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Integrated production of fresh water, sea salt and magnesium from sea water

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ABSTRACT

Seawater desalination is becoming an important source of fresh water in several 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. An integrated production of fresh water and salts may be achieved using the discharge brine from a desalination plant as a feed for conventional salt ponds, with the advantages of using brine more concentrated than sea water and, in the case of thermal desalination plants, warmer than sea water. By doing so, the process is faster as a consequence of the enhancement of evaporation rate on the surface of ponds. The above concept has been proposed already several years ago, but only rare examples exist of real applications. A pilot test has been performed in the last 4 years in Trapani (Italy), where a 36,000-m^3/d multiple effects desalination with thermal vapour compression plant is operating very close to a traditional salt pond normally fed with sea water. 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. Results have shown a very promising enhancement of the salt pond production capacity, keeping at the same time the very high quality standards required for the production of food-grade salt from sea water. On the other side, laboratory experiments indicated the actual possibility of producing high-purity magnesium salts, thus encouraging towards further investigation for the development of a pilot process development and installation.

Keywords: Environment; Seawater desalination; Brine disposal; Salt recovery; Magnesium

1. Introduction and literature review

Nowadays, seawater and brackish water desalination processes are considered more and more suitable non-conventional water sources for the supply of high-quality drinking water in areas affected by water scarcity and drought problems.

In the last years, several concerns have been raised regarding the environmental impact of desalination

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processes, mainly due to the production of a concentrated effluent (blowdown brine) that must be accurately managed. In the case of seawater desalination plants, installed nearby the coast, the brine is commonly discharged back to the sea. The reject stream could be discharged in the shoreline area or offshore by means of dense effluent diffuser [1,2].

In this case, plant location is a crucial parameter for the estimation of environmental impacts. The following can be the possible risky scenarios [3]:

- brine discharged in a closed basin, with low mixing processes and/or long turnover times (e.g. Red Sea or small seas in general);
- brine discharged close to sensible environments, like coral reefs or natural reserves (e.g. some Australia shore lines, small island in the Mediterranean sea, etc.);
- very high concentration of desalination plants or other industrial activities in a certain area (e.g. Persian/Arabian Gulf).

In general, increasing the process recovery ratio will significantly reduce 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 and features of the desalination process.

Typically, seawater reverse osmosis plants produce waste brine with concentration in the range 65,000–85,000 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 10–15% higher than that of feed sea water.

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 [3–5].

On the other side, in the case of brackish water desalination (from wells and salt water springs in inland sites), the option of disposal back to the sea is not feasible most of the times; thus, some other options for brine disposal have been investigated in the literature [6], namely:

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

Although injection wells are used in various regions of the United States for the disposal of hazardous and non-hazardous fluids (e.g. municipal wastewater in South Florida), the use of this technology for brine disposal strongly depends on the geological conditions of the plant site and is not always feasible.

The disposal of brine into surface waters (lakes, ponds, rivers) is applicable only for small desalination plants in order to avoid any significant impacts on the aquatic species. Irrigation of halophyte plants can lead to salinisation of soil and therefore can be used only for small amounts of brine.

Finally, disposal into municipal sewers may cause an increase in the total dissolved solids of domestic sewage that could make impossible the use of treated effluent for irrigation purposes [7].

Normally, the cost of brine disposal ranges from 5 to 33% of the total cost of desalination [8], depending on the amount of brine, the level of treatment before disposal, the nature of the surrounding environment and the disposal method. Thus, minimisation of brine volumes 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 and 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 [9]. 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. [10] have worked on the development of a novel process: the Wind Aided Intensified eVaporation (WAIV). 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 [11,12].

Another example of enhancing natural evaporation is reported in the work of Arnal et al. [13], who used capillary adsorbents for increasing evaporation rate, in order to improve the 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 [14]. 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 presents an integrated approach for the solution of brine disposal problem and exploitation of brine potentials, which has been adopted and experimented in the Mediterranean site of Trapani (Sicily, south of Italy). The concept idea is that of using the brine exiting from a MED-TVC desalination plant to feed small experimental saltworks. The saturated exhausted brine, eventually, exiting from the final basins of the saltworks, can be used for the extraction of magnesium salts, thus providing a further added value to the overall integrated process.

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 of magnesium recovery from exhausted saturated brines also giving some ideas of the tremendous exploitation potentials of such approach.

2. The singular framework of Trapani MED plant and saltworks

Trapani is a small city in the west coast of Sicily (Fig. 1), in the heart of Mediterranean Sea. Since the Romans time, it has been an important centre for the

Fig. 1. Google Maps view of Trapani position with a zoomed view of the area hosting the MED-TVC desalination plant and the experimental saltworks "Mariastella".

production of salt from sea water, thanks to the natural presence of saltworks, which have been readapted and optimised for the production of large quantities of salt and still operating since more than 2000 years ago.

Nowadays, one of the major problems of Trapani and surrounding villages is the water supply, due to severe drought periods occurred in the last decades. For this reason, a MED-TVC desalination plant was constructed in the 1990s 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.

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, each one with a capacity of 9,000 m^3/day [15]. Each unit consists of 12 horizontal tubes evaporation effects, with parallel feed configuration, and a thermal vapour compressor (middle pressure steam ejector) as sketched in Fig. 2.

Inlet sea water undergoes a basic pre-treatment step with some screening and sand removal. Shock chlorination was preformed at the intake, although recently no chlorination at all is performed. Pre-treated sea water reaches two plate heat exchangers where it is preheated, while exiting distillate and brine (this latter 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.

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 there acting as motive steam.

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

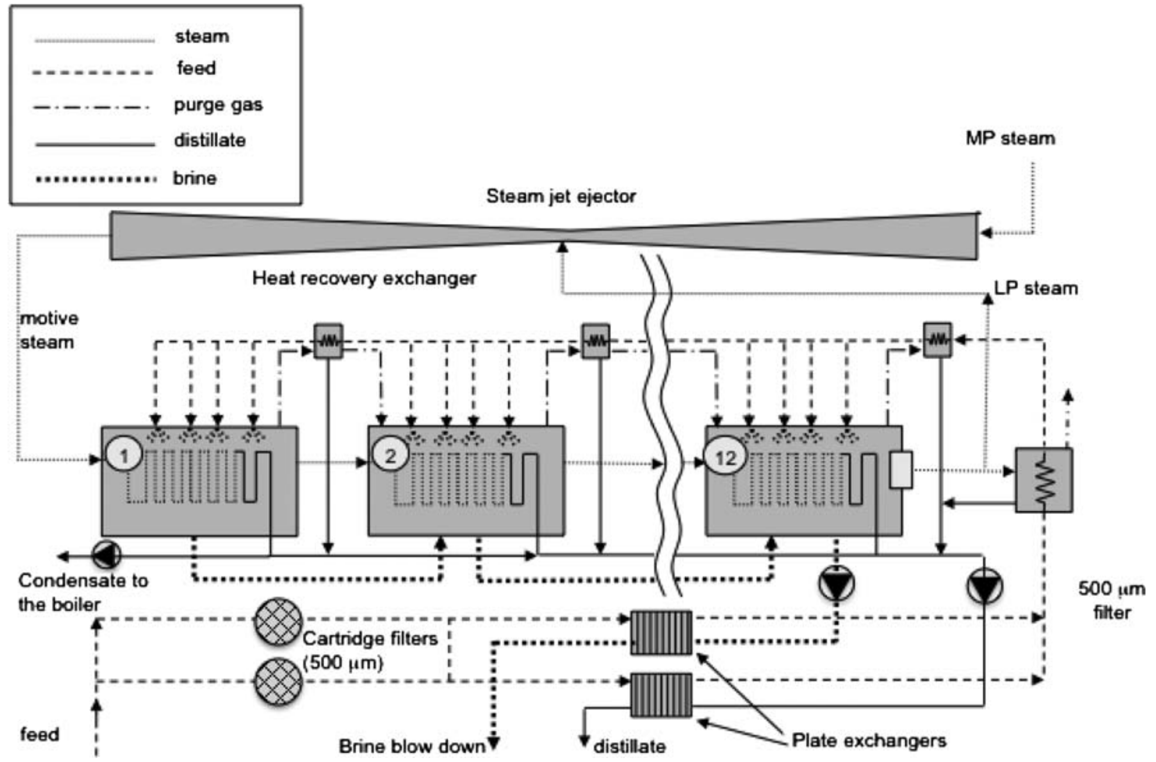

Fig. 2. Sketch of a MED-TVC unit of the desalination plant in Trapani [15].

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 sea water, and partially recompressed by a steam ejector with motive steam at 45 bar. In such a way, the recompressed vapour can act as motive steam to the first effect, thus enhancing the gain output ratio of the process.

The first evaporation effect operates at a maximum temperature of 62°C in order to minimise 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.

Fig. 3. A picture of evaporation effects of one of the MED-TVC units. Red circle indicates one of the six cylinders containing two subsequent effects.

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 g/l. 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 53–55 g/l. 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).

As it concerns the use of chemical additives, only low-temperature antiscalant (Belgard EV2050) and antifoaming (Nalco 131S) agents at very low concentrations are added to the feed sea water.

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 (see Fig. 3).

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 3.7% (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 in the meanwhile 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 orders of ponds, each order being characterised by a well-defined density range:

Fig. 4. View of a basin of "Mariastella" saltworks with the MED-TVC plant in the background.

- 1st order, called "cold ponds" (FR1 and FR2 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 50–100 cm;
- 2nd order, so-called driving ponds (VAC, VG1, VG2 and VG3 in Fig. 5). The number of ponds depends on the saltwork design. The density grows

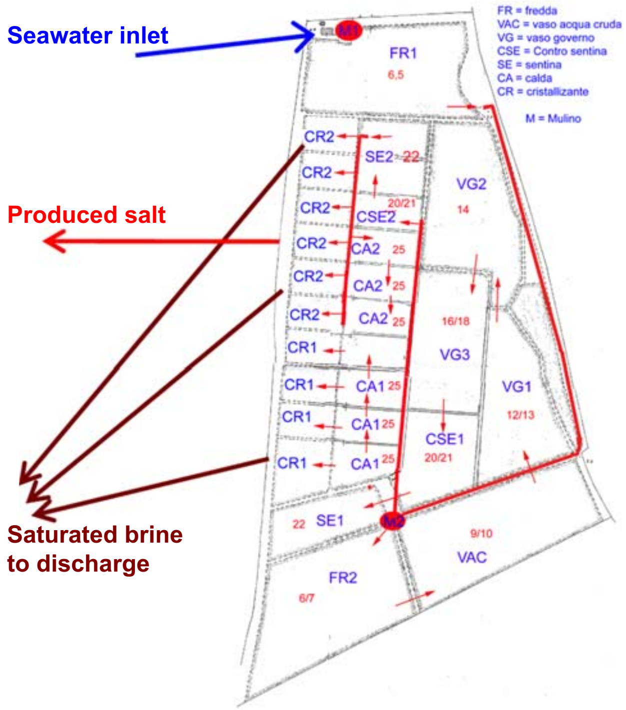

Fig. 5. Schematic process flow layout of "Mariastella" saltworks in the traditional configuration.

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 <50 cm;

- 3rd order (hot ponds, CSE1, CSE2, SE1, SE2, CA1, CA2 in Fig. 5), made by several small and shallow (<40 cm) ponds, covering 40–45% of the total saltwork surface. Here, the pond segmentation is very fine. Each pond has a surface of 1,000–2,000 m^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 with saturated brine one or two crystallisation ponds, which represents the 4th and last order of ponds;
- 4th order, made by several crystallisation ponds (CR1, CR2). Each of them has roughly the same dimension of the hot ponds. They are very shallow (<25 cm) with very flat floor. The salt crystallises only in this order of ponds. During the hot season, a crust of ~10 cm is grown in 40–45 days in the crystallisation ponds, where it is harvested once or twice per year according to the season's climatic behaviour. The crystallisation ponds cover not more than 15% of the total saltwork surface.

The flow of the water, 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, the 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 to 98.5%.

The production cycle is repeated with yearly frequency. Saltwork feeding starts at the end of April, when the evaporation rate starts to be significant (it will stay between 1 and 1.5 cm/day up to September, with peaks up to 2 cm/day) and the rainfall is correspondingly reduced (<100 mm total rainfall from May to September). Every year, 12–15 cm of salt crust is grown, with a typical figure for the production/Hectare of $(1–1.2) \times 10^3$ ton/$10^4 m^2$. Harvesting is done twice, or even three times in a year, in case of very dry seasons.

Table 1
Geometrical features and operating data of Mariastella saltwork

	Cold ponds		Driving ponds		Hot ponds		Crystal. ponds		Total surface	
	m^2	%	m^2	%	m^2	%	m^2	%	m^2	%
	39,187	21.94	50,401	28.22	61,023	34.16	28,017	15.68	178,628	100
Production historical data										
Year	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Prod. (ton)	2,370	0	1,941	1,934	1,694	1,630	1,765	1,686	2,000	2,000

As far as the Mariastella saltwork is concerned, Table 1 summarises the main figures of its layout and the production historical data in the period 2000–2007.

Fig. 6 graphically presents the surface distribution of Mariastella saltwork, which is typically maintained in most seawater saltworks. It is worth noting how the surface required for the first evaporation steps (cold basins, where salt concentration is increased from about 35 to 50–60 g/l) is more than 20% of total surface. Thus, the use of already concentrated brine exiting from a desalination plant would easily allow a saving of 20% of total saltworks area or, on the other side, a corresponding increase in potential surface for the "enhanced" evaporation process.

The yearly productivity of saltworks can dramatically vary according to the meteorological conditions occurring during the productive season (in Trapani, normally from May to October). Nevertheless, for Mariastella saltwork in the 10 years from 1998 to 2007, the production has ranged within values of about 1,600–2,350 ton/year (Fig. 7), with an average production of 1,800 ton/year.

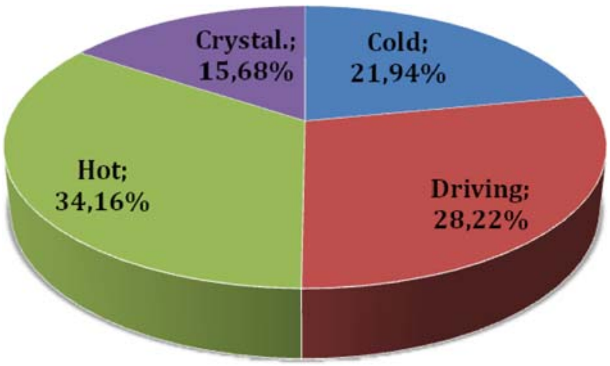

Fig. 6. Surface distribution of the different basin types within a conventional saltwork.

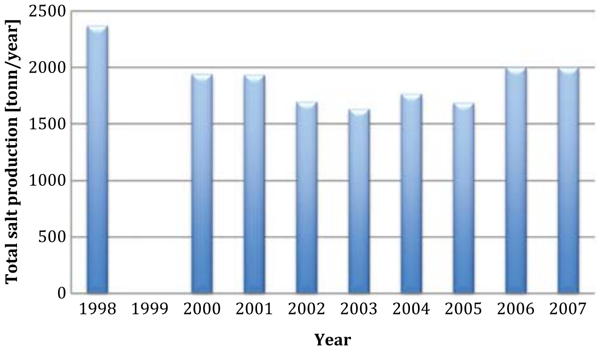

Fig. 7. Yearly salt production of Mariastella saltwork from 1998 to 2007.

3. Feeding the Mariastella saltwork with the MED plant brine: a four-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 saltwork by using the brine from a desalination plant as a feed to the saltworks itself.

This has been done within the above-described Mariastella saltwork, where the output flow of one of the four MED-TVC units has been intercepted and sent, through a 30-m-long pipeline, to the Mariastella VAC pond, thus substituting the direct seawater intake. The saltworks feeding is thus made with 5.5Bè brine instead of 3.5Bè fresh sea water. 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 its first part is concerned, to the new intake point. As shown in Fig. 8, 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.

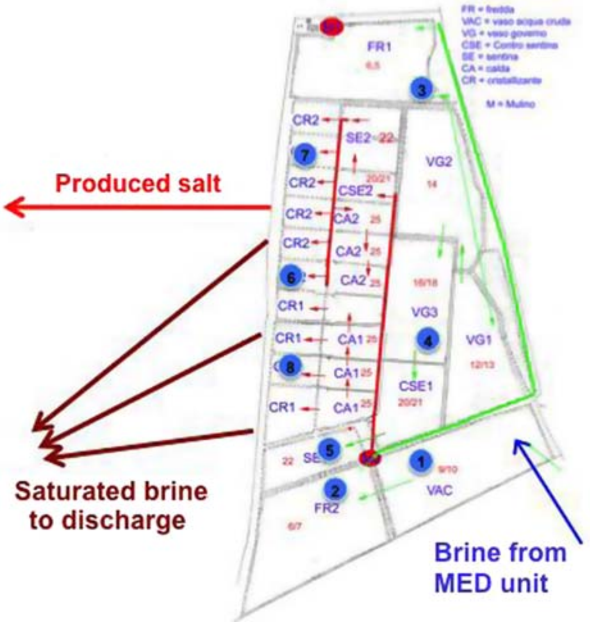

Fig. 8. Schematic process flow layout of "Mariastella" saltworks in the novel configuration, where brine from the MED-TVC plant is used as feed stream. Blue circles indicate sampling for IC analysis with the relevant basin identification number.

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 of the crystallisation surface C to the total saltworks area T (C/T), which should be not 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 C/T ratio was equal to 15.68%, which has been practically reduced to 12.54% if considering the (fictitious) basin area $T' = T \times 1.25$, 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 in 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 in salt production with respect to the average values registered in all the saltworks of the area. Production of raw salt of 2,900 tons has been estimated in the Mariastella saltwork, to be compared with a mean value of 1,815 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 saltwork, which is obviously not significative and caused a strong depletion also on 2010 data. In 2010, in fact an estimated production of 1,650 tons has been registered. These results are again a very poor one, which cannot be compared with the result of other saltworks in the area. The hurricane of 16 September 2009, which has a repetition time, in the area, of less than 1 event/50 years (last recorded event is of 3 September 1965), was in fact very localised and affected Mariastella saltwork to a much larger extent than affecting 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 salt workers 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. Preliminary data concerning the production confirm a definite strong enhancement of the production. A total production of 2,500 tons has been registered, 38% 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 17% larger in 2011 than the mean value[1] taken in the same reference period. Although the relevant data concern only two years of production and therefore only preliminary conclusions can be drawn, a benefit of 20–30% production increase turns out in using the outlet brine of the Trapani desalination plant.

As it concerns possible drawbacks generated by the new configuration (in terms of both 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 experiences already presented in 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 [14] 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:

- use of chemical additives within the desalination plant pre-treatment stages (particularly in the case of a reverse osmosis (RO) brine, which may contain inorganic or organic flocculants, antiscalant and antifouling agents), which may dramatically influence the biological growth within the saltworks basins;

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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.

- different brine composition (in the case of the Eilat plant, the RO unit treated a seawater/brackish water mixture with a composition fairly different from sea water, thus affecting the fractionated crystallisation steps normally designed for saltworks operated with sea water);
- 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 sea water, thus maintaining basically the same feed composition of traditional saltworks.

The lucky location of the MED plant, basically beside the Mariastella saltwork, 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 thermogravimetric 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 present 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. 9 and 10 show 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. On the contrary, K^{+} and Mg^{2+} concentrations still rises up to values between 700 and 900% higher than initial values, that is, up to concentrations of 8 g/l for potassium and more than 35 g/l for the magnesium.

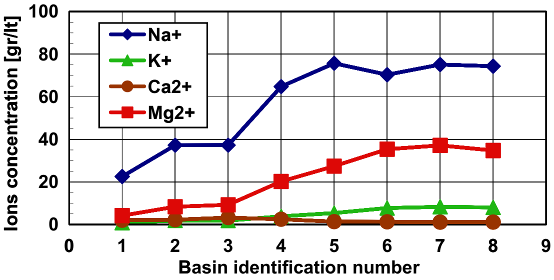

Fig. 9. Increase in cations concentration (expressed in gr/lt) along Mariastella basins. Basin identification numbers are reported in Fig. 8.

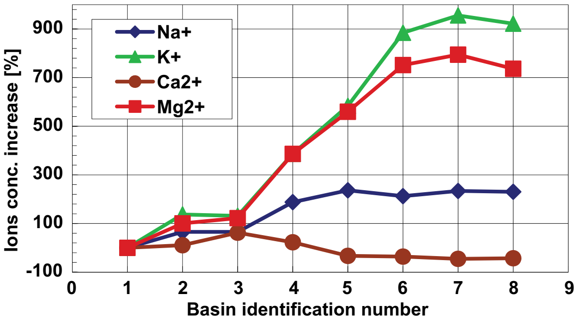

Fig. 10. Increase in cations concentration (expressed as a percentage increase with respect to the initial value) along Mariastella basins. Basin identification numbers are reported in Fig. 8.

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. With this regard, an experimental investigation has been performed by laboratory tests for the 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 sea water for energy production. This topic has been recently addressed in the EU-FP7-funded project REAPower [16], which aims at the development of a Salinity Gradient Power–Reverse Electrodialysis (SGP–RE) prototype to be installed and operated within the saltworks facilities in Trapani using sea water and exhausted brines as dilute and concentrate solutions, respectively.

4. Exploitation of saltworks-exhausted brine for magnesium production

Given the above consideration on the large potential for the 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 a saltwork 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 a homemade bench-scale reactive precipitation apparatus (Fig. 11).

The reactor was simply constituted by a glass becker (Vol. 500 ml), mechanically stirred by a small marine impeller, which was loaded with 50 ml of brine, with a composition reported in Table 2, 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 of Aldrich analytical grade.

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

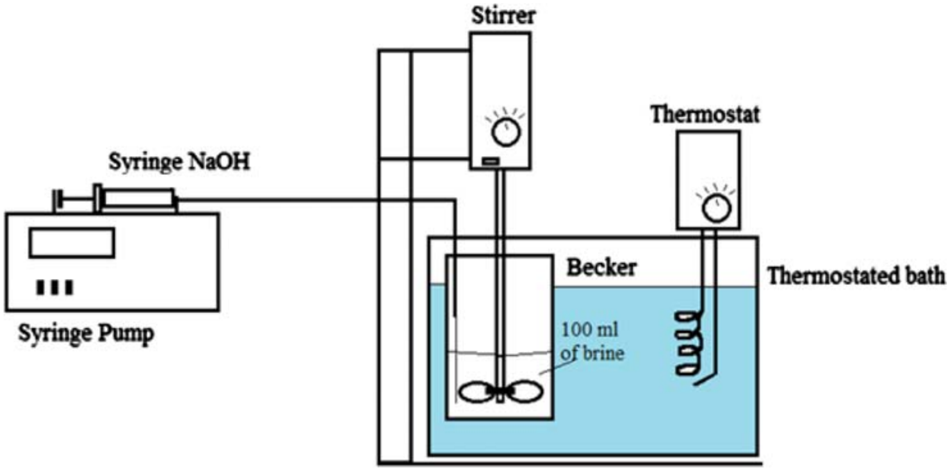

Fig. 11. A schematic view of the experimental apparatus adopted for the reactive precipitation tests.

Table 2
Composition of exhausted brine adopted for reactive precipitation tests

Brine source	pH	Concentration of main cations and anions in solution [gr/lt]						
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Br^-
Exhausted brine from Trapani saltworks	7.1	48.30	8.62	0.46	36.06	166.1	52.32	1.76

Analysis performed using ionic chromatography, after dilution 1:4,000 of sampled brine

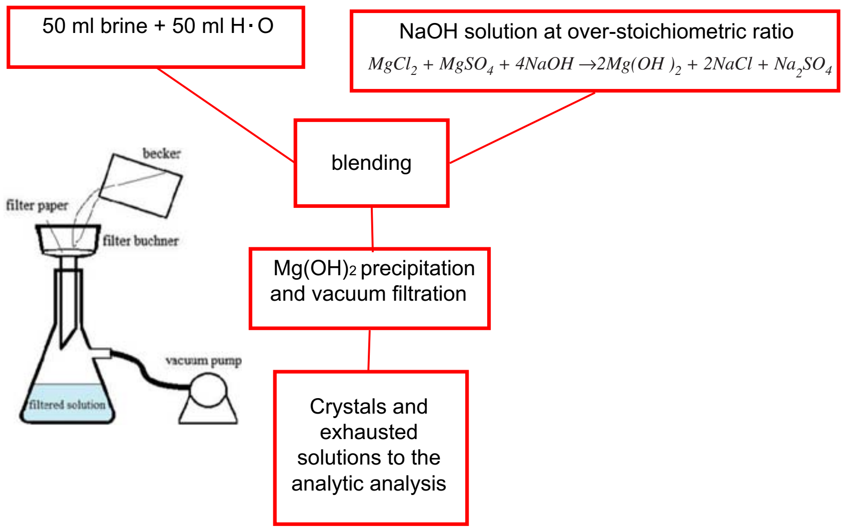

Fig. 12. Schematic description of the experimental procedure adopted for the reactive precipitation and solid separation steps.

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 1 M HCl solution. The morphology of solid crystals was analysed and imaged with a Philips scanning electron microscope (SEM). Samples were sputter-coated with gold to a thickness of 200 Å.

A schematic graphical description of the experimental procedure adopted for the solid precipitation and collection is reported in Fig. 12.

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.

Filtration times 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 in 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 with the amount initially measured in the exhausted brine, and their ratio was considered as the complement to one of precipitation efficiency.

4.3. Results and discussion

Laboratory tests were performed under varying operating conditions in the ranges reported below:

- *NaOH solution concentration*: 0.5 and 1 M;
- *NaOH solution injection flow rate*: 1.5, 2.5, 3.5, 7 (ml/min);
- *Impeller speed*: 400, 570, 710 RPM;
- *Thermostatic bath temperature*: 25 and 40˚C.

Filtration time was significantly influenced by process parameters, thus indicating a strong influence of these latter on crystals nucleation/growth kinetics. In particular, Fig. 13 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 more 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. 14). Finally, the effect of bath temperature led to an increase in filtration time when operating at higher temperature, as shown in Fig. 15.

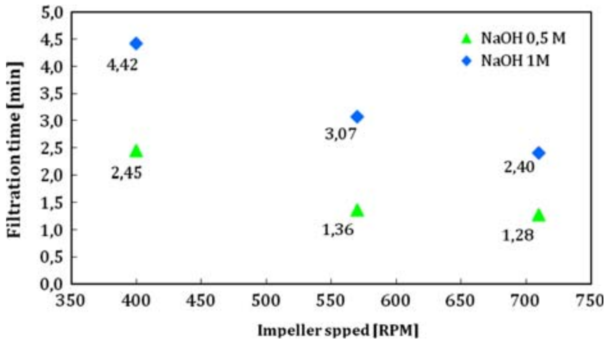

Fig. 13. Dependence of filtration time on impeller speed and NaOH solution concentration: NaOH solution injection rate 3.5 ml/min.

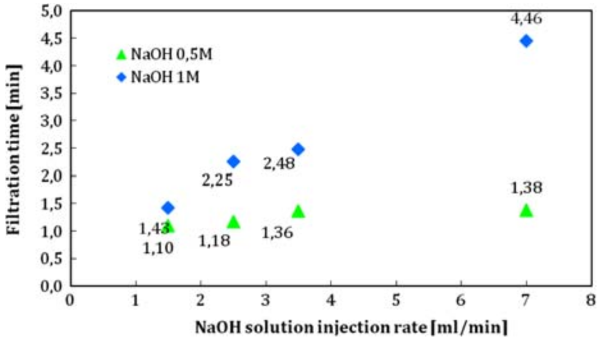

Fig. 14. Dependence of filtration time on NaOH solution injection rate and concentration: impeller speed 570 RPM.

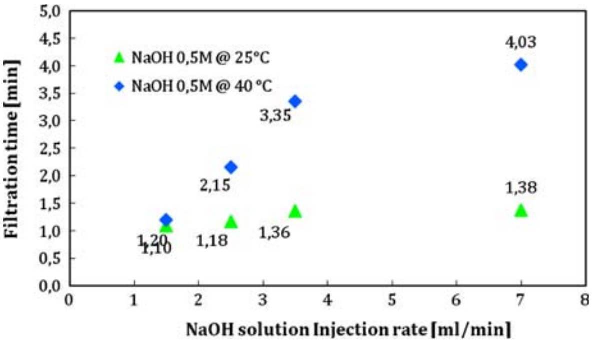

Fig. 15. Dependence of filtration time on NaOH solution injection rate and temperature: impeller speed 570 RPM.

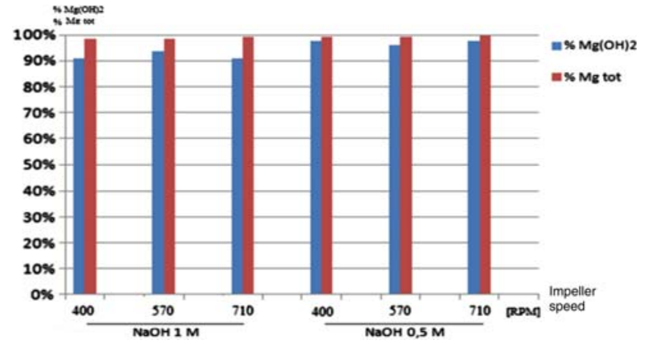

Fig. 16. Obtained magnesium salts' purity varying impeller speed and NaOH solution concentration: injection rate 3,5 ml/min, temperature 25˚C.

Concerning 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. 16–18), and only slight increases in purity with the lower NaOH concentration (0.5 M) were found.

The last performance parameter analysed for the characterisation of precipitation tests was the

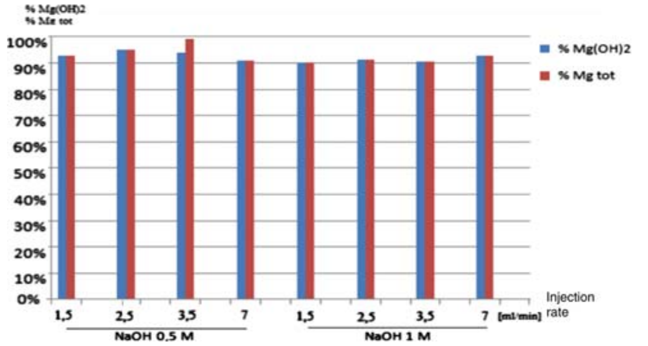

Fig. 17. Obtained magnesium salts' purity varying NaOH solution injection rate and concentration: impeller speed 570 RPM, temperature 25°C.

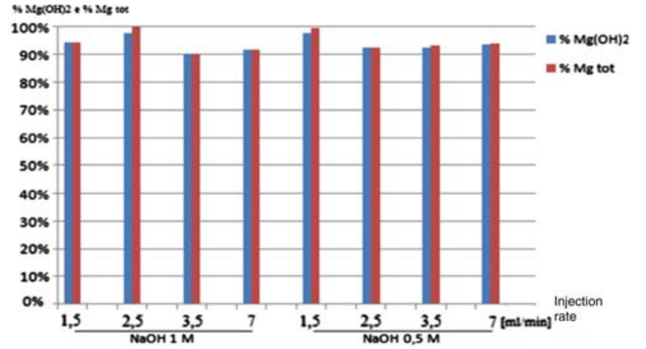

Fig. 18. Obtained magnesium salts' purity varying NaOH solution injection rate and concentration: impeller speed 570 RPM, temperature 40°C.

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/l, corresponding to a precipitation efficiency higher than 99.7%), thus indicating an almost unitary efficiency of the process. Fig. 19 reports the calculated values of efficiency, indicating a random variation of this parameter, with values always above 99%.

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 [17].

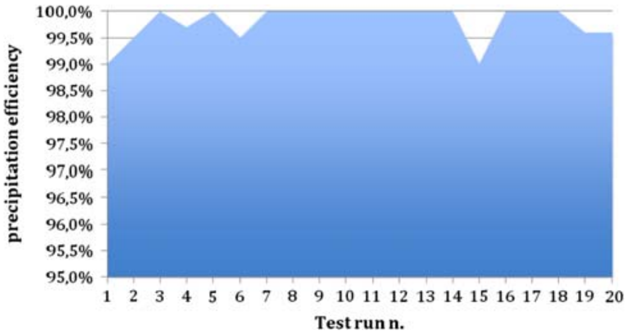

Fig. 19. Precipitation efficiency of all laboratory test runs.

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.

As a starting point, it is necessary to consider that the total salt production of Trapani saltworks is about 90,000 tons/year, with a relevant exhausted brine production of about 36,000 m^3/year (assuming that about 50% of NaCl entering the saltworks is actually precipitated, while the remaining brine is discharged back to the sea). Assuming a Mg^{2+} concentration in the brine of 30 kg/m^3 and a 100% recovery of $Mg(OH)_2$, it is possible to estimate a potential production of $Mg(OH)_2$ of about 27,000 tons/year, that is, 10,800 tons/year of magnesium.

Considering that the total world annual production of magnesium is around 600,000 tons/year (data referred to 2010, [18]), with a production of about 500,000 tons/year in China and about 37,000 tons/year in Russia (2nd producing country), it is interesting to note how the above-estimated production would achieve the 2% of world production, that is, the 30% of Russian production, thus being potentially an enormous resource for the local and national economy.

5. Conclusions

The problem of brine disposal from desalination plants has recently been addressed as 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 is presented.

The peculiar context of Trapani (a city in Sicily, south of Italy) saltworks, 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-years 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.

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