Magnesium oxide (MgO or periclase) is among the most important industrial magnesium compounds. Approximately 20% of the world’s production comes from seawater, brines and desalination of reject brine [1]. Magnesium oxide is used as an exceptionally important material in catalysis [2,3], toxic waste remediation [4], or as additives in refractory products, paint, manufacture of fertilizers, animal foodstuff, building materials (Sorel cement, lightweight building panels) and superconductor products [5-7]. A panel of fundamental and applied studies exists in literature reviews [7-11]. It particularly shows that magnesium hydroxide production from seawater or brines is precipitated by the addition of a strong base (e.g. ammonia). Later on, separation is calcined to produce MgO. It is important to note that magnesia qualities may differ depending on the physico-chemical conditions of preparation and on the compound type, which is why two compounds were selected to be tested: magnesium chloride and magnesium sulphate. The respective final products are compared on the basis of their X-ray diffractograms, specific surface area and microstructural differences.

To accomplish this task, we first performed a DTA/DTG decomposition study of Mg(OH)\textsubscript{2} (brucite). After that, XRD results were used to study the impact of calcination temperature, the impact of calcination time and finally the impact of Mg(OH)\textsubscript{2} reaction temperature. Additionally, X-ray diffractograms were used to calculate MgO crystallite size depending on some physical parameters such as calcinations temperatures.
and reaction times. At a later stage, the specific surface area was determined in order to confirm the particles’ crystallite size variations. Finally, MgSO₄·7H₂O was selected as the compound used for MgO preparation.

EXPERIMENTAL

Methodology

The industrial exploitation of the abundant natural brines in the Sebkhas and Chotts of the Tunisian South is conditioned by the development of specific processes, the technique and economic viabilities of which have to be demonstrated beforehand. For this purpose, we agreed to study this kind of saline solutions previously studied by many authors [12,13], assimilated to a quinary system represented by Na⁺, K⁺, Mg²⁺/Cl⁻, SO₄²⁻/H₂O.

Natural Brine is a highly concentrated complex aqueous solution. In the case of the brine called Sebkha El Melah, magnesium, chloride and sulphate ions seem to be sufficiently high to recover magnesium salts like epsomite (MgSO₄·7H₂O) and bischofite (MgCl₂·6H₂O) useful in a wide range of applications (such as fertilizers, Sorel cement, and refractory compounds).

Epsomite is obtained by polythermal crystallization conducted in two steps. The first one is completed at 35 °C, temperature during which the brine is evaporated to reach a density of 1.29 g.cm⁻³ and the maximum concentrations of magnesium and sulphate ions. The second step consists in cooling the above-mentioned pretreated solution at 0 °C in order to crystallize MgSO₄·7H₂O.

Purification of the product, realized by washing it with a saturated solution of Epsom salts, provides epsomite of 99% purity [14].

For bischofite synthesis, the concluded process is mainly composed of six stages based on two main unit operations, firstly isothermal evaporation and crystallization and then chemical precipitation.

The resulting brine, composed mainly of magnesium chloride, is concentrated by isothermal evaporation at 35 °C to precipitate magnesium chloride. The recovered product, collected from the final stage, is mainly composed of bischofite the purity of which exceeds 90% [15].

MgO powders preparation is done in two steps starting from two different precursors: bischofite (MgCl₂·6H₂O) and epsomite (MgSO₄·7H₂O) successfully produced from Tunisian natural brines.

At first, each reactant was dissolved in deionized water at room temperature to produce a 0.8 M Mg²⁺ solution. After that, an excess of ammonium hydroxide was added and vigorously stirred at 50 °C with pH 10. A white precipitate of Mg(OH)₂ was obtained which was thoroughly washed with distilled water and dried at 100 °C during 2 h. At this stage, the following reaction takes place:

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2
\]

In the second step, magnesium hydroxide powders were calcined to produce MgO. The heating treatment was carried out in an electric furnace by raising the temperature 10 °C/min. Therefore, the following thermal reaction takes place:

\[
\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}
\]

Materials

An X-Ray diffractometer with a Philips PW 3040 generator, goniometer PW 3050/60 2θ/2θ and a cathode of copper PW 3373/00 was used to distinguish MgO from two different precursors. Microstructural differences between MgO agglomerates were examined using SEM FEI Quanta 200. The decomposition of precipitated Mg(OH)₂ was analysed by DTA/TGA (DSC) Setaram Setsys Evolution. The specific surface area was determined by a Quantachrome Autosorb-1 apparatus.

RESULTS AND DISCUSSION

Starting from the two compounds prepared from the natural brine Sebkha El Melah as described above (MgCl₂·6H₂O and MgSO₄·7H₂O), the two successive steps of brucite and magnesia preparation were performed as previously indicated. The thermogravimetric decomposition (DTA/DTG) of Mg(OH)₂ was studied. The recovered products were characterized by XRD and SEM.

Mg(OH)₂ characterization

Mg(OH)₂ decomposition (DTA/DTG) study

The start of Mg(OH)₂ decomposition was studied using DTA/DTG experiments. Mg(OH)₂ experimental diagrams related to the compounds magnesium chloride and magnesium sulphate are respectively presented in Figures 1a and 1b. It becomes possible to compare the mass losses of the two obtained powders to the theoretical ones from these two diagrams.

The two DTA-DTG analyses show two endothermic peaks respectively related to dehydration process and to magnesium hydroxide decomposition. The second phenomenon occurs at 362 and 385 °C, respectively, for the compounds magnesium chloride and magnesium sulphate. However, in terms of bru-
Figure 1. DTA/DTG of Mg(OH)$_2$ obtained from two different precursors: a) MgO from chloride and b) MgO from sulphate.
cite (Mg(OH)₂) theoretical decomposition, 30.864% mass loss should be achieved, which is slightly larger than the observed one 29.883 and 23.022%, respectively. This is due to the incompleteness of the decomposition reaction within this temperature range. These results are in good agreement with others presented elsewhere [16-18].

As a preliminary conclusion, it comes into view that Mg(OH)₂ prepared from the two studied compounds is of good chemical purity, but its morphology varies from one compound to another. Furthermore, the starting decomposition temperature differs depending on the compound's nature. In order to clarify the compound's impact on the final product, we studied MgO prepared under different physical conditions.

Mg(OH)₂ X ray diffraction description

Magnesium hydroxide prepared from the two above-mentioned compounds was characterized by X-rays, it was found that the produced compounds correspond to Mg(OH)₂ regardless of the considered compound. Figure 2 shows a marked diffractogram of the compound obtained from MgSO₄·7H₂O; an identical one is produced when MgCl₂ is used as the precursor.

Mg(OH)₂ SEM description

The morphology of Mg(OH)₂ from different precursors is explored by SEM analysis. Brucite was dried accordingly at 100 °C and observed after cooling. Microstructural differences were detected for the two compounds (Figure 3). This observation indicates that magnesium oxide products may present different physical properties related to the compound.

Magnesium hydroxide derived from magnesium sulphate shows a plate-like shape, the particles were joined to each other forming spherical particles around 15 µm, which tend to form large agglomerates (30 µm).

MgO characterization

MgO X-ray diffraction study

X-ray diffraction allows, in the first step, a qualitative comparison of the crystallinity of the obtained materials; such a parameter is related to the peaks' intensity and their affinities. In the second step, the diffractograms are used to calculate the average crystallite size of the prepared MgO in a more quantitative term. Regarding these two parameters, the following effects were investigated: calcination temperature, calcination time and reaction temperature.

Calcination temperature effect. As previously concluded, Mg(OH)₂ decomposition starts at the range varying from 362 to 385 °C, thus a calcination temperature ranging from 500 to 1000 °C for a duration of 2 h was operated in order to study the effect of such a factor on the different obtained products from the two studied compounds. Figures 4a and 4b illustrate
X-ray diffractograms for the precursors magnesium chloride and magnesium sulphate, respectively. Figure 5 shows that all samples were magnesium oxide formed with CFC structure (NaCl type). The best crystallinity corresponds to the calcination temperature of 1000 °C with regard to the two compounds. Nevertheless, it is important to note that MgO, obtained from MgSO₄·7H₂O, shows the highest...
intensity and the sharpest peak at the same temperature. In addition, unlike the MgCl₂ compound, MgSO₄·7H₂O shows a gradual increase of intensity parallel to that of temperature. These remarks clearly indicate the influence of the compound on the properties of the final product (MgO).

**Calcination time effect.** MgO calcination time is studied in the range from 2 to 48 h. Figure 5 illustrates XR diffractogramms for MgO obtained from magnesium sulphate at 1000 °C (a similar result is concluded for the other compound). Therefore, increasing the calcination time improves the crystallinity. As a result, 48 h of calcination time gave the best results. CFC magnesium oxide was always obtained.

**Reaction temperature effect.** Mg(OH)₂ reaction temperature parameter was studied in the range 25-75 °C. Figure 6 illustrates only XRD results for MgO obtained from the compound magnesium sulphate at 1000 °C and with 48 h of calcination time. The variations of the peak intensities, which play the function of temperature, are irregular. However, in terms of crystallinity, the below diffractograms enable us to deduce that 40 °C is the best reaction temperature for the two compounds.

**Average crystallite size.** The above diffractograms were handled to determine the average crystallite size, L, of the prepared powders. For this purpose, we applied the Scherrer formula:

\[
L = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where: \(\lambda\) is the wavelength of the X-ray, \(\theta\) is the diffraction angle associated with a Bragg peak, \(\beta = (\beta_m\alpha - \beta_m^2)^{\frac{1}{2}}\) is the corrected full width at half maxi-

![Figure 5. Diffractogram showing the calcination time on MgO obtained from magnesium sulphate precursor.](image)

![Figure 6. MgO obtained from magnesium sulphate diffractograms vs reaction temperature.](image)
mum (FWHM), $\beta_m$ being the FWHM of the well defined (200) Bragg peak and $\beta_s$ being that of a standard crystallized sample of MgO (across sample).

Considering the two tested reactants, the crystallite sizes with calcination temperature, calcination time and reaction temperatures are shown respectively in Figures 7-9.

Figure 7 shows that for the two precursors, the crystallite size increased in accordance with the increase of calcination temperature. Crystallite sizes were within the ranges: (64.7 to 115.4 nm) and (18.1 to 86.3 nm) for magnesium chloride and magnesium sulphate, respectively. Therefore, the MgO obtained from magnesium sulphate had the smallest particle size. This result enhances the relation between the full width at half maximum of Bragg peaks and crystallite size. In fact, the FWHM is the result of the convolution of an instrumental contribution and a size effect.

For the compound magnesium sulphate, the crystallite size increased with calcination time (Figure 8). For the other one (magnesium chloride), the evolution of crystallite was irregular. The final sizes were lower than those obtained from magnesium sulphate after 48 h of calcination time. The calcination time effect on crystallite size seems to be more important than the temperature effect (150 nm in 48 h and 80 nm at 1000 °C).

Figure 9 shows that MgO produced from magnesium chloride has an irregular evolution of crystallite sizes. It is therefore difficult to confirm the previous conclusion, but for energy considerations 40 °C was retained as the reaction temperature.

**BET Specific surface.** In order to confirm the above results, the specific surface areas by BET for MgO powders burnt-off at 1000 °C during 24 h were set up. The obtained results were 9.31 and 16.87 m²g⁻¹ for magnesium chloride and magnesium sulphate, respectively. These results confirm that the sample obtained from the magnesium sulphate has the highest specific surface area which is in concordance with the data [19-22] indicating that small particles have the highest surface areas.

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**Figure 7. Development of crystallite size with temperature on the crystallisation of MgO.**

**Figure 8. Development of crystallite size with calcination time on the crystallisation of MgO.**
The morphology of MgO powders obtained from different compounds is explored by SEM analysis. Periclase powders (MgO) obtained at 1000 °C during 48 h from the two compounds after cooling and SEM examination show the presence of fine particles, less than 1 µm, forming agglomerates (less than 5 µm) with homogeneous distribution (Figure 10).

At 1000 °C, a well-defined plate-like morphology was observed which can be related to periclase phase, a similar morphology has been reported elsewhere [23].

CONCLUSION

The results of this study demonstrate that the MgO obtained from the two compounds has different physical properties such as the crystallite size, shape, and structure. A set of parameters like calcination temperature, calcination time and temperature of brucite precipitation has to be controlled to produce a high quality product.

Intermediate and final products were characterized by X-ray diffraction, DTA/DTG analysis, BET and SEM.

This study shows that 40 °C is an appropriate temperature to obtain Mg(OH)₂ from the compounds used in the experiments.

The calcination temperature for MgO production with high crystallinity is set to be within the range 800-1000 °C. Within this interval, the maximum brucite decomposition into periclase is achieved. Calcination time of 48 h confirm this result with a very pure product. Finally, magnesium oxide obtained from magnesium sulphate is the best approach to obtain the ideal product, due to its higher surface area, and eventually, to its smallest primary particle size at the limits of calcination temperature. Besides, the specific area value can be related to the microstructure of the sections disposed around a central nucleus. According to these results, we select magnesium sulphate as the precursor to obtain magnesium oxide.

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MAGNEZIJUMOVE SOLI KAO JEDINJENJA ZA DOBIJANJE MAGNEZIJUM OKSIDA IZ TUNIŠKIH PRIRODNIH SLANIH VODA


Ključne reči: kristalnost; veličina kristala; Mg(OH)₂; MgO; specifična površina.