|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. xxx, 2025*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: David Bogle, Flavio Manenti, Piero Salatino  Copyright © 2025, AIDIC Servizi S.r.l. **ISBN** 979-12-81206-21-2; **ISSN** 2283-9216 | |

A Novel Pilot-scale Crystallizer for the Production of Mg(OH)2 Powders from Saltworks Bitterns

Ferdinando Micilettaa, Giuseppe Battagliaa,\*, Giuseppe Scelfoa, Fabrizio Vassallob, Fabrizio Vicarib, Alessandro Tamburinia, Andrea Cipollinaa, Giorgio Micalea

a Dipartimento di Ingegneria, Università degli Studi di Palermo, Palermo, Viale delle Scienze ed 6, 90128, Italy

b ResourSEAs SrL, Via Notarbartolo n. 38, 90141 Palermo, Italy

giuseppe.battaglia03@unipa.it

Magnesium hydroxide suspensions and powders are widely used products in several industrial fields. Among the various synthetic methods, the reactive crystallization technique from saline solutions has low environmental impact, although difficulties are often encountered to obtain products with high technical specifications. In this study, Mg(OH)₂ suspensions and powders were synthesized using an innovative crystallizer called 2nd generation "Magnesium Crystals Granulometry Controlled Reactor". Two bitterns with a Mg2+ concentration of 2 M were used, a real one collected from the Trapani saltworks (Italy) and an artificial one. 0.5 M NaOH solutions were employed as the alkaline stream. The obtained solids were characterized by mass purities greater than 98%, with magnesium ions recoveries exceeding 99%. The produced suspensions exhibited excellent settling and filtration properties: in the best scenario, the initial settling velocity and the filtration rate were 433 mm/h and 58.8 kg/m²·h, respectively. Results mark the considerable potential of the innovative pilot-scale crystallizer in producing Mg(OH)₂ suspensions with excellent solid/liquid separation properties, as well as highly pure solids in line with market standards.

Introduction

In last decades, there has been a growing interest in extracting minerals from unconventional sources. Magnesium, one of the most widely adopted industrial metal, has been listed as a critical raw material by the European Union (Walter & Wajer, 2022). Magnesium is employed in numerous industrial applications as a metal or in the form of hydroxides, i.e. magnesium hydroxide (Mg(OH)2), oxides, namely magnesium oxide (MgO), or carbonates compounds. Mg(OH)2 powders have been gaining significant attention in the field of flame retardant fillers as an environmental friendly compound to replace toxic halogenated substances. Mg(OH)2 suspensions have been also tested as reliable means for acid wastewater treatment and for the absorption of heavy metals contained in wastewater (Jiang et al., 2019). Today, magnesium hydroxide is mainly produced through the calcination of carbonate-bearing magnesium minerals and their further hydration (Shand, 1980). This synthetic route, however, has several issues such as the uneven global distribution of magnesium carbonate ores, a significant energy demand and an high environmental impact. In this context, the possible supply of magnesium hydroxide suspensions/powders from unconventional sources has been investigated. In this context, the chemical precipitation process of Mg(OH)2 from saline solutions, such as seawater, lake brines, or waste brines from desalination plants, has been considered as a promising approach. Although, the precipitation of Mg(OH)2 compounds is a simple process, the technique presents several challenges: (i) if strong alkaline solutions are adopted, the reactive process is almost instantaneous hindering the control of local supersaturation and crystallization kinetics, (ii) the synthesized suspensions, in most of the cases, are characterized by scarce settling and filterability performances, and (iii) the presence of multiple ionic species in saline solutions can affect the purity of the targeted products. Dong et al. (2018) studied the recovery of Mg(OH)2 powders from reject brine produced by a desalination plant in Singapore. NaOH solutions were used as the alkaline agent. Mg(OH)2 powders had a purity of ~90%, not complying with commercial standards, due to the co-precipitation of Ca ions, contained in the brine. Lee & Lim (2007) investigated the synthesis of Mg(OH)2 suspensions from waste bittern discharged by salt purification plant employing NaOH solutions. Suspensions exhibited low settling characteristics reaching a thickening degree of only 25% after 40 minutes. The authors adopted a carboxy methyl cellulose solution, as an additive, to enhance the settling process of the suspensions leading to an increase of the sedimentation performance up to 3 times. On the other hand, the purity of the solids was ~92% due to the use of the additive, which was effectively removed only after six washing steps (purity of the powders of 98%). Turek’ & Gnot (1995) explored the precipitation process of Mg(OH)2 suspensions and powders from hard coal mine brines via NaOH solutions. The process achieved scarce settling and filtration rates of roughly 117 mm/h and 7 kg/m²·h, with a good final purity of ~98%.

In the last 10 years, there has been a growing focus in recovering magnesium hydroxide from saltworks bitterns. Bitterns are highly concentrated waste solutions by-product of the table salt production in saltworks. Mg2+ concentration in bitterns is considerably high, reaching values up to 50-60 g/L (about 35 times the Mg2+ concentration in seawater). Battaglia et al. (2022) produced Mg(OH)2 powdersfrom real saltworks bitterns by adopting a T-mixer device to ensure fast mixing of the reagents. The authors successfully synthesized Mg(OH)2 nanoparticles characterized by a purity always higher than 99 % and mass purity values ranging from 90 % and 95 %. The same research group, Romano et al. (2023), has studied a possible synthesis route for the production of well-grown Mg(OH)2 hexagonal platelets through precipitation for flame retardant applications. Several reactor configurations have been investigated on a laboratory scale. A synthetic MgCl2 solution characterized by a Mg2+ concentration of 0.5M, mimicking the composition of a diluted real bittern, was let to react with a 1.0 M NaOH solution. The use of a double feed semi-batch system, operated at low inlet flow rates of the reagents, favored the growth of the Mg(OH)2 crystals. Battaglia et al. (2023) developed a pilot scale crystallizer to treat saltworks bitterns as Mg2+ source and using NaOH as the alkaline reactant. The authors demonstrated the possibility of recovering all the Mg2+ contained in the bittern and producing high-purity Mg(OH)2 solids (purity >99%). However, synthesized suspensions exhibited very low settling times (order of tens of hours) and filtration performance not adequate for industrial production. The authors attributed the scarce performance of the synthesized suspensions to a low control of the supersaturation level in the reaction environment.

In the present work, the performance of a novel pilot-scale crystallizer, the 2nd generation “*Magnesium Crystals Granulometry Controlled Reactor*", Mg-CGCR, was addressed for the industrial production of Mg(OH)2 suspensions/solids from real saltworks for the first time. The crystallizer was purposely designed, constructed and tested by ResourSEAs SrL and the University of Palermo within the activities of the European-granted Horizon Europe SEArcularMINE project. The prototype is also currently adopted in the MareMag LIFE European project to produce magnesium minerals through a sustainable, replicable and renewable-energy-based process.

The performances of the novel pilot-scale crystallizer were evaluated in terms of (i) settling and filtration rates of the synthesized suspensions, (ii) the magnesium recovery and (iii) the purity of the powders. The investigated parameters were (i) the nature of the bittern (either real or artificial), (ii) the final pH value of synthesized suspensions and (iii) the fluid dynamics in the reaction environment.

**2 Materials and Methods**

Mg(OH)2 suspensions and solids were produced through the reaction between Mg2+ ions, contained in bitterns, and OH- ions provided by a sodium hydroxide aqueous solution (NaOH):

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

The 2nd generation Mg-CGCR prototype is a tubular reactor made of two co-axial tubes. Reagents are injected into the annular region through nozzles along the reactor length. The system adopts an innovative dilution strategy to control the supersaturation levels. This includes a pre-dilution step of the reagents by mixing them with recirculated produced suspension, a proprietary injection system of the reactants and a recirculation strategy of the suspension within the reaction environment (the annular region) to manage suitably the supersaturation. A schematic representation of the recirculation strategy is shown in Figure 1.

Immagine che contiene testo, diagramma, linea, Carattere

Il contenuto generato dall'IA potrebbe non essere corretto.

Figure 1: Schematic representation of the recirculation strategy adopted in the crystallizer

In the experimental campaign, artificial and real bitterns were employed. Real solutions were collected from Margi saltworks (Trapani, Italy), while the artificial ones were prepared by dissolving hexahydrate magnesium chloride solids (Chem-Lab, Belgium technical grade) in softened tap water. In both cases, the Mg2+ concentration was ~50 g/L (~2M). NaOH solutions 0.5 M, synthesized in situ by an Electrodialysis with Bipolar Membrane unit, were adopted in all cases. Mg2+ and OH- concentrations were measured by titration through Ethylenediaminetetraacetic acid (EDTA) and 0.1 M standard hydrochloric acid, respectively.

**2.1 Experimental tests**

Five tests were conducted to evaluate: (i) the influence of the use of artificial and real bitterns (tests 1 and 3), (ii) the effect of the value of the pH of synthesized suspensions , namely 10.0, 10.8 and 12.0 (tests 2, 3, and 4), and (iii) the influence of the recirculation flow rate of the suspension in the reaction system, i.e. 130 and 60 L/min (tests 4 and 5). The brine flow rate was selected to comply with the Mg(OH)2 target production rate of the SEArculrMINE project. The NaOH flow rate was then adjusted to (i) ensure a stochiometric amount of hydroxyl ion, leading to a pH of 10.8, and (ii) an 15% excess, reaching a pH value of 12. Higher NaOH flow rates were not investigated since they would lead to expensive operating conditions. The performance parameters were (i) the settling and filtration rates of Mg(OH)2 suspensions, (ii) the mass purity of the powders, and (iii) the Mg2+ recovery. In the outlet stream of the reactor, the pH of the suspensions was monitored with an in-line pH meter (KROHNE PH 8320), while flow rates were evaluated by magnetic flowmeters (KROHNE 4100 C and 4300 C). Table 1 reports the operating conditions of performed tests.

Table 1: Operating conditions adopted in the experimental campaign. The Mg2+ concentration in real and artificial saline solutions was always ~2 M. In all tests, a 0.5M NaOH solution was adopted

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Test | Mg2+ solution | Mg2+ solution flow rate [L/min] | OH- solution flow rate [L/min] | Recirculation flow rate [L/min] | pH of suspension |
| 1 | Real bittern | 0.33±3% | 2.80±3% | 130 | 10.8±2% |
| 2 | Artificial solution | 0.33±3% | 2.64±3% | 130 | 10.0±2% |
| 3 | Artificial solution | 0.33±3% | 2.80±3% | 130 | 10.8±2% |
| 4 | Artificial solution | 0.33±3% | 3.06±3% | 130 | 12.0±2% |
| 5 | Artificial solution | 0.33±3% | 3.06±3% | 60 | 12.0±2% |

**2.2 Analytical procedures**

In each test, a 500 mL glass cylinder was filled with the Mg(OH)2 suspension exiting the crystallizer. Sampling was performed after 30 minutes (4-5 times the residence time) since the beginning of the test to guarantee the system stability. The settling velocity was recorded for 24 h, then the initial settling rate was determined as the slope of data from the 2nd to 20th minute in a height [mm] vs time [h] plot. The residual magnesium content in the clarified solution was assessed through complexometric titration with Ethylenediaminetetraacetic acid (EDTA) and the magnesium recovery, , was calculated as follows in Eq (2):

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

where and are the molar concentration of Mg2+ ions in the bittern and in the clarified solution after thickening, respectively. The dilution factor (DF) has been calculate to express the extent of the mixing of inlet and outlet streams in the mass balance concerning Mg2+ ions. DF is expressed as follows in Eq (3):

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

where and are the bittern and alkaline solution flow rates, respectively.

After 24 h, the suspension was washed several times using deionized water, until the electrical conductivity of the clarified solution was below 200 µS/cm. 100 mL of the washed and concentrated suspension, namely the thickened suspension, were filtered in a Buchner funnel, adopting a 1.6 µm fiberglass filter (Whatman GF/A grade, GE Healthcare Life Sciences) of 70 mm diameter at an absolute pressure of 0.5 bar, using a vacuum pump (BUCHI, VACUUM V700). The filtration rate per unit of time and area was expressed as:

|  |  |
| --- | --- |
|  | (4) |

where is the filtered volume of suspension [m3], is the magma density of the suspension [kg/ m3], is the area of the filter [m2] and is the filtration time [h]. Then, the filtered cake was dried in an oven at 120 °C for 24h. Powders were analyzed via thermogravimetric analysis, TGA (STA 449 F1 Jupiter analyzer, NETZSCH), to assess the mass purity. TGA analyses were performed with a heating rate of 10 °C/min, in the temperature interval ranging 30 - 900 °C, under a steady nitrogen flow of 20 mL/min. The mass purity was determined as:

|  |  |
| --- | --- |
|  | (5) |

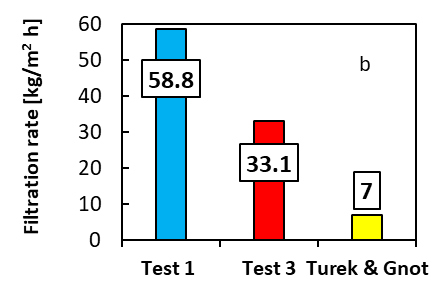
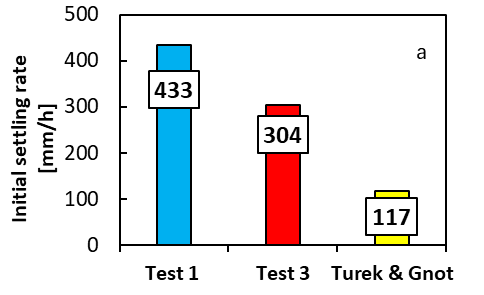
where is the mass loss from 320 °C to 480 °C (decomposition to oxide) and is the theoretical mass loss of pure Mg(OH)2 solids, namely 30.85 %.

**3 Results and Discussion**

In this section, the initial settling rate, the filtration rate, the mass purity, and the Mg2+ recovery obtained in each test will be presented.

**3.1 Influence of the type of bittern solution**

The influence of the type of magnesium solution was evaluated by using, under the same operating conditions, a real bittern (test 1) and an artificial solution containing only Mg2+ and Cl- ions (test 3), see Table 1. Figure 2 shows the calculated initial settling and filtration rates for tests 1 and 3. For the sake of comparison, data from Turek & Gnot (1995) are also reported.



*Figure 2:* Initial settling rate (a) and filtration rate (b) values obtained in test 1, test 3. For the sake of comparison, data from Turek & Gnot (1995) are also reported

Mg(OH)2 suspension synthesized in test 1 exhibited an initial settling rate of 433 mm/h, while the suspension obtained in test 3 reached a value of 304 mm/h, which was about 40% lower than that achieved in test 1. A similar trend was observed for filtration rate values that were 58.8 kg/m²h and 33.1 kg/m²h in tests 1 and 2, respectively. Using the best data from Turek & Gnot (1995) as a benchmark, the settling rates and the filtration rates were 3.7 and 2.7, and 8.4 and 4.7 times higher those of Turek & Gnot (1995), respectively. Note that, for the best of author’s knowledge, there are no comparisons between settling and filtration data for Mg(OH)2 particles synthesized from real and synthetic solutions. However, an explanation of the reported here results can be associated to the higher ionic strength of the real bittern. According to the DLVO theory (Agmo Hernández, 2023), a high ionic strength causes a reduction of the thickness of the electric double layer around a particle in a liquid. This phenomenon decreases the repulsion action between particles thus favoring the establishment of strong bonds among them leading to big aggregates with faster settling and filtration characteristics, as also reported in nanoparticles systems by Dai et al. (2022).The initial magma density, final settled volume and the final magma density of the suspensions, the Mg2+ recovery and the mass purity of the produced solids are reported in Table 2.

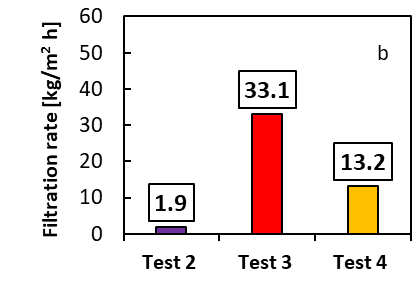
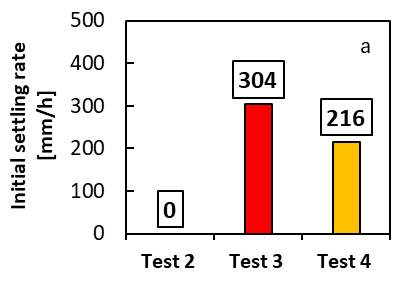
Table 2: Initial magma density, final volume of thickened suspension, final magma density, Mg2+ recovery (Eq.2) and mass purity (Eq.5) values for tests 1 and 3. The initial volume of suspension in the cylinder was 500 mL.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Test | Initial magma density [g/L] | Final settled volume [mL] | Final magma density [g/L] | Mg2+ recovery [%] | Mass purity [%] |
| 1 | 11.7 | 105 | 55.7 | 98.7 | 98.65 |
| 3 | 11.7 | 125 | 46.7 | 98.5 | >99 |

The highest final magma density value of 55.7 g/L was observed in test 1. Recovery was > 98.5% in both tests. Mass purity was high in both cases. The high purity from real solutions is a fundamental parameter for the commercialization of the Mg(OH)2 solids, moreover, the high purity of powders synthesized from artificial solutions marked the efficiency of the washing step to remove impurity of the by-product, i.e. NaCl.

**3.2 Influence of the pH of synthesized Mg(OH)2 suspensions**

The influence of the pH value of the final Mg(OH)2 suspensions was studied by producing three suspensions at different pH values, namely 10.0, 10.8 and 12.0, see Table 1. In all tests, the artificial solution was used. Figure *3* shows the initial settling and filtration rates values measured in tests 2, 3, and 4.



*Figure 3: Initial settling rate (a) and filtration rate (b) values for tests 2 (pH 10.0), 3 (pH 10.8) and 4 (pH 12.0)*

Increasing the pH value from 10.0 to 10.8, the initial settling rate increased from 0 to 304 mm/h, while a further increase of the pH to a value of 12 caused a reduction down to 216 mm/h. A similar trend was observed for the filtration rate. Filtration rate increased from a value of 1.9 kg/m2/h up to 33.1 kg/m2h to further decrease to 13.2 kg/m2h. This behavior can be related to the isoelectric point of Mg(OH)2 suspensions, which is between 11.6 and 12 (Lin & Wang, 2009.)*,*the local supersaturation and the pH of the reaction environment. At a pH of 10, Mg(OH)2 particles reject each other preventing aggregation, thus hindering the settling and filtration processes. Conversely, at pH 12, the system is close to its isoelectric point, however, the excess of OH⁻ ions causes a high local supersaturation level leading to the precipitation of tiny particles. These particles form large agglomerates entrapping mother liquor, namely the lyosorption phenomenon. Lyosorption phenomenon is favored at high pH value leading to lyosphere that are characterized by scarce filtration and settling characteristics. Therefore, the best conditions were observed at the intermediate case at pH 10.8. Table 3 reports the initial and final magma density values, the final settled volume, the recovery of Mg2+ ions in the inlet solution and the mass purity of the solids.

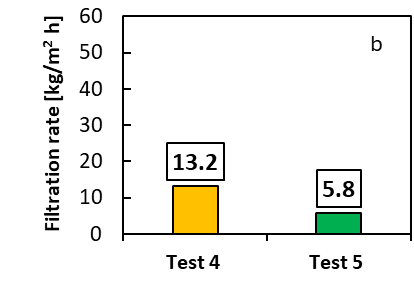
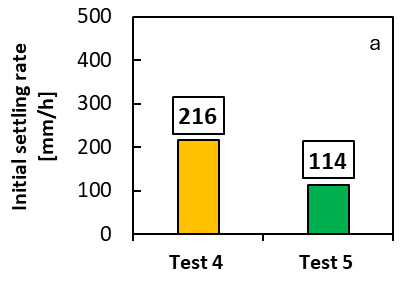
*Table 3: Initial magma density, final volume in the cylinder, final magma density,* Mg2+ recovery (Eq.2) *and mass purity (*Eq.5*) for tests 2 (pH=10.0), 3 (pH=10.8) and 4 (pH=12.0).* The initial volume of suspension in the cylinder was 500 mL

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Test | Initial magma density [g/L] | Final volume of thickened suspension [mL] | Final magma density [g/L] | Recovery [%] | Mass purity [%] |
| 2 | 9.8 | 275 | 17.8 | 77.0 | >99 |
| 3 | 11.7 | 125 | 46.7 | 98.5 | >99 |
| 4 | 11.1 | 45 | 123.3 | 99.7 | / |

The final magma density increased by increasing the pH of the suspensions probably due to easier particle packing, with measured values of 17.8, 46.7, and 123.3 g/L at pH 10, 10.8, and 12, respectively. Recovery was 77.0% at pH of 10, 98.5% at pH of 10.8 and >99 at the pH value of 12. The mass purity was always 99%, regardless of the operating conditions.

**3.3 Influence of recirculation flow rate**

The effect of the fluid dynamics in the reactor volume was investigated by producing two Mg(OH)2 suspensions (pH 12.0) at different recirculation flow rates, , of 130 L/min and 60 L/min. Figure 4 shows the initial settling rate and filtration rate values for tests 4 (130 L/min) and 5 (60 L/min).



*Figure 4: Initial settling rate (a) and filtration rate (b) for tests 4 (=130 L/min) and 5 (=60 L/min)*

In test 4, the Mg(OH)₂ suspension exhibited an initial settling rate of 216 mm/h, whereas in test 5, the initial settling rate decreased to 114 mm/h (a reduction of ~47 %). A similar behavior was observed for the filtration rate, showing a reduction from 13.2 kg/m²/h, in test 4, to 5.8 kg/m²/h, in test 5 (a decrease of 56%).

A possible explanation of the observed behavior can lie on (i) the intensity of the flow rate in the reaction volume, and (ii) the probability of collision of particles in the reaction environment. Specifically, the higher the fluid flow intensity and the collision probability (both promoted by the higher flow rate of the recirculating product), the higher the aggregation phenomena among particles, thus leading to big aggregates with faster settling and filtration properties, as observed in test 4 compared to test 5. Likewise, the final magma density of the suspension in test 5 decreased to 77.4 g/L. Also in this case, the purity of the powders was > 99%.

Conclusions

In this work, the performance of a novel pilot scale crystallizer for magnesium hydroxide production from saltworks bittern, the 2nd generation Mg-CGCR, was evaluated. The effect of reaction pH, the recirculation flow rate and the nature of the bittern was assessed on settling, filtration, recovery, and purity of the Mg(OH)2 suspension and dry solids produced. Using real bittern resulted in faster settling and filtration rates i.e. 433 mm/h and 58.8 kg/m²/h, with respect to that observed by adopting an artificial MgCl2 solution, which resulted in 304 mm/h and 33.1 kg/m²/h, at a fixed pH of 10.8. This was attributed to the higher ionic strength of the real bitterns. Settling and filtration rates of suspensions produced at pH values from 10 to 12 exhibited a settling and filtration rates values of 304 mm/h and 33.1 kg/m²/h at pH of 10.8, probably due to the zeta potential of the Mg(OH)2 particles. A reduction of the recirculation flow rate from 130 L/min to 60 L/min, at a pH of 12, caused a decrease of the settling and filtration rates from 216 mm/h and 13.2 kg/m²h to 114 mm/h and 5.8 kg/m²h, respectively. This was ascribed to the lower turbulence in the reaction environment. Mg2+ recovery was always greater than 98% for pH values higher than 10.8 and mass purity of solids were always ~99%, regardless of the saline solution.

Results demonstrated the high performance of Mg(OH)2 suspensions and solids synthesized by adopting the novel 2nd generation Mg-CGCR prototype showing settling and filtration features significantly higher of those reported in the literature so far.

Acknowledgments

This project has received funding from the European Union’s LIFE 2021-2027 programme under Grant Agreement 101147407 - LIFE23-ENV-IT-MAREMAG LIFE. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor CINEA can be held responsible for them.

References

Agmo Hernández, V. (2023). An overview of surface forces and the DLVO theory. *ChemTexts*, *9*(4).

Battaglia, G., Domina, M. A., Romano, S., Tamburini, A., Cipollina, A., & Micale, G. (2022). Magnesium Hydroxide Nanoparticles Production from Natural Bitterns. *Chemical Engineering Transactions*, *96*, 43–48.

Battaglia, G., Ventimiglia, L., Viggiano, F. P. M., Vassallo, F., Cipollina, A., Tamburini, A., & Micale, G. (2023). Mg(OH)2 Recovery from Real Bitterns: a Proof of Concept at Pilot Scale. *Chemical Engineering Transactions*, *105*, 1–6.

Dai, H., Han, T., Cui, J., Li, X., Abbasi, H. N., Wang, X., Guo, Z., & Chen, Y. (2022). Stability, aggregation, and sedimentation behaviors of typical nano metal oxide particles in aqueous environment. *Journal of Environmental Management*, *316*.

Dong, H., Unluer, C., Yang, E. H., & Al-Tabbaa, A. (2018). Recovery of reactive MgO from reject brine via the addition of NaOH. *Desalination*, *429*, 88–95.

Jiang, D., Yang, Y., Huang, C., Huang, M., Chen, J., Rao, T., & Ran, X. (2019). Removal of the heavy metal ion nickel (II) via an adsorption method using flower globular magnesium hydroxide. *Journal of Hazardous Materials*, *373*, 131–140.

Lee, S. W., & Lim, J. H. (2007). Recovery of Magnesium Oxide and Magnesium Hydroxide from the Waste Bittren. *Advanced Materials Research*, *26–28*, 1019–1022.

Lin, J. X., & Wang, L. (2009). *Adsorption of dyes using magnesium hydroxide-modified diatomite*.

Shand, M. A. (1980). *THE CHEMISTRY AND TECHNOLOGY OF MAGNESIA*.

Turek’, M., & Gnot, W. (1995). Precipitation of Magnesium Hydroxide from Brine. In *Ind. Eng. Chem. Res* (Vol. 34).

Walter, M. D., & Wajer, M. T. (2022). *Overview of Flame Retardants Including Magnesium Hydroxide*.