Mg(OH)$_2$ Recovery from Real Bitterns: a Proof of Concept at Pilot Scale

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Water, energy, and minerals are fundamental pillars for the future of humankind. Sustainable and renewable productive processes and resources are the only possibility to face the continuously growing global population and high living standards requirements. The present work introduces a proof of concept for the pilot scale production of magnesium hydroxide, Mg(OH)$_2$, from waste saltworks bitterns located in the district of Trapani, Italy. Mg(OH)$_2$ was produced by adopting a proprietary "*Magnesium Crystals Granulometry Controlled Reactor*", Mg-CGCR. The influence of several parameters was investigated on Mg(OH)$_2$ suspensions and powders characteristics: (i) the bittern flow rate, (ii) alkaline sodium hydroxide, NaOH, concentrations solutions (adopted as the precipitant agent) and (iii) the final suspension pH value (stoichiometric or OH$^-$ excess amounts). A Mg^{2+} recovery >99 % can be achieved thanks to the adoption of a product recycling strategy in the reactor. Furthermore, highly pure Mg(OH)$_2$ powders, addressed by cationic purity, were synthesized. Results demonstrate the possibility of producing highly pure Mg(OH)$_2$ products from waste-concentrated saline solutions, thus turning waste into valuable compounds.

1. Introduction

Minerals are employed in a broad variety of applications related to construction, manufacturing, agriculture, and energy supply. The continuously growing global mineral demand results into a considerable consumption of limited land mining sources. In addition, mineral ores are not equally geographically worldwide spread. As a matter of fact, since 2011, the European Union has identified and updated a list of critical raw materials (CRMs) due to the scarce EU supply and their criticality for the EU economy and social development. Desalination brines, lake brines and saltworks bitterns have been recently identified as the ideal sustainable and environmentally low-impact mineral sources (Battaglia et al., 2023). Magnesium is a grey mineral extensively employed in numerous fields. Magnesium derivatives, such as magnesium hydroxide, Mg(OH)$_2$, magnesium carbonate, MgCO$_3$, and magnesium oxide, MgO, are also widely adopted in numerous industrial applications: (i) as flame retardant agents in polymeric materials, (ii) in wastewater treatments or (iii) as catalysts (Balducci et al., 2017). Nowadays, magnesium compounds are mainly produced from mineral ores, however, a strong effort has been put into their recovery from salty concentrated solutions. Gong et al. (2018) analysed the feasibility of mineral recovery from seawater brines marking the high economic, social and environmental benefits associated with the brine's exploitation. Yousefi et al. (2020) studied the recovery of Mg^{2+} from an Iranian Khur Potash Complex brine containing ~50 g/L of Mg^{2+} and ~182 g/L of Ca^{2+}. Mg(OH)$_2$ was produced by letting the brine react with sodium hydroxide solutions, NaOH, accurately controlling the reaction pH (kept between 9 and 9.5). The pH strategy avoided the co-precipitation of Ca^{2+} compounds leading to Mg(OH)$_2$ powders characterized by a purity of ~86%. Alamdari et al. (2008) studied the Mg(OH)$_2$ precipitation phenomena from sea bitterns collected from a salt production unit of a local petrochemical complex. Particle nucleation was found to be the dominant mechanism, resulting in a large number of small crystals that exhibit slow sedimentation rates. Mg(OH)$_2$ production from seawater and industrial waste brines was also investigated by employing an innovative ionic exchange membrane crystallizer (Cr-IEM) able to selectively mix brines with low-

cost alkaline solutions, such as calcium hydroxide, $Ca(OH)_2$ (Vassallo et al., 2021a). The anionic membrane allows the passage of only hydroxyl ions, blocking the flux of undesired cations, i.e. Ca^{2+}, which could impair $Mg(OH)_2$ purity. The same research group also proposed a purposely designed multi-feed plug flow reactor able to accurately control the reaction pH environment to selectively precipitate Ca^{2+} and Mg^{2+} ions using NaOH (Vassallo et al., 2021b). Mg^{2+} and Ca^{2+} recoveries >99 % and >95 %, respectively, were obtained with $Mg(OH)_2$ and $Ca(OH)_2$ cationic purities above 95 % when treating a retentate of a nanofiltration unit using a spent brine from an industrial water production plant. Lately, Morgante et al. (2022) thoroughly analysed the filtration and sedimentation characteristics of $Mg(OH)_2$ suspensions produced adopting the same reactor. Suspensions sedimentation and filtration times considerably decreased by recycling part of the product inducing a seeded precipitation process. In the last couple of years, mineral extraction from saltworks bitterns has been investigated. Specifically, bitterns collected from the final basins of the saltworks operating in the district of Trapani (Sicily, Italy) were analysed within the activities of the European-funded SEArcularMINE project. Bitterns are by-products of the sea salt production from seawater, whose discharge poses environmental concerns. Battaglia et al. (2023) thoroughly investigated, at a laboratory scale, $Mg(OH)_2$ powder purity synthesized from two real bitterns of Trapani saltworks. Powders were characterized by cation purity values >99 % and mass purities >95 %. These values reach market requirements for commercial $Mg(OH)_2$ applications. In addition, $Mg(OH)_2$ nanoparticles of pharmaceutical interest were also produced thanks to the high mixing intensity attained in a T-mixer (Battaglia et al., 2022b).

The present work aims at assessing, for the first time, the $Mg(OH)_2$ production scale-up from the laboratory to the pilot scale, treating real saltworks bitterns. A proprietary multi-feed plug flow reactor designed by ResourSEAs (Palermo, Italy), and denominated "*Magnesium Crystals Granulometry Controlled Reactor*", Mg-CGCR, was employed under different operating conditions. $Mg(OH)_2$ production rates scaled from a few gram per hour (laboratory scale) to kilogram per hour (pilot scale). The exploitation of Mediterranean saltworks bitterns would be able to produce ~1.2 million tonnes of $Mg(OH)_2$ per year covering 30 % of the $Mg(OH)_2$ global demand. No mineral ore resources will be consumed, in contrast with typical $Mg(OH)_2$ production processes. Furthermore, the flexibility of the Mg-CGCR prototype is an innovative aspect that would overtake the use of classical stirred tank reactors. The Mg-CGCR prototype is going to be re-adapted based on computational fluid dynamics simulations coupled with population balance equations for precipitation description in the second phase of the SEArcularMINE project, aiming at producing different $Mg(OH)_2$ products, whose characteristics will comply with several market sectors.

2. Material and methods

Saltworks bitterns are highly concentrated solutions in numerous chemical elements (Vicari et al., 2022). In bitterns, Mg^{2+} concentration can reach values up to 20-60 times that in seawater. In the present work, the bittern collected from the Margi saltwork located in Trapani, Italy, was chosen as a potential Mg^{2+} source. Mg^{2+} concentration of the Margi bittern is reported in Table 1.

In the process, Mg ions react with hydroxyl ones, OH^-, provided here by synthetic NaOH solutions:

$$Mg^{2+} + 2NaOH = Mg(OH)_2 + 2Na^+ \tag{1}$$

NaOH solutions were prepared by dissolving NaOH pellets (Inovyn, technical grade) in softened tap water. The softening process was aimed at removing any bivalent ions, i.e. Mg^{2+} and Ca^{2+}, that would falsify experimental results. $Mg(OH)_2$ precipitation occurred in the innovative Mg-CGCR tubular multiple feed plug flow pilot scale reactor. The Mg-CGCR is made of two adjacent volumes where the bittern and NaOH solutions flow. The bittern is injected into the NaOH compartment through multiple nozzles to guarantee a well-supersaturation homogenization all over the reactor volume. The $Mg(OH)_2$ suspension exiting the reactor is partially mixed with fresh alkaline solution and recycled back to the inlet section of the reactor. The recycling strategy has been reported to induce a seeded $Mg(OH)_2$ precipitation and promote a total conversion of Mg ions. A whole description of the employed pilot plant was presented by Morgante et al. (2022).

2.1 Experimental tests

The influence of (i) bittern flow rates (Cases #1 and #2), (ii) NaOH concentrations (Cases #1 and #3) and (iii) the final suspension pH values (Cases #a-b) was examined on the sedimentation, filterability and purity of the produced $Mg(OH)_2$ suspensions and powders.

Table 1 lists concentrations and flow rates of the Margi bittern and NaOH solutions adopted in Cases #1, #2 and #3. Letters a and b distinguish cases characterized by final pH values of 10.8 (stoichiometric precipitation conditions) and 12.8 (OH^- excess amount conditions), respectively. NaOH concentrations were validated by

titration; the outlet suspensions pH was monitored in-line by a pH-meter (PH 8320, KROHNE); Mg²⁺ bittern concentration was obtained by ion chromatography (IC, 882 Compact IC plus, Metrohm).

Table 1 Operating parameters and characteristics of the adopted real bitterns and synthetic NaOH solutions. The final pH value of the Mg(OH)₂ suspension is also reported.

Case	Bittern Mg²⁺ [M]	Bittern Flow rate [L/h]	NaOH concentration [M]	NaOH Flow rate [L/h]	Final suspension pH
#1a	2.04±2 %	12±3 %	0.50±2 %	96±3 %	10.8±2 %
#1b	2.04±2 %	12±3 %	0.50±2 %	155±3 %	12.8±2 %
#2a	2.04±2 %	30±3 %	0.50±2 %	235±3 %	10.8±2 %
#2b	2.04±2 %	30±3 %	0.50±2 %	338±3 %	12.8±2 %
#3a	2.04±2 %	12±3 %	1.00±2 %	47±3 %	10.8±2 %
#3b	2.04±2 %	12±3 %	1.00±2 %	94±3 %	12.8±2 %

2.2 Mg(OH)₂ suspensions and powders characterization

Mg(OH)₂ suspensions were collected at the outlet of the reactor after a start-up phase of about 15 minutes. In settling tests, two 100 mL graduated cylinders were filled, and the settled volume was recorded for about 48 h. Suspensions were then re-suspended and filtered. Specifically, the filtration time required to obtain an 80 mL filtered clarified solution was recorded for each sample. Filtration tests were conducted at a constant vacuum pressure of 0.5 bar using a vacuum pump (Buchi V-100), a Buchner funnel and 1.8 µm glass fiber filters (GE Healthcare Life Science Whatman™). After, the Mg(OH)₂ cake was accurately washed with distilled water (~10 µS/cm) until the filtered water reached a conductivity <150 µS/cm. The washing step removed mother liquor and reaction by-products entrapped in the cake. The Mg(OH)₂ cake was dried for 24 h in an oven. Finally, ~150 mg was dissolved in 2 wt%. nitric acid (Trace SELECT, 65 wt%, Honeywell Fluka) solution and powder cationic purity was assessed via IC. Filtered clarified solutions were analyzed by Ethylenediaminetetraacetic acid (EDTA) complexometric titration to determine Mg²⁺ recovery.

Mg²⁺ recovery, namely the amount of magnesium ions extracted from the bittern in the process, was defined as the difference between the initial Mg²⁺ concentration in the bittern and that in the filtered clarified solutions over the initial Mg²⁺ concentration in the bittern, as follows:

$$Mg^{2+}recovery = \frac{Mg^{2+}_{BITTERN} - Mg^{2+}_{CLARIFIED} \cdot DF}{Mg^{2+}_{BITTERN}} \tag{2}$$

The Mg²⁺ concentration in the filtered clarified solutions was appropriately multiplied by a dilution factor, $DF = (Q_{BITTERN} + Q_{NaOH})/ Q_{BITTERN}$, that considers the dilution phenomenon caused by mixing between the bittern and the NaOH flow rates (Q). Cation purity was calculated as the ratio between the Mg²⁺ amount, Mg^{2+}_{IC}, over the sum of all the cations, c_i, detected by IC in the dissolved Mg(OH)₂ powders:

$$Cation\ purity = \frac{Mg^{2+}_{IC}}{\sum_i^N c_i} \tag{3}$$

where N is the number of all cations measured by the IC.

3. Results

In this section, sedimentation trends and filtration times of produced Mg(OH)₂ suspensions are discussed along with Mg²⁺ recoveries and Mg(OH)₂ purity values. Sedimentation trends report the normalized settled volume, V_N, defined as:

$$V_N = \frac{V_{Actual} - V_{Final}}{V_{Inital} - V_{Final}} \tag{4}$$

where V_{Actual} is the recorded volume occupied by the Mg(OH)₂ suspension at a certain time over the 48 h of sedimentation; V_{Inital} and V_{Final} are the initial (100 mL) and final volume occupied by the Mg(OH)₂ suspension. The V_N quantity allows a better evaluation of suspension sedimentation behaviors as it emphasizes the sedimentation trend required to reach the final volume occupied by the Mg(OH)₂ suspension.

3.1 Influence of bittern flow rate

The influence of bittern flow rate on $Mg(OH)_2$ suspension sedimentation and filterability properties was studied by increasing the bittern flow rate from 12 L/h (Cases #1) to 30 L/h (Cases #2).
Figure 1a and Figure 1b show the normalized settled volume, V_N, see Eq. (4), trends and filtration times required for obtaining 80 mL of clarified filtered solutions, respectively.
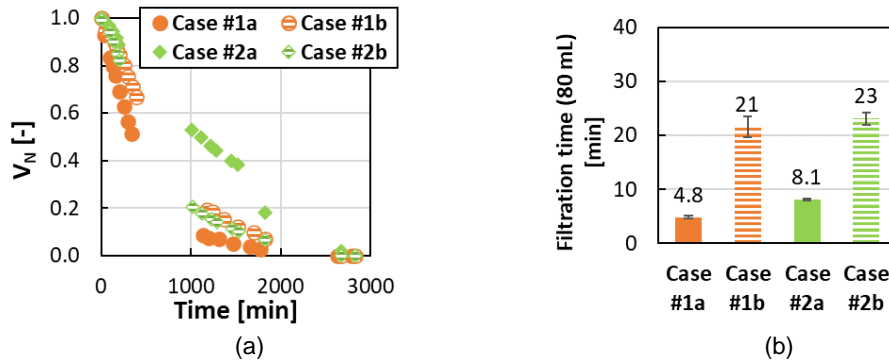

(a)   (b)

Figure 1 Normalized settled volume, V_N, Eq. (4), trends, (a); and filtration times, (b), required to obtain 80 mL of clarified filtered solutions at 0.5 bar for Cases #1 (bittern flow rate of 12 L/h) and Cases #2 (bittern flow rate of 30 L/h). Cases #a and #b were characterized by a final suspension pH of 10.8 and 12.8, respectively.

Cases #1b and #2b show similar sedimentation trends, regardless of the different bittern flow rates. Case#1a exhibits the fastest sedimentation performance, while Case #2a is characterized by the slowest one. This behaviour can be related to the higher bittern flow rate adopted in Cases #2. The higher flow rate increases the reactants mixing degree that reduces aggregation phenomena, leading, eventually, to more easily breakable particles that are more difficult to be sedimented and filtered (Battaglia et al., 2022a; Morgante et al., 2022). This is in accordance with recorded filtration times, see Figure 1b. Specifically, filtration time is almost two times higher for Case #2a, 8 minutes, than for Case #1a, 5 minutes. Interestingly, Cases #a (suspension pH of 10.8) are almost 4 times faster than Cases #b (final suspension pH of 12.8), despite their higher $Mg(OH)_2$ concentration (suspension magma density), as reported in Table 2. This can be caused by the final suspension pH that influences (i) particle zetapotential (Battaglia et al., 2022a), and (ii) particle tendency at adsorbing more liquid phase creating agglomerates characterized by internal pores containing more mother liquor (Turek and Gnot, 1995). These phenomena can lead to even more easily breakable aggregates than Case #2a, considerably hindering the filtration process. Table 2 reports the normalized final settled volume, sedimentation concentration factors, i.e. the inverse of the normalized final settled volume, and final magma densities. Final magma densities were calculated by multiplying initial magma densities by concentration factors. Higher final magma densities are always observed for Cases #b (final pH suspension of 12.8) as for concentration factors, probably due to their lower initial suspension magma densities.

Table 2 Initial magma densities, normalized final settled volumes, concentration factors and final magma densities for Cases#1a, #1b, #2a and #2b.

Case	Magma density [g/L]	V_{Final}/V_{Inital}	Concentration factor	Final magma density [g/L]
#1a	13.2	0.38	2.6	34.5
#1b	8.5	0.22	4.5	38.9
#2a	13.5	0.45	2.2	30.0
#2b	9.7	0.23	4.5	44.2

3.2 Influence of NaOH concentration

The NaOH concentration influence on $Mg(OH)_2$ suspension sedimentation and filterability properties was investigated by adopting 0.50 M (Cases #1) and 1.00 M (Cases #3) NaOH solutions.
Figure 2a and Figure 2b report the normalized settled volume, V_N, Eq. (4), trends and filtration times required for obtaining 80 mL of clarified filtered solutions, respectively.
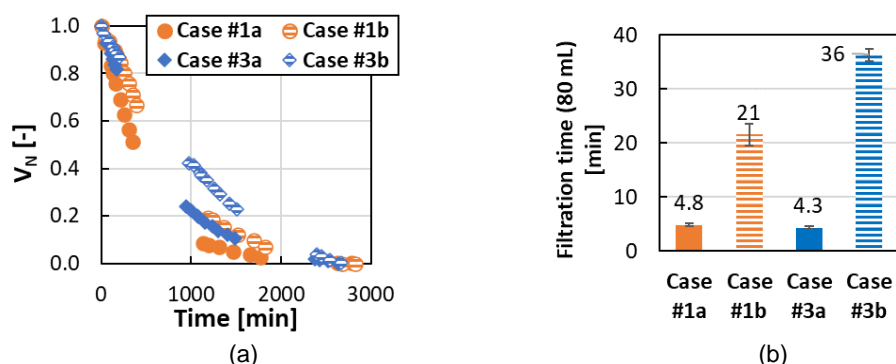
(a)   (b)

Figure 2 Normalized settled volume, V_N, Eq. (4), trends, (a); and filtration times, (b), required to obtain 80 mL of clarified filtered solution at 0.5 bar for Cases #1 (0.50 M NaOH) and Cases #3 (1.00 M NaOH). Cases #a and #b were characterized by a final suspension pH of 10.8 and 12.8, respectively.

$Mg(OH)_2$ suspensions produced in Cases #3 sedimented slower than those of Cases #1. This can be due to the higher magma densities of Cases #3, see Table 3.The slower sedimentation trends can also be attributed to the higher local supersaturation level achieved in the reactor due to the higher employed NaOH concentration. Higher local supersaturation levels lead to the nucleation of smaller particles that entrap a higher mother liquor amount, eventually, producing more isodense particles characterized by slower sedimentation rates (Turek and Gnot, 1995). Concerning filtration times, Case #3a requires a similar filtration time, 4.5 minutes, than that of Case #1, 4.8 minutes, see Figure 2b. The filtration time of Case #3 b is almost 9 and 1.5 times higher than those of Cases #1a and #1b, probably due to the use of the more concentrated NaOH solutions. Table 3 reports the initial magma densities, the final normalized settled volume, concentration factors and final magma densities for Cases #1 and #3. Case#3a reaches the highest final magma density of ~57.6 g/l, while Cases #3 exhibit the lowest concentration factors probably due to their higher initial magma densities.

Table 3 Initial magma densities, normalized final settled volumes, concentration factors and final magma densities for Cases#1a, #1b, #3a and #3b.

Case	Initial magma density [g/L]	V_{Final}/V_{Inital}	Concentration factor	Final magma density [g/L]
#1a	13.2	0.38	2.6	34.5
#1b	8.5	0.22	4.5	38.9
#3a	24.2	0.42	2.4	57.6
#3b	13.5	0.36	2.7	36.6

3.3 Mg^{2+} recovery and $Mg(OH)_2$ purity assessment

Mg^{2+} recoveries and $Mg(OH)_2$ powder purities were analysed for each test. Table 4 reports Mg^{2+} recovery values calculated using Eq. (2) after analyzing the Mg^{2+} concentration in the filtered clarified solutions. Table 4 also lists Mg^{2+} and Na^+, the only identified cations, concentrations in dissolved $Mg(OH)_2$ powders detected by IC measurements. Cationic purity is calculated employing Eq. (3).

Table 4 Mg^{2+} recovery evaluated using Eq. (2) based on filtered clarified solutions EDTA analysis. Mg^{2+} and Na^+ concentrations measured by IC in dissolved $Mg(OH)_2$ powders along with cation purity calculated by Eq.(3).

Case	Mg^{2+} recovery [%]	Mg^{2+} [mg/g]	Mg^{2+} SD [mg/g]	Na^+ (mg/g)	Na^+ SD [mg/g]	Cationic Purity [%]
#1a	>99	392.0	0.4	<5*	-	>99
#1b	>99	387.6	0.9	<5*	-	>99
#2a	94	382.9	0.4	<5*	-	>99
#2b	>99	387.2	0.2	<5*	-	>99
#3a	>99	385.9	0.2	<5*	-	>99
#3b	>99	389.2	0.5	<5*	-	>99

*Concentration values lower than their Limit of Quantification (LOQ).

Magnesium recovery is always higher than 99 % when the final suspension pH is equal to 12.8. Results are in accordance with findings reported by Morgante et al. (2022) when a recycling strategy is employed for the $Mg(OH)_2$ precipitation process. Cationic purity was always higher than 99 % confirming previous data collected at a laboratory scale on real saltworks bitterns (Battaglia et al., 2023). Overall, results demonstrate the possibility of producing highly $Mg(OH)_2$ powders from real bittern at a pilot scale.

4. Conclusions

$Mg(OH)_2$ production from waste saline solutions was investigated at a pilot scale by adopting a novel "*Magnesium Crystals Granulometry Controlled Reactor* ", Mg-CGCR. The reactor was purposely developed within the Europan SEArcularMINE project to treat waste saltworks bitterns. $Mg(OH)_2$ suspensions sedimented faster (Case #1a) when (i) the final suspension pH was 10.8, (ii) low reactants mixing degree is attained in the reactor and (iii) low NaOH concentrations are employed. Suspensions characterized by a final pH value of 10.8 (Cases #a) required almost one-fourth of the time recorded by those having a final pH value of 12.8 to obtain 80 mL of clarified filtered solutions. This behaviour was attributed to the influence of the final suspension pH on particle stability and characteristics. Mg^{2+} recovery was found to be higher than 99 % (final suspension pH of 12.8) thanks to the slurry recycling strategy adopted in the reactor. Cation purity was higher than 99 % in all cases.
Results demonstrate the actual possibility of producing highly pure $Mg(OH)_2$ compounds at a pilot scale treating real bitterns paving the road to a valuable manufacturing alternative of $Mg(OH)_2$ compounds.

Acknowledgments

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