An integrated cycle for the production of fresh water, minerals and energy from sea

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ABSTRACT Seawater desalination is becoming an important source of fresh water in several different countries all around the world. One of the main drawbacks of desalination processes, however, is related to the disposal of large quantities of concentrated brine, which is an always-present by-product of the process, yet characterised by huge potentials of exploitation as a source of valuable raw materials and energy stored in the form of salinity gradient.

A first integrated production of fresh water and salts can be achieved using the brine produced from a desalination plant as a feed for conventional salt ponds, with the advantages of using brine more concentrated than seawater and, in the case of thermal desalination plants, warmer than seawater. By doing so, the process is faster as a consequence of the evaporation rate enhancement on the surface of ponds. The above concept has been investigated for several years, but only rare examples exist of real applications. A pilot-scale investigation has been performed in the last 5 years in Trapani (Italy), where a 36000 m^3/d MED-TVC plant is operating very close to a traditional salt pond normally fed with seawater.

Furthermore, the use of fractionated crystallisation process, typically adopted in conventional salt ponds, allows for the easy separation of salts like Calcium Carbonates and Sulphates, Sodium Chloride and a final saturated brine which is extremely rich in Magnesium as a sole bivalent cation. Thus, the possibility of a further exploitation of such saturated brine has been experimentally analysed by laboratory tests in order to produce high purity Magnesium to be commercialised in the pharmaceutical, food and metal industries.

Finally, concentrated brines from any of the final stages of such processing cycle can be adopted within a Salinity Gradient Power generation process for the production of energy through the Reverse Electrodialysis technology, as demonstrated within the EU-FP7 REAPower project (www.reapower.eu).

A complete overview of the activities so far carried out in these three directions will be presented, highlighting the big potentials for the enhancement of salt pond production capacity, recovery of important raw materials from a non-conventional "mining" source and production of renewable, clean and safe energy from solar/wind generated natural salinity gradients.

Key words: Environment; seawater desalination; brine re-use; sea salt; magnesium recovery; salinity gradient power

1. INTRODUCTION

In recent years, seawater desalination processes have been considered more and more suitable non-conventional water sources for the supply of high quality drinking water in areas affected by water scarcity and droughts problems.

However, several concerns have been raised regarding the environmental impact of desalination processes, mainly due to the production of a concentrated effluent (blow down brine) that must be accurately managed. In the case of sea-water desalination plants, installed nearby the coast, the brine is commonly discharged back to the sea.

In general, increasing the process Recovery Ratio will reduce significantly the volumes of brine to be disposed, but on the other side it will also increase the concentration of salts in the brine to be discharged. Moreover, the Recovery Ratio is strongly limited by the feed water salinity of and the features of the desalination process.

Typically Sea Water Reverse Osmosis plants produce waste brine with concentration in the range 65000-85000 ppm, while Thermal desalination plants (MED, MSF) usually discharge a more diluted brine, also due to the high consumption of cooling water, which is very often mixed with the brine before its disposal. In this case typical values of brine salinity are around 10-15% higher than feed seawater.

In all cases, the continuous release of a reject stream, often characterised by high salinity and/or temperature, can be dangerous for marine life, especially in protected marine environments [Latteman, 2009; Peters and Pintò, 2008].

Normally the cost of brine disposal ranges from 5 to 33% of the total cost of desalination [Glueckstern and Priel, 1996], depending on: the amount of brine, the level of treatment before disposal, the nature of the surrounding environment and the disposal method. Thus, brine volumes minimisation is a fundamental target for reducing both potable water costs and at the same time the environmental impact of the desalination process.

The easiest way for reducing brine volume is the use of an evaporation process. To this regard, the use of evaporation ponds for brine disposal and/or concentration has several advantages compared with the other options listed above. Ponds are relatively easy to construct, require low maintenance and no mechanical equipment is required except for the pump conveying the brine to the pond. Of course, the main problem of evaporation ponds is related to the large amount of land required for the brine disposal, but also the potential of contaminating underground potable water sources by seepage from the pond [Truesdal *et al.*, 1995]. The use of an evaporation pond for brine reduction is therefore feasible in dry and warm sites where land cost is low, evaporation rates are high and no risk of natural underground water sources is present.

In order to overcome some drawbacks of evaporation ponds Gilron et al. [Gilron *et al.*, 2003] have worked on the development of a novel process: the WAIV (Wind Aided Intensified eVaporation). In WAIV process brine evaporation surface is increased by distributing the brine over vertical tissues, reducing in this way the evaporation device land requirements. A bench pilot unit with a footprint of 0.17 m^2 and an evaporation area of 1 m^2 has been tested by the mentioned research group and a rotating frame has been designed for positioning of the evaporation surfaces parallel to the main wind direction in order to further increase the evaporation rate [Katzir *et al.*, 2010].

Another example of enhancing of natural evaporation is reported in the work of Arnal et al. [Arnal *et al.*, 2005], who used capillary adsorbents for increasing evaporation rate, in order to improve the evaporation productivity of an evaporation pond.

The exploitation of brine potentials has been raising interest among scientific communities worldwide. The use of standard methodologies for salt (NaCl) production can be sometimes coupled with the recovery of brines from desalination plants and significant advantages can arise, as shown in some works recently presented in the literature [Ravizky and Nadav, 2007]. Moreover, the increasing cost of raw materials and continuous technological development of separation processes are also pushing towards the recovery of higher value minerals, such as Magnesium salts, in competition with the standard minerals sources related to mining facilities.

The present paper focuses on the description of an integrated approach to the solution of brine disposal problem and exploitation of brine potentials (Fig.1), which has been adopted and experimented in the Mediterranean site of Trapani (Sicily, south of Italy) [Cipollina *et al.*, 2012]. The concept idea is that of using the brine exiting from a MED-TVC desalination plant to feed a small experimental saltworks. The saturated exhausted brine, eventually, exiting from the final basins of the saltworks can be used for extraction of magnesium salts, thus providing a further added value to the overall integrated process. Finally, very concentrated brines at the various stages of the integrated process, can be used for energy generation within Salinity Gradient Power Reverse Electrodialysis (SGP-RE) systems, as demonstrated within the EU-funded REAPower project.

Field investigation has allowed the characterisation of the new operating conditions within the experimental saltworks "Mariastella" after feeding with brine from the MED-TVC plant. At the same time laboratory tests have been performed for assessing the potential for Magnesium recovery from exhausted saturated brines also giving some ideas of the tremendous exploitation potentials of such approach. Finally, a prototype unit for Salinity Gradient Power generation has been installed and operated in the saltworks of Marsala (Trapani, Italy), being the first example of pilot system operating in such conditions.

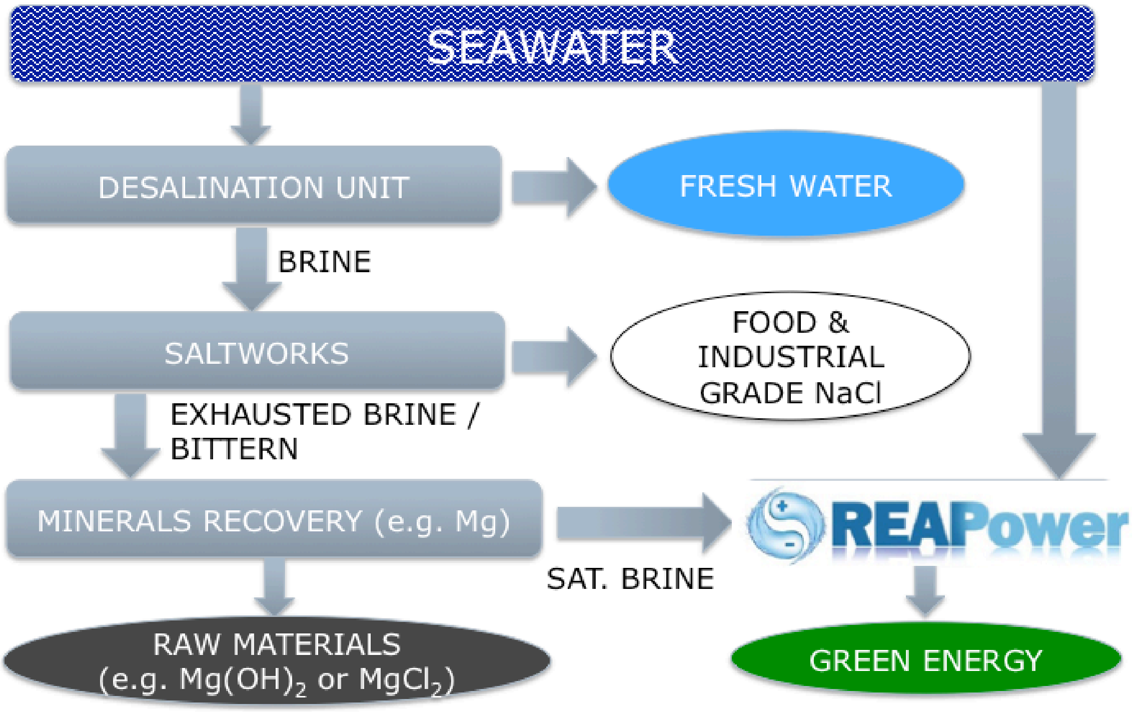


Fig.1 Schematic view of the integrated process for the production of fresh water, salts, minerals and energy from seawater.

2. THE SINGULAR FRAMEWORK OF TRAPANI MED PLANT AND SALTWORKS

Trapani is a small city in the west coast of Sicily (Fig.2), in the heart of Mediterranean Sea. Since the Roman times, it has been an important center for the production of salt from seawater, thanks to the natural presence of saltworks, which have been readapted and optimized for the production of large quantities of salt and still operating for more than 2000 years.

Nowadays, one of the major problems of Trapani and surrounding villages is the water supply, due to severe drought periods that occurred in the last decades. For this reason, a MED-TVC desalination plant was constructed in the ‘90s to provide about 36,000 m^3/day of fresh water to be mixed with other conventional sources and distributed to the population.

A peculiarity of this site is the closeness of the desalination plant to the conventional Trapani’s saltworks, which has allowed the assessment of the integrated approach presented in this study, as it will be illustrated in the following paragraphs.

Fig. 2 Google maps view of Trapani position with a zoomed view of the area hosting the MED-TVC desalination plant and the experimental saltworks "Mariastella".

2.1. Description of the MED-TVC plant

The desalination plant in Trapani, started-up in 1995 with the financial support of the Sicilian Regional Government (also owner of the plant), is constituted by 4 MED-TVC units with a capacity of 9,000 m^3/day each [Cipollina *et al.*, 2005]. Each unit consists of 12 with horizontal tubes evaporation effects, with parallel feed configuration, and a thermal vapour compressor (middle pressure steam ejector) as sketched in Fig.3 .

Inlet seawater undergoes a basic pre-treatment step with some screening and sand removal. Shock chlorination was performed at the intake, although recently no chlorination at all is performed. Pre-treated seawater reaches two plate-heat exchangers where it is pre-heated, while exiting distillate and brine (only in winter season) are cooled before storage and disposal, respectively. Then, the feed reaches the down condenser where it is further heated, while condensing part of the vapour exiting from the last stage, and eventually goes through the distributors of each stage.

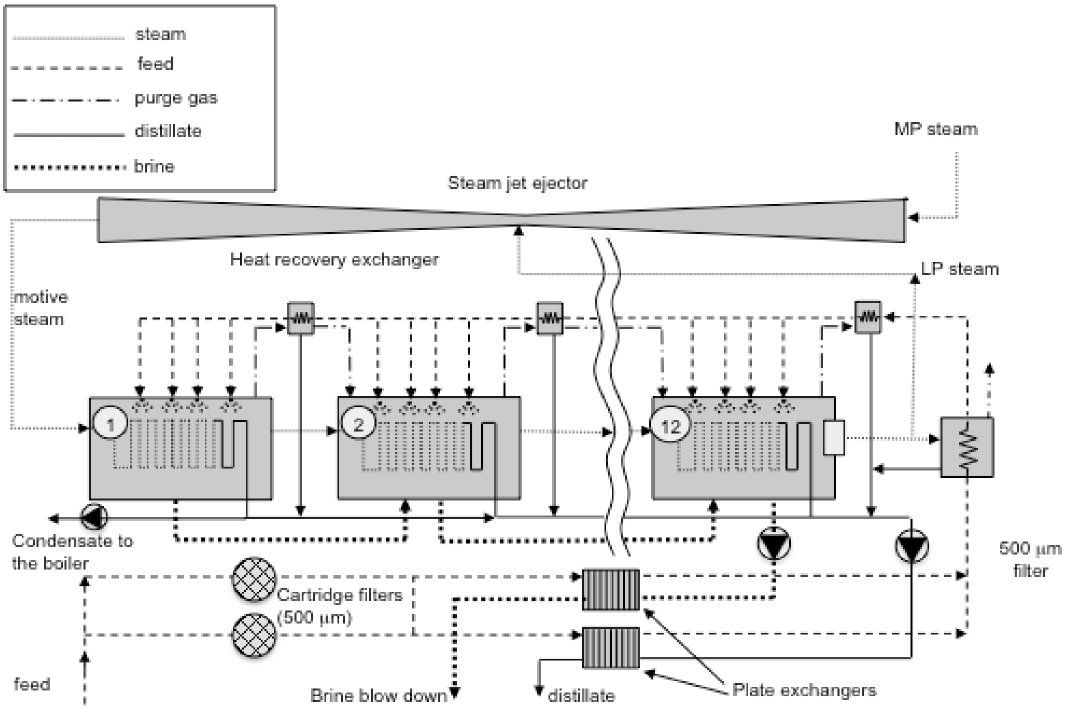


Fig. 3 Sketch of a MED-TVC unit of the desalination plant in Trapani [Cipollina *et al.*, 2005].

The plant has got a parallel feed configuration, with heat recovery exchangers positioned every two effects, where the feed is heated again before entering evaporation stages, by recovering heat from a mixture of vapour and non-condensable gases extracted from the effects. In each stage the feed is sprayed on the tube-bundle evaporator and the formed vapour leaves the chamber to enter in the tube side of the following effect.

The brine passes from each effect to the following one incurring in a sudden pressure reduction and flashing process which produces an extra amount of vapour. The distillate condensing inside the tube bundle of each stage is collected and eventually pumped to the post-treatment section.

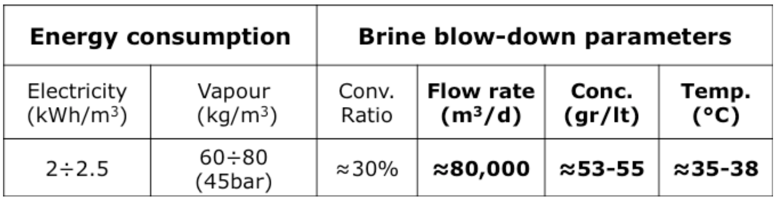
Vapour produced in the last effect passes through a demister and, after being split, is partially sent to the down condenser, where it is condensed and cooled by the cold feed seawater, and partially re-compressed by a steam ejector with motive steam at 45 bar. In such a way, the re-compressed vapour can act as motive steam to the first effect, thus enhancing the GOR of the process.

The first evaporation effect operates at a maximum temperature of 62°C in order to minimize scaling problems in the tube bundle. Thanks to the optimised thermal integration of the plant and the high efficiency of the thermal vapour compression system, the nominal Gain Output Ratio of the unit is of 16.6 kg of distillate/kg of vapour, which is normally reached and sometimes exceeded during standard plant operation.

2.1.1. Parameters of interest for the use of process brine to feed the saltworks

The process nominal Recovery Ratio is about 30%, with an inlet seawater salinity of 37 gr/lt. Thus the brine exiting from the last stage has got a nominal flow rate of about 21,000 m^3/day (per each unit) and a salinity of approximately 53 gr/lt. Exiting brine temperature can vary of several Celsius degrees during the year, however values up to 35-38°C are common in summer season, thus being significantly higher than seawater temperature (normally below 24°C). Table 1 summarises the main operating parameters of interest for this study.

Table 1. Main operating parameters of the MED-TVC plant under study



Energy consumption		**Brine blow-down parameters**			
Electricity (kWh/m^3)	Vapour (kg/m^3)	Conv. Ratio	**Flow rate (m^3/d)**	**Conc. (gr/lt)**	**Temp. (°C)**
2÷2.5	60÷80 (45bar)	≈30%	**≈80,000**	**≈53-55**	**≈35-38**

As it concerns the use of chemical additives, only low temperature anti-scalant (Belgard EV2050) and anti-foaming (Nalco 131S) at very low concentrations are added to the feed seawater.

Feed disinfection was performed only as shock treatment at the seawater intake, but in the last years no disinfection at all was done. However, given the long path and the relatively high temperatures inside the evaporation units, residual effects in exiting brines can be normally considered negligible in thermal plants.

2.2. Description of “Mariastella” saltworks

Mariastella saltwork is a typical saltwork of the western Sicilian coast for sea salt production (Fig. 4). In such saltworks the salt density grows from the initial value of 3.5% (sea water) up to the saturation point of sodium chloride (25.7) by means of the evaporation induced by the sun energy. The water flows through several order of ponds within the saltwork while that the density grows. In the typical design of such a saltwork (reference is given to the Mariastella layout of Fig. 5 in what follows) there are four order of ponds, each order being characterized by a well-defined density range:

- 1st order, called “cold ponds” (FR1,2 in Fig. 5, with reference to the Mariastella saltwork): 3,5Bè to 5-6Bè, it covers 20-25% of the total saltwork surface, with a depth of 50-100cm;
- 2nd order, so called “driving ponds” (VAC, VG1,2,3 in Fig.5). The number of ponds depends from the saltwork design. The density grows in this kind of ponds from 5-6Bè to 10-12Bè. Their total surface covers 20-25% of the total saltwork surface. The pond depth is here reduced to <50cm;

- 3^{rd} order, (hot ponds, CSE1,2, SE1,2, CA1,2 in Fig. 5) made by several small and shallow (<40cm) ponds, covering 40-45% of the total saltwork surface. Here the pond segmentation is very fine. Each pond has a surface of 1000-2000m^2. A sequence of four (not less than three) ponds is fed with the water coming from the "driving ponds" at a density of 10-12Bè. In the last pond of the sequence the water reaches the saturation point of sodium chloride (25.7Bè). The number of parallel sequences depends on the saltwork design and dimension. Each sequence of hot ponds feeds one or two crystallisation ponds with saturated brine, that represents the 4^{th} and last order of ponds;
- 4^{th} order, made by several crystallisation ponds (CR1,2. Each of them has roughly the same dimension as the hot ponds. They are very shallow (<25 cm) with very flat soil. The salt crystallises only in this order of ponds. During the hot season a crust of ~10cm is grown in 40-45 days in the crystallisation ponds, where it is harvested once or twice according to the season's climatic behaviour. The crystallisation ponds cover not more than 15% of the total saltwork surface.

Fig. 1 View of a basin of "Mariastella" saltworks with the MED-TVC plant in the background.

The water flow, mainly driven by gravity through the ponds, and its correct distribution, are guaranteed by small canals connecting the ponds and, whenever needed, by small low prevalence pumps. The saltwork master regulates the water flux feeding the "cold pond" with fresh water and shifting the brine from one order of ponds to the other according to the evaporation rate. This ensures that each order of ponds represents, at any time, a storage of concentrated water with a well-defined density range. Moreover, salts other than sodium chloride precipitate in different ponds according to their own saturation point. The resulting NaCl content of the produced salt ranges from 97-98.5%.

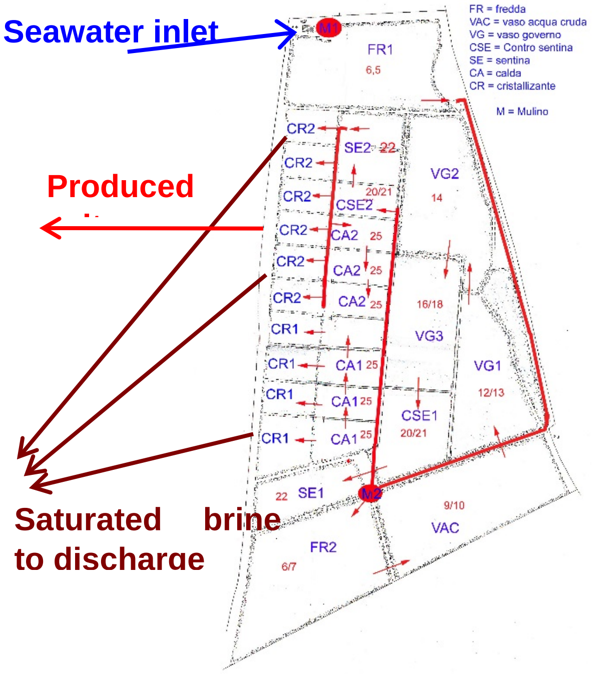


Fig. 2 Schematic process flow layout of "Mariastella" saltworks in the traditional configuration [Cipollina *et al.*, 2012].

The production cycle is repeated with yearly frequency. Saltworks feeding normally starts at the end of April, when the evaporation rate starts to be important (it will stay between 1 and 1.5cm/day up to September, with peaks up to 2 cm) and the rainfall is correspondingly reduced (<100mm integrated rainfall from May to September). 12-15 cm of salt crust is grown every year with a typical figure for the production/ha of (1-1,2)×10^3 ton/10^4m^2. Harvesting is done twice, or even three times a year, in case of very dry seasons.

As far as the Mariastella saltworks are concerned, Table 2 summarises the trend of salt production historical data in the period 2000-2007.

Table 2 Geometrical features and operating data of Mariastella saltworks

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

The saltworks yearly productivity can dramatically vary according to the meteorological conditions occurring during the productive season. Nevertheless, for Mariastella saltworks in the 10 years from 1998 to 2007 the production has ranged from values of about 1600 tons/year to values of 2350, with an average production of 1700 tons/year.

3. Feeding the Mariastella saltworks with the MED plant brine: a three-year experience

3.1. The new operating configuration of the experimental saltworks

In 2008 a novel feeding scheme has been adopted for testing the possibility of enhancing the production of salt in an experimental saltworks by using the brine from a desalination plant to feed the saltworks itself.

This has been done within the above described Mariastella saltworks, where the output flow of one of the four MED-TVC units has been intercepted and sent, through a 30m-long pipeline, to the Mariastella VAC pond, thus substituting the direct seawater intake. The saltworks feeding is thus made with a 5,5Bè brine instead of 3,5Bè fresh seawater. This allows the entire concentration process to be shortened and fastened. The logical process of the brine flow is, from now on, absolutely unchanged. The brine path through the ponds is instead adapted, as far as its first part is concerned, to the new intake point. As shown on Fig. 6, after the VAC pond the brine is sent to FR2 and, with the aid of the low prevalence pump M1, to FR1 (the first pond of the path in the former configuration) and from here to the VG1 pond. From this point on, the path is unchanged, repeating exactly the process layout of the traditional configuration.

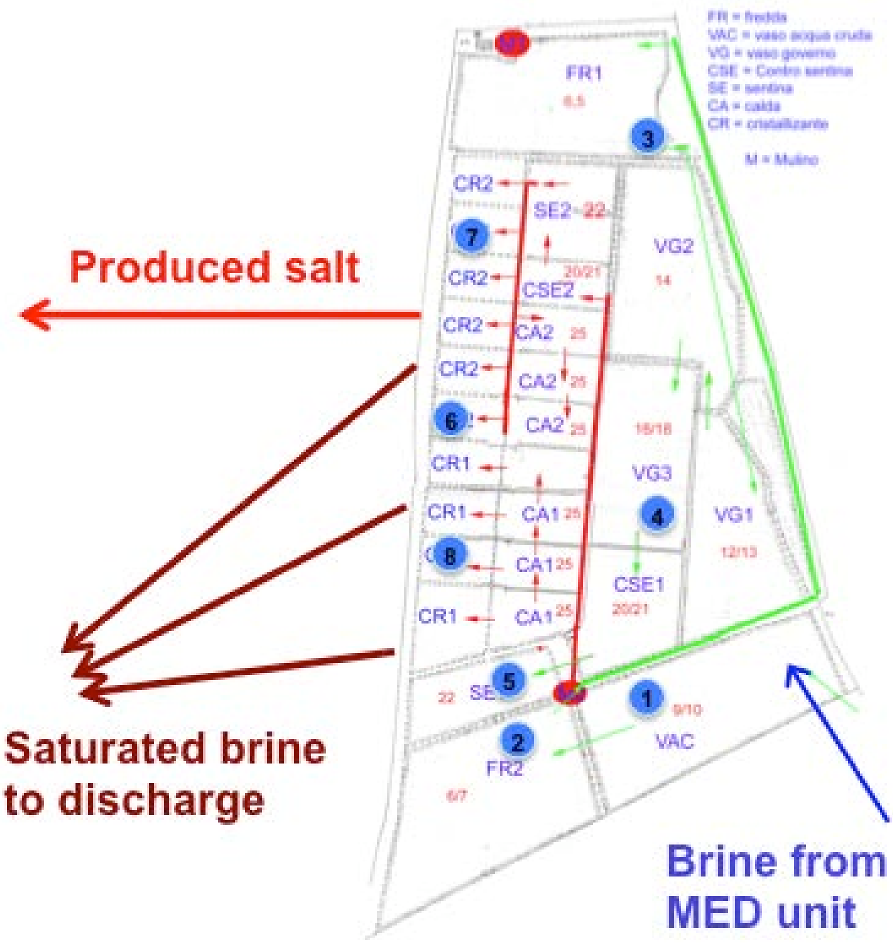


Fig. 6 Schematic process flow layout of "Mariastella"saltworks in the novel configuration, where brine from the MED-TVC plant is used as feed stream. Blue circles indicate sampling for IC analysis with the relevant basin identification number [Cipollina *et al.*, 2012].

As it is obvious, since the density starting point is higher, and the path length the same, the saturation point of the brine is reached before (in terms of progressing basins) and in a shorter time. The production is therefore enhanced. This advantage can be in principle managed in two ways:

- Increasing the crystallisation surface, by adding some new crystallisation ponds. The main requirement to be respected for an efficient saltworks design is the ratio C/T between the crystallisation surface C and the total saltworks area T, which should be no larger than 15%, with an *optimum* value of 1/8. Since the so-called cold pond of a traditional saltworks covers a surface of >20% to let the density increase from 3.5Bè to 5.6Bè, this means that the effective saltworks area is *de facto* increased by a factor 1.25 when the process starts at 5.6Bè as it happens by feeding it with the outlet of the desalination plant. For the traditional Mariastella saltwork the ratio C/T was equal to 15.68%, which has been practically reduced to 12.54% if considering the (fictitious) basins area

T’=T×1.25, also taking into account the first evaporation step occurred within the MED unit. This almost leads to the achievement of the *optimum* value of 1/8, thus indicating that a further increase of the crystallisation surface C would unbalance such optimal ratio.

- The second way to manage the enhanced evaporation process is to let a larger salt crust grow in a shorter time on the same crystallisation surface. This has been the preferred solution in the Mariastella case.

3.2. Benefits and problems of the new operating configuration

The first test season for the new method has been 2008, when exceptional climatic conditions allowed a 30% increase of salt production with respect to the average values registered in all the saltworks of the area. A production of raw salt of 2900 tons has been estimated in the Mariastella saltworks, to be compared with a mean value of 1815 tons over the last 10 years[1], which means an increase of ~60%. At the beginning of 2009 harvesting season, a huge hurricane bet the Western Sicilian coast. Only 30% of the production has been saved in the Mariastella saltworks, which is obviously not significant and caused a strong depletion also on 2010 data. In 2010 in fact an estimated production of 1650 tons has been registered. This results is again a very poor one, that cannot be compared to the result of other saltworks in the area.

The hurricane of September 16, 2009, that has a repetition time, in the area, of less than 1 event/50years (last recorded event is of September, 3, 1965) was in fact very localised and affected Mariastella saltworks to a much larger extent than the other saltworks of the area both for its localisation and for the position of Mariastella, very close to public roads and less protected by guard rings canal than the others. This means that the usual concentrated water storage done by the saltworkers in the winter period was completely spoiled-out in the 2009-2010 winter and, despite the new feeding method, the 2010 production was also strongly depressed.

A normal situation was restored in 2011 and 2012, confirming a definite strong enhancement of the production. A total production of 2500 and 3000 tons has been registered, in 2011 and 2012 respectively, more than 60% larger than the 1997-2007 mean value[1], to be compared with the results of other saltworks of the area, whose production showed a value 15-20%% larger than the mean value[1] taken in the same reference period. Despite the relevant data concern only three years of production, and therefore only preliminary conclusions can be drawn, a benefit of 20-30% production increase turns out in using the outlet of the Trapani desalination plant.

As it concern possible drawbacks generated by the new configuration (both in terms of quality of the salt and possible effects of the chemical additives used in the MED-TVC plant pre-treatment stage), on the basis of similar past experience already presented in

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[1] The mean value is always calculated taking the last 11 years data and discarding the worst result, assuming that once every 10 years there is a singularity, which significantly affects the production of a single unit.

the open literature regarding the use of desalination brine to enhance saltworks productivity, a number of different aspects were monitored during these three years of experiments in Trapani.

In particular Ravizky and Nadav in 2007 presented the experience of using a reverse osmosis brine for feeding a saltwork in Eilat. According to such experience, a number of problems may arise due for example to:

- The use of chemical additives within the desalination plant pre-treatment stages (particularly in the case of a RO brine, which may contain inorganic or organic flocculants, anti-scalant and anti-fouling agents), which may dramatically influence the biological growth within the saltworks basins;
- Different brine compositions (in the case of the Eilat plant, the RO unit treated a seawater/brackish water mixture with a composition fairly different from seawater, thus affecting the fractionated crystallisation steps normally designed for saltworks operated with seawater);
- Salt precipitation when brine has to be transported for long distances.

In the present case, most of the above presented concerns have been faced and solved before the field tests started in 2008.

The MED-TVC plant in Trapani has always operated with seawater, thus maintaining basically the same feed composition of traditional saltworks.

The lucky location of the MED plant, basically beside the Mariastella saltworks, has allowed the use of a simple 30 m long pipe for brine transportation.

As it concerns the presence of chemical additives present in the brine, pre-treatment in the MED-TVC unit is rather limited to the use of a discontinuous shock disinfection procedure at the seawater intake (which does not leave any residual chloride in the brine, and has been stopped in the last 2 years of operation) and the addition of very small quantities of commercial antiscalant and antifoam agents. Both of them are classified as “no environmental risk and food-grade” products, thus not representing a significant risk even if residual amounts would be entrained by the brine. Moreover, qualitative analysis have been performed by means of thermo-gravimetric measurements and no detectable amounts of these compounds have been found, also due to the large quantity of other small traces of organic matter normally available in sea-salt. Moreover, the possibility that traces of these compounds could be trapped during crystallisation process is very low, also given the washing procedure normally performed before packing the salt.

Finally, no effect has been observed in the biological parameters monitored in the saltworks. No algae bloom has occurred, while normal fauna (e.g. *artemia salina*) living in low and medium concentration basins still remained alive and active in promoting the correct operation of the saltworks, being this latter a real complex and delicate bioreactor.

3.3. Monitoring of process water composition and potentials for further exploitation of brines

Process waters along the evaporation basins were also continuously monitored in order to check for possible variation from standard operating performances. Figs. 7 shows the trend of concentration of different cations in processed brines along the evaporating basins of the saltworks. It is clear how most cations concentrate progressively along the first 5 monitored points (i.e. until crystallisation basins), with the exception of Ca^{2+}, which starts precipitating in the VG basins as calcium carbonate and sulphate salts. Na^{+} concentration is then stabilised in the crystallisation ponds, where NaCl starts precipitating. At the contrary K^{+} and Mg^{2+} concentration still rises up to values between 700 and 900% higher than initial values, i.e. up to concentrations of 8 g/l for potassium and more than 35 g/l for magnesium.

Given the above considerations, it emerges the huge potential for recovery of such materials, in particular magnesium. This is, in fact, significantly facilitated by the high concentration of Mg^{2+} achieved in the exhausted brine and by the almost complete absence of Ca^{2+} ions, which would be somehow competing in any process involving the separation of bivalent cations. Some experimental investigation has been performed by laboratory tests for precipitation of magnesium hydroxide, as it will be presented in the next section.

Another interesting application for brine exploitation potentials is the use of salinity gradients between brine and seawater for energy production. This topic has been recently addressed in the EU-FP7 funded project REAPower [www.reapower.eu], which aims at the development of a Salinity Gradient Power - Reverse Electrodialysis (SGP-RE) prototype installed and operated within the saltworks facilities in Trapani using seawater and exhausted brines as salinity gradient generating solutions.

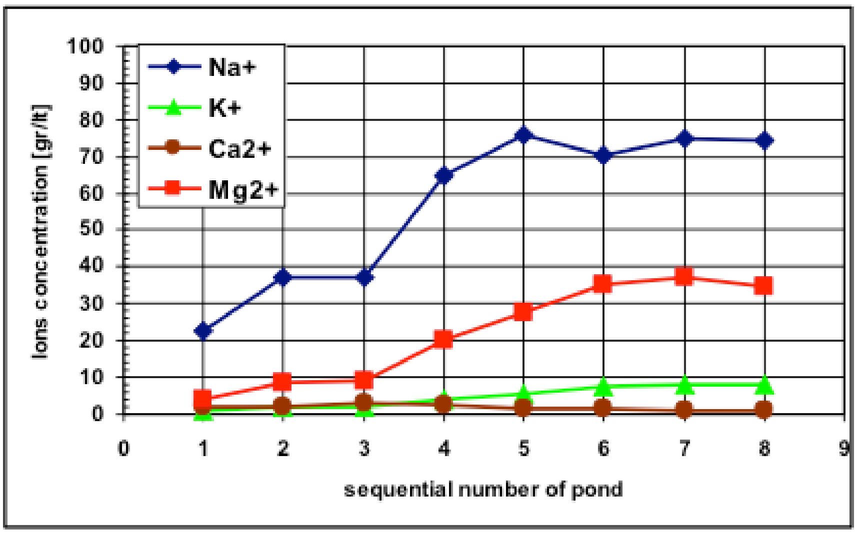

Fig.7. Increase in cations concentration (expressed in g/l) along Mariastella basins. Basin identification numbers are reported in Fig. 8.

4. Exploitation of saltworks exhausted brine for magnesium production

Given the above consideration on the large potential for exploitation of saturated brines from saltworks, some preliminary tests have been performed aiming at the feasibility assessment of performing magnesium recovery from brines by means of reactive precipitation induced through reaction with an alkaline solution. The final goal of such approach would be the quantitative recovery of magnesium salts (in this case mainly magnesium hydroxide) with high purity and with crystal sizes high enough to allow rapid separation of the precipitated phase by settling or fast filtration.

In the presented preliminary tests, the concentration and flow rate of the alkaline solution and the stirring rate of the reaction medium were changed to investigate their effect on the purity and nucleation/growth rates of magnesium hydroxide crystals. Experiments were performed at 25 and 40°C, the latter being a temperature easily accessible in saltworks just using solar irradiation.

Finally, vacuum filtration was adopted instead of gravity sedimentation to assess in a faster manner the effect of operative conditions on the size of precipitated magnesium hydroxide grains since higher filtration time can be attributed to smaller average size of precipitated particles.

In the following paragraphs a detailed description of experimental apparatus and procedures is reported along with the results of laboratory tests performed.

4.1 Experimental set-up and procedures

Experimental tests were carried out in an home-made bench scale reactive precipitation apparatus adopting two systems at different scales (mixed tank reactor volume of 0,5 l and 5 l).

In the smaller scale reactor, the system was simply constituted by a glass Becker (vol. 500 ml), mechanically stirred by a small marine impeller, that was loaded with a 50 ml of brine, with a composition reported in Table 3, diluted by a further addition of 50 ml of distilled water. The temperature of the solution was fixed by an electronically controlled thermostatic bath. A syringe pump was used to feed with controlled flow rate an over-stoichiometric (a 25% increase was used with respect to the stoichiometric quantity of NaOH required) amount of aqueous solution of NaOH used as co-reagent for the reactive precipitation. The sodium hydroxide used for the preparation of NaOH solutions was Aldrich analytical grade.

Table 3. Composition of exhausted brine adopted for reactive precipitation tests.

Brine source	pH	Concentration of main cations and anions in solution [gr/lt]						
Exhausted brine from Trapani saltworks	7.1	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Br^-
		48.30	8.62	0.46	36.06	166.1	52.32	1.76
		Analysis performed using Ionic Chromatography, after dilution 1:4000 of sampled brine						

The precipitated solid was separated from the residual aqueous phase by filtration under vacuum. The solid was carefully washed using deionized water and dried under vacuum overnight.

Both solid and liquid phases were analysed by Perkin Elmer Optima 2010 DV ICP. To this purpose a weighed amount of the solid sample was dissolved in a 1M HCl solution. The morphology of solid crystals was analyzed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter coated with gold to a thickness of 200Å.

A schematic graphical description of the experimental procedure adopted for the solid precipitation and collection is reported in Fig. 8.

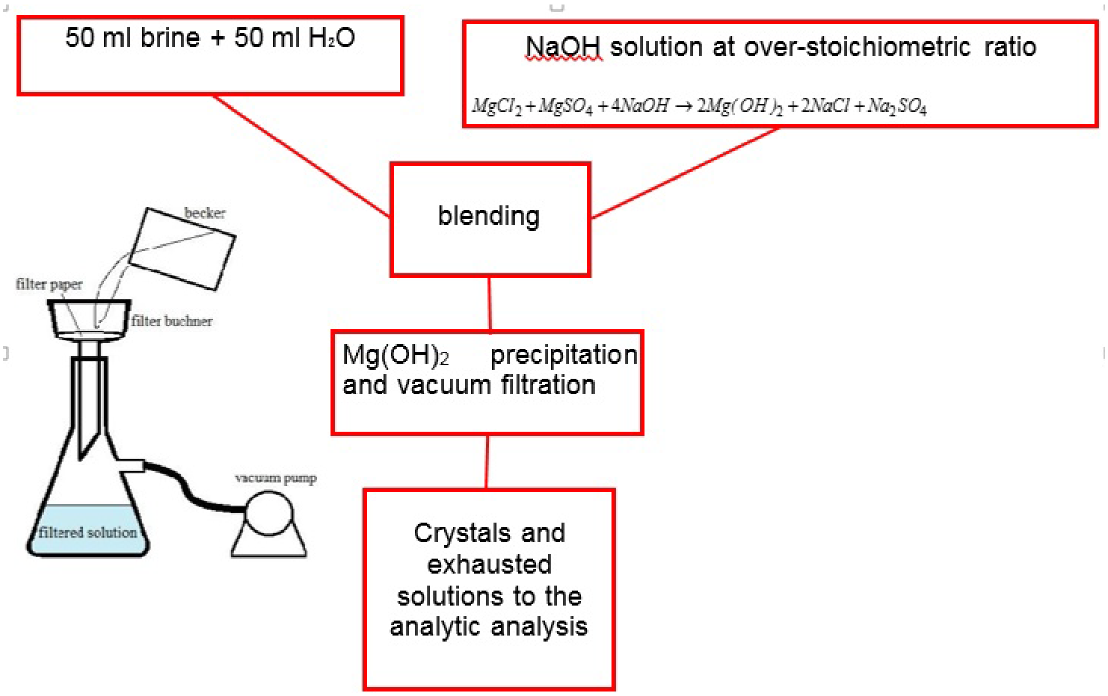

Fig. 8. Schematic description of the experimental procedure adopted for the reactive precipitation and solids separation steps.

A slightly different procedure was adopted for the 5 l reactor [Cipollina *et al*, 2014], where the volume was kept constant during the precipitation experiment by continuously purging a volumetric flow rate of reacting suspension equal to the injected NaOH solution flow rate.

Finally, a continuous precipitation test was also performed with the 5 l reactor, in order to assess the process feasibility for a continuous industrial production [Cipollina *et al*, 2014].

4.2 Process performance parameters

In order to analyse process performances, three different performance parameters were taken into account, namely:

- filtration times;
- purity of magnesium salts produced;
- efficiency of the precipitation process.

As it concerns filtration times, they were simply measured during the vacuum filtration step of the final suspension obtained after reactive-precipitation.

Purity of magnesium salts was estimated starting from the composition of main ions measured by Ionic Chromatography in the solid samples and calculating the amount of magnesium salts likely present in the precipitate. The presence of potassium and calcium ions n the precipitate has been found to be negligible in all experimental runs. Moreover, as a simplifying assumption, the quantity of different salts has been estimated starting from the quantity of Na^+ ions and associating a relevant stoichiometric quantity of ions Cl^- and, when an excess of Na^+ ions still remained, also to SO_4^{2-} ions (as NaCl and Na_2SO_4, respectively). Eventually, the remaining quantities of Cl^- and SO_4^{2-} ions were associated with a stoichiometric part of Mg^{2+} (as $MgCl_2$ and $MgSO_4$, respectively). Finally, all the “non-associated” Mg^{2+} ions were considered to be precipitated as $Mg(OH)_2$.

The efficiency of the precipitation process was estimated by IC analysis of filtered solution after precipitation. The amount of Mg^{2+} ions still present in the solution was compared to the amount initially measured in the exhausted brine and their ratio was considered as the complement of precipitation efficiency.

4.3 Results and discussion

Laboratory tests with the small scale system (0.5 l reactor) were performed varying operating conditions in the ranges reported below [Cipollina *et al.*, 2012]:

- NaOH solution concentration: 0.5M and 1M;
- NaOH solution injection flow rate: 1.5, 2.5, 3.5, 7 (ml/min);

- Impeller speed: 400, 570, 710 RPM;
- Thermostatic bath temperature: 25°C and 40°C.

Filtration time was significantly influenced by process parameters, thus indicating a strong influence of theses latters on crystals nucleation/growth kinetics. In particular, Fig.9 shows how the promotion of mixing (i.e. impeller rotational speed) significantly reduced filtration times, as it probably reduces the oversaturation of brine in proximity of the NaOH injection point and, therefore, it reduced the primary nucleation rate thus allowing an increase in crystals size.

Higher filtration times were always recorded when using concentrated NaOH solutions, while the increase in injection rate also increased filtration times likely causing a faster primary nucleation in proximity of the needle (Fig. 10). Finally, the effect of bath temperature led to an increase in filtration time when operating at higher temperature, as shown in Fig.11.

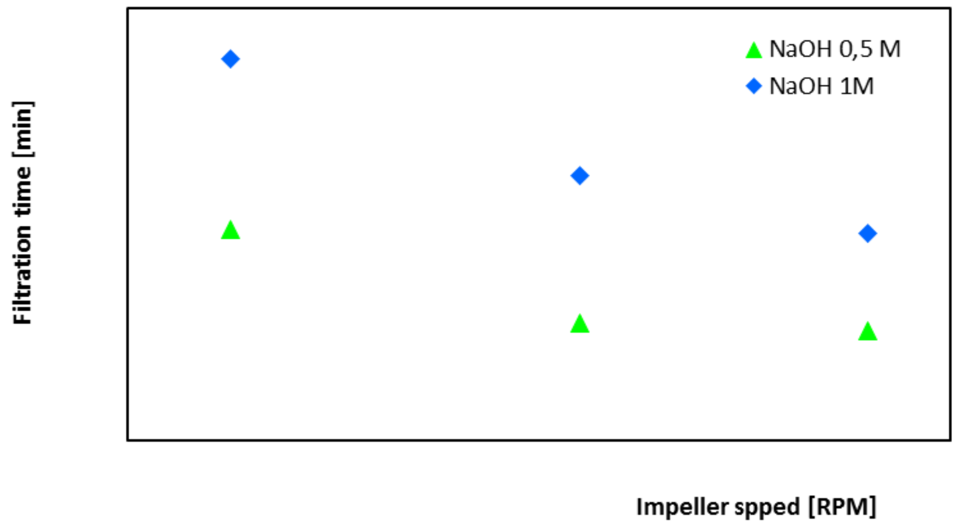

Fig. 9 Dependence of filtration time on impeller speed and NaOH solution concentration. NaOH solution injection rate 3.5 ml/min.

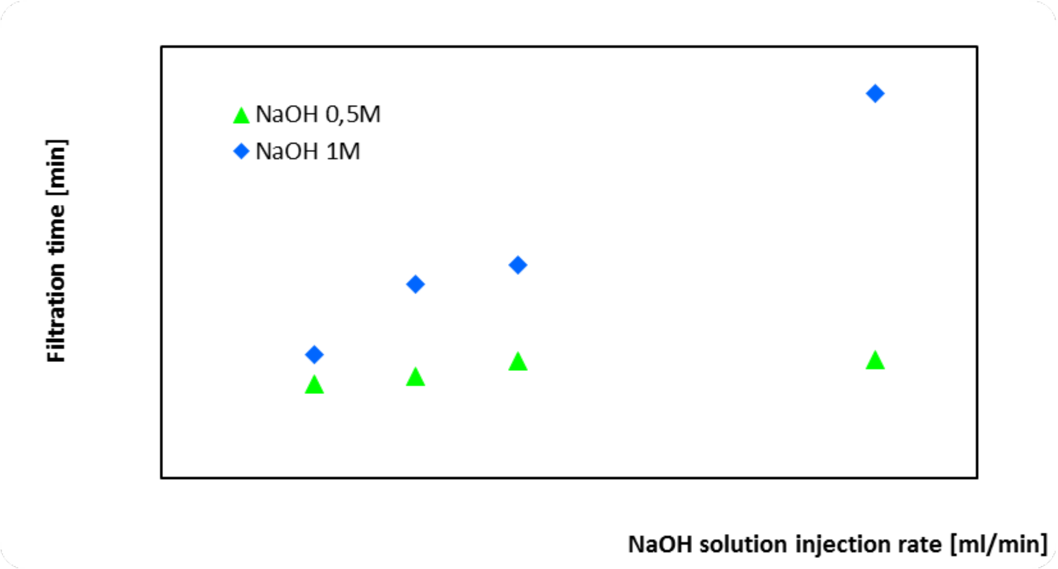

Fig. 10. Dependence of filtration time on NaOH solution injection rate and concentration. Impeller speed 570 RPM.

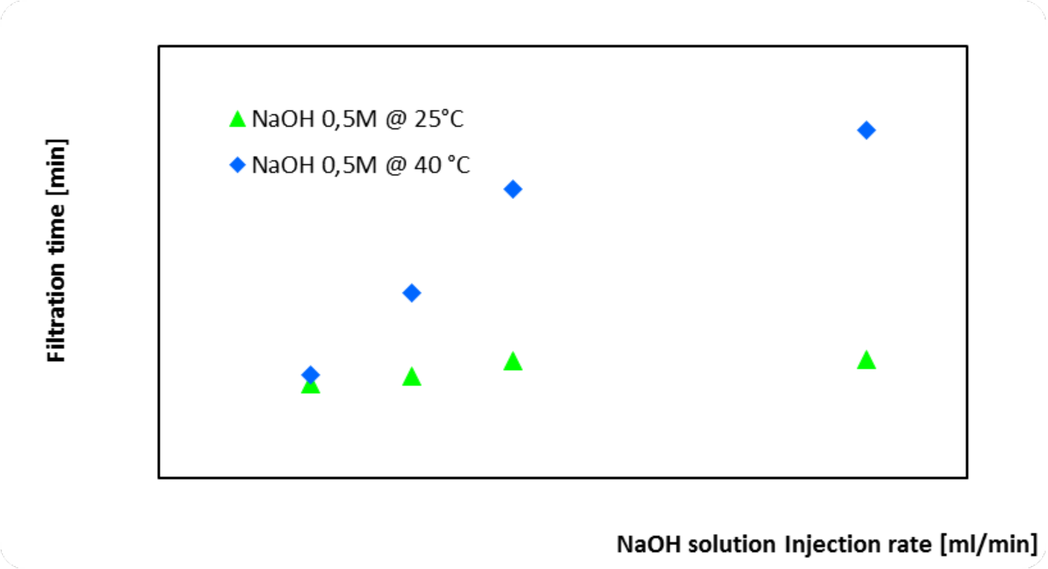

Fig.11. Dependence of filtration time on NaOH solution injection rate and temperature. Impeller speed 570 RPM.

As it concerns the content of magnesium salts in the precipitate, quite high purity values (in all tests values higher than 90%) were found, with peaks of more than 98% in terms of $Mg(OH)_2$.

Also in this case, operating conditions influenced the purity of precipitated product; however, the effect was not so relevant as in the case of filtration times (Figs. 12-14) and only slight increases of purity with the lower NaOH concentration (0.5M) and higher temperature (40°C) were found.

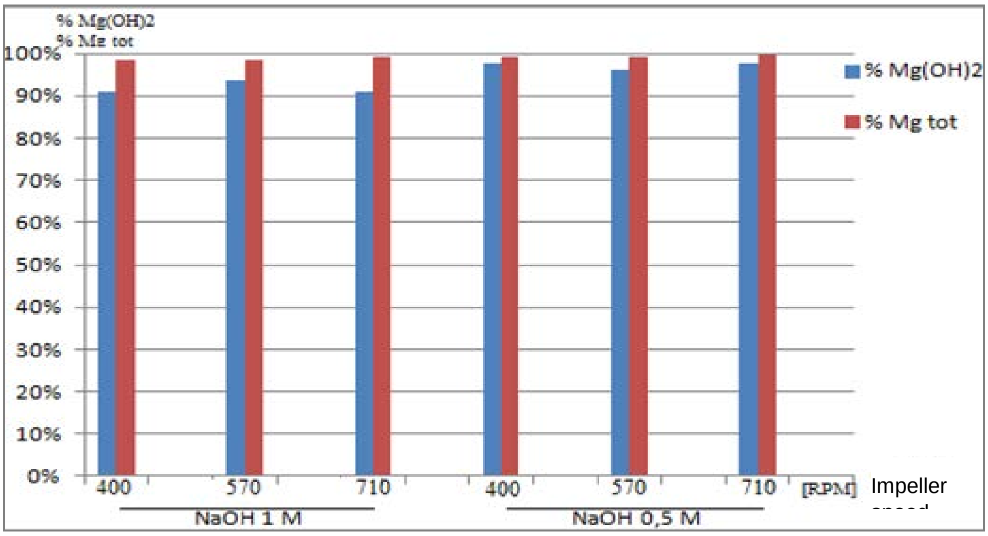

Fig.12. Obtained magnesium salts purity varying impeller speed and NaOH solution concentration. Injection rate 3,5 ml/min, temperature 25°C.

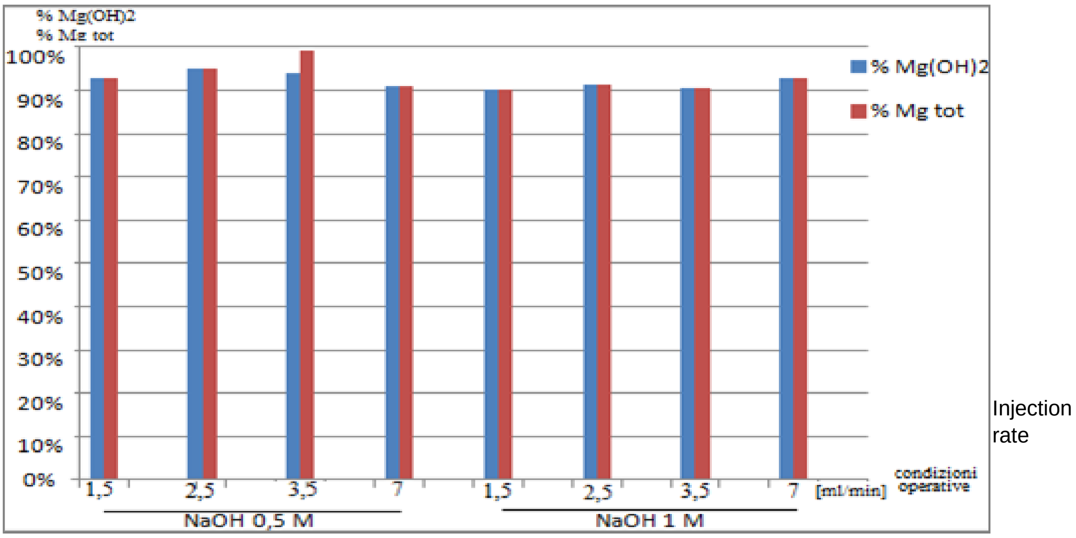

Fig. 13. Obtained magnesium salts purity varying NaOH solution injection rate and concentration. Impeller speed 570 RPM, temperature 25°C.

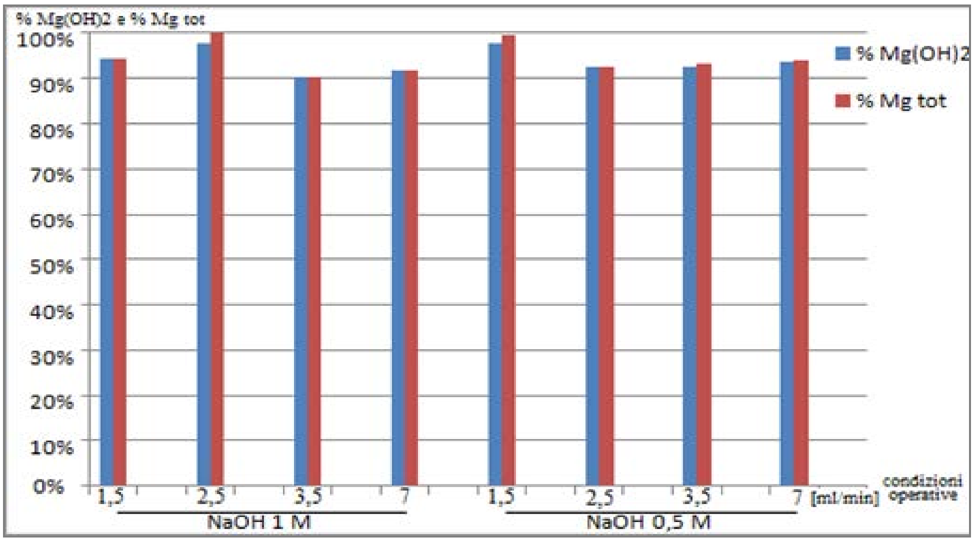

Fig.14. Obtained magnesium salts purity varying NaOH solution injection rate and Concentration. Impeller speed 570 RPM, temperature 40°C.

The last performance parameter analysed for the characterisation of precipitation tests was the efficiency of reactive precipitation (i.e. the reaction yield). To this regard, very small quantities of Mg^{2+} were detected in the filtered solution and, in several cases, these were under the detection limit of the instrument (due to the very high concentration of sodium chloride in the solution, the dilution required before IC analysis did not allow the detection of Mg^{2+} concentration in the filtered solution below 10 mg/lt, corresponding to a precipitation efficiency higher than 99.7%) thus indicating an almost unitary efficiency of the process

Very similar achievements were found also operating the semi-batch experiments with the 5 l reactor (not reported here for the sake of brevity), for which detailed information can be found in a recent paper by the same authors [Cipollina *et al.*, 2014].

Finally, the continuous crystallisation test have shown that $Mg(OH)_2$ crystallisation can be performed in a CSTR reactor, though the smaller size of particles and long residence time in the reacting system would indicate that other types of continuous reactors (I.e. Plug flow reactors) may perform better in the same operating conditions [Cipollina *et al.*, 2014].

On the basis of this first experimental campaign, it emerges how magnesium extraction from brine is feasible and can lead to the production of high purity magnesium hydroxide, which can then be sent to a further processing step for the production of metallic magnesium by thermal or electrochemical reduction [Friedrich and Mordike, 2006].

In order to give a rough idea of the economic potentials for the application of such idea in Trapani saltworks, some preliminary calculations have been made to estimate the quantity of magnesium obtainable from exhausted brine in a national area such as Italy or extending the area of interest to the whole Mediterranean basin.

As a starting point it is necessary to consider that the total salt production in Italian saltworks is about 1,000,000 tons/year, with a relevant exhausted brine production of about 4,500,000 m^3/year (assuming that about 50% of NaCl entering the saltworks with seawater is actually precipitated, while the remaining brine is discharged back to the sea). Assuming a Mg^{2+} concentration in the brine of 35kg/m^3, and a 100% recovery of $Mg(OH)_2$, it is possible to estimate a potential production of $MgO_{equivalent}$ of about 270,000 tons/year. Extending the calculation to the whole Mediterranean basin, with a total saltworks capacity more than 10 times large than the Italian one, a total potential production of almost 3,000,000 tons/year of $MgO_{equivalent}$ can be estimated, counting for about 30% of Magnesium world production (estimated to be around 11 million tons/year of MgO equivalent in 2011 [Bray, 2013]).

5. Energy generation from brines through the Reverse Electrodialysis process

5.1 *The REAPower project*

The final stage of the proposed integrated cycle, is the production of energy from salinity gradients generated by the use of concentrated brines/bitterns and sea or brackish water. With this respect, a cooperation research project, namely the REAPower project (www.reapower.eu), has been recently financed by the EU, with the final aim of developing an innovative system for power production by Salinity Gradient Power – Reverse Electrodialysis (SGP-RE) process, to be tested in the framework of Trapani saltworks, using sea (or brackish) water as diluted solution and brine as concentrate [Tedesco, Cipollina, *et al.*, 2014].

As depicted in Fig. 15, a Reverse Electrodialysis unit is constituted by a number of anionic and cationic exchange membranes alternatively positioned into a stack, forming rectangular channels, in which saline solutions at different concentrations can flow. The concentration gradient between them forces the ions to move through the membranes. This ionic flux is regulated by ions mobility and membrane permselectivity, i.e. the selectivity towards cation/anion transport through Cation Exchange Membranes/Anion Exchange Membranes, respectively, which generate a net ionic current through the stack. Finally, this ionic current is converted into electric current by means of redox reactions at the electrodes, positioned at the two ends of the stack, and can be collected by an external load.

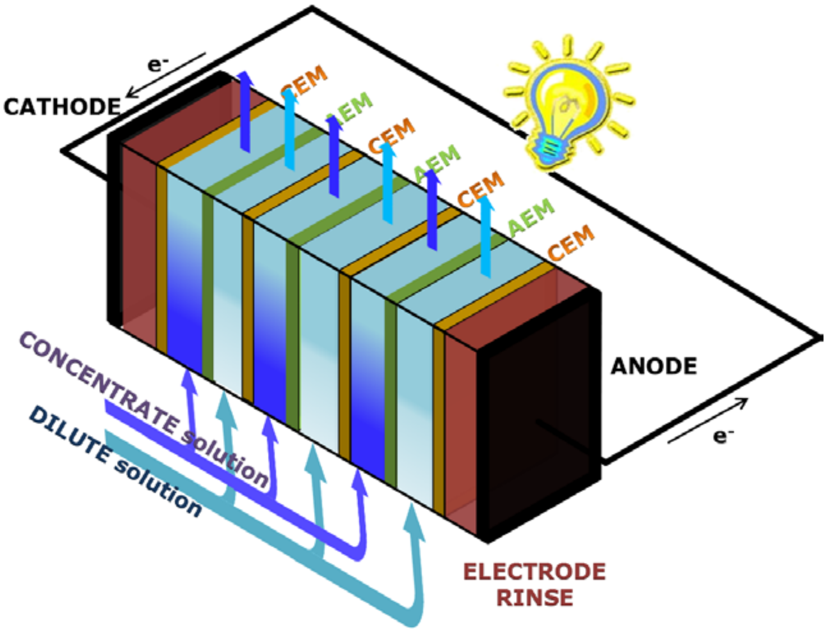

Fig.15. Schematic view of the Reverse Electrodialysis (RED) process

Within the complex organisation of R&D activities of the REAPower project, the main task were focused on:

- ✓ 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 for the design and simulation of the project prototype.
- ✓ Construction and testing of a prototype to be operated with real brines
- ✓ Economic analysis & process sustainability on large scale

Fig. 16 gives a clear idea on the significant scale-up steps planned within the 4 years of activities. It is worth noting how the starting RED unit with a total cell pair area of 0.5 m^2 has been scaled-up to a second generation stack with a cell pair area of about 5 m^2, still adopted for laboratory testing and R&D. Passing to the prototyping phase, the single stack size passed from a small unit of about 25 m^2 and, then, to the large stack equipped with about 100 m^2 of cell pair area. Finally, the prototype equipped with three large stacks will count on a total cell pair are of about 300 m^2, successfully achieving a scale-up of almost 3 orders of magnitude from the first generation laboratory RED stack.

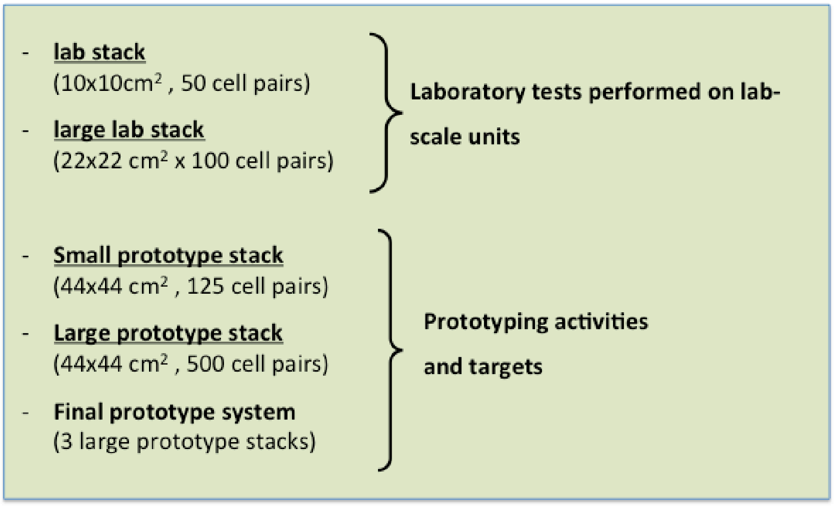

Fig.16 Technology development stages within the REAPower project.

In the following paragraph, an overview on the main achievements and perspectives relevant to the prototype installed and operated in Trapani saltworks will be presented.

5.2 Installation and testing of the REAPower prototype

Installation activities started in January 2014, within an old-restructured windmill located at the Ettore e Infersa saltwors in Marsala, TP, Italy (Fig. 17). The first installation phase was completed in April 2014 with the small prototype stack (44cmx44cm, 125 cell pairs) installed and operated.

Fig. 16. The installation site of the REAPower prototype: the windmill at the Ettore e Infersa saltworks, Marsala (TP), Italy.

The prototype stack was positioned on a test bench (Fig. 18) equipped with all necessary auxiliary and measuring systems, such as circulation pumps, flow maters, pressure, temperature and conductivity controllers (positioned both at the inlet and outlet of the feed solutions), all connected with a data acquisition system able to monitor continuously the main operating parameters of the prototype.

Fig. 18. View of the prototype installation, with the first operating stack equipped with 100 cell pairs of 22cmx22cm membrane area.

The first weeks of operation allowed to collect valuable information on the performances of the system, which has been so far the first and largest installed reverse electrodialysis prototype operating with real saline solutions and concentrated brines. For the sake of brevity, only the working ranges of the main operating parameters are reported in Table 4. Notably, the power output registered during these operations has varied in the range 40-60 W, with higher values achieved with the optimised artificial solutions. This figure has to be considered a milestone for the RED technology, being at least one order of magnitude larger than the power outputs so fare presented in the relevant literature.

Table 4 Working range of the main operating parameters of the prototype system equipped with the small prototype stack (44cmx44cm with 125 cell pairs).

Feed streams	**Conductivity [mS/cm]**	**Flow rate [l/min]**	**Temperature [°C]**	**Power output [W]**
Natural or artificial brine	180-230	6-12	25-30	**40-60**
Natural or artificial brackish water	1-6	6-12	22-25	

Project activities will continue until September 2014, with the final goal of installing and testing the prototype system at its maximum provisional capacity, when equipped with three large prototype stacks (each one with 44cm x 44cm 500 cell pairs).

Simulations were performed, with a purposely-developed simulation tool, in order to optimise the layout and the operating conditions of the system [Tedesco, Mazzola, *et al.*, 2014]. Model predictions indicate how the three different layouts analysed for the final prototype plant, will allow in principle the achievement of the target of 1kW power output.

However, it is worth noting that the first collected experimental results (with the small prototype stack) already indicate some reductions of the output power with respect to the predicted theoretical values, mainly due to parasitic phenomena related to the use of real solutions (containing a very heterogeneous ions mixture, instead of only NaCl) and to non-ideal flow distribution inside the stack, 8 times larger than the one tested in the lab and used for model validation.

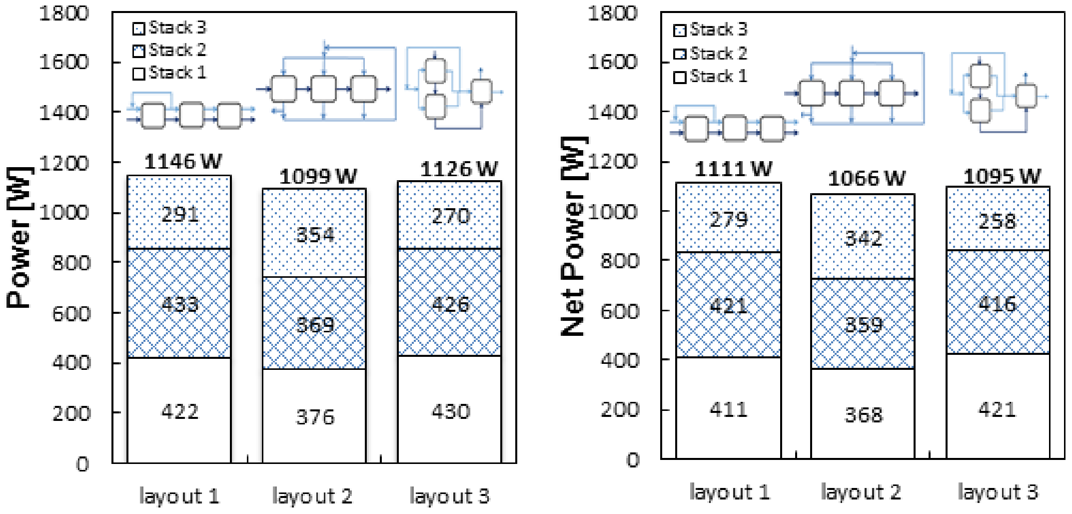

Fig. 19 Provisional gross and net power outputs of the final REAPower prototype [Tedesco, Mazzola, *et al.*, 2014]. Simulations of 3 stacks (500 cells) equipped with Fujifilm membranes 44×44 cm^2 and 270 µm woven spacers; C_{HIGH} = 5 M (NaCl); Q_{HIGH} =29.4 lt/min; make-up of brackish water, Q_{MU} = 40 lt/min, C_{MU} = 0.03 M (NaCl).

6. Conclusions

The problem of brine disposal from desalination facilities has recently been addressed by converting it into a potential resource for the recovery of raw materials and energy.

In the present work a case study for the design and application of a concept for the production of fresh water, salt and magnesium by means of an integrated cycle involving a desalination facility, traditional saltworks and a precipitation step for the final recovery of magnesium hydroxide.

The peculiar context of Trapani and Marsala saltworks (in Sicily, south of Italy), where a desalination MED-TVC facility already exists, has been chosen for an experimental campaign focused on the use of desalination brine as a feed solution for an experimental saltworks. A 4-year experience has demonstrated the feasibility of the concept also highlighting possible risks and the large potential for the enhancement of the evaporation-driven process for salt production.

At the same time, some preliminary tests were performed at laboratory scale, for the feasibility analysis of magnesium recovery from exhausted brines being discharged from saltworks. Also in this case, results have shown that the reactive-precipitation process is a viable solution for the recovery of high purity magnesium hydroxide with extremely high precipitation efficiency.

Finally, the potential for energy production through Salinity Gradient Power Reverse Electrodialysis technology have been explored within the EU-funded research project REAPower. After a complex and fruitful 4-years period of activities in the laboratories (for performing experimental and modelling analysis for the development of the RED technology), a prototype unit has been installed in Ettore e Infersa saltworks (Marsala-TP) and operated using saltworks brines/bitterns and sea or brackish water as feed solutions. Never explored potentials for energy generation from saltworks brine have been assessed. Moreover, the prototype size and the measured power output values are to be considered the highest ever achieved for the RED technology, thus making the prototype installation and operation a milestone for the development of salinity gradient power technologies.

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