

Chemical processing of dolomite associated with the phosphorites for production of magnesium sulfate heptahydrate

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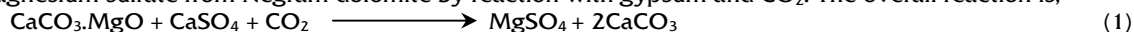
ABSTRACT

Egyptian dolomite ($\text{CaMg}(\text{CO}_3)_2$) associated with Abu-Tartur phosphorites, New Valley was leached with sulfuric acid to produce magnesium sulfate heptahydrate and calcium sulfate dihydrate (gypsum). Magnesium sulfate heptahydrate containing 16.23% MgO was obtained at the following optimum conditions The particle size was 100% - 150 μm , temperature of the reaction was 60°C, time of reaction 50.0 minute, solid/liquid ratio 1:4g/ml and mole ratios of sulfuric acid to calcium oxide and magnesium oxide was 1.0 and pH 8.5 for removal of precipitated iron, manganese, aluminum. The magnesium sulfate was separated from calcium sulfate dihydrate by filtration. The factors affecting on the filtration rate was studied and the filtered magnesium sulfate was concentrated at density from 1.35-1.45g/ml at temperature 103-110°C and then crystallized as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by cooling at room temperature. The purity of the produced magnesium sulfate heptahydrate was 99.2%. © 2005 SDU. All rights reserved.

Keywords: Magnesium sulfate heptahydrate; Dolomite; Leaching

1. INTRODUCTION

Magnesium sulfate heptahydrate as a source of magnesium has a wide application in medical, textile, tanning and agricultural industry (fertilizers). It forms a raw material for manufacturing various chemicals containing magnesium. These materials, when doped with selected activators yield efficient luminescent properties. The crystallization of magnesium sulfate heptahydrate is influenced by supersaturation, temperature, pH of the solution, cooling rate, agitation, viscosity, initial state of the seed crystals, and the presence of impurities (Ramalingom *et al.*, 2001). Magnesium sulfate heptahydrate exists in a stable rhombic and in an unstable monoclinic form. The rhombic form is the stable phase in aqueous solutions at normal temperatures. The unstable monoclinic form crystallizes below 21°C under certain conditions (Kirk Othmer, 1969). Many processes was adapted to preparation of magnesium sulfate heptahydrate from dolomite, Maria *et al.* (1978) prepared magnesium sulfate fertilizer containing 17.4% MgO by decomposition of Mg carbonate, oxide or silicate containing raw materials with sulfuric acid. Stainslaw *et al.* (1987) produced magnesium sulfate used in fertilizers by treating of dolomitic wastes with waste sulfuric acid from manufacturing of TiO_2 pigment and showed that the formation of magnesium sulfate dependent on the amount and concentration of sulfuric acid, temperature and independent on the reaction time. Ilie (1973) produced high purity magnesium sulfate by treating of suspension of calcined dolomite with sulfuric acid at temperature does not exceed 80°C and pH 3-3.5 and then pH 6.5-7 to remove all impurities. The produced magnesium sulfate solution is filtered, concentration and crystallized. Grigor (1969) prepared magnesium sulfate from Negram dolomite by reaction with gypsum and CO_2 . The overall reaction is;



Satisfactory results were obtained only when partially decarbonated dolomite is used. The optimal exposure 6 hours and a further increase have practically effect on the yield of magnesium sulfate with increasing carbon dioxide pressure. The maximum yield of magnesium sulfate is 76.6%.

Vendelin and Miroslav (1991) treated semiburnt dolomite with ammonium sulfate in presence of water at temperature from 80-200°C with separating the produced calcium sulfate hydrated from magnesium sulfate solution. Wiedeman *et al.* (1990a,b) produced magnesium sulfate but using crushing dolomite in vertical reactor with the waste gases from combustion of sulfur containing fuels with simultaneous feeding of oxygen and steam of 650-800°C and the product used as fertilizer. On the other hand, Urbanek (1989) used sulfur trioxide for production of magnesium sulfate.

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Approximately two million tons of dolostone associated with the phosphorite ores of Abu-Tartur area, New Valley, as beds and lenses. These dolomites are extracted during the mining of phosphorites and considered as gangue minerals since it decreases the P_2O_5 contents and increases the MgO contents, which decrease the economic potential of the produced ores. The present study aims to utilize these dolomites of to produce magnesium sulfate by treatment of the ore with sulfuric acid, so that increase the economic potential of these dolomites and add values to the phosphorite deposits of Abu Tartur area. This treatment consists namely of three stages, namely leaching and purification, solid/liquid separation and finally crystallization. All the parameters affecting the efficiency of each stage were systematically studied and the optimum conditions were determined.

2. EXPERIMENTAL

2.1. Raw materials and apparatus

Dolomite samples from Abu-Tartur area, New Valley was supplied from Abu-Tartur phosphate project and commercial sulfuric acid 98% from Abu-Zaabal Company for fertilizer and chemical industries were used in these studies as the leaching materials. Anionic polyacrylamide A 100, from American Cyanamid Company used in improvement of the filtration rate and was prepared by dissolving 0.1g in 20ml ethyl alcohol and 80ml H_2O with magnetic stirrer for 15 minute at room temperature. The reaction between dolomite and sulfuric acid was performed in a 500ml round bottom flask placed in a thermostatically controlled water bath. The slurry was mechanically agitated at a rate of 500rpm. The magnesium sulfate was filtered and washed under vacuum in a Buchner-type filter using polypropylene filter cloth of 200 mesh (75 μ m) size.

2.2. Procedure

Amount of dolomite ore was added gradually with constant agitation to the sulfuric acid in the reaction vessel. After the elapse of the reaction time, the slurry was controlled at pH 8.5 to remove ferric hydroxide, manganese hydroxide and aluminum hydroxide and phosphates, then filtered and washed three times and then the produced magnesium sulfate concentrated and crystallized as $MgSO_4 \cdot 7H_2O$.

In industry, the filtration rate is expressed as ton of MgO produced per square meter per day. So, the same expression is used to express the filtration rate applying the following equation (Abdel-Aal, 1995):

$$\text{Filtration rate} = W \cdot F / T \cdot A \quad (2)$$

where:

W: Weight of MgO in filtrate and wash liquor in gram

F: Filtration rate factor related to effective filter area in m^2 and conversion of g to ton and seconds to days.

T: Total times of filtration, washing and drying in seconds

A: Filter area, cm^2

The produced magnesium sulfate solutions were concentrated by evaporation to obtain magnesium sulfate crystals. The solution was transferred into the concentration flask, which was heated under reduced pressure and temperature. The condensed vapors were collected and the concentrated solution was cooled for magnesium sulfate crystallization. X-ray diffraction technique was used to examine the phase of the crystallized salt.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of dolomite ore

The chemical analysis of New-Valley dolomite ore is given in Table 1. It is clear that, the theoretical MgO content in pure dolomite mineral is 21.875%, this indicates that, the purity of dolomite ore is about 75.66%. The ore contains a high amount of calcium oxide which causes the problems after solid/liquid separation due to high content of produced calcium sulfate dehydrate. In addition, the ore contains a high amount of carbon dioxide, which causes excessive foams during the acid leaching process and consequently decreases the effective capacity of the reactor. In industry, the process can control by increasing retention time, calcinations of the ore before leaching and addition of antifoaming agent during the acid leaching stage.

Table 1
 Chemical analysis of Abu-Tartur dolomite

Constituent	%
MgO	16.55
CaO	29.11
SiO ₂	8.40
Al ₂ O ₃	1.54
Fe ₂ O ₃	4.34
MnO	0.49
Na ₂ O	0.02
K ₂ O	0.08
P ₂ O ₅	1.05
L.O.I	38.35

X-ray diffraction analysis Figure 1 indicates that four minerals are present, namely dolomite as a major mineral having the maximum relative intensity line, francolite, quartz and pyrite as a minor minerals.

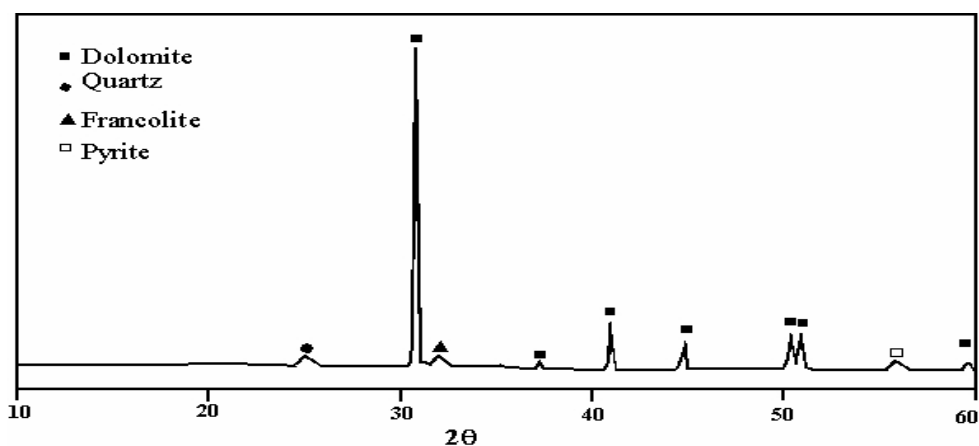


Figure 1. X-Ray diffraction analysis of dolomite samples

Sieve analysis of the dolomite minerals is shown in Table 2. The sample runs to pass from (0.355mm, 355µm) and the weights of the ores remaining over various sieves (0.355mm, +355µm to -0.07mm, -75µm) were recorded and chemically analyzed for MgO content. The results reveal that there is no change in the content of MgO in any of the fractions investigated.

Table 2
 Sieve analysis of Abu-Tartur dolomite.

Particle size, µm	Weight, %	MgO content
+ 355	26.5	16.45
-355 + 180	23.5	16.53
-180 + 150	4.2	16.57
-150 + 106	7.9	16.51
-106 + 75	12.2	16.61
-75	25.7	16.57

3.2. Production of magnesium sulfate

- The process of production of magnesium sulfate from dolomite ore involves the following steps:
- Leaching the ore with sulfuric acid and purification of the magnesium sulfate from dissolved impurities
 - Separation of precipitated impurities from magnesium sulfate solution
 - Concentration and crystallization of magnesium sulfate solution
- All steps were systematically studied.

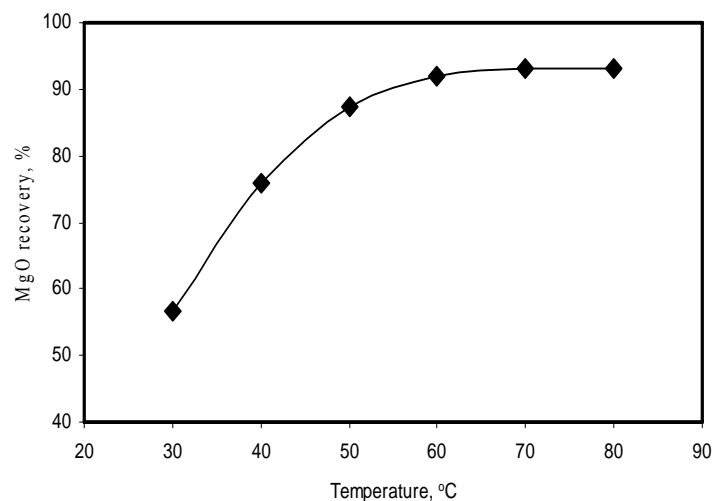


Figure 2. Effect of temperature on MgO recovery, %

3.2.1.3. Effect of reaction time

A series of experiments was carried out for different periods from 10-90 minutes under the following conditions:

Particle size, $-150\mu\text{m}$: 100 Temperature, °C : 60
Solid/liquid ratio, g/ml: 1:10 H_2SO_4 : MgO+CaO: 1

The obtained results are given in Figure 3. They reveal that the increasing the reaction time led to increase in MgO recovery. This is attributed to the liberation of the trapped magnesium cations from the ore cavities. The optimum reaction time is 50 minutes which given 97% MgO recovery. Further increase in the reaction time has no pronounced effect on increasing MgO recovery.

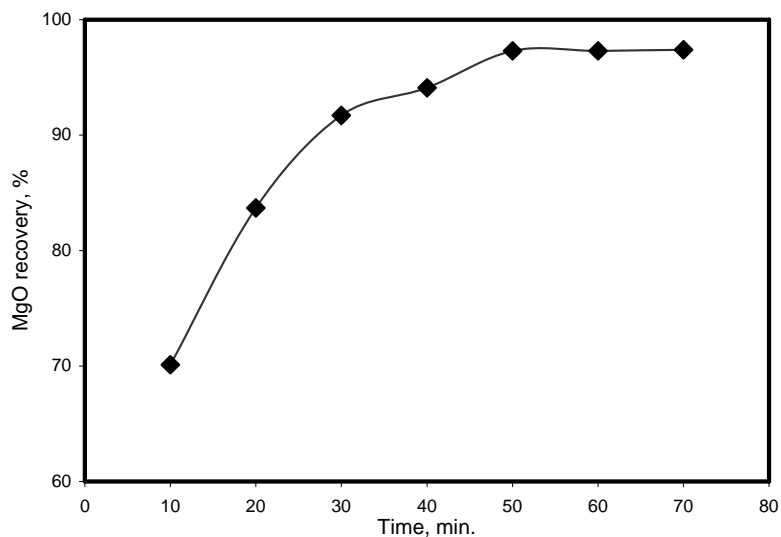


Figure 3. Effect of reaction time on the MgO recovery

3.2.1.4. Effect of solid/liquid ratio

To study the effect of liquid/ratio ratio on the MgO recovery, a series of experiments was performed at solid/liquid ratios ranging from 3:1 to 10:1ml/g. The experiments were carried out under the following conditions:

Particle size: 100% - $150\mu\text{m}$ Temperature: 60°C
Reaction time: 50 min. H_2SO_4 : MgO+CaO mole ratio: 1

The results given in Table 4 reveal that the recovery of MgO was not affected by changing the L/S ratio. Only, the concentration of magnesium sulfate solution is changed at the same recovery. At higher solid/liquid ratios (10:1), the magnesium sulfate concentration is (6.27%) which needs higher energy for evaporation. On the other hand, at lower liquid/solid ratio, the obtained solution is saturated with magnesium sulfate and the salt crystallizes on standing thus increasing MgO losses during filtration. Moreover, the filterability was very low due to the high viscosity of the solution.

Table 4
 Effect of solid/liquid ratio on MgO recovery and magnesium sulfate concentration

Solid/liquid ratio, g/ml	MgO Recovery, %	MgSO ₄ Conc., %
1:3	97.1	18.58
1:4	97.3	15.99
1:5	97.2	12.67
1:6	97.3	10.70
1:8	96.9	8.78
1:10	97.3	6.27

3.2.1.5. Leaching and purification parameters

The stoichiometric mole ratio of H₂SO₄: MgO+CaO is constant at unity to achieve pH 8.5 for removal of iron oxide, manganese oxide and aluminum oxide. The conditions of dolomite ore with sulfuric acid are summarized as the following: 100% -150µm particle size, temperature 60°C, reaction time 50 minute, solid/liquid ratio 1:4 g/ml. The obtained MgO recovery is 97.3%.

3.2.2. Filtration

After leaching, the slurry was filtered to separate calcium sulfate dihydrate (gypsum), ferric hydroxide, aluminum hydroxide, phosphates, manganese hydroxide and insoluble materials. The percentage of solids removed was about. The solid residue was washed three times. The following filtration and washing conditions were applied:

Type of filter: Buchner-type funnel	Diameter of filter: 7.4cm
Filter area: 43cm ²	Filter cloth: Polypropylene
Aperture of filter cloth: 200 mesh	Temperature of slurry: 50°C
Temperature of wash water: 50°C	Washing: 2 times
Number of filter cloth layers: 2	Volume of wash water: 100ml

3.2.2.1. Effect of pressure difference

To study the effect of pressure difference on the filtration rate, a series of experiments was performed under pressure differences ranging from 200 to 650mm.Hg. The experiments were carried out under the following conditions:

Number of washing: 2	Wash liquor temperature, °C: 50
Cake thickness, mm: 16	

The results given in Table 5 show that the filtration rate increased by increased the applied pressure difference up to 600mm. Hg. Higher pressure (> 600mm.Hg) results in boiling of the pregnant liquor. Also, the filtration rate decreased at higher pressure difference (650mm.Hg) due to increase of cake compressibility and consequently blocking of pores (Coulson and Richardson, 1968). The optimum pressure difference achieved is 600mm.Hg which gave the highest filtration rate of 1.2 ton MgO/m².day.

Table 5
 Effect of pressure difference on the filtration rate

Pressure difference		Filtration rate, ton MgO/m ² .day
mm.Hg	inch.Hg	
300	11.81	0.5
350	13.78	0.6
400	15.75	0.8
450	17.72	0.9
500	19.68	1.0
600	23.62	1.2
650	25.59	0.9

3.2.2.2. Effect of cake thickness

A series of experiments was carried out at different value of cake thickness. The experiments were carried out under pressure difference of 600mm.Hg. The results reveal that the optimum filtration rate of 1.2ton MgO/m².day at 16mm cake thickness was achieved. Lower cake thickness results in cracking and channeling of the cake, which offer a preferential passage of wash water without efficient washing.

Table 6
Effect of cake thickness on the filtration rate

Cake thickness, mm	Filtration rate, ton MgO/m ² .day
8	1.4
16	1.2
24	0.9
32	0.7
40	0.4
48	0.3

3.2.2.3. Effect of additives

The filtration process was performed with pressure difference 600mm.Hg and Cake thickness 16mm using different doses of anionic polyacrylamide A 100 (superfloc A 100) using different doses of 10, 20, 25, 30ml of (0.001 % concentration). The filtration rate is given in Table 7 and the results noticed that, the filtration rate is increased at 20ml of superfloc A100 due to the formation of a filter cake with an open structure, with high permeability with no fines to block the channels of the filter medium (Laskowski and Ralston, 1992). Increase of the dose concentration from 25-30ml led to decrease of the filtration rate due to the increase of filtrate viscosity.

Table 7
Effect of anionic polyacrylamide doses on the filtration rate

Volume of Superfloc A 100	Filtration rate, ton MgO/m ² .day
0	1.2
10	1.5
20	2.1
25	1.4
30	1.3

3.2.3. Concentration and crystallization

Magnesium sulfate pregnant liquor of 1.14g/ml density was concentrated under atmospheric pressure to different densities from 1.35-1.51g/ml and then crystallized by cooling. The densities achieved and corresponding magnesium sulfate are represented in Table 8. The crystals formed by cooling contain different amounts of water of crystallization based on concentration conditions. These results reveal that by increasing concentration time, the magnesium sulfate concentrations as well as the densities of pregnant liquor are increased. Cooling of pregnant liquors of from 1.35 to 1.45g/ml density gave MgSO₄. 7H₂O crystals and further increase in the density up to 1.5 gave a mixture of MgSO₄.7H₂O and MgSO₄.6H₂O. XRD data of the crystals are given in Figure 4. The results reveal that the crystallinity of MgSO₄.7H₂O increased by increased the density from 1.35 to 1.45g/ml.

Table 8
 Variation of magnesium sulfate concentration with concentration time under atmospheric pressure
 (Temperature range: 103-110°C, Density of pregnant liquor, g/ml: 1.14)

Concentration time, min.	Vapors, %	Density of pregnant liquor, g/ml	MgO, %	MgSO ₄ concentration, %
0	0	1.140	5.36	15.99
6	10	1.172	5.96	17.78
12	20	1.212	6.70	19.99
18	30	1.245	7.66	22.85
24	40	1.275	8.93	26.64
30	50	1.315	10.72	31.98
33	53	1.357	11.36	33.90
37	58	1.424	12.76	38.08
40	60	1.456	13.40	39.99
42	63	1.513	14.48	43.21

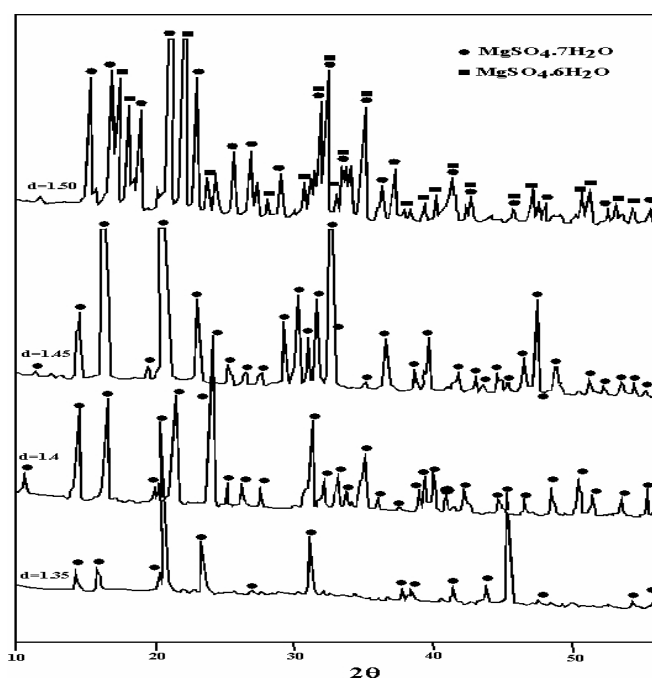


Figure 4. X-Ray diffraction analysis of magnesium sulfate at different densities

3.3. Quality of magnesium sulfate

The produced magnesium sulfate crystals were chemically analyzed and the results are given in Table 9. The chemical analysis shows that, the purity of produced magnesium sulfate heptahydrate is 99.15 %.

Table 9
 Chemical analysis of the produced magnesium sulfate heptahydrate

Constituent	%
MgO	16.23
SO ₃	32.58
P ₂ O ₅	0.05
CaO	0.21
Na ₂ O	0.01
K ₂ O	0.02
Fe ₂ O ₃	0.002
Al ₂ O ₃	0.001
SiO ₂	0.001

3.4. Evaluation of solid residue

The obtained solid residue after filtration and washing was dried and chemically and mineralogically analyzed. The chemical analysis given in Table 10 shows that the solid cake residue contains mainly CaO, SO₃, SiO₂.

The results of XRD analysis given in Figure 5 show that the solid cake residue contains gypsum as a major component and iron oxide and quartz as minor component. The gypsum residue may be suitable in the building industry and improvement of soil in the area of New Valley by mixing with phosphate slimes from Beneficiation plant of Abu-Tartur phosphate project.

Table 10
Chemical analysis of gypsum by product

Constituent	%
CaO	26.79
SO ₃	38.70
SiO ₂	8.10
Fe ₂ O ₃	4.75
Al ₂ O ₃	2.16
MgO	1.44
Na ₂ O	0.068
K ₂ O	0.015
MnO	0.97

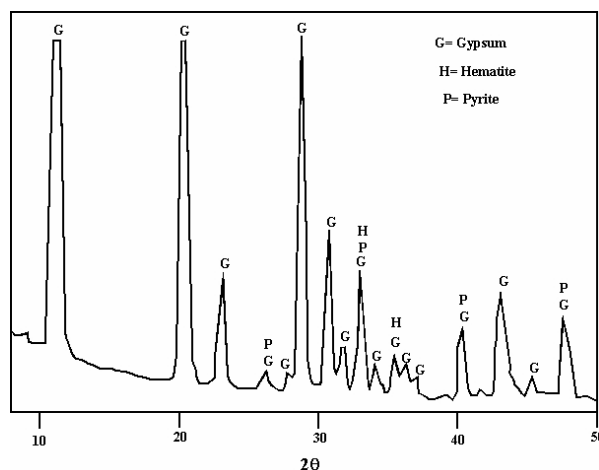


Figure 5. X-Ray diffraction analysis of produced gypsum

4. CONCLUSIONS

Leaching of Abu-Tartur dolomite with sulfuric acid to produce magnesium sulfate heptahydrate and gypsum was applied. The leaching conditions are particle size 100% -150µm, temperature 60°C, reaction time 50min and liquid/solid ratio 4:1g/ml. Recovery values of about 97% were achieved. The produced magnesium sulfate heptahydrate was separated from calcium sulfate dihydrate (gypsum) by filtration. The filtration rate was 2.1ton MgO/m².day at pressure difference 600mm.Hg, cake thickness 16mm and 20ml of 0.001% anionic polyacrylamide concentration. The filtered magnesium sulfate heptahydrate was crystallized by concentration to densities 1.35-1.45 g/ml and then cooling. The crystallinity of magnesium sulfate heptahydrate was increased by increased the density to 1.45. Increasing the density to 1.50g/ml led to a mixture of magnesium sulfate heptahydrate and hexahydrate. The purity of the produced MgSO₄.7H₂O was 99.2%.

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