UNIVERSITÀ DEGLI STUDI DI PALERMO

SOSALT DAL MARE DI TRAPANI

Scuola Politecnica
Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica

Integrated cycle for the production of fresh water, minerals and energy

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European Commission

REAPower

INTRODUCTION

Environmental issues are more and more crucial in the design strategies of new desalination plants.

Two possible alternatives are proposed:

- Novel and low-impact brine disposal strategies to be implemented;

- Re-use and exploitation of brines as a non-conventional source of minerals and energy.

Alternative brine disposal strategies

Proposed strategies for brine disposal in coastal sites:

- Pre-mixing with seawater (usual for thermal plants);
- Use of a dense jet diffuser.

Proposed strategies for brine disposal in in-land sites:

- deep well injection;
- disposal into surface water bodies;
- irrigation of plants tolerant to high salinities;
- disposal to municipal sewers;
- evaporation ponds (concentration into solid salts).

Alternative brine disposal strategies

Potential resources to be exploited from brines:

❖ **Recovery of salts:**

-for the production of commercial food-grade salt;

-for the production of commercial industrial salt;

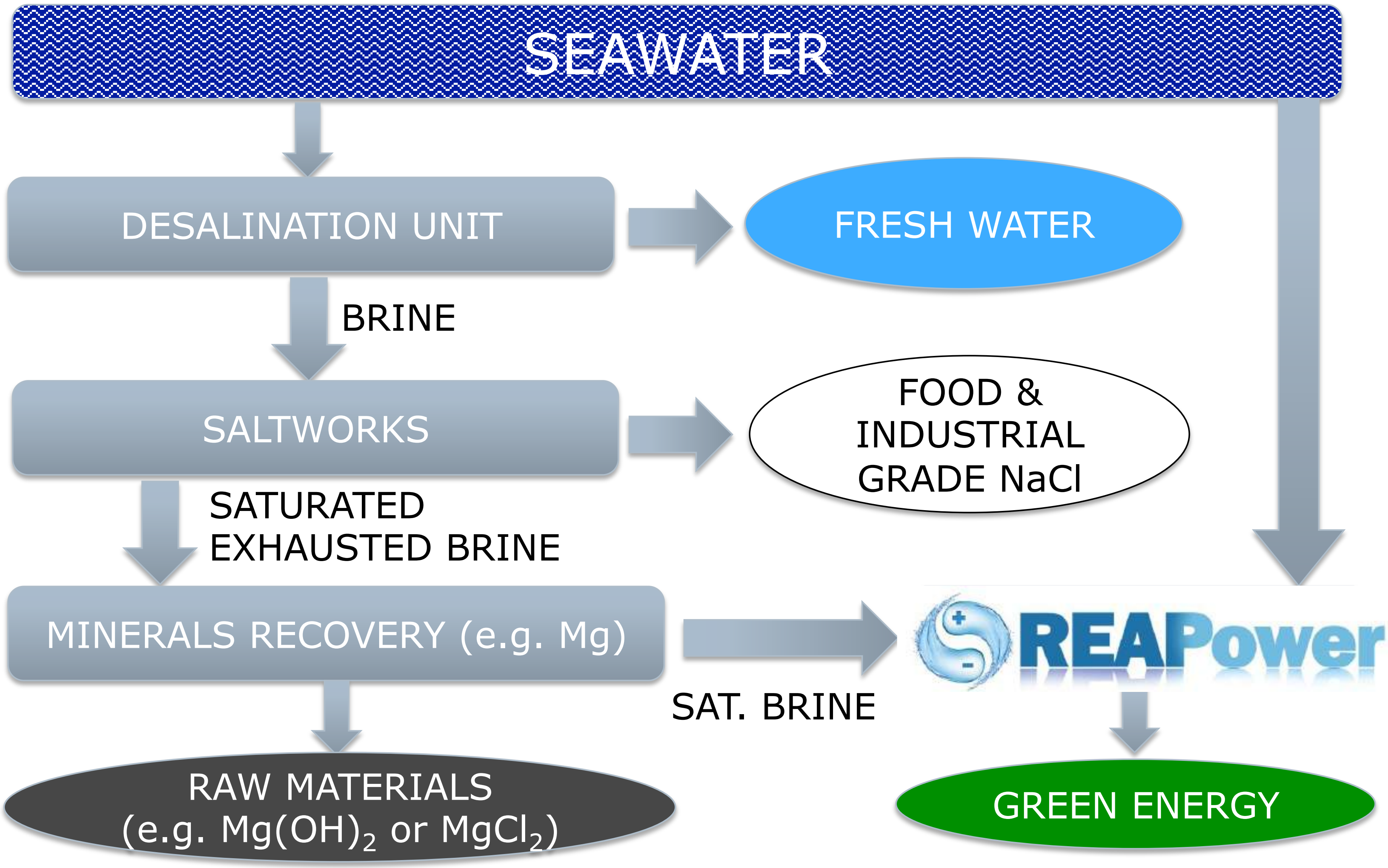
-for the production of high value compounds (e.g. Magnesium);

❖ **Recovery of the energy contained in the brine through:**

-Osmotic processes (e.g. Pressure Retarded Osmosis);

-Electrochemical processes (e.g. Reverse Electrodialysis & Capacitive Mixing);

The idea of an integrated cycle



The experience of Trapani site

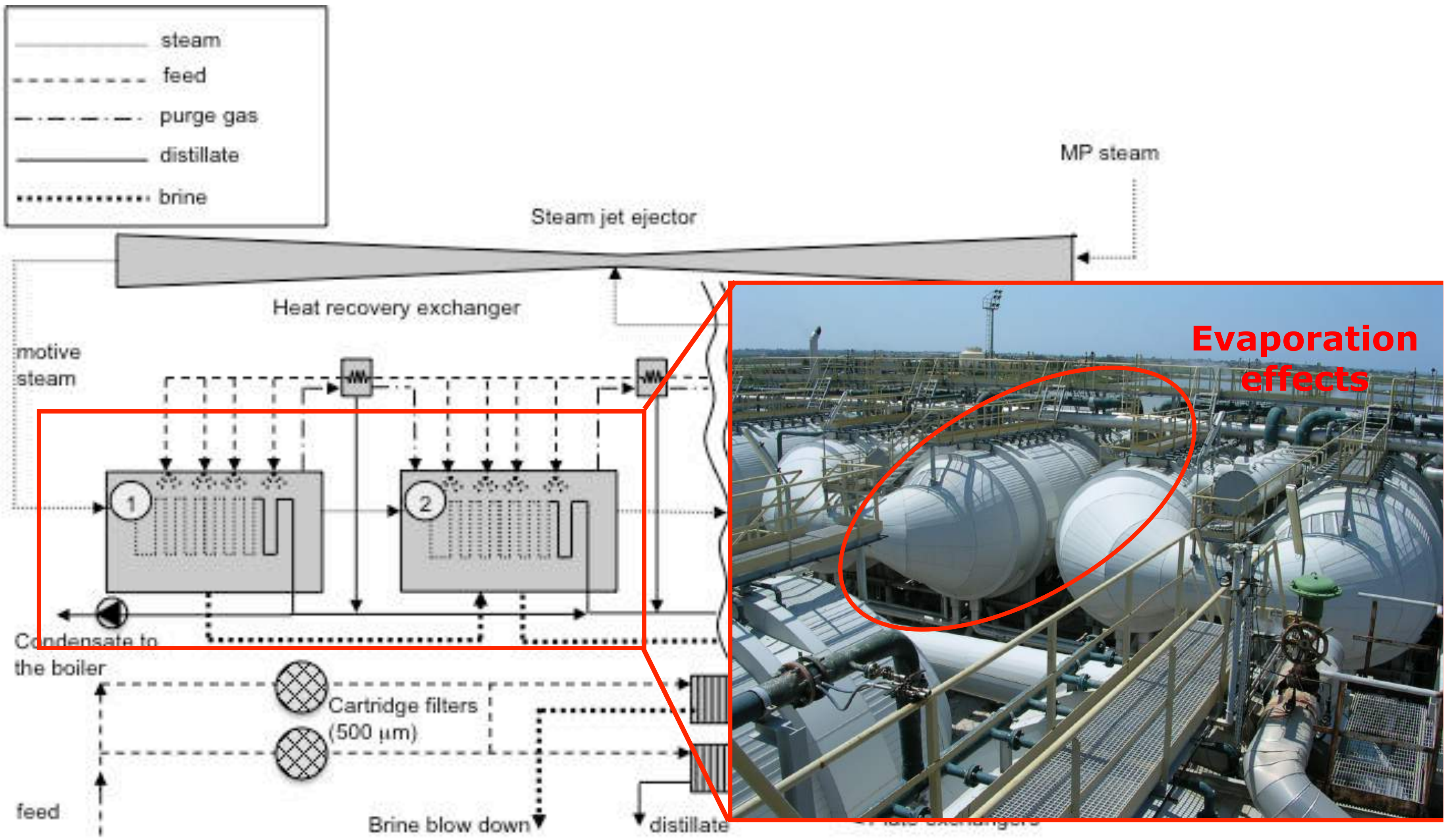
MED-TVC plant

- In 1995 **4 MED-TVC units** started-up with a nominal production of **9000 m^3/d each**;

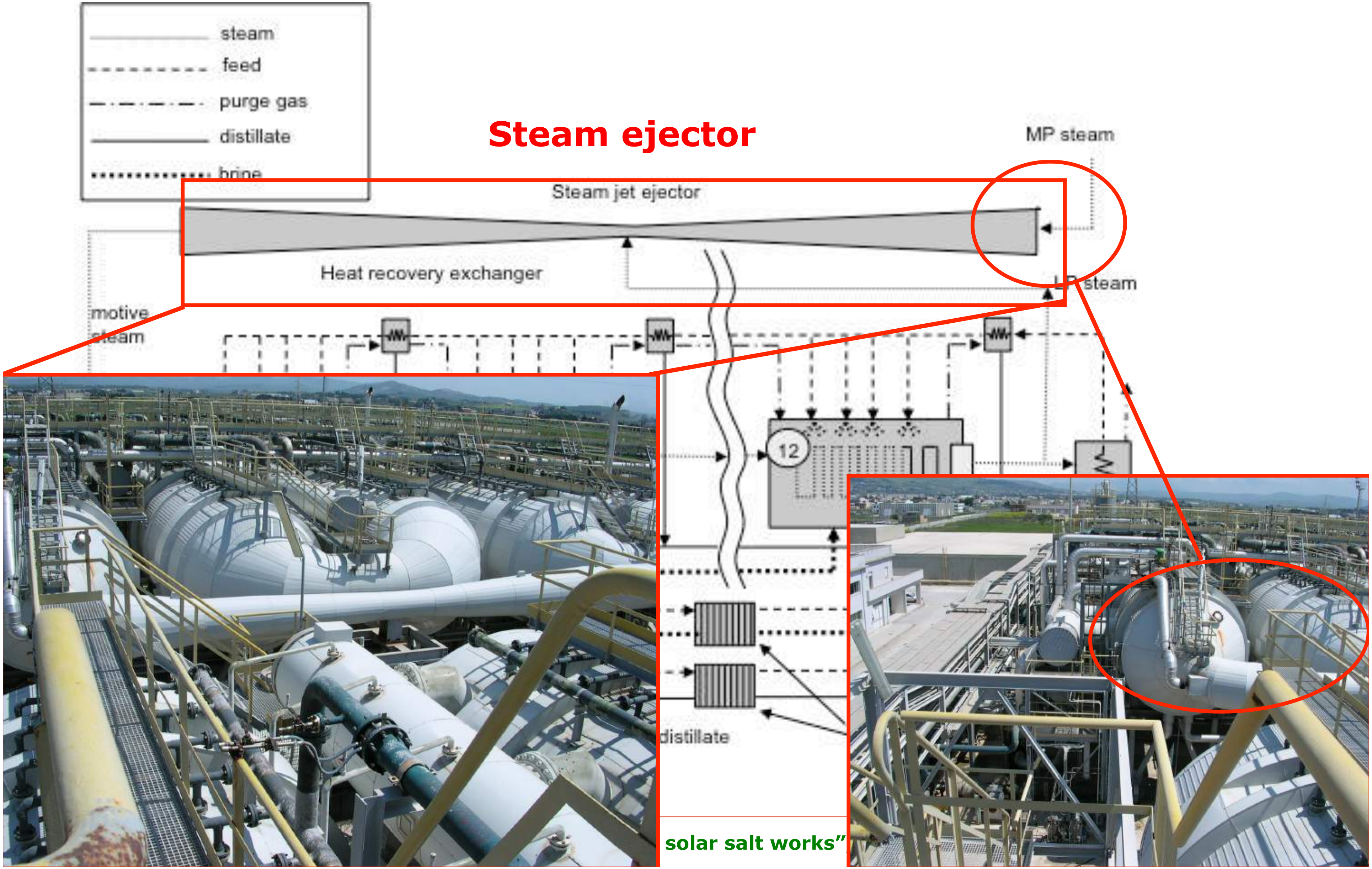
- Each unit has got **12 effects** and a Vapor Ejector for the **Thermal Vapor Compression**;

- The first Stage Temperature is around 65°C and the **nominal Performance Ratio** of the unit is up to **16 kg of distillate/kg of vapor**;

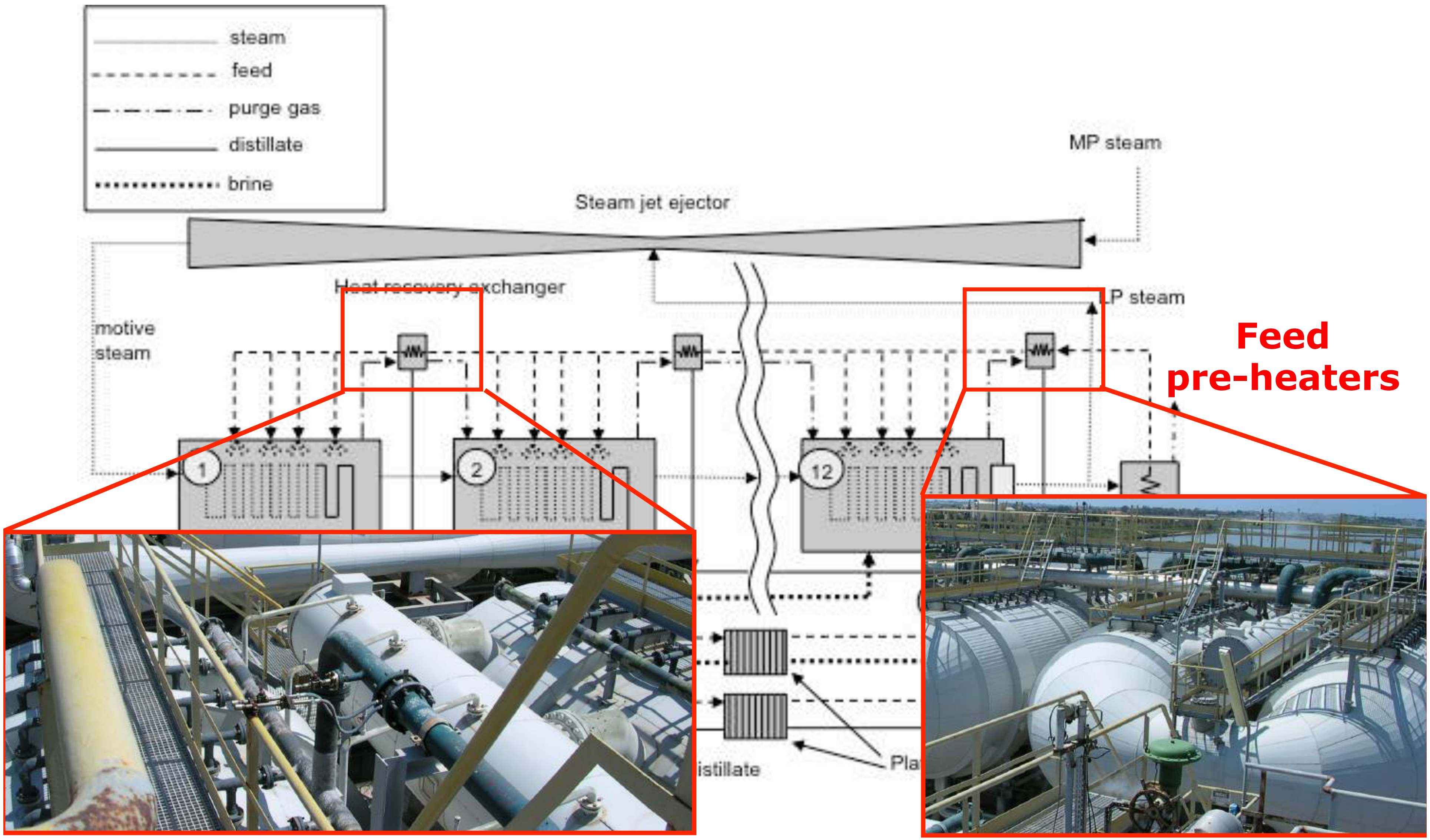
MED-TVC plant



MED-TVC plant



MED-TVC plant



MED-TVC plant

Plant operating and performance parameters

Energy consumption		Brine blow-down parameters			
Electricity (kWh/m³)	Vapour (kg/m³)	Conv. Ratio	**Flow rate (m³/d)**	**Conc. (gr/lt)**	**Temp. (°C)**
2÷2.5	60÷80 (45bar)	≈30%	**≈80,000**	**≈53-55**	**≈35-38**

Chemicals used in the plant are:

-**Anti-foam: few ppm in the feed;**

-**Anti-scaling: few ppm in the feed;**

-**Disinfection: Sodium hypochlorite, produced *in situ* and injected with "shock frequency" (disinfection procedures stopped in the last years)**

MED-TVC plant

Saltworks "Mariastella"

Salt pond

≈ 150,000 m²

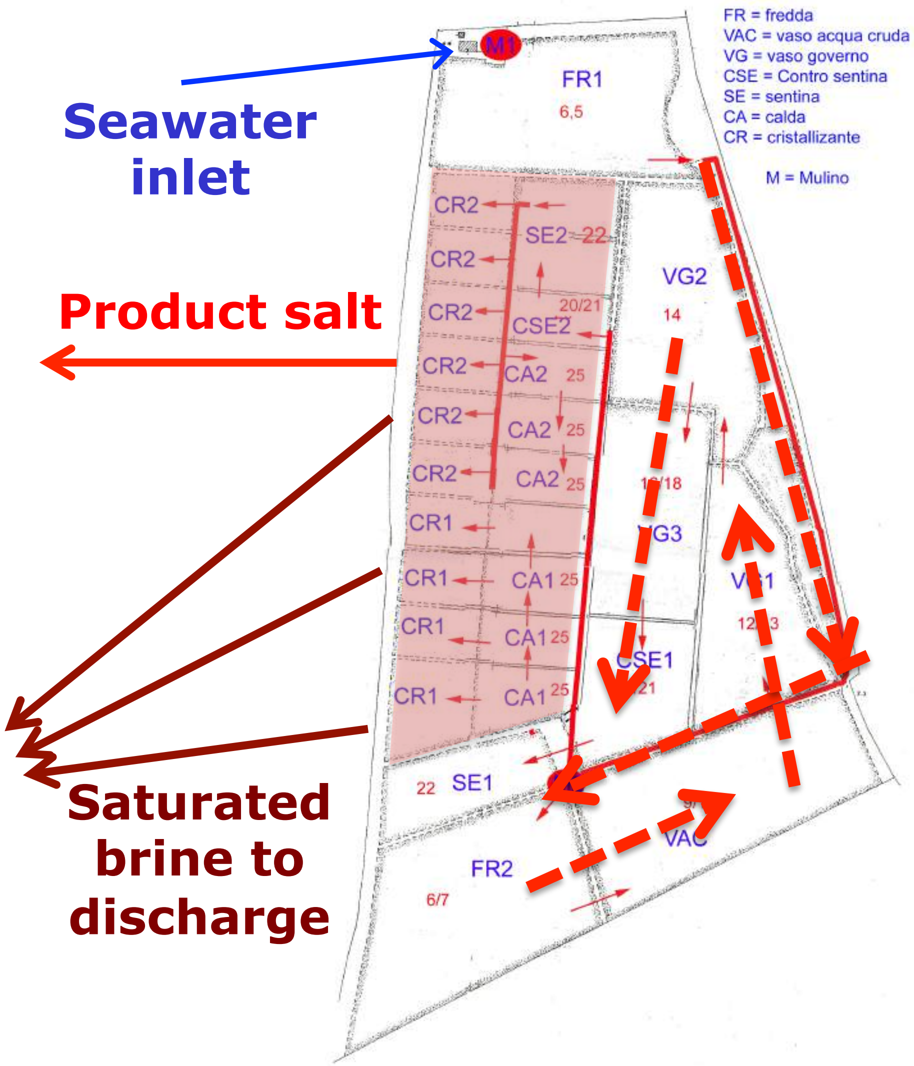
MED-TVC plant

Saltworks "Mariastella"

Saltworks "Mariastella"

Flow chart of the conventional saltworks operations:

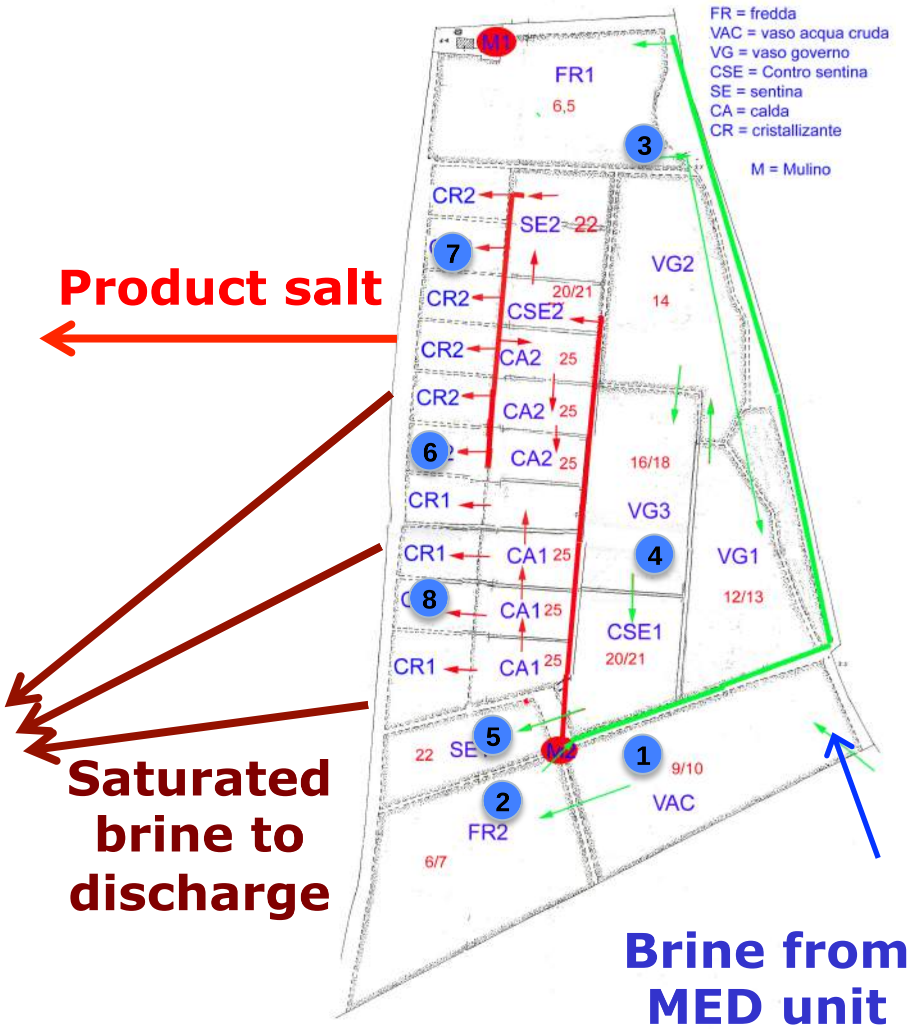
- Seawater enters the first pond (FR1), then it starts evaporating/ concentrating flowing in the basins;
- In middle basins (VG2 & VG3) Calcium Carbonates and Sulfates precipitate, thus removing quantitatively Ca^{2+} from the solution;
- Almost Ca^{2+}-free brine passes through warm basins (CSE1, CSE2, CA) preparing for NaCl crystallisation;
- Ready saturated brine is stored in service basins (SE1 and SE2);
- It feeds crystallization basins (CR), where NaCl is precipitated and collected



Saltworks “Mariastella”

NOVEL EXPERIMENTAL SALTWORKS FLOW CHART (from 2008):

- Brine from the MED unit enters the first pond (VAC) at 5°Be and 35°C;
- It continues evaporating/ concentrating, with a slight variation in the basins sequence;
- NaCl crystallisation stage is anticipated in time and basin sequence;
- A double/triple collection step may be required to avoid crystallisation basins overflow



Saltworks “Mariastella”

BENEFITS OF THE NOVEL SALTWORKS CONFIGURATION:

CONVENTIONAL OPERATIONS:

Production historical data										
Year	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Prod. (ton)	2370	0	1941	1934	1694	1630	1765	1686	2000	2000

NOVEL CONFIGURATION:
Brine in ≈ 600 m^3/d

2008 → **2900 t***

2009-2010 → **???**

2011 → **2500 t**

2012 → **3000 t***

A production increase by 20-30% can be estimated!!!

*An average production increase of 10-20% was registered in all Trapani saltworks in these years

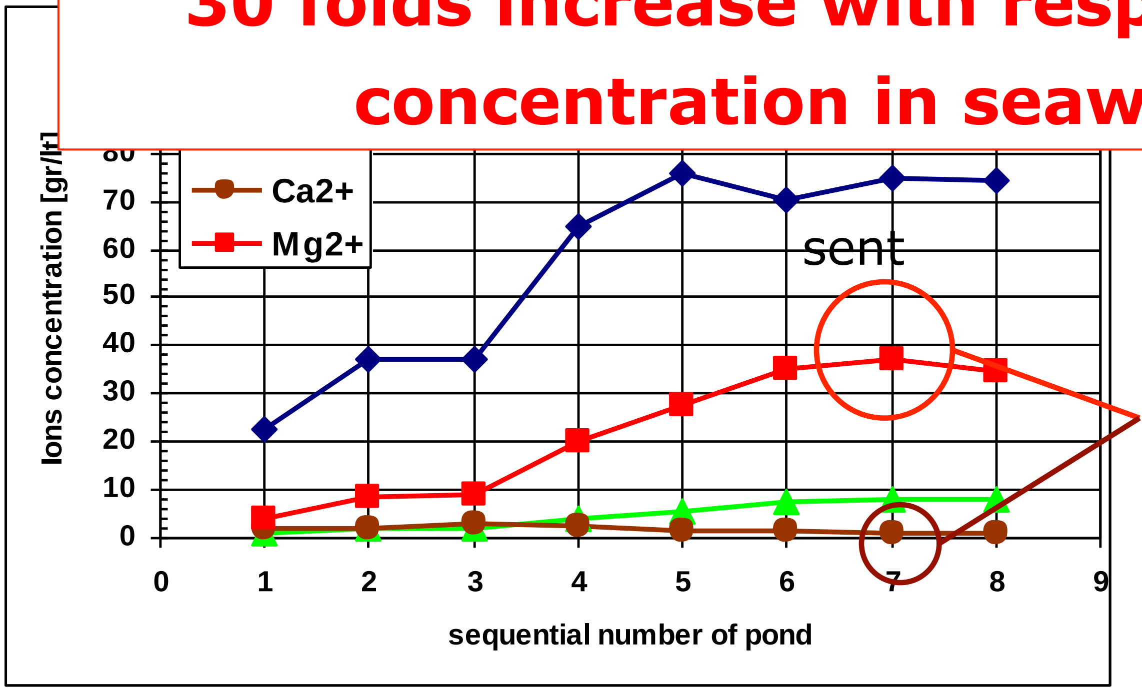
No variation in salt quality has been observed;

Biological life within saltworks basins still continues, not affected by the variation in feed stream

Saltworks “Mariastella”

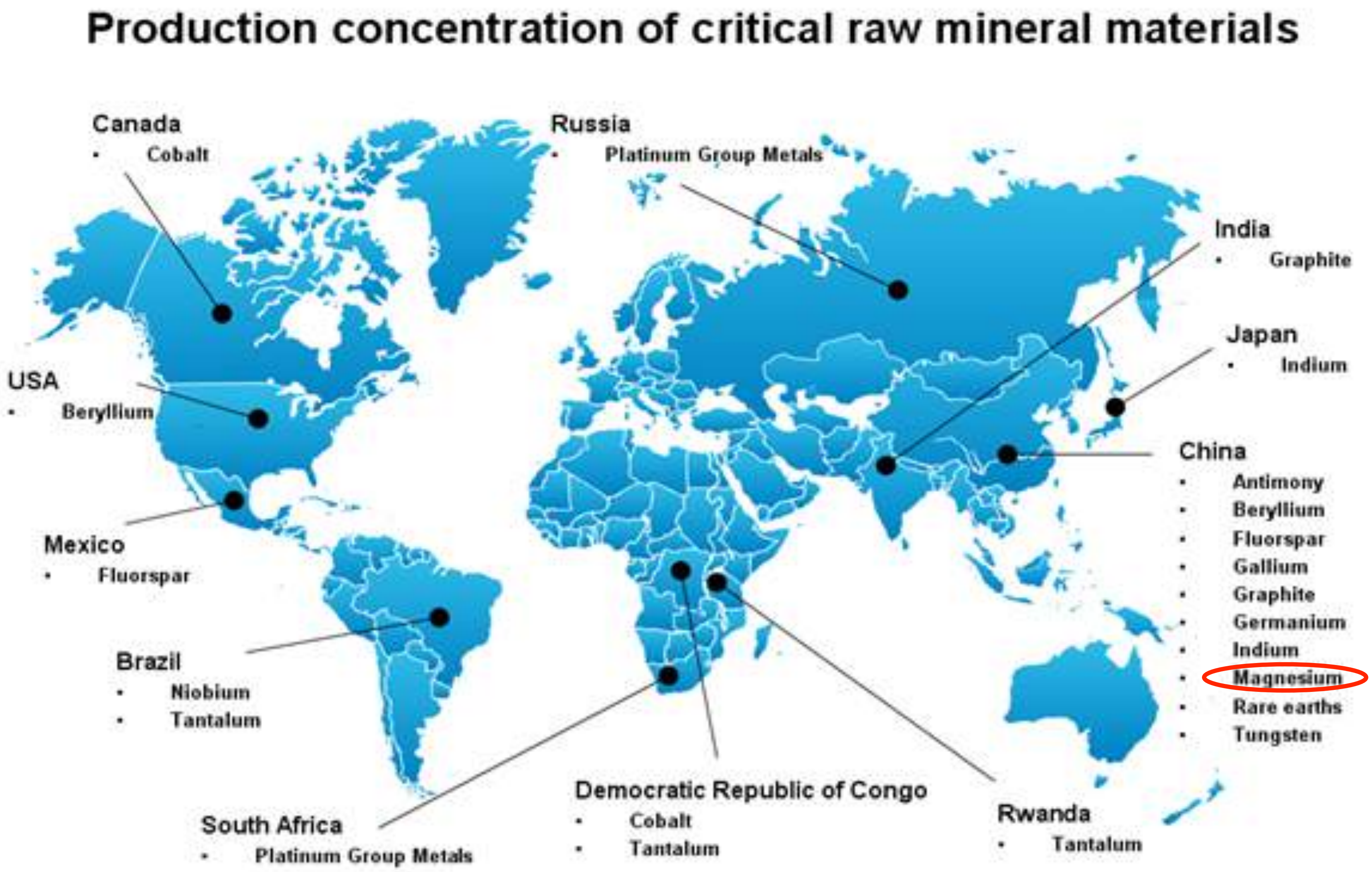
Ions concentration along the basins of the experimental saltworks (samples collected on the 27th of May 2008)

30 folds increase with respect to Mg concentration in seawater!



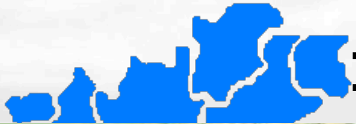
More than **35 gr/lt** of **Mg^{2+}** ($free of Ca^{2+}$) available for recovery

Mg recovery from exhausted brine



Mg recovery from exhausted brine

Potentials of exploitation of brines from saltworks



Italian sea-salt production facilities

A total potential of about

<u>3,000,000 tons/year of MgO</u>

extracted from saltworks brines can be estimated for the whole Mediterranean basin

...

Practically around **30% of world production**

Mg recovery from exhausted brine

Experimental procedure for batch tests

50 ml brine + 50 ml H_2O

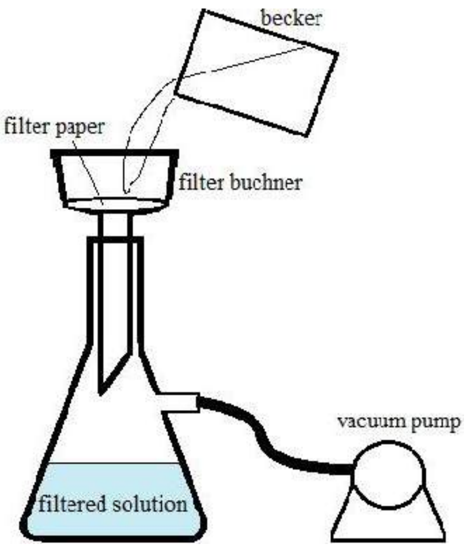
NaOH solution at over-stoichiometric ratio

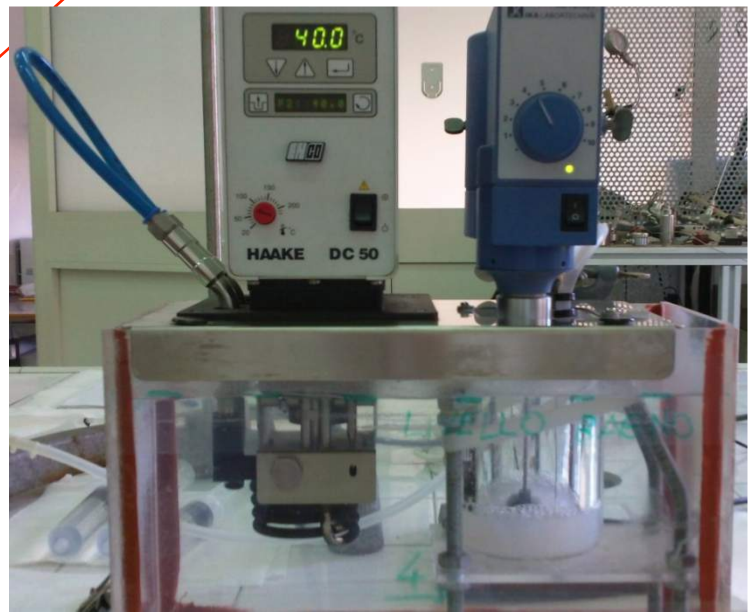
$$MgCl_2 + MgSO_4 + 4NaOH \rightarrow 2Mg(OH)_2 + 2NaCl + Na_2SO_4$$

blending

$Mg(OH)_2$ precipitation and vacuum filtration

Crystals and exhausted solutions to the analytic analysis



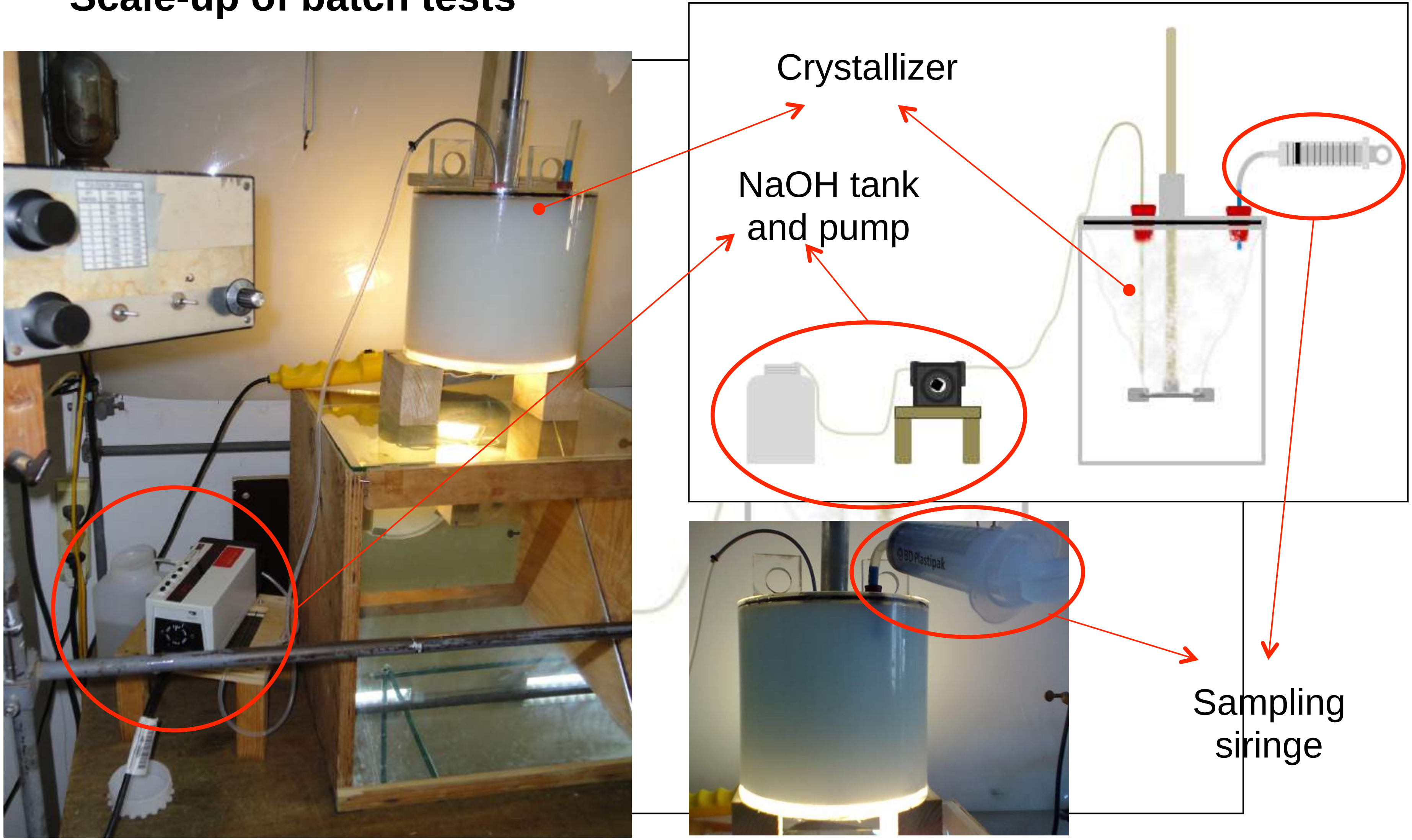


Precipitate

Filtered solution

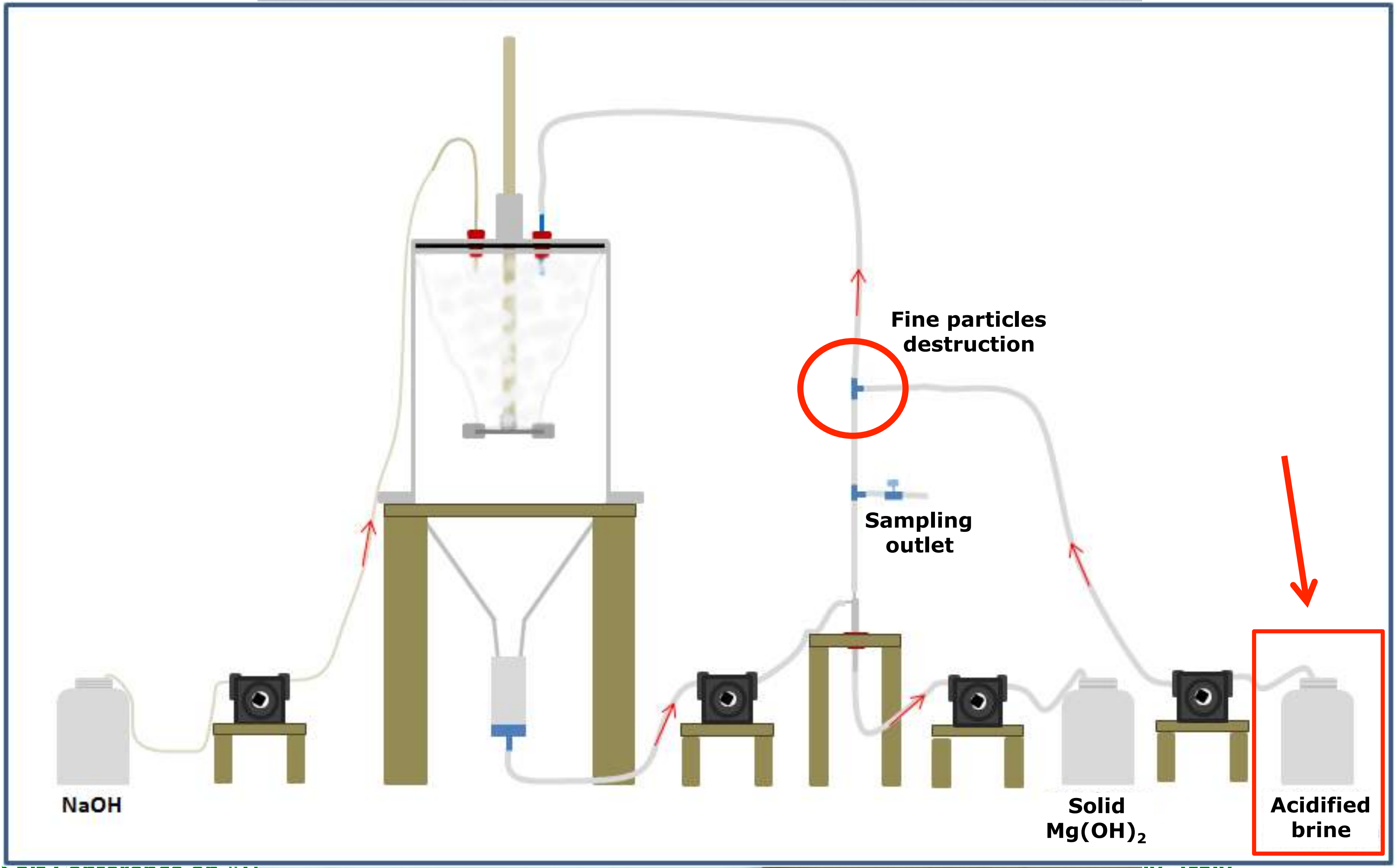
Mg recovery from exhausted brine

Scale-up of batch tests



Mg recovery from exhausted brine

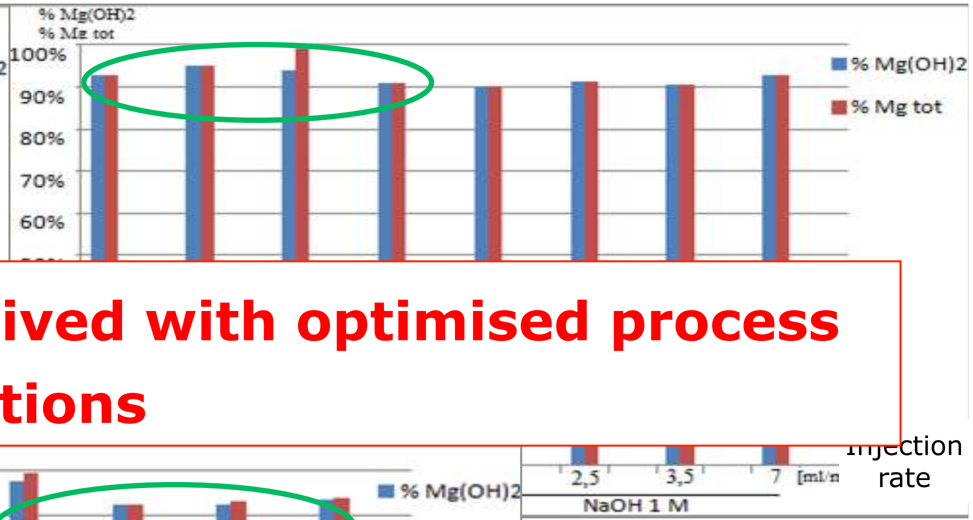
Pilot system for continuous crystallization



Mg recovery from exhausted brine

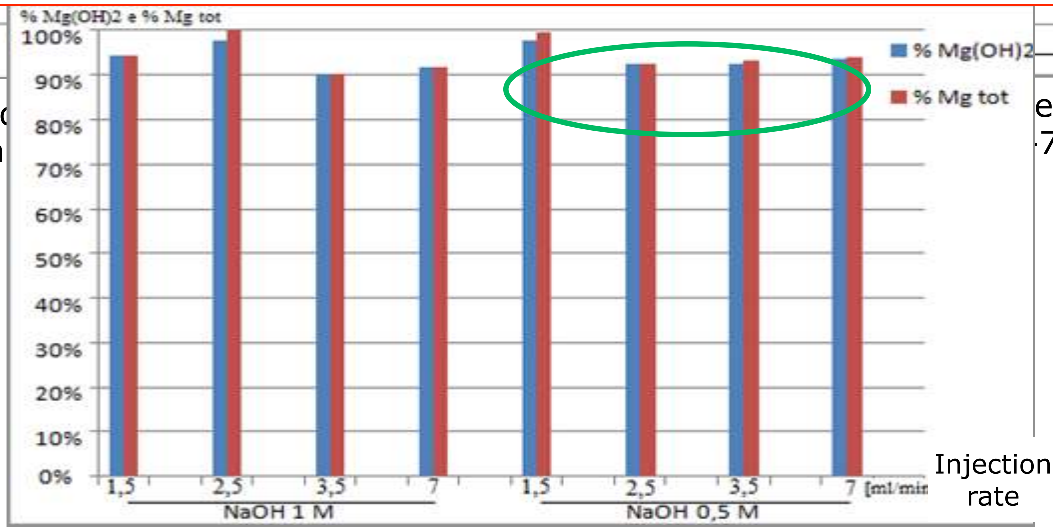
Lab-batch tests results: magnesium purities

T= 25°C; impeller speed
injection rate: 3,5 ml/m



ed: 570 RPM; NaOH
-7 ml/min

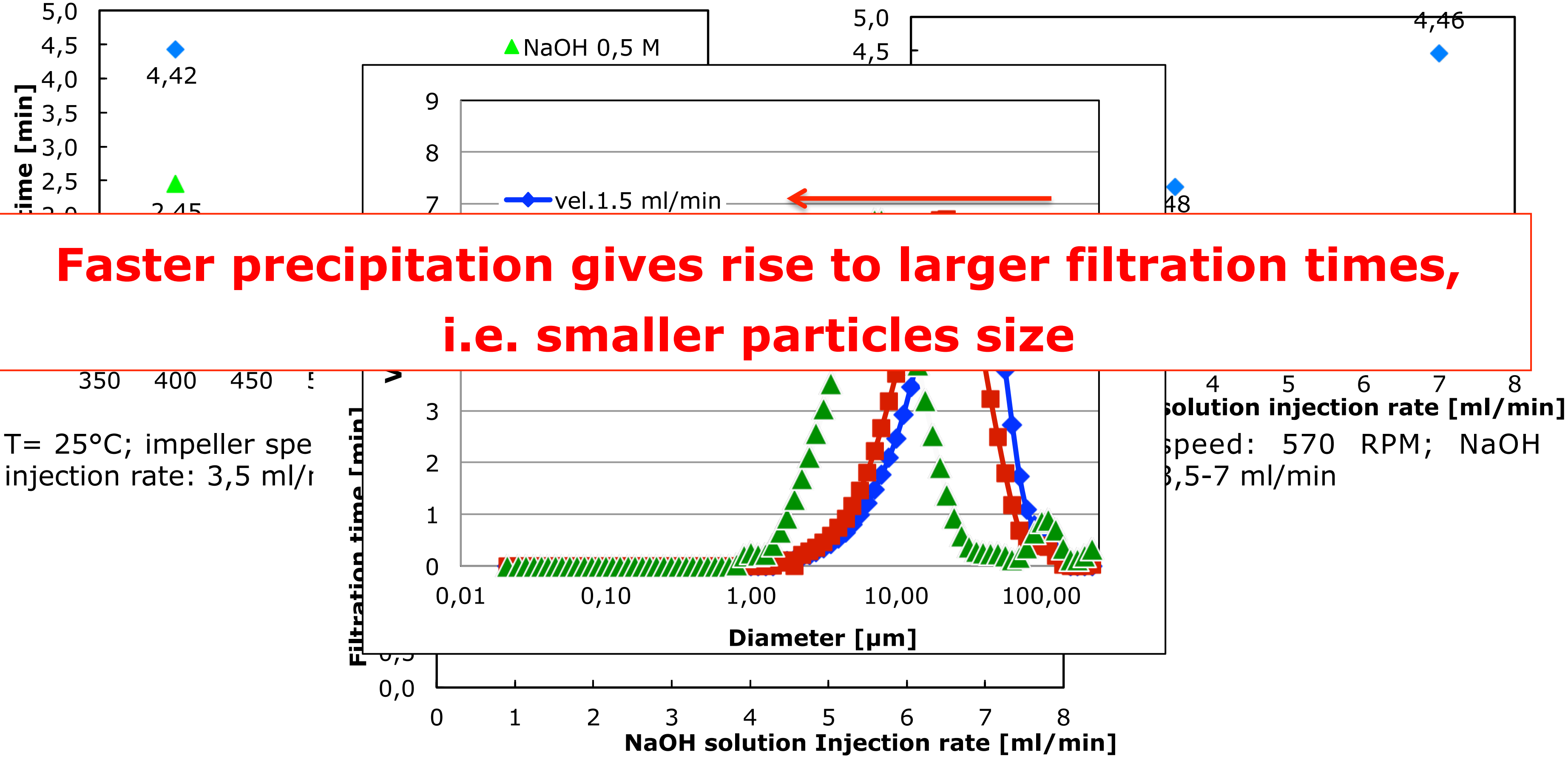
Purities up to 99% were achived with optimised process conditions



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

Mg recovery from exhausted brine

Lab-batch tests results: filtration times



Faster precipitation gives rise to larger filtration times, i.e. smaller particles size

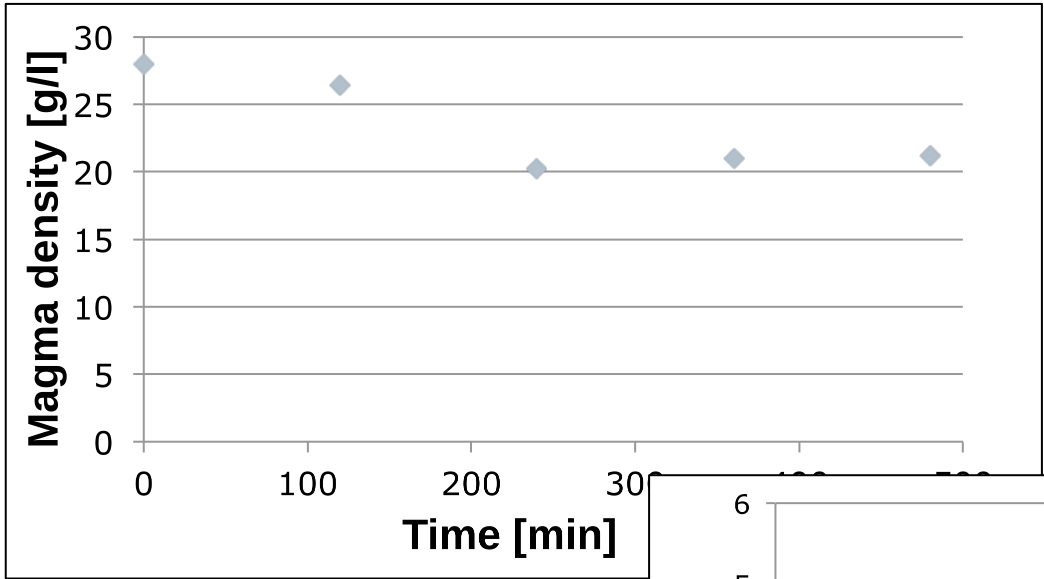
T= 25°C; impeller spe
injection rate: 3,5 ml/

speed: 570 RPM; NaOH
3,5-7 ml/min

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

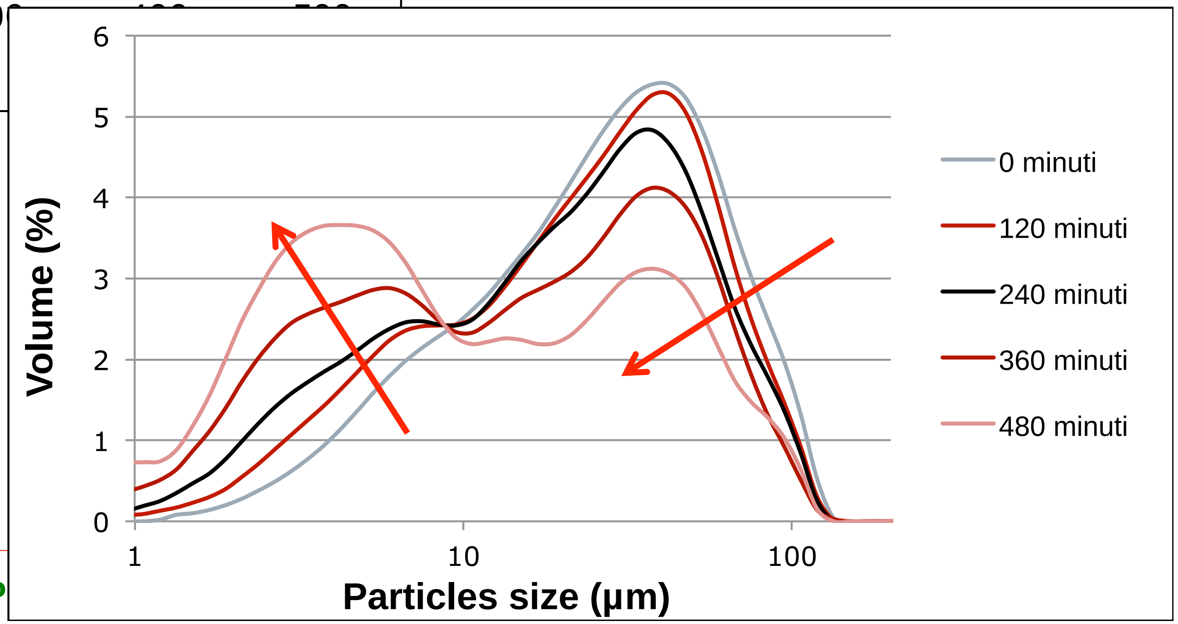
Mg recovery from exhausted brine

Pilot system results: suspension density and granulometry



Steady state achieved for the magma density

Transitory conditions still observed for the particles granulometry



Mg recovery from exhausted brine

Pilot system results: magnesium purities & process yield

Pilot test n.1		
Normalised time	Mg purity (%)	η_{yield} (%)
0	99.9	100
0.8	100	100
1.6	100	100
2.4	100	100
3.2	99.8	100

Mg purity (%)
99.8 – 100 %

Mg recovery efficiency
100%

Pilot test n.2		
Normalised time	Mg purity (%)	η_{yield} (%)
0	99.9	100
1.1	99.9	100
2.2	99.9	100
3.3	100	100

Pilot test n.3		
Normalised time	Mg purity (%)	η_{yield} (%)
0	99.9	100
1.1	99.9	100
2.2	99.8	100
3.3	99.9	100

Mg recovery from exhausted brine

Laboratory tests results: precipitation efficiency

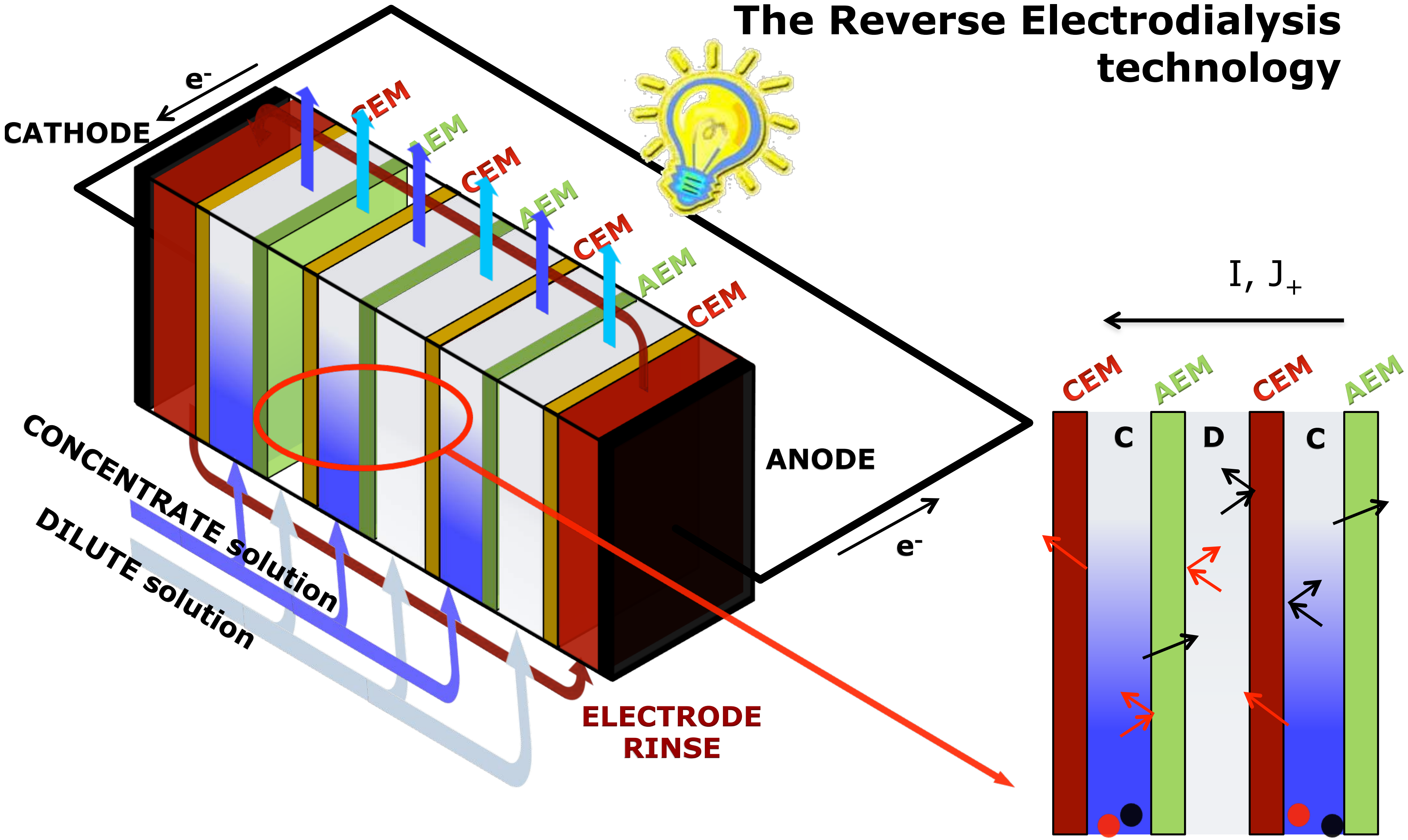
In all tests the efficiency of Mg removal has been between 99 and 100%

Ca^{2+}- & Mg^{2+}-free brine is obtained, perfectly suitable for feeding a Salinity Gradient Power - Reverse Electrodialysis (SGP-RE) unit

REAPower

Energy production from brines

The Reverse Electrodialysis technology

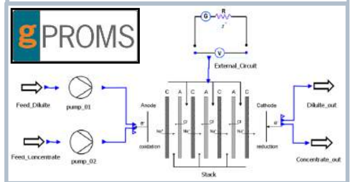


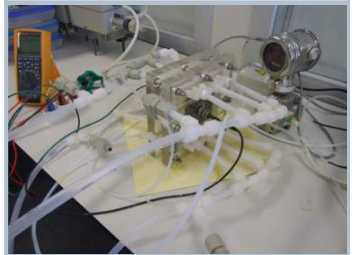
Energy production from brines

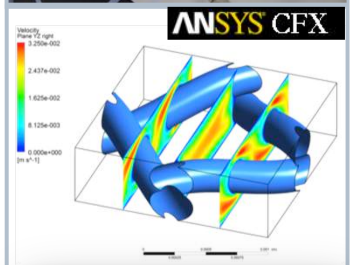
Salinity gradient power from brines: the REAPower project

The idea

to produce energy from salinity gradients generated by sea/brackish water and ultra-concentrated brines







R&D strategy

- ✓ Development of new **Ion Exchange Membranes** for highly concentrated solutions
- ✓ Selection of best conditions for **redox couple/stack design**
- ✓ Wide **experimental investigation** on lab-scale stack
- ✓ Development/validation of a **predictive modelling tool**
- ✓ **Economic analysis** & process sustainability on large scale

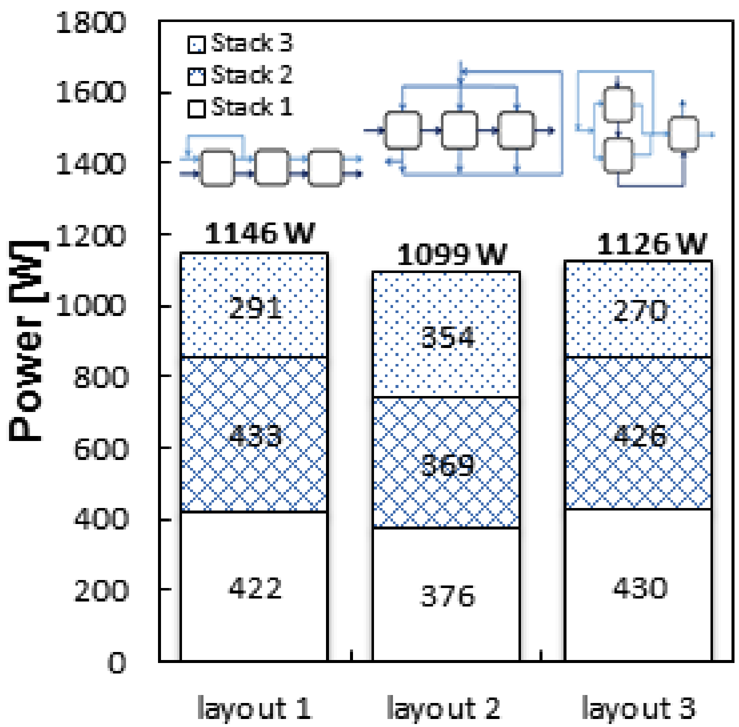
, Italy

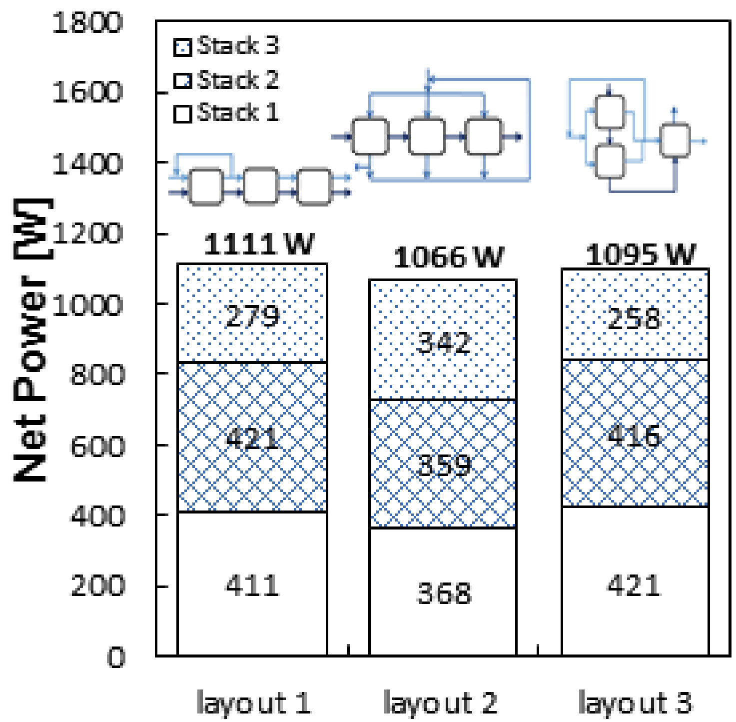
Energy production from brines

Prototype commissioning

Energy production from brines

REAPower final **TARGET** : **1000 W**





Simulations of 3 stacks (500 cells) equipped with Fujifilm membranes 44×44 cm^2 and 270 μm woven spacers; C_{HIGH} = 5 M; Q_{HIGH} =29.4 lt/min; make-up of brackish water, Q_{MU} = 40 lt/min, C_{MU} = 0.03 M.

Conclusions

Exploitation of desalination brines can be a significant resource if an effective integrated production cycle is design and realised

An experimental saltworks has been tested in Trapani (Italy) for the production of about 3000ton/year of NaCl from 600m^3/day MED brine

A capacity increase by 20-30% was registered in the saltworks with respect to conventional operation cycles

Exhausted brines from saltworks can be further exploited for the production of minerals, such as Mg, as demonstrated by batch and continuous precipitation tests carried out at lab-scale

Concentrated brines can also be used for power generation from salinity gradients, as demonstrated by the SGP-RE prototype installed and operated within the EU-FP7 funded REAPower project

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THANKS

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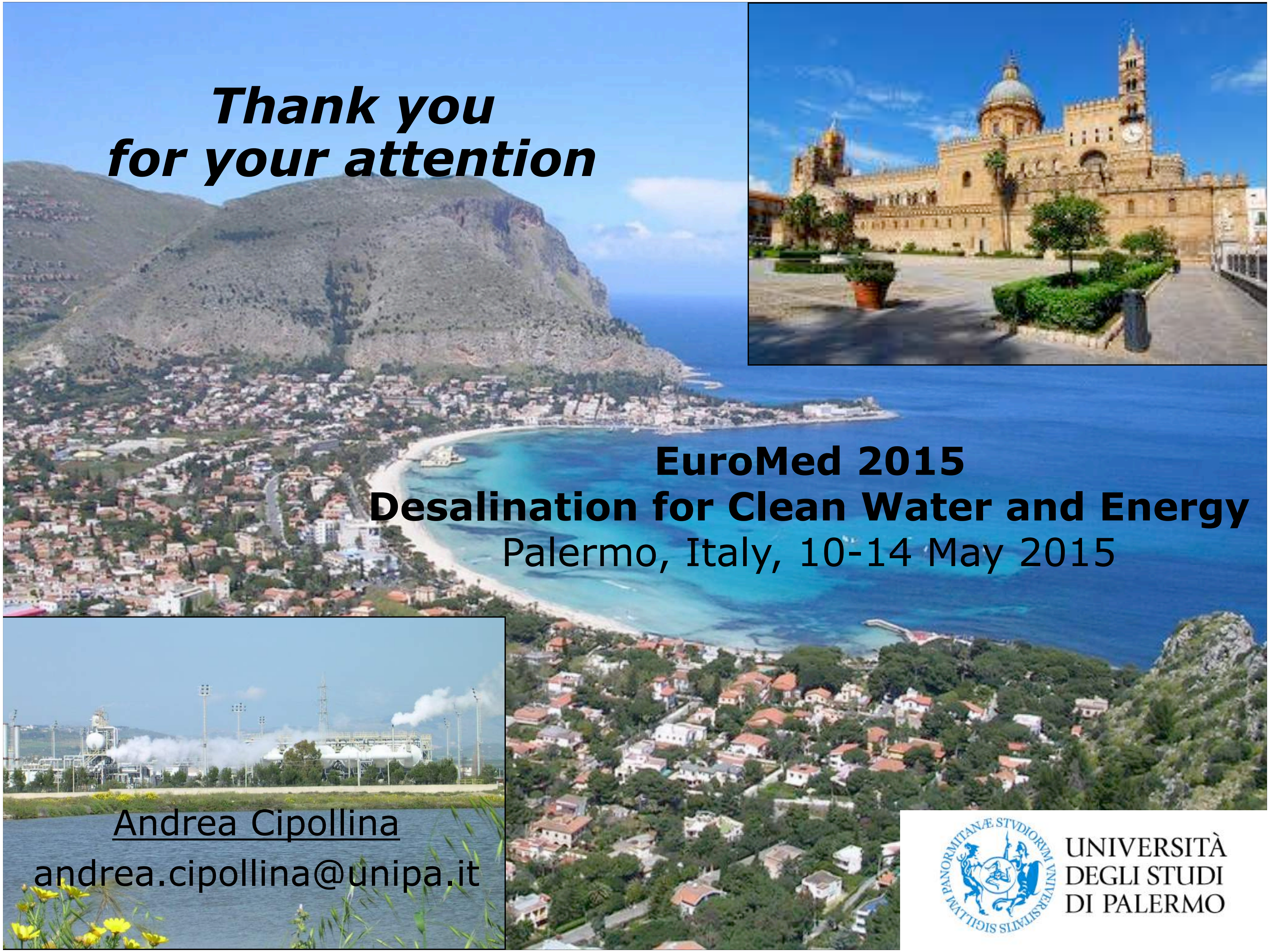
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