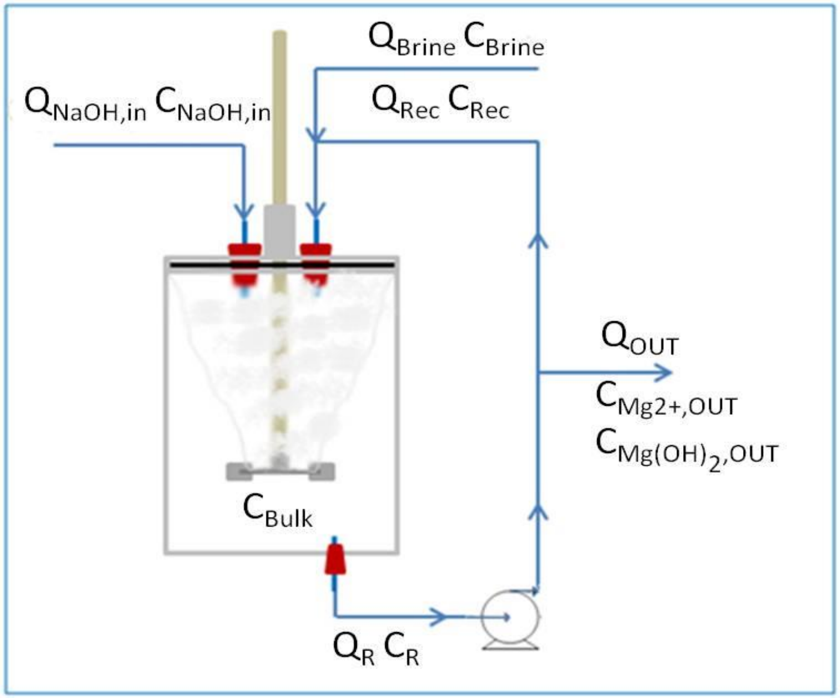
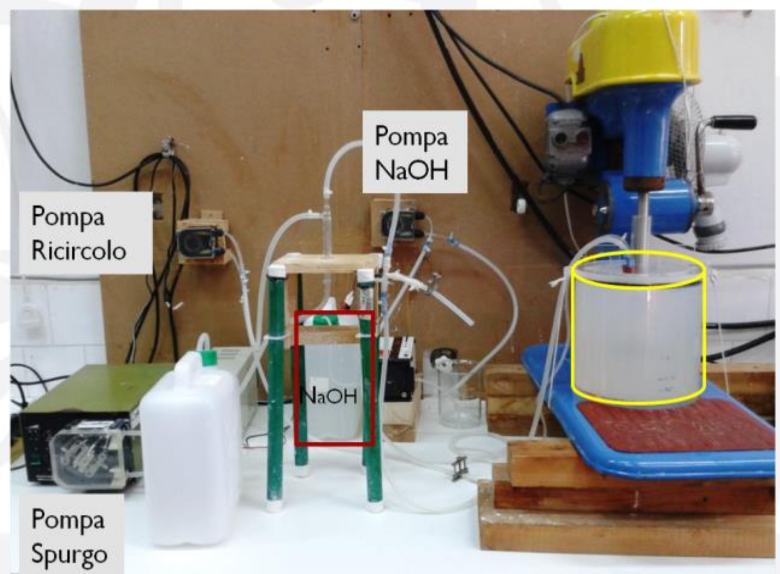
CSTR REACTOR



- **Same reactor as in batch tests;**
- **Continuous injection of feed brine and alkaline reactant;**
- **Continuous purging of the suspension**



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ANALITYCAL INSTRUMENTS

Ionic chromatography

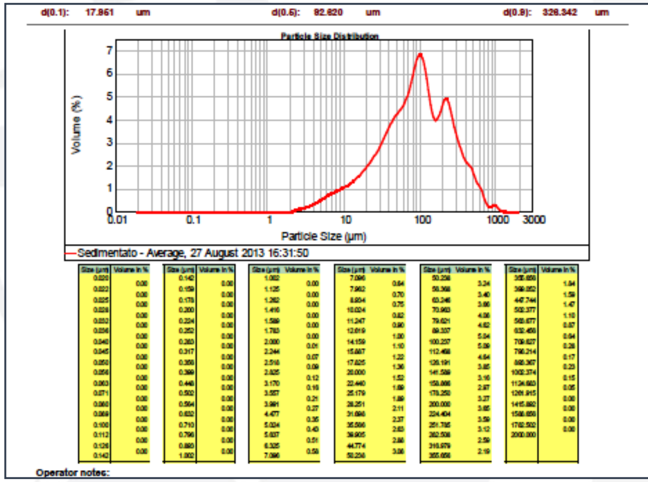
- Mg purity
- Recovery efficiency

$$Mg\_purity[\%] = \frac{[Mg^{2+}]}{[all\_cations]}$$

$$h_{recovery}[\%] = \frac{[Mg^{2+}]_{filtered\_solution}}{[Mg^{2+}]_{feed\_brine}}$$

Laser Granulometry

- Particle size distribution



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Summary of semi-batch tests conditions

SET	TEST n.	C_{NAOH} [mol/l]	Q_{NaOH} [ml/min]	C_{Mg2+} [mol/l]	Impeller
1°set	1	**4**	**7**	1	Rushton
	2	**2**	**14**	1	Rushton
	3	**0.5**	**57**	1	Rushton
2°set	4	**4**	14	1	Rushton
	2	**2**	14	1	Rushton
	5	**1**	14	1	Rushton
3°set	6	2	14	**2**	Rushton
	2	2	14	**1**	Rushton
	7	2	14	**0.5**	Rushton
4°set	8	4	14	1	**Rushton**
	4	4	14	1	**Marine impeller**
	9	4	14	1	**Pitched-blade**

Magnesium recovery from concentrated brines.
Results: semi-batch tests

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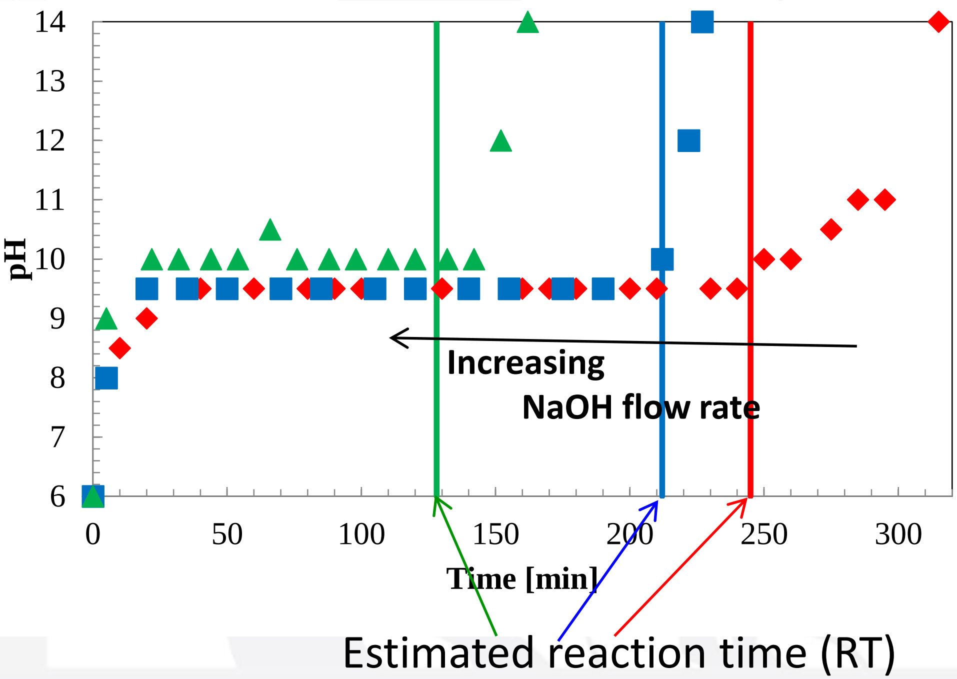
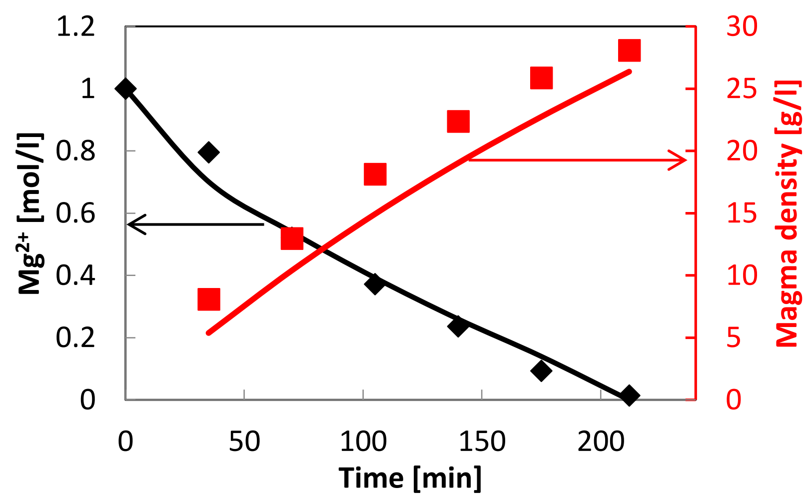
Sampling intervals during the reaction

1/6 RT | 2/6 RT | 3/6 RT | 4/6 RT | 5/6 RT | 1 RT

1B | **2B** | **3B** | **4B** | **5B** | **6B**





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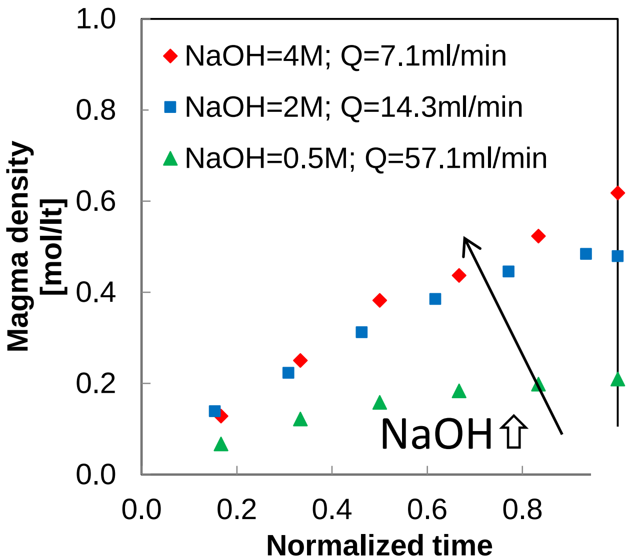
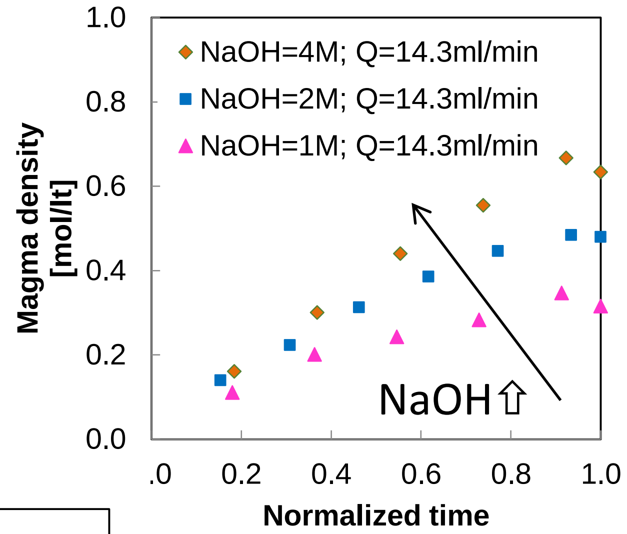
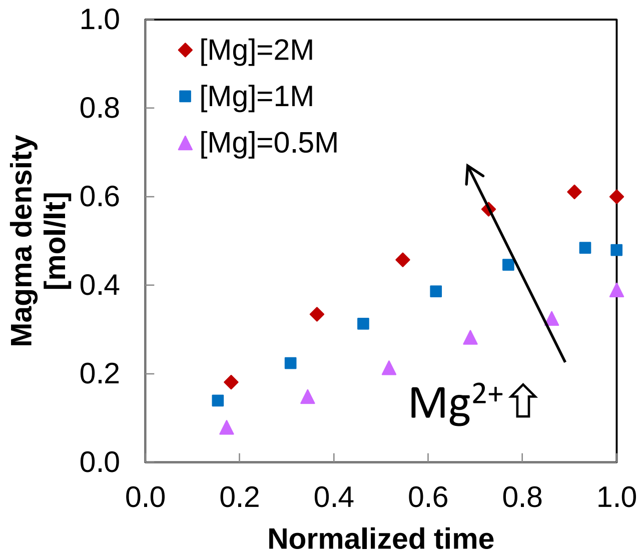
Trends of magma density







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Magnesium recovery from concentrated brines.
Results: semi-batch tests

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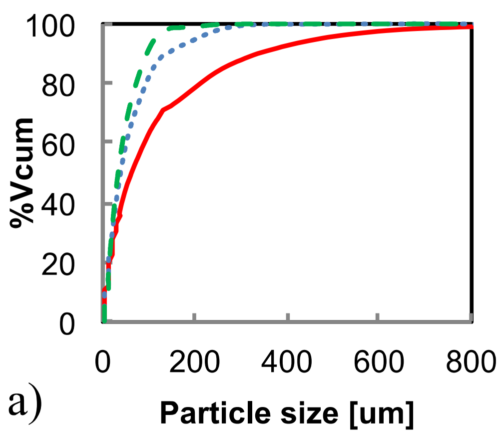
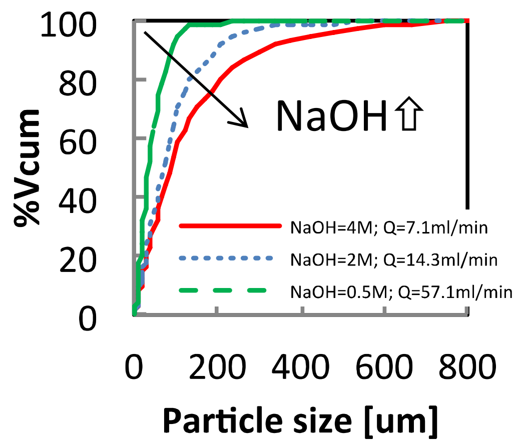
Cumulative granulometric distribution (1/2)

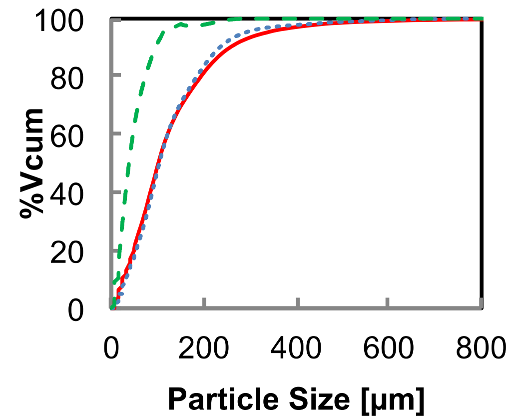
Particle size decreases with time

1° SET

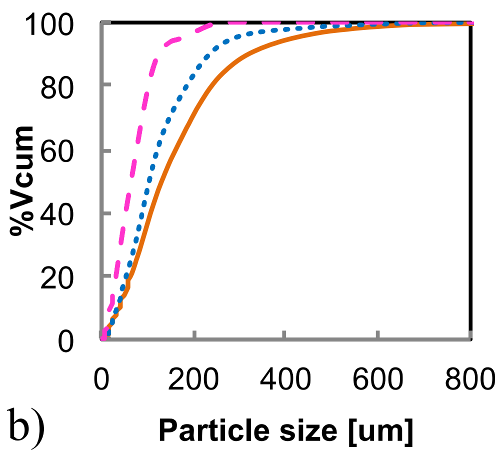


a)

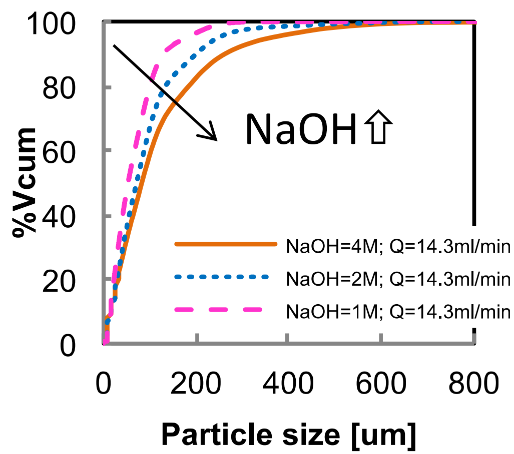


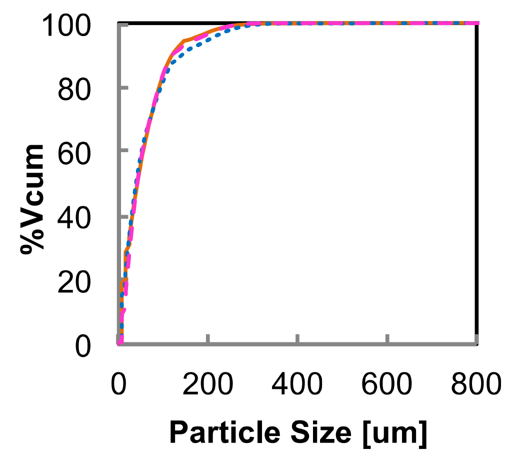


2° SET



b)





1/6 RT → 1/2 RT → RT

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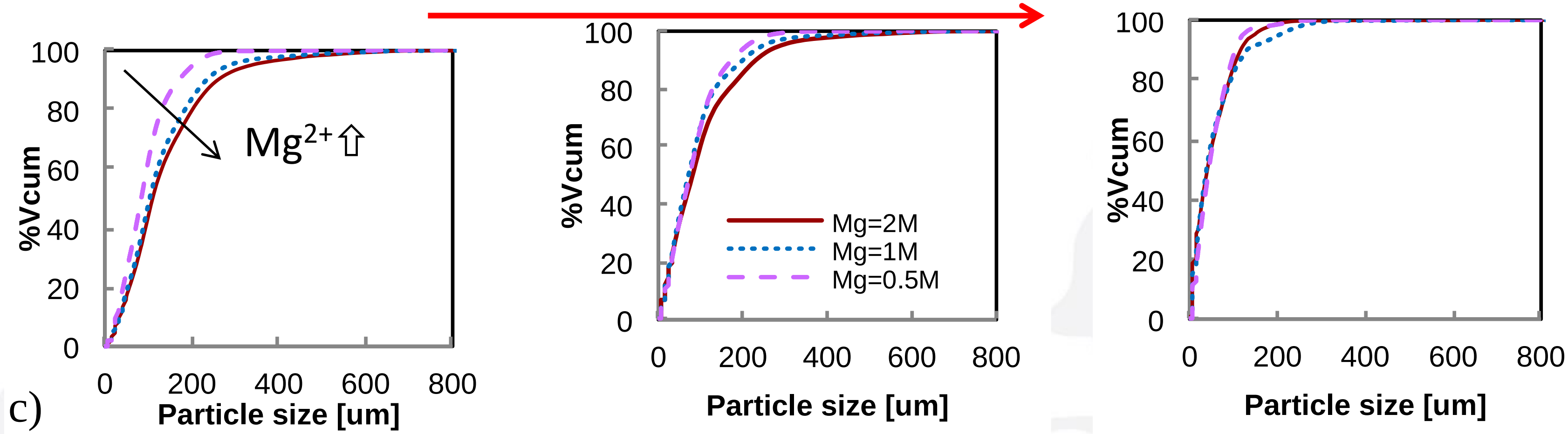
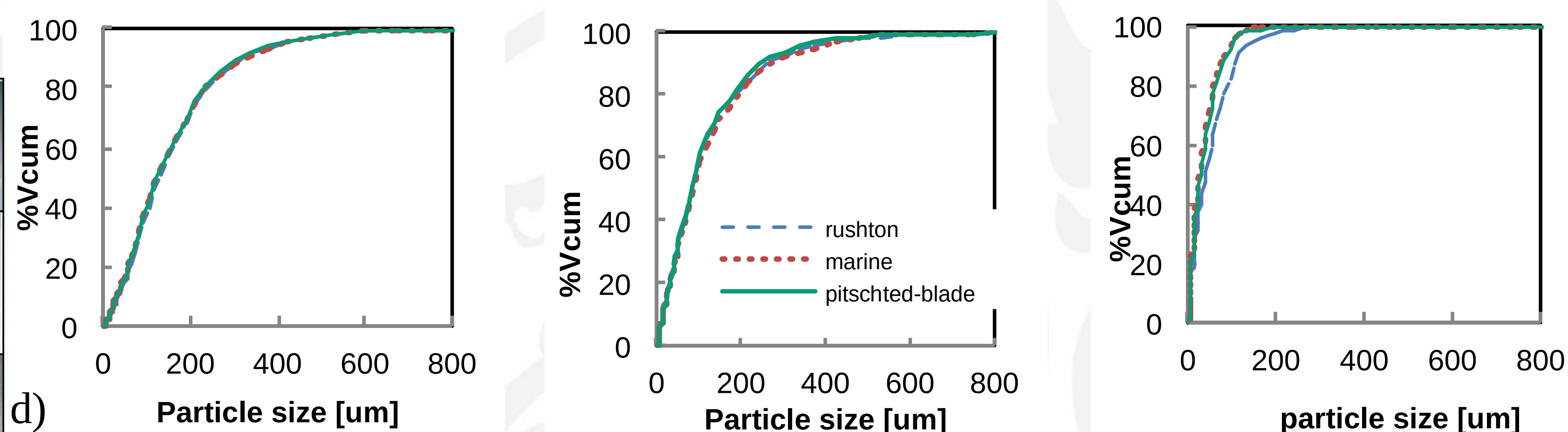
Cumulative granulometric distribution (2/2)

Particle size decreases with time

3° SET



4° SET



1/6 RT | 1/2 RT | RT


Trapani: mulino Maria Stella (foto di M.Vento)

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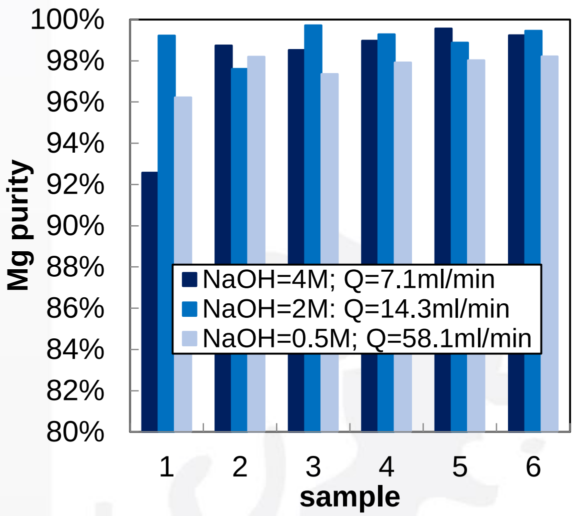
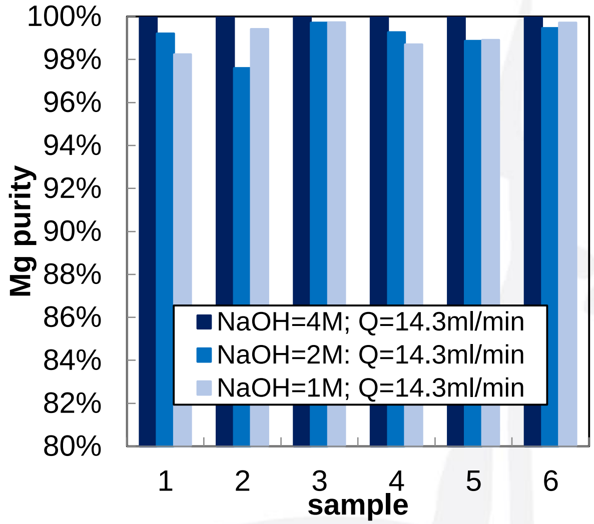
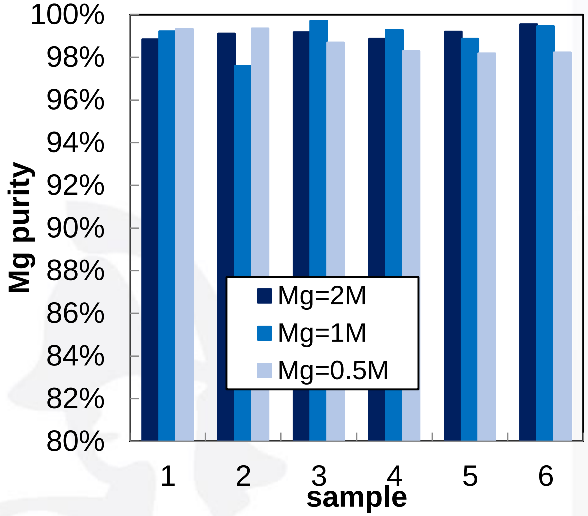
Magnesium purity







Mg recovery efficiency

Filtered solution from samples collected in TEST n.2					
sample	Na^{+} (ppm)	K^{+} (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	Mg recovery (%)
2B1	45399	6068	19076	125	**27.99%**
2B2	40550	4763	12483	281	**52.88%**
2B3	40893	4321	8909	342	**66.37%**
2B4	40957	3825	5661	158	**78.63%**
2B5	33622	2796	2226	345	**91.60%**
2B6	44399	3356	333	480	**98.74%**
2B7	41827	2992	0	702	**100.00%**

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CSTR REACTOR

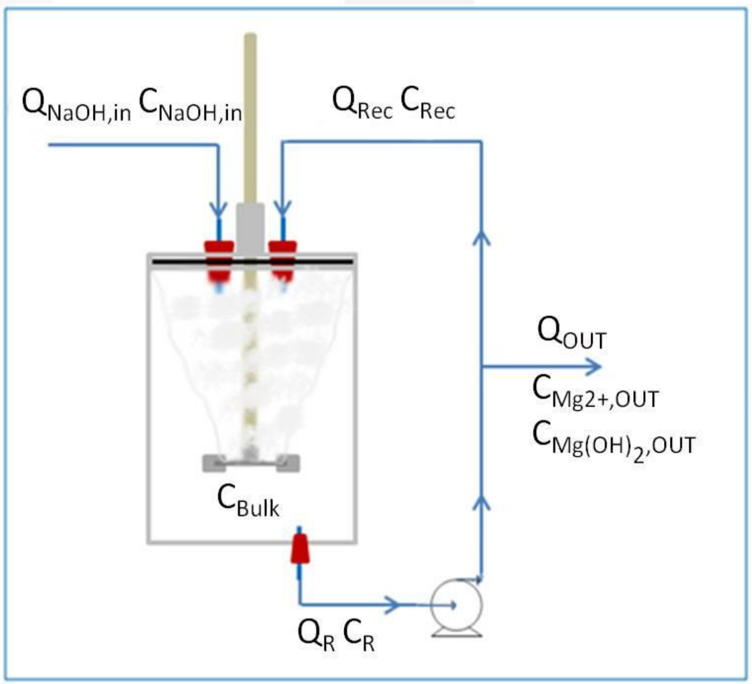
Final suspension of a batch test with:

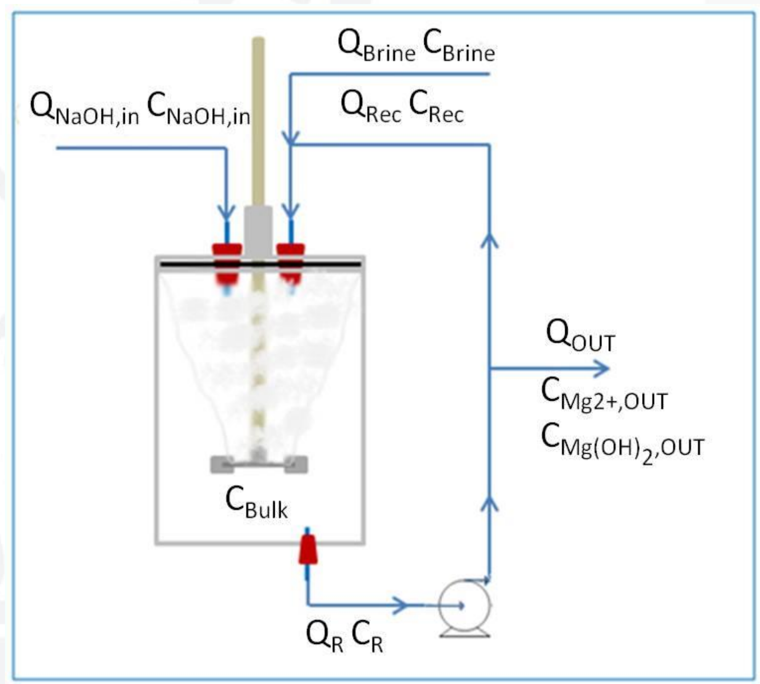
- Volume = 5 lt
- Magma density = 28 gr/lt
- Granulometric distribution 1-100 μm

CSTR @ t=0

Continuous react. conds.:

- NaOH 4M;
- τ = 150 s;
- NaOH stoichiometric with Mg^{2+}





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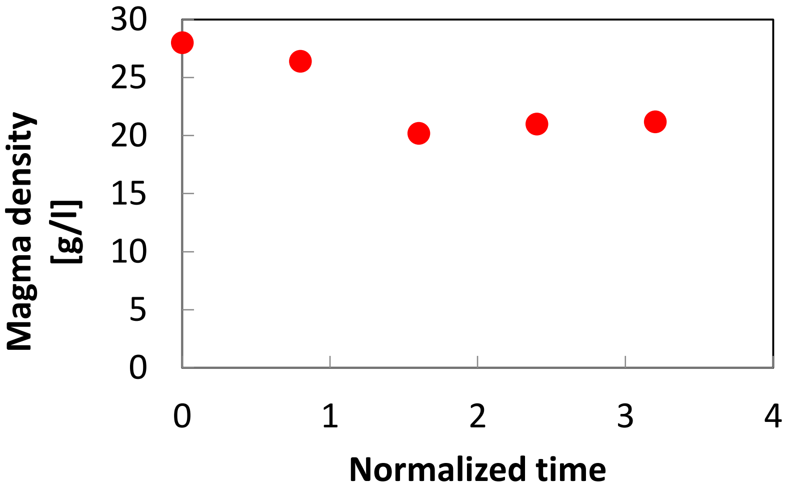
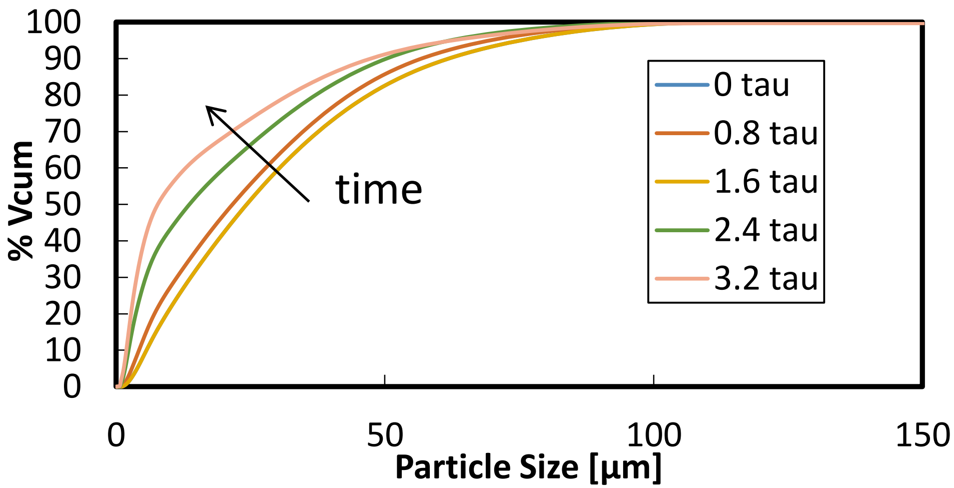
CSTR REACTOR

Trend of magma density



Granulometric distributions



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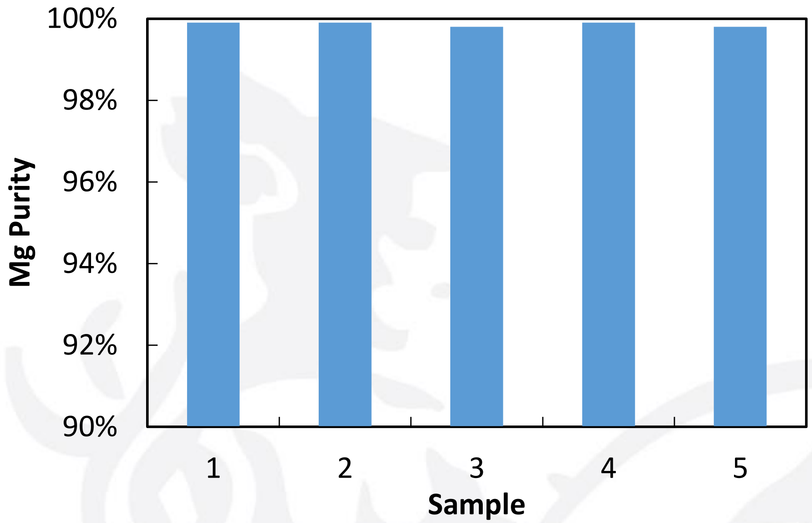
CSTR REACTOR

$Mg(OH)_2$ product purity



Mg Recovery was 100% in all sampled suspensions

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Works achievements

- ✓ **From waste stream, saltworks brine turns-out to be a huge resource of raw materials**

- ✓ **$Mg(OH)_2$ precipitation tests performed with semi-batch and CSTR reactors, thus piloting the potential of such exploitation**

- ✓ **Granulometric distribution with larger particles can be obtained using high concentrations of the two reactants (OH^- and Mg^{2+})**

- ✓ **Mg precipitate purities above 98% were observed in most samples**

- ✓ **Mg recovery from the brine is practically 100%**

Magnesium recovery from concentrated brines.
Acknowledgments

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Thank you

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