Reactive crystallisation process for magnesium recovery from concentrated brines

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ABSTRACT

Seawater brines, generated either by natural or anthropic processes, often cause significant environmental issues related to their disposal. A clear example is the case of brines from desalination plants, which can have severe environmental impacts on the receiving water body. On the other side, brines can represent a rich and appealing source of raw materials, especially when they are very concentrated, as it happens with bitterns (i.e. exhausted brines) produced in saltworks. In particular, magnesium concentration can reach values up to 30–40 kg/m^3 of brine, which is 20–30 times that of typical seawater. An experimental campaign has been carried out in the present work for assessing the potentials for magnesium recovery from concentrated brines. Real brines were collected from the final basins of the saltworks operating in the district of Trapani (Sicily, Italy). Experiments were performed both in a semi-batch and in a continuous 5 liters crystalliser operated by a reactive precipitation process. NaOH solutions were adopted as standard alkaline reactant in order to assess the influence of all operating parameters and reactor configuration on the recovery efficiency and purity of the Mg(OH)$_2$ powder produced. Results have highlighted a very promising strategy for the recovery of Mg from concentrated brines, which could be scaled up and applied to a number of different scenarios, including existing saltworks and newly designed integrated cycles for Zero Liquid Discharge desalination.

Keywords: Brine disposal; Magnesium; Minerals recovery; Saltworks; Reactive crystallisation

1. Introduction

In recent years, a rising interest has been addressed to the problem of concentrated brines from industrial processes. In fact, while in the past, brines were treated as a simple waste to be just disposed back into a receiving water body or to be treated before disposal; nowadays, a major concern has been raised both in terms of environmental safety and process sustainability [1–3]. This is, in fact, related to a bigger attention to environmental problems generated

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by brine disposal, as well as to the interest in performing process integrations, which may increase the profitability of any industrial process. On this basis, brines have recently been considered more and more as a potential resource for the extraction of salts, raw materials and energy [4–6].

One of the most important anthropic brine sources is certainly related to the desalination industry. A recent estimate of global desalination capacity indicates [6] that almost $80 \times 10^6 \, m^3/d$ of desalinated water is produced, which leads to the need of disposing a quantity of concentrated brine in the order of $100 \times 10^6 \, m^3$ every day. Such huge amount is normally discharged back into the sea, although a few examples of plants exist where brine is reused for the production of salts and minerals [4,7].

Among these, magnesium plays a fundamental role in seawater chemistry, being the second most abundant cation after sodium.

On the other side, the global market of magnesium minerals has recently seen a rapid increase in demand and production, with a world production of about 11 million tons/year of equivalent MgO in 2012 [8]. However, given the very heterogeneous distribution of Mg producers in the world, with more than seven million tons/year produced by China, Russia and USA, magnesium has been recently classified by the EU [9,10] among the 14 most critical raw materials, which are subject to a high risk of supply interruption, thereby recognising the importance of researching alternative ways for the supply of such material.

In this respect, a recent work [4] has highlighted the potential of recovering magnesium from exhausted brines. In fact, while magnesium concentration in seawater can vary between 1.1 and $1.7 \, kg/m^3$, it can normally be up to two times more concentrated in the brine exiting from the desalination plant. This figure becomes even more impressive when exhausted brines from production processes are considered, such as saltworks for the production of sea salt. In this case, magnesium concentration can reach values up to $30–40 \, kg/m^3$, 30 folds larger than in seawater. Italian production of sea salt from saltworks accounts for almost 10^6 tons/year of NaCl (>97% purity), with an estimated quantity of magnesium (in terms of MgO equivalent) in the exhausted brines of about 150,000 tons/year. This figure can rise by about 10 times if the overall capacity in the Mediterranean sea is considered, thus becoming a dramatically important potential source of this raw material for Europe.

A number of works concerning the recovery of magnesium from brines are reported in the literature. Already at the end of the 80s, Al Mutaz [11] analysed the technical feasibility of recovering minerals from the brine discharged from desalination plants in Gulf countries, starting from concentrations of total dissolved salts greater than the seawater standard. The conceptual analysis of processes for the recovery of sodium chloride, potassium salts and potassium, chlorine, bromine and magnesium, was performed underlining the importance of such application, also with regard to the large volume of brine produced in those years in Saudi Arabia (about 1,450 mgd).

Three years later, the same author [12] focused his research on the recovery of magnesium (in 1988, the production of magnesite was around 9 million ton per year, with about 33% of this coming from seawater). The world's largest producers of magnesium were the United States, Norway and the USSR. The idea was inspired by the fact that although about 60% of global desalination plants were installed in Gulf Countries, no magnesium extraction was performed. Several methods were analysed for the production of magnesium, and for the first time, cost estimation was proposed for the production of 2,000 tons/year of magnesium considering the particular case of brine produced in a desalination plant in the Arabian Gulf. Adding up all cost items, a hypothetical value of 2,357 US $/ton was obtained, which was lower than the selling price of magnesium (3,370 US$/ton in the United States). In a different context, i.e. the treatment of waste brines from chlorine production industry, Turek and Gnot [13] proposed a two-stage system capable to give magnesium hydroxide (commonly used in refractories industry) as a by-product. In order to industrially precipitate magnesium hydroxide, mainly calcined dolomite, burnt lime or ammonia were employed. However, in this case, these reagents could not be used because of the risk of calcium precipitation, when employing calcined dolomite or burnt lime, or danger of explosions in the electrolytic step, when running the process with ammonia. For this reason, the use of sodium hydroxide was proposed, leading to technological complications due to the slow sedimentation of the $Mg(OH)_2$ suspension obtained (resulting in difficult filtration procedures). The experimental campaign highlighted that the formation of the first crystalline germs was virtually instantaneous. The primary crystals of magnesium hydroxide formed had the flat structure characteristic of brucite. It was found also that, if an excess of hydroxide ions was maintained during crystallisation, the sedimentation speed was low and the filterability was worse than in the case of magnesium ions excess.

About 10 years later, Sung-Woo and Jun-Heok [14] proposed a multi-step reactive process for recycling magnesium chloride from brines derived from an industrial membrane process for the production of

NaCl. In this case, sulphuric acid was first added in order to precipitate calcium ions, thereby leading to a higher purity product. Then, the alkaline base (NaOH) was added for precipitating magnesium hydroxide. The result was a magnesium hydroxide with a purity of 98% and a structure of hexagonal flat platelets. Furthermore, the main outcome of the work was to demonstrate how the rate of sedimentation could be improved by adding appropriate sedimentation agents and aggregation inhibitors such as carboxy methyl cellulose and sodium stearate, respectively (added in small dosage as they can remain as impurities in the final product). Results showed that halved sedimentation times can be achieved by this addition. A final product with a magnesium purity of 99.5% and with crystal size of 0.5 microns was achieved.

More recently, Henrist et al. [15] investigated how the operating conditions in a magnesium hydroxide precipitation process from artificial brines, using alkaline aqueous solutions (NaOH or NH_4OH), affects the size, shape and level of agglomeration of $Mg(OH)_2$ crystals. The use of NaOH leads to the formation of cauliflower-shaped globular agglomerates, while the synthesis carried out with aqueous ammonia results into platelet-shaped particles, characterised by a higher mechanical resistance. The temperature also plays an important role, mainly on the agglomeration behaviour and particles size, which show a tendency of small crystals to agglomerate more about 60°C, while lower temperatures lead to larger but fewer single particles in the shape of circular platelet. This influence was confirmed also by the study conducted by Cipollina et al. [4].

In 2011, Liu et al. [16] developed a linear regression model for a the precipitation of magnesium hydroxide from brines using NaOH, $Ca(OH)_2$ or ammonia as reactants. Interestingly, these authors propose the use of ammonia as an alkaline reactant, which can eventually be regenerated, after the $Mg(OH)_2$ precipitation, by means of a thermal treatment (NH_3 is very volatile and tend to evaporate shifting NH_4^+/NH_3 equilibria towards NH_3). Authors found that a much more regular shape of crystals as well as a high degree of purity were guaranteed using NaOH, compared to the case in which calcium hydroxide or ammonia are used. However, the authors also found that particle agglomerate in the form of flakes, containing large quantities of water, leading to difficult filtration process as already reported in previous literature works [15]. In order to address this problem, several authors [15,17,18] investigated the use of magnesium hydroxide precipitation with hydrothermal treatment. However, this technology, characterised by high temperatures, high pressures and long residence time, does not seem to be suitable for large-scale production.

The use of organic additives and catalysts was also investigated [19,20], but this leads to an inevitable increase of impurities in the final product.

In 2011, Song et al. [21] analysed the batch precipitation process of high-purity $Mg(OH)_2$ through concentrated artificial solutions containing sodium chloride. Through an in-depth analysis of process performance dependences on operating conditions, the optimal ones were identified in order to achieve $Mg(OH)_2$ crystals with spherical shape, purity higher than 99% and an average particle sizes distribution ranging from 6 to 30 μm. More recently, the same authors [22] performed experiments in a continuous Mixed Suspension Mixed Product Removal crystalliser. Also, in this case, the main identified drawback was that $Mg(OH)_2$ nanoparticles can easily aggregate forming gelatinous precipitates, which create filtration difficulties, as already underlined by some of the previous works.

A fundamental study was carried out by Alamdari et al. [23] in 2008 on the kinetics of $Mg(OH)_2$ precipitation from artificial solutions and sea bittern (i.e. very concentrated brines generated from the evaporation of seawater). The authors identified three different kinetics for nucleation, growth and agglomeration, respectively. Nucleation rate was found to be the dominant phenomenon in the consumption of Mg^{2+}, while growth is comparatively slow, especially when high super-saturation is maintained. This is even more enhanced with real sea bittern, although the agglomeration rate seems to be improved in this latter case, which gives rise to larger particles more easily separated in the final separation stage.

Notwithstanding the significant number of laboratory investigations on reactive crystallisation of $Mg(OH)_2$ from concentrated solutions, little information is available in the literature on the investigation of precipitation phenomena from real saltworks brines. On this basis, in the present work, an experimental campaign has been carried out for assessing the potentials and the limits of magnesium recovery from real exhausted brines, collected in saltworks for the production of sea-salt (Trapani, Italy). On the basis of literature findings, highlighting the main drawback of reactive crystallisation, being the formation of very small crystals leading to the formation of particles flakes, incorporating large amounts of water and being very difficult to separate by simple precipitation, a specific focus was given to the analysis of precipitates crystals size distribution. Experiments were conducted both in semi-batch and continuous crystallisers, thus providing a fundamental insight in the crystallisation processes and eventually, highlighting, the main features contributing to increase product purity and particle size, in order to facilitate the final separation.

2. Experimental apparatus and procedures

2.1. Test-rig and procedures for semi-batch experiments

The first experimental campaign was carried out with a 5 liters semi-batch reactor, made of an unbaffled tank (diameter $(T) = 190$ mm, height $(H) = 190$ mm), equipped with a Rushton turbine with a diameter (D) equal to $T/3$. Unbaffled mixed tanks are, in fact, very suitable for crystallisation reactions, thanks to the sufficient mixing capacity coupled with a low energy consumption at the shaft, and to the minimum impeller-fluid relative velocity, which dramatically reduces secondary nucleation [24,25]. A description of the experimental procedure is given with reference to the schematic representation of Fig. 1.

The reactor was initially filled with the feed brine. At time $t = 0$, the injection of NaOH solution started
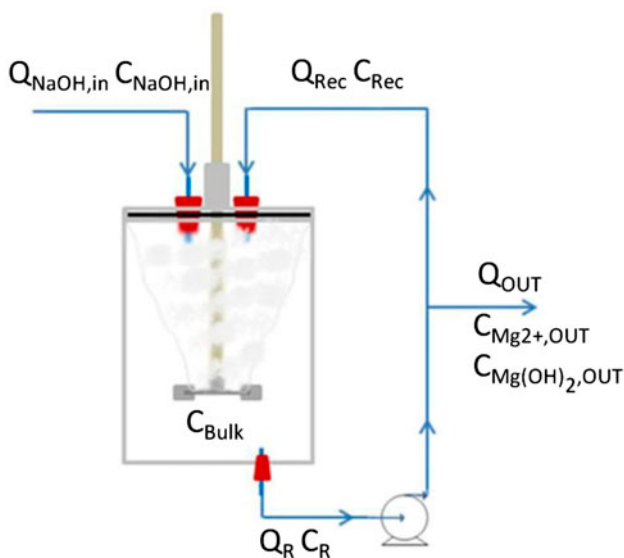

Fig. 2. Picture of the semi-batch reactor.

by means of a peristaltic pump (Verderflex OEM M025) and a long needle (internal diameter 1.5 mm) in order to inject the solution close to the impeller, where mixing phenomena are maximised (a picture of the reacting suspension in the stirred tank is shown in Fig. 2). The volume of the suspension in the reactor was controlled by a continuous purge of reacting suspension from vessel bottom.

In order to investigate the effect of impeller geometry on the granulometric distribution of crystals, tests with three different impellers were performed, namely: a Rushton turbine, a marine propeller and a 45°-pitched four-blade impeller (Fig. 3).

The solution pH was monitored during the precipitation reaction and typically showed an initial increase followed by a plateau at a pH around 9–10 (at which, practically complete precipitation of Mg occurred). A final sudden increase of pH up to values of 13–14 indicated the exhaustion of Mg^{2+} ions, which led to the increase of OH^- concentration following the addition of alkaline reactant. Fig. 4 illustrates an

Fig. 1. Schematic representation of the semi-batch reactor.

Fig. 3. The three impellers adopted in the semi-batch experiments. (a) Rushton turbine; (b) marine propeller; and (c) pitched-blade impeller.
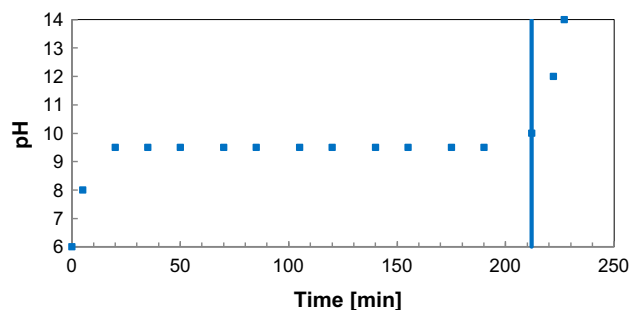
Fig. 4. Typical trend of solution pH during a crystallisation experiment. Symbols: experimental data. Vertical line: expected end of crystallisation reaction. Operating conditions: $Q_{NaOH} = 14 \, ml/min$, $C_{NaOH} = 2 \, M$ and $C_{Mg^{2+}} = 0.9 \, M$.

example of such trend, with experimental points, indicating the pH at the sampled instants and the vertical line indicating the theoretically predicted end of the reaction (see paragraph 2.3), which actually coincides with a rapid increase in pH generated by the excess addition of alkaline solution.

2.2. Sampling procedures and processing

The reacting suspension was sampled at six regular intervals throughout the reaction time. For each sample, a volume of 100 ml of suspension was extracted from the bottom of the stirred tank. A small amount of the suspension was directly used for the granulometric analysis (Laser Granulometer Malvern 2000), while the remaining part was filtered using a laboratory vacuum filtration system. The filtered solution was stored for the chromatographic analysis (Ionic Chromatograph Metrhom 882 Compact IC plus, with Cationic Exchange column Metrosep C4-250/4.0) to characterise the cationic composition of the process solution. The filtered solids were washed twice with 50 ml of distilled water (to remove trapped brine, which eventually led to the precipitation of soluble salts, thereby affecting the product purity), and finally dried in an oven kept at 60°C for 24 h.

In order to be prepared for chromatographic analysis, filtered solutions were first diluted at 1:1,000, and then micro-filtered (0.45 μm filter). 50 milligrams of dried solids were first dissolved using 1.7 ml of 1 M HCl solution, then diluted in to 0.5 liters, and eventually micro-filtered before injection in the chromatograph.

2.2.1. Definition of the main reaction performance parameters

A number of performance indicators were considered for the full characterisation of experiments. In

particular, visual inspection allowed the qualitative observation of crystallisation phenomena, while pH monitoring indicated the starting time and depletion of Mg^{2+} ions in the brine. Other quantitative parameters were identified as follows:

- magma density of the reacting suspension, expressing the solids concentration in the reactor, measured by dry weighing the filtered solid samples and dividing by the filtered suspension volume;
- granulometric distribution of the particulate suspension, indicating the particle size distribution of suspended particles within the reactor, measured by means of laser granulometric analysis of the suspension after dilution;
- magnesium purity of the product, expressing the percentage of Mg^{2+} ions on the total amount of cations revealed by the ionic chromatographic analysis of precipitate samples; and
- crystallisation yield, expressing the ratio between precipitated magnesium and magnesium inlet or fed with the brine, estimated from IC analysis of the sampled filtered solution (where the quantity of residual Mg^{2+} ions could be detected).

2.3. Theoretical estimation of time-dependent concentration profiles within the reactor

In order to predict the time-variation of species concentration inside the reactor and to better design the experimental tests, a simple model based on mass balance equations was developed. Specific assumptions were made regarding the stirred tank behaviour and reaction/precipitation kinetics:

- A constant volume of the suspension is kept by purging a flow rate equal to the inlet alkaline solution flow rate.
- An instantaneous reaction was assumed, i.e. precipitation rate was controlled only by the inlet rate of the alkaline reactant.

The equations adopted in the model are:
Mass balance on the Mg^{2+}:

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

where Q_{out} is the flow rate of the suspension exiting from the system (purge stream, equal to $Q_{NaOH,in}$), $C_{Mg^{2+},out}$ is the molar concentration of the magnesium ions exiting from the system (equal to the bulk

concentration, $C_{Mg^{2+}}$, assuming a perfect mixing in the tank), $Q_{NaOH,in}$ is the flow rate of the inlet alkaline solution, C_{NaOH} is the NaOH molar concentration in the inlet alkaline solution, V the is reactor volume and $C_{Mg^{2+}}$ is the Mg^{2+} concentration of the bulk solution (equal to $C_{Mg^{2+},out}$).

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

where $C_{Mg(OH)_2,out}$ is the molar concentration of the magnesium hydroxide in the suspension.

Rearranging and integrating Eq. (1) leads to:

$$-Q\left(C_{Mg^{2+}} + \frac{C_{NaOH}}{2}\right) = V\frac{dC_{Mg^{2+}}}{dt} \Rightarrow \int_{t_o}^{t}\frac{dC_{Mg^{2+}}}{\left(C_{Mg^{2+}} + \frac{C_{NaOH}}{2}\right)}$$

$$= \int_{t_o}^{t}\frac{Q}{V}dt \quad (3)$$

where Q=Qout=QNaOH, and, eventually, to:

$$\ln\left(\frac{C_{Mg^{2+}} + \frac{C_{NaOH}}{2}}{C_{Mg^{2+}}^o + \frac{C_{NaOH}}{2}}\right) = -\frac{Q}{V}t \quad (4)$$

$$\Downarrow$$

$$C_{Mg^{2+}} = \left(C_{Mg^{2+}}^o + \frac{C_{NaOH}}{2}\right)e^{-\frac{t}{\tau}} - \frac{C_{NaOH}}{2} \quad (5)$$

where $\tau = \frac{Q}{V}$ is the residence time of the alkaline solution in the reactor and $C_{Mg^{2+}}^o$ is the initial concentration of Mg^{2+} ions in the brine.

In a similar way, assuming that no $Mg(OH)_2$ is present in the initial brine and noting that the range of validity is limited to the time frame in which Mg^{2+} concentration is greater than zero, integrating Eq. (2) leads to:

$$C_{Mg(OH)_2} = \frac{C_{NaOH}}{2} - \left(\frac{C_{NaOH}}{2}\right)e^{-\frac{t}{\tau}} = \frac{C_{NaOH}}{2}\left(1 - e^{-\frac{t}{\tau}}\right) \quad (6)$$

Based on the above equations, a trend of species concentration along time was predicted for each batch test, which fits well the experimentally observed trends (Fig. 5), thus confirming the validity of the assumption of instantaneous reaction/precipitation kinetics, as well as all the measuring techniques adopted.

This model was adopted also to determine the duration of each batch test, thus allowing to correctly define the sampling times during the crystallisation.
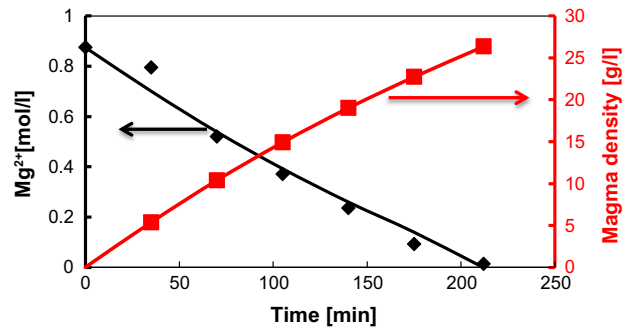

Fig. 5. Trend of dissolved Mg^{2+} ions concentration and magma density during a crystallisation experiment. Symbols represent experimental points and lines represent the theoretically expected trend. Operating conditions: Q_{NaOH} = 14 ml/min, C_{NaOH} = 2 M and $C_{Mg^{2+}}$ = 0.9 M.

It is worth mentioning that the above mass balances cannot provide information about crystals' size distribution for which a suitable population balance equation should be solved, provided that information on nucleation and growth kinetics was available. In the present work, crystals size distribution was only experimentally assessed as discussed in the next paragraphs.

2.4. Test-rig and procedures for CSTR reactor experiments

The same reactor above described was adopted for continuous crystallisation experiments, with some minor modifications to the system layout.
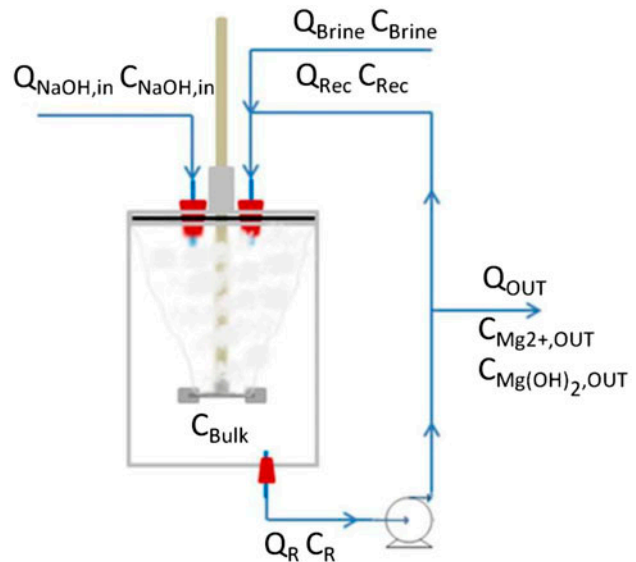

Fig. 6. Schematic representation of the continuous CSTR reactor.

The Continuous Stirred Tank Reactor (CSTR) configuration was adopted, which is characterised by having a perfectly mixed reaction fluid volume, with the bulk average conditions exactly equal to the outlet stream conditions.

A schematic diagram of the system is reported in Fig. 6. The main modification was the addition of a continuous injection of feed brine in the reacting suspension. The injection was performed by mixing the feed brine with the recirculating suspension, continuously extracted and recirculated to the reactor as in the case of the semi-batch tests. The injection of alkaline solution and extraction of the samples were performed as in the previous set-up, thus guaranteeing the same operating conditions and fluid flow distribution inside the reactor.

In order to avoid long transient start-up operations, the continuous test was performed starting from a final suspension of a batch test performed starting from 3.6 liters of brine, 0.8 M in Mg^{2+}, and adding 4 M NaOH solution up to 5 liters total volume.

In the continuous run, the volumetric flow rate of the feed brine was set to 24 ml/min, while it was set to 9.4 ml/min for the 4 M NaOH solution (4 M concentration was chosen in order to reduce the volumetric inlet flow rate of the alkaline solution), thus generating a residence time of about 150 min inside the reactor.

Sampling procedure was maintained as for semi-batch tests, although the sampling time was fixed to 2 h, and the duration of the experiment was extended to 8 h.

Assuming, also in this case, that all reaction kinetics are instantaneous, the CSTR reactor works with almost nil concentration of reacting species (Mg^{2+} and OH^-). On the other side, nucleation, growth and agglomeration/separation phenomena can dramatically influence the size of crystals and agglomerates, thus affecting the granulometric distribution showing a time-dependent behaviour, which will be illustrated in the following paragraphs.

3. Results and discussion

3.1. Semi-batch experiments

A comprehensive experimental campaign was carried out with the semi-batch reactor in order to characterise crystalliser performances under different operating conditions. The influence of three main operating parameters was investigated, namely the inlet NaOH solution flow rate, its molar concentration and the Mg^{2+} ions concentration in the feed brine. Moreover, the effect of three different impeller geometries was investigated.

Table 1 summarises the tests performed with relevant operating conditions.

Among the above-mentioned performance indicators (paragraph 2.2), three of them were considered and reported in the following graphs, namely: (1) magma density of the reacting suspension; (2) granulometric distribution of the particulate suspension; and (3) Mg purity of the precipitated product.

Fig. 7 reports the dependence of magma density as a funciton of the normalized time (i.e. time divided by the total duration of the experiment) for the first three sets of experiments. In all cases, magma density increases with time, as expected due to the reaction progress, which seems to be almost linear until the final plateau reached at the end of the reaction. However, the use of a more concentrated alkaline solution gives rise to larger magma

Table 1
Summary of experimental conditions and tests

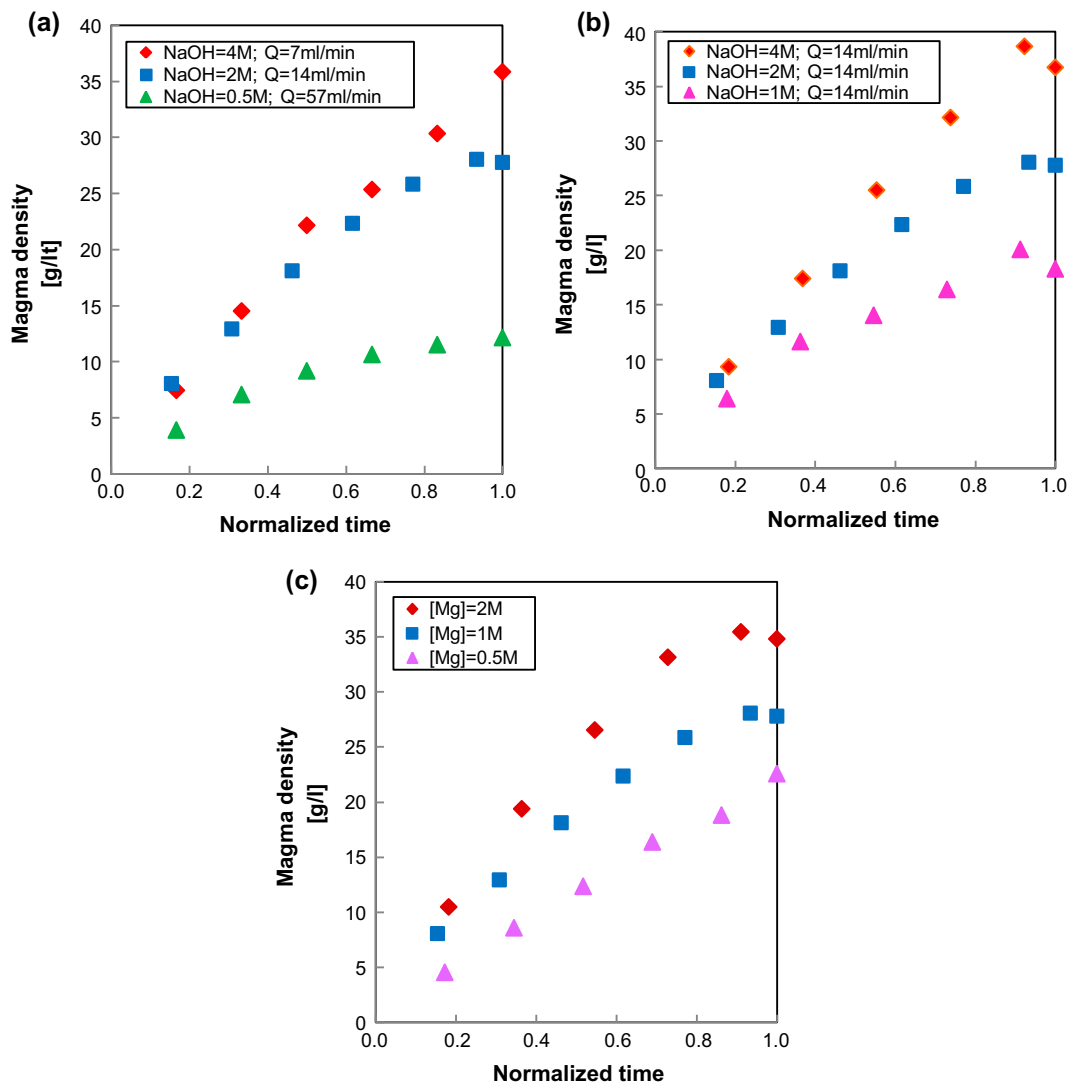| Set	Test no	C_{NaOH} [mol/l]	Q_{NaOH} [ml/min]	$C_{Mg^{2+}}$ [mol/l]	Impeller
1°set	1	4	7	1	Rushton
	2	2	14	1	Rushton
	3	0.5	57	1	Rushton
2°set	4	4	14	1	Rushton
	2	2	14	1	Rushton
	5	1	14	1	Rushton
3°set	6	2	14	2	Rushton
	2	2	14	1	Rushton
	7	2	14	0.5	Rushton
4°set	8	4	14	1	Marine
	4	4	14	1	Rushton
	9	4	14	1	Pitched-blade

Fig. 7. Time variation of the magma density during the semi-batch tests. (a) Influence of NaOH concentration and volumetric flow rate (fixing a constant NaOH molar flow rate); (b) influence of NaOH concentration; and (c) influence of Mg^{2+} concentration in the brine. Non-variable parameters are fixed as standard conditions: $V_{NaOH} = 14.3$ ml/min; $[NaOH] = 2$ M; and $[Mg^{2+}]_{brine} = 1$ M.

density. Such trend can also be explained due to the larger inlet (and, therefore, purge) flow rate required in the first set for lower NaOH concentration, which led to a greater dilution of the suspension. On the other side, in set N.2, the larger NaOH concentration allowed the achievement of the total precipitation in shorter times (though in the graph only normalized times are reported), leading again to a minor dilution of the suspension.

Finally, the presence of a larger quantity of Mg^{2+} ions in the solution leads to greater magma densities, as a larger amount of magnesium hydroxide can be formed, although requiring a longer reaction time for a fixed molar flow rate of NaOH injected.

All these outcomes, although being quite predictable, indicates that the presence of larger concentrations of reactants normally lead to denser suspensions, while reaction kinetics are practically not affected by such operating parameters, being basically controlled by the molar flow rate of NaOH (the alkaline reactant adopted for the reactive crystallisation) injected in the reacting suspension.

A much more complex behaviour was observed in terms of particle size distribution of the reacting suspension sampled at different instants during the reaction run.

The cumulative granulometric distributions are reported in Fig. 8 for each experimental set. The first
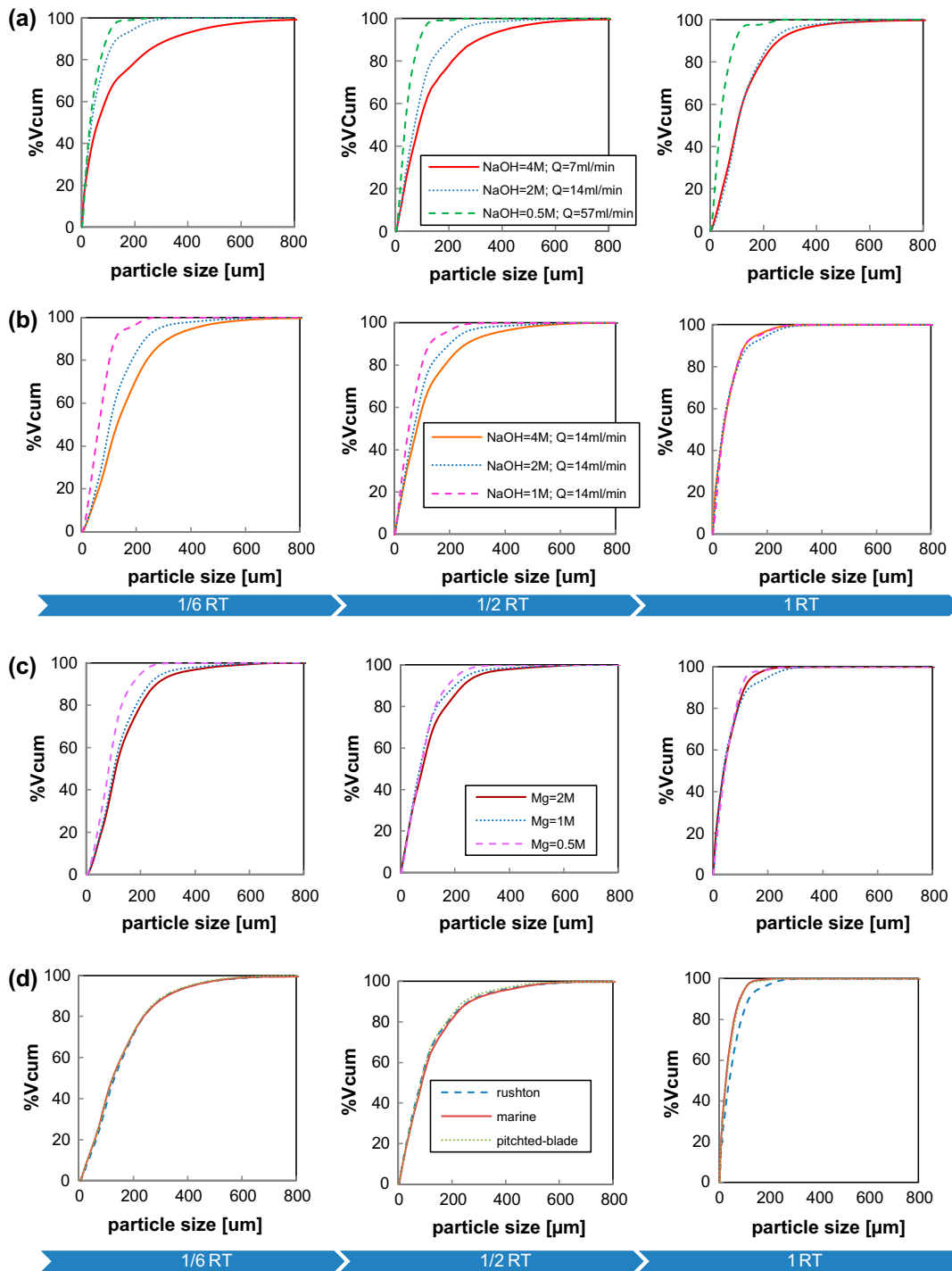
Fig. 8. Cumulative granulometric distribution of the particles precipitated at time $t = 1/6$ RT, $1/2$ RT and 1 RT (RT = total Reaction Time). (a) Influence of NaOH concentration and volumetric flow rate (fixing a constant molar flow rate); (b) influence of NaOH concentration; (c) influence of Mg^{2+} concentration in the brine; and (d) influence of impeller geometry. Non-variable parameters are fixed as standard conditions: $V_{NaOH} = 14.3$ ml/min; [NaOH] = 2 M; $[Mg^{2+}]_{brine} = 1$ mol/l; and impeller type = six-blade Rusthon turbine.

two sets of experiments indicate that higher concentrations of NaOH contribute to obtain larger particles, although the difference is more evident in the first phase of the experiment, when Mg^{2+} ions concentration in the suspension is still high. A similar behaviour has also been observed with respect to Mg^{2+} initial concentration in the brine. More concentrated brine gives slightly larger particles, although the influence is less evident than that with NaOH concentration. A very interesting, yet unexpected, phenomenon can be observed looking at the time variation of granulometric curves. In fact, in all cases, particle sizes range from few microns to 300–400 μm, with a larger percentage of particles size >100 μm in the initial phase of the batch experiment ($t \leq 1/2$ RT) and a lower percentage (in some cases negligible) at the end of the precipitation test, indicating that the lower the Mg^{2+} concentration, the smaller is the mean size of formed particles.

Such findings apparently strike with previous literature findings. These, in fact, indicate a typical size distribution of $Mg(OH)_2$ crystals up to few microns [15,20–22]. Moreover, the apparent increase in particle size while increasing reactant concentration is opposite to the usual dependence of nucleation and growth kinetics with super-saturation. Extreme supersaturation normally leads to and nucleation rate higher than growth rate, while, at the contrary, low supersaturation conditions should lead to higher growth rate and bigger crystals formed. On the other side, agglomeration phenomena are known to have an important role in precipitated $Mg(OH)_2$ particle size distribution, which could explain such a behaviour. However, further investigation is required for a better understanding of these aspects.

Also, the dependence of Mg purity of the precipitated product on reaction conditions was analysed
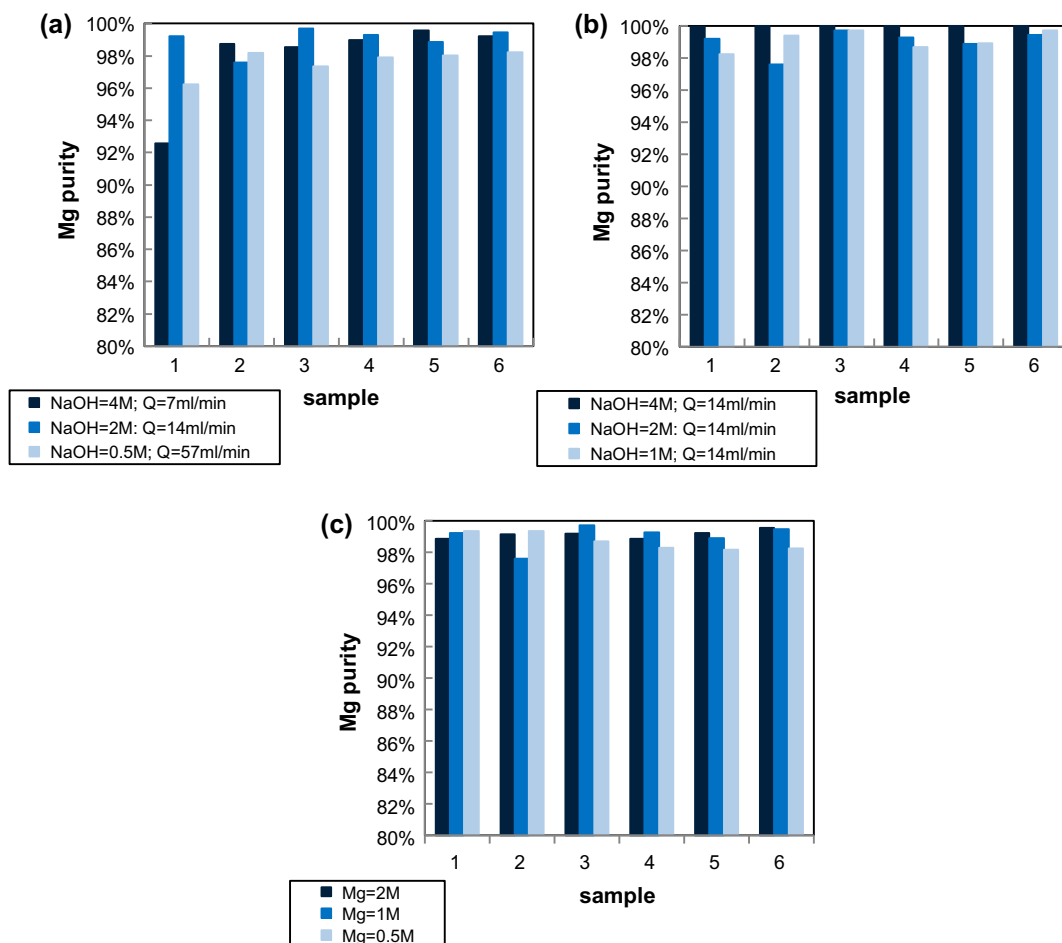

Fig. 9. Purity in Mg of the precipitate in the samples of semi-batch tests. (a) Influence of NaOH concentration and volumetric flow rate (fixing a constant molar flow rate); (b) influence of NaOH concentration; and (c) influence of Mg^{2+} concentration in the brine. Non-variable parameters are fixed as standard conditions: $V_{NaOH} = 14.3$ ml/min; [NaOH] = 2 M; and $[Mg^{2+}]_{brine} = 1$ M.

and reported in Fig. 9. The first, most important, finding is that magnesium purity is very high in all conditions and experimental tests. Apart from a few samples in the first set of experiments, purity between 98 and 100% was obtained. Also, in this case, a larger concentration of alkaline solution injected in the reactor apparently leads to higher purities, although such trend is not perfectly regular for all samples.

A less pronounced dependence was found on the initial concentration of Mg^{2+} in the brine, although in the final samples, a slightly higher purity is obtained starting from more concentrated brines.

Finally, it is worth noting that in all batch experiments, a practically complete conversion of Mg^{2+} was achieved, with a precipitation yield equal to almost 100%. This indicated that precipitation yield only depends on the amount of alkaline reactant added. In fact, by dosing a slightly over-stoichiometric quantity of NaOH, no Mg^{2+} ions left were found in the final solutions sampled from the reactor.

3.2. Continuous precipitation in the CSTR reactor

A continuous crystallisation test was also performed in the CSTR reactor as described in paragraph 2.4. Time-dependent variation of the main performance parameters was investigated and is presented in Figs. 10 and 11 for magma density and granulometric distribution, with respect to a normalized time calculated as the ratio between the sampling time ($t = 0$, 120, 240, 360 and 480 min) and the flow residence time in the reactor ($\tau = 150$ min).

Fig. 10 shows how the magma density stabilises after 1.5 τ to a value around 20 g/l, slightly lower than the one reached in the preparatory batch test. At the contrary, a continuous reduction in the particles size can be observed from Fig. 11 for the whole duration of the run (8 h), in accordance with the previous experimental findings and the discussed precipitation mechanism. In fact, due to the very low Mg^{2+} and OH^- concentrations kept in the CSTR reactor, agglomeration mechanisms are slower and less effective, leaving room to the fast nucleation of crystals, thus continuously displacing the cumulative particle size distribution towards smaller particles.

Mg purity was between 99 and 100% for all samples analysed, thus indicating a very effective mechanism of separation.

Finally, total recovery of Mg^{2+} was obtained by continuous dosing of a stoichiometric quantity of NaOH with the inlet brine.
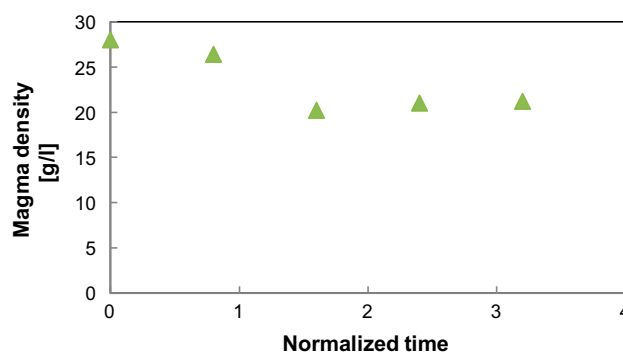

Fig. 10. Time variation of the magma density in a continuous CSTR reaction experiment.
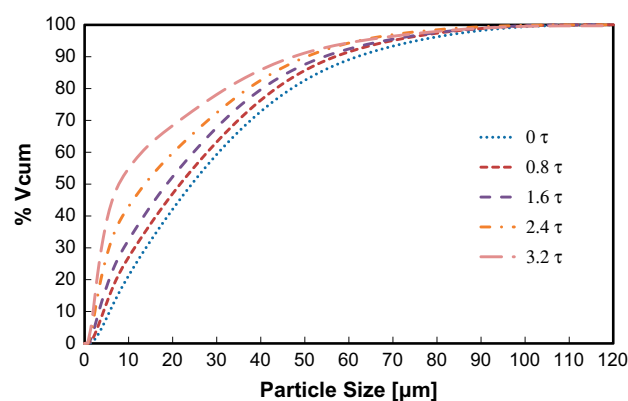

Fig. 11. Time variation of the magma density in a continuous CSTR reaction experiment.

4. Conclusions

In the world scenarios of alternative mining processes of raw materials, the recovery of minerals from waste brines can have a role of paramount importance, especially in the Mediterranean area, where the presence of traditional saltworks and the growing number of desalination plants installed guarantee the availability of large amounts of brines that have to be either disposed or reused. Under this respect, magnesium represents one of the most interesting elements to be recovered from seawater brines for two reasons: (i) the large quantities of Mg^{2+} ions in seawater brines and (ii) the great importance of identifying new sources of such material, which has recently been classified by EU as a "critical raw material".

On this basis, the present work assessed the feasibility and highlighted the potentials of using reactive

precipitation for recovering magnesium hydroxide from real exhausted brines from Trapani saltworks (Sicily, Italy). An experimental campaign has been carried out in semi-batch and continuous reactors, in order to identify the main dependencies of process performance on operating conditions, confirming that reactive precipitation is a feasible way for recovering magnesium from brines. Previous literature findings on the main technological issues, consisting in the formation of particles flakes incorporating large amounts of liquor and making it difficult their separation by simple sedimentation, were also confirmed. For this reason, a focused investigation of the influence of operating conditions on particle size distribution was performed, leading to the conclusion that higher concentrations of alkaline reactant and Mg^{2+} ions allows the formation of larger particles. Mg purity of precipitates was found to be extremely high, with values ranging from 98 to 100%, in most experimental runs. Reactive precipitation also allowed a total recovery of magnesium from the brine, just keeping a stoichiometric injection of alkaline reactant.

Acknowledgements

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