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Mg(OH)2 Production from Seawater and Saltworks Brines

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Desalination and saltworks are widely adopted to produce freshwater and table salt. On the other hand, these processes generate waste saline solutions, named brine or bitterns, that have been managed so far following the linear economy approach. Only in the last 10 years, more attention has been paid on the valorisation of these waste streams for the recovery of high added value compounds, such as magnesium hydroxide, Mg(OH)2. Although several scientific efforts have investigated the precipitation of Mg(OH)2 compounds from brines and bitterns, literature still lacks of comparative studies under similar operating conditions. With this respect, the present work aims at filling this gap by testing two types of real saline waste solutions: (i) a reverse osmosis (RO) brine outcoming from the desalination plant located in the Lampedusa Island (Italy) and (ii) a bittern collected from Margi saltworks (located in Trapani, Italy). Synthetic sodium hydroxide (NaOH) solutions were employed as alkaline reagent. Tests were carried out using a continuous-flow stirred-tank laboratory reactor (CSTR). Mg(OH)₂ suspensions synthesized from desalination brines exhibited faster settling velocities, but lower filtration rates with respect to suspensions synthesized from saltworks bitterns. The purity of Mg(OH)2 solids produced from saltworks bittern was > 98.5%, whereas the purity of Mg(OH)2 solids synthesized from desalination brines was below 95%, due to calcium co-precipitation.

* 1. Introduction

The continuous world population growth has led to a high demand for raw materials, causing an overexploitation of land and water resources. This has prompted the search for novel and sustainable sources of raw materials, promoting the transition from the linear economy to a circular economy. In fact, the linear economy concept is based on the linear consumption of a product. Specifically, raw materials are typically used for the manufacture of new products that, at the end of their lifecycle, are discharged into the environment or in landfills. However, end-life products can be still valorised and reused. This is the case of saline solutions produced by the desalination industry, namely brines, or by the table salt production in saltworks, bitterns. Sodium, chlorine, magnesium, calcium, and sulphate ions are the most abundant species in brines. Among them, magnesium has been classified as a Critical Raw material (CRM) for its supply risk and importance for the social and economic development of the European Union (Battaglia et al., 2024). Mg2+ concentration in seawater is about ~1.3 g/L, it almost doubles in desalination brines, while it can be up to 40 times larger in saltworks bitterns. The valorisation of these waste solutions, often discharged back into the sea, represents an opportunity to produce magnesium hydroxide and other magnesium-based goods, reducing, at the same time, the environmental impact of desalination and saltworks processes. As an example, today 95.37 million m³/day of freshwater and 141.5 million m³/day of brine are worldwide produced by desalination plants (Jones et al., 2019). Such high brine volumes can significantly harm local marine ecosystems due to their high salinity content (Panagopoulos et al., 2019). Magnesium hydroxide is a chemical compound adopted in several industrial fields as a flame-retardant agent, an antibacterial agent, a neutralization reagent for the treatment of acidic liquid waste, an environmentally friendly material for heavy metal extraction from water. Mg(OH)2 suspensions/solids also serve as paper preservatives and precursors for magnesium oxide preparation (Balducci et al., 2017).Yousefi et al. (2024) used a natural brine, collected from a solar evaporation pond in Khur Potash Complex (Iran) to synthesize Mg(OH)2 nanostructures. Sun et al. (2024) studied a two-step method to completely extract magnesium from sea bitterns. Sodium hydroxide (NaOH) solids were added into the sea bittern to convert magnesium ions into magnesium hydroxide Mg(OH)2 intermediate. Mg(OH)2 solids were hydrothermally transformed to Mg(OH)2 hexagonal crystals suitable as flame retardant agent in epoxy resin (EP) compounds. Dong et al. studied the Mg(OH)2 precipitation process from reject brine of desalination plants using both NaOH (Dong et al., 2018) and ammonium hydroxide, NH4OH, (Dong et al., 2017) as alkaline reagents. Although several studies have investigated the precipitation of Mg(OH)2 compounds from brines and bitterns, in most of the cases, the literature lacks comparative studies under identical conditions. The present work aims at filling this gap by thoroughly assessing the features of Mg(OH)2 suspensions/solids synthesized from a reverse osmosis (RO) brine from the desalination plant located in the Lampedusa Island (Italy) and a waste bittern collected from the Margi saltworks (Trapani, Italy), under the same operating conditions. Activities were carried out within the Italian-funded CARMEn and the European-funded REWAISE projects. The CARMEn project focuses on developing an innovative circular strategy to recover critical raw materials and energy from spent seawater brines (*CARMEn Project*, 2023). The REWAISE project aims to create a new smart water ecosystem to embrace the true value of water, reducing freshwater and energy use, and demonstrating innovative recovery of raw materials and minerals from water desalination (*REWAISE Project*, 2020). The bittern solution was more concentrated in magnesium ions, while calcium ions were more concentrated in the brine one. Mg(OH)2 suspensions/solids were synthesized at two final pH values of 10.6 and 12.5. Settling and filtration rates, the recovery of magnesium ions and the purity of Mg(OH)₂ powders were analysed.

* 1. Material and methods

Magnesium hydroxide precipitation tests were carried out by using a laboratory continuous stirred tank reactor system (CSTR), as shown in Figure 1. A 1L plexiglass reactor was filled up to a volume of 750 mL to comply with the standard geometry configuration. The reactor had a diameter of 10 cm and a height of 15 cm. A six blade Rushton turbine of 5 cm diameter was used to ensure proper mixing. The stirring speed was 400 rpm (LLG LABWARE). Reagents were injected by two peristaltic pumps (Kronos, 50). The pH of magnesium hydroxide suspensions was monitored by a portable pH-meter (WTW, mod. 3320).

Immagine che contiene schermata, diagramma, testo, design

Il contenuto generato dall'IA potrebbe non essere corretto.

**a)**

**b)**

Figure 1: a) Schematic representation of the adopted experimental set-up; b) post-treatment procedure of produced Mg(OH)2 slurries (a volume of the slurry of 500 mL was used).

Two different saline solutions were investigated: (i) a RO brine from the desalination plant of Lampedusa Island (Italy) and (ii) a waste bittern from the Margi saltwork in the Trapani district (Italy). Mg2+ and Ca2+ concentrations in the solutions were measured by complexometric titration with ethylenediaminetetraacetic acid, see Table 1.

Synthetic sodium hydroxide solutions were prepared by dissolving NaOH pellets (Inovyn, purity grade >99%) in deionized water. The concentration of hydroxyl ions was measured by acid-base titration.

* + 1. Experimental tests and analytical procedures.

The features of Mg(OH)2 suspensions synthesized from the reverse osmosis (RO) brine and the waste bittern were investigated under the same operating conditions. Mg(OH)2 suspensions were produced at two final pH values of 10.6 and 12.5. Settling and filtration rates, recovery of magnesium ions and the purity of Mg(OH)₂ powders were analyzed. At a pH value of 10.6, magnesium ions are assumed to be quantitatively extracted (Vassallo et al., 2021), while, a pH value of 12.5 would ensure a complete reaction of all Mg2+, although the co-precipitation of Ca2+ is expected to take place. The concentration of the reagents and details of the operating conditions adopted in all tests are reported in Table 1.

* + 1. Experimental tests and analytical procedures.

The features of Mg(OH)2 suspensions synthesized from the reverse osmosis (RO) brine and the waste bittern were investigated under the same operating conditions. Mg(OH)2 suspensions were produced at two final pH values of 10.6 and 12.5. Settling and filtration rates, recovery of magnesium ions and the purity of Mg(OH)₂ powders were analyzed.

Table 1: Details of the operating conditions of performed experimental tests

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| TEST | Waste saline solution | Ca2+ [g/L] | Mg2+ [g/L] | OH- [g/L] | Brine flow rate [mL/min] | NaOH flow rate [mL/min] | Final pH |
| Case #1-a | brine | 0.72±0.01 | 2.07±0.01 | 6.8±0.1 | 40.0±0.5 | 40.0±0.5 | 10.6±0.1 |
| Case #1-b | bittern | 0.08±0.001 | 24.3±0.1 | 40.0±0.1 | 40.0±0.5 | 80±1 | 10.6±0.1 |
| Case #2-a | brine | 0.72±0.01 | 2.07±0.01 | 10.8±0.1 | 40.0±0.5 | 40±0.5 | 12.5±0.1 |
| Case #2-b | bittern | 0.08±0.001 | 24.3±0.1 | 40.0±0.1 | 40.0±0.5 | 104±2 | 12.5±0.1 |

The outlet Mg(OH)2 suspensions were collected in a 500 mL glass cylinder to evaluate their settling velocity within 24 hours. Then, the initial settling rate was estimated as the slope of data from the 2nd to 20th minutes in a height [mm] vs. time [h] plot. Clarified solutions were analysed to evaluate the magnesium and calcium recovery, calculated by Eq. (1):

|  |  |
| --- | --- |
|  | (1) |

where and are the molar concentration of Mg/Ca ions in the initial saline solution and in the clarified solution after thickening, respectively, Mg and Ca ions were measured by complexometric titration with ethylenediaminetetraacetic acid. DF is the dilution factor which considers the dilution phenomena in the reactor due to the mixing of brines and NaOH solutions, expressed by Eq. (2):

|  |  |
| --- | --- |
|  | (2) |

where and are the inlet flow rates of the brine and the NaOH solution in the reactor, respectively. After thickening, Mg(OH)2 suspensions were washed with deionized water until the conductivity of the clarified water was below 200 S/cm. 100 mL of washed suspension was filtered in a Büchner funnel with a 1.6 µm fiberglass filter (70 mm of diameter) at an absolute pressure of 0.5 bar using a vacuum pump (BUCHI VACUUM V700).The filtration rate was calculated following Eq (3):

|  |  |
| --- | --- |
|  | (3) |

where is the filtered volume of suspension [m3], is the magma density of the suspension [g/L], is the area of the filter [m2] and is the filtration time [h]. Cakes were dried at 120°C in an oven.

The purity of synthesized Mg(OH)2 powders was determined by dissolving ~150 mg of solids in 0.10 mol/L ultrapure hydrochloric acid (Honeywell-Fluka;>30% for trace analysis) and further diluted in a 1L of ultra-pure water. Liquids were analysed by Ion Chromatography technique (IC, Metrohm model 882 compact IC plus). Cationic purity was calculated as the ratio between the Mg2+ concentration and the sum of the concentration of all cations, , as followed by Eq. (4):

(4)

The purity of solids was also analyzed by Fourier-transform infrared spectroscopy (Shimazdu IRTracer-100).

* 1. Results and discussion
     1. Influence of the saline solution and of the final pH.

The influence of the (i) different concentration of magnesium and calcium ions, (ii) the nature of the saline solutions and (iii) the reaction pH was investigated. The recovery of calcium and magnesium ions, Eq.2, the initial magma density and filtration times are reported in Table 2.

T*able 2: A summary of Mg2+ recovery, Ca2+ recovery, Eq.2, initial magma densities and filtration times of all tests*

|  |  |  |  |
| --- | --- | --- | --- |
| TEST | Initial magma density [g/L] | Ca2+ recovery [%] | Mg2+ recovery [%] |
| Case #1-a | 2.5±0.1 | >13 | >97 |
| Case #2-a | 2.5±0.1 | ⁓100 | ⁓100 |
| Case #1-b | 19.4±0.2 | >23 | >97 |
| Case #2-b | 19.4±0.2 | >78.8 | ⁓100 |

At a pH of 10.6, the Mg2+ recovery was 97 % in Cases #1-a and b, regardless of the adopted saline solution. Ca2+ recovery was 23% and 13% in RO brine and bittern, most likely due to the formation of calcium carbonate compounds, whose precipitation occurs at a pH of 9 (Dong et al., 2018). Notably, due to the very low concentration of Ca2+ in the bittern, the amount of possible precipitated calcium carbonate compounds is expected to be negligible compared to that of Mg(OH)2 one. Calcium and magnesium recoveries were 100 % at pH values of 12.5, Cases #2-a and b, thanks to the excess of OH- ions that ensured the consumption of all metallic cations. Figure 3 reports the initial settling velocity and the filtration rate of synthesized Mg(OH)2 suspensions.

Figure 2: Settling velocity (a) and filtration rate (b) values of tests conducted at a pH value of 10.6 (Cases 1) and 12.5 (Cases 2), adopting RO brine, Cases #a, and saltworks bittern, Cases #b, solution

a)

At a pH value of 10.6, the initial settling velocity of suspensions synthesized in Case #1-a was 693 mm/h, while the initial settling velocity of the suspension produced in Case #1-b reached a value of 48 mm/h (14 times lower). On the other hand, the suspensions of Case #1-b showed a faster filtration rate, i.e. 30.3 kg/m2 h, with respect to that of Case #1-a (3.9 kg/m2·h). This was attributed to (i) the local supersaturation in the reaction environment and (ii) the concentration of particles in the suspension. In Case #1-b, the higher Mg2+ and OH- concentrations led to high local supersaturation levels that are expected to favor the nucleation of particles and their aggregation (strong bonds among primary particles). Bigger aggregates are characterized by faster settling and filtration characteristics, in accordance with the observed filtration rates. On the other hand, the higher magma density of suspensions in Case #1-b promotes electrostatic interactions between particles that enclose the surrounding mother liquor. The enclosed mother liquid decreases the specific density of the particles, hindering the settling process (Gregory, 1997). The increase of the final pH value of the suspensions from 10.6 to 12.5 caused a considerable reduction of the settling velocity and the filtration rates. Initial settling velocity values decreased from 693 mm/h and 48 mm/h to 24 mm/h and 8 mm/h, respectively, while filtration rates varied from 3.92 kg/m2h and 30.3 kg/m2 h to 0.2 kg/m2 h and 0.8 kg/m2 h, in Cases #a and #b, respectively. This behaviour was attributed to the higher local supersaturation level, promoting nucleation phenomena, caused by the use of more concentrated NaOH solutions, and the lyosorption phenomenon. The lyosorption phenomenon is favoured in high pH environments and promotes the formation of agglomerates made by small particles (Battaglia et al., 2023). Small particles tend to absorb the surrounding liquid phase (mother liquor), reducing their density; consequently, settling velocities and filtration rates decrease.

* + 1. Purity assessment by FT-IR and IC techniques.

Figure 3 shows FT-IR spectra of synthesized Mg(OH)2 powders.

C=O bonds

Figure 3: FT-IR spectra of Mg(OH)2 powders produced in tests conducted at a pH value of 10.6 (Cases 1) and 12.5 (Cases 2), adopting RO brine, Cases #a, and saltworks bittern, Cases #b, solutions

The analysis revealed that magnesium hydroxide is the predominant compound in all samples. Specifically, the peak at 3600 cm⁻¹ is attributed to the OH⁻ ions of Mg(OH)₂. The presence of calcium carbonate in the sample synthesized from RO brines was confirmed by the peaks at 1355 cm⁻¹, associated with the asymmetric stretching of C=O bonds, and at 806 cm⁻¹, corresponding to the bending mode of the CO₃²⁻ group (Samanta et al., 2016). In Case #2-a, due to the high value of pH, the amount of calcium is greater than Case #1-a, in accordance with Ca2+ recovery.

FT-IR data were confirmed by cationic purity analysis. Table 3 reports cation concentrations measured by IC in dissolved Mg(OH)2 powders, along with calculated cationic purity values, Eq. (4).

Table 3: *Cationic purity*, measured by IC, of *Mg(OH)2 solids precipitated from brine, Cases #a, and bittern, Cases #b, suspensions. LOQ states for Limit of Quantification*

|  |  |  |  |
| --- | --- | --- | --- |
| TEST | Ca2+  (mg/g, IC) | Mg2+  (mg/g, IC) | Mg2+ cationic purity [%] |
| Case #1-a | 10.8±0.5 | 276.9±1 | ⁓96 |
| Case #2-a | 28.7±0.5 | 368.4±2 | >93 |
| Case #1-b | LOQ | 397.7±1 | >98 |
| Case #2-b | LOQ | 400.6±2 | >100 |

In Cases #b, calcium concentration values were below their limit of quantification (LOQ) of 1.5 mg/g, whereas in Cases #a calcium concentrations were 10.7 mg/g and 28.7 mg/g at pH values of 10.6 and 12.5, respectively. Cationic purity was always higher than 98% in Cases #b, indicating the production of highly pure compounds from bittern. Overall, purity values agreed with data reported for Mg(OH)2 production from bitterns, i.e. purity >98 % (Battaglia et al., 2022), and reverse osmosis brines, purities between 90.6 and -95.4% Dong et al. (2018).

* 1. Conclusions

The recovery of Mg(OH)₂ solids from real Mg2+-rich solutions was investigated, focusing on a RO brine from the desalination plant located in Lampedusa (Italy) and a saltwork bittern collected from Margi pond, in Trapani (Italy). The aim of this work was to assess the initial settling velocity and the filtration rate of Mg(OH)2 suspensions, the Mg2+ recovery and the purity of Mg(OH)2 powders using different exhausted saline solutions under the same operating conditions. Mg(OH)2 suspension produced from the RO brine at pH of 10.6 exhibited a faster initial settling velocity (693 mm/h) with respect to suspensions synthesized from the bittern (48 mm/h, 14 times lower). Conversely, suspensions from bitterns had a higher filtration time, namely 30.3 kg/m2 h against 3.9 kg/m2·h. Initial settling velocities and filtration rates decreased of one order of magnitude at high pH values of 12.5. The presence of calcium in the RO brine affected the purity of particles. Cationic purity of Mg(OH)2 solids produced from the bittern was >99%, while the cationic purity of solids synthesized from the RO brine was in the range between 93 % and 96 %. The present study demonstrated the detrimental effect of operating at high pH levels that caused a decrease of the performance of settling velocities, filtration rates and cationic purity values. Moreover, the study clearly marks the high purity of Mg(OH)2 powders synthesized from bitterns.

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