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## **HYDROMETALLURGICAL PROCESSING OF EGYPTIAN MAGNESITE ORE**

Egyptian magnesite ore (43.32% MgO) from the Eastern Desert was leached with aqueous hydrochloric acid. The following optimum conditions of leaching were determined: ore particle size  $-0.5$  mm, temperature  $60^{\circ}\text{C}$ , leaching time 15 min, HCl to MgO molar ratio 1.06, and liquid/solid ratio of 2.5:1 ml/g. These conditions lead to recovery of about 99.1% MgO. Resultant liquor was first treated with calculated amount of sulphuric acid in order to precipitate calcium ions and then was neutralized to remove ferric ions. Optimum conditions of this purification procedure were determined. Purified magnesium chloride solution was evaporated and magnesium chloride crystals of 99.5% purity were obtained. Block flowsheet of this process was proposed.

### **INTRODUCTION**

Many processes have been adapted to produce magnesium chloride from magnesites by leaching with hydrochloric acid. Pertl (1973) treated crude magnesite calcined at  $800^{\circ}\text{C}$  of 0.1–1.0 mm particle size with water followed by passage of HCl gas through this suspension at about  $100^{\circ}\text{C}$  to produce magnesium chloride. Horak et.al. (1974) leached calcined ore containing more than 8.6% MgO with HCl (16–25%). Harris et. al. (1988) first ground magnesite to 60% less than 6 mesh particle size, calcined it at  $700^{\circ}\text{C}$  for 2 hours and then treated with 35.5% HCl solution in a stirred tank. On the other hand, Jeny et.al. (1976) dissolved magnesium minerals without calcination countercurrently with 18–21% HCl solutions. Sen et.al. (1984) leached Jhiroli magnesite ore (MgO 45%) of 100% less than 60 mesh particle size at  $100^{\circ}\text{C}$  for 45 minutes. Mejdal et.al. (1990) leached magnesite with 30% HCl at relatively low temperature of  $85\text{--}90^{\circ}\text{C}$ . Ya et.al. (1990) prepared magnesium chloride from boromagnesite using a salting out process.

In this study a sample of Egyptian magnesite was leached with aqueous hydrochloric acid, treated with calculated amount of sulphuric acid, neutralized and then filtered. Resultant filtrate was evaporated to obtain hydrated magnesium chloride. The block flowsheet of the process is proposed.

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## EXPERIMENTAL

### Raw material and apparatus

A sample of magnesite from the Eastern Desert (Egypt) and 32% pure hydrochloric acid were used. The reaction was performed in a 500 ml round bottom thermostated flask. Reaction mixture was agitated at a rate of 500 r.p.m. and then filtered under vacuum in a Buchner-type filter using polypropylene filter cloth of 200 mesh aperture size.

### Procedure

Calculated amount of magnesite was added gradually into agitated hydrochloric acid solution in the reaction flask. After the desired reaction time, slurry was treated with calculated amount of sulphuric acid to precipitate calcium, neutralized to pH 7.0–7.5, and filtered from silica, calcium sulphate, ferric oxide and other impurities. The filtrate was analysed for MgO content and then evaporated. Resultant crystals were analysed for total MgO content. The residue was washed two times with warm water. Filtration and washing times were recorded to calculate the filtration rate. At applied pressure difference 600 mm Hg the rate of filtration (in tonnes of MgO produced per square meter per day) is given by the equation:

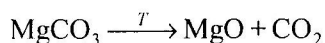
$$F = W \cdot 10^{-6} \cdot 86400 / A \cdot 10^{-4} \cdot 0.8T$$

where:

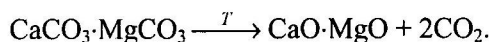
- $F$  – filtration rate, tonne MgO/m<sup>2</sup>·day,
- $W$  – weight of MgO in filtered solutions,
- $A$  – filter area, cm<sup>2</sup>,
- $T$  – filtration and washing times in seconds,
- 0.8 – ratio of effective filter area to total filter area.

### Characterisation of magnesite ore

Chemical, X-ray diffraction, thermal and sieve analyses of the magnesite ore were performed and the results were published elsewhere, Abdel-Aal et.al. (1994). The sample contained 43.32% of MgO and low contents of CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. X-ray diffraction of ore indicates that the major mineral is magnesite (MgCO<sub>3</sub>) while dolomite (CaCO<sub>3</sub>·MgCO<sub>3</sub>) and antigorite (3MgO·2SiO<sub>2</sub>·2H<sub>2</sub>O) are minor minerals. Thermal analysis of the ore shows two endothermic reactions, one at 550 °C due to the decomposition of magnesite:



and the second at 850 °C due to the decomposition of dolomite:

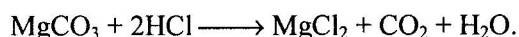


Particle size distribution of the crushed ore as received reveals that the ore contains little (12.4%) of fine fraction ( $-0.5$  mm). The MgO content in different fractions are roughly similar.

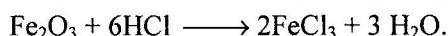
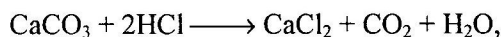
## RESULTS AND DISCUSSION

### Leaching

Leaching is based on the decomposition of the magnesite with hydrochloric acid according to the following equation:



Moreover, hydrochloric acid reacts with some impurities e.g.:



The main factors affecting the leaching are: particle size, reaction temperature, reaction time, liquid/solid ratio and stoichiometric ratio of hydrochloric acid to MgO. These factors were systematically studied.

### Effect of particle size

Decrease in the particle size leads to the increase in surface area, which promotes the reactivity. On the other hand, size reduction is a costly operation and should be

Table 1. Effect of particle size of tested magnesite on the MgO recovery

Particle size, % ( $-0.5$ mm fraction*)	MgO recovery %
0	79.10
25	83.90
50	86.60
75	88.40
100	90.65
100**	91.31

\* The remaining was  $-4.0 + 0.5$  mm fraction.

\*\* 100% of  $-0.335$  mm fraction.

avoided, if possible. A series of experiments was carried out using different proportions of ore of different particle sizes from  $-0.5$  mm and  $-4.0+0.5$  mm. Additionally,

relatively fine ore ( $-0.335$  mm) was tested. The experiments were conducted at  $50\text{ }^{\circ}\text{C}$  for 30 minutes at liquid/solid ratio 4:1 ml/g with about 18% hydrochloric acid and at stoichiometric ratio  $\text{HCl}:\text{MgO} = 1$ . Reaction products were analysed and the MgO content was referred to the original MgO content in the ore in order to calculate the MgO recovery. Results given in Table 1 revealed that the optimum particle size of the magnesite ore for leaching is  $-0.5$  mm ( $-35$  mesh) where 90.65% MgO recovery was achieved. Further grinding of the ore to  $-0.335$  mm particle size gives insignificant increase in MgO recovery.

#### Effect of reaction temperature

Experiments were performed at temperature ranging from  $30$  to  $80^{\circ}\text{C}$ . At lower temperatures, where the viscosity of liquid phase is higher which leads to a decrease in the mobility of reacting ions and consequently lowers the reaction rate. On the other hand, higher temperatures result in excessive foam formation together with increasing corrosivity of hydrochloric acid. The leaching was examined under the following conditions:

- Particle size – 100%  $-0.5$  mm,
- Reaction time – 30 min,
- Liquid/solid ratio – 4:1 ml/g,
- Stoichiometric ratio  $\text{HCl}/\text{MgO} = 1.0$ ,
- Acid concentration – 18%.

Results are given in Fig. 1 which reveal that the MgO recovery increase with increasing temperature. The optimum temperature is  $60\text{ }^{\circ}\text{C}$  which gives 94.18% MgO recovery. Further increase of the temperature gave no increase in MgO recovery.

#### Effect of reaction time

To study the effect of reaction time on the MgO recovery, experiments were carried out under the above conditions for different periods (5–60 min). Results are given in Fig. 2 which reveal that the reaction of magnesite with hydrochloric acid is a spontaneous reaction of a high rate. Practically, the recovery of MgO equal to 82.23% was obtained after 5 minutes. It is obvious that recovery of MgO increases with the increasing reaction time. The optimum reaction time is 15 minutes where 93.38% of MgO recovery is achieved. Increase of reaction time over 15 minutes gives no appreciable increase in MgO recovery.

#### Effect of liquid/solid ratio

To study the effect of liquid/solid ratio on MgO recovery and  $\text{MgCl}_2$  concentration, experiments were carried out at liquid/solid ratio changing from 6.0:1 to 2.5:1 ml/g. Results are presented in Fig. 3 which shows that higher liquid/solid ratio leads to lower magnesium chloride concentration (14.18%) which requires more energy to evaporate. On the other hand, at lower liquid/solid ratio (2.1:1), the filtrate becomes supersaturated which results in crystallization and losses of  $\text{MgCl}_2$  during filtration.

The optimum liquid/solid ratio is 2.5:1 ml/g which gives 94.66% MgO recovery and 32.98% of  $\text{MgCl}_2$  in the filtrate.

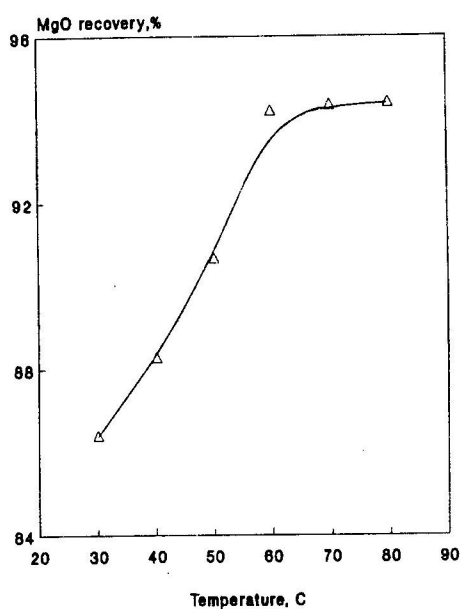


Fig. 1. Effect of temperature on MgO recovery

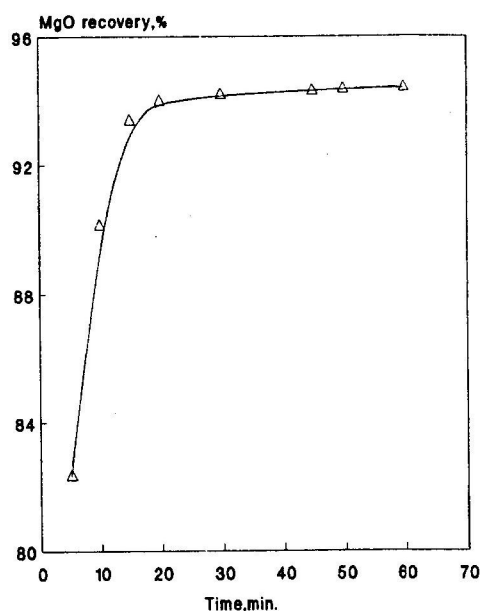


Fig. 2. Effect of reaction time on MgO recovery

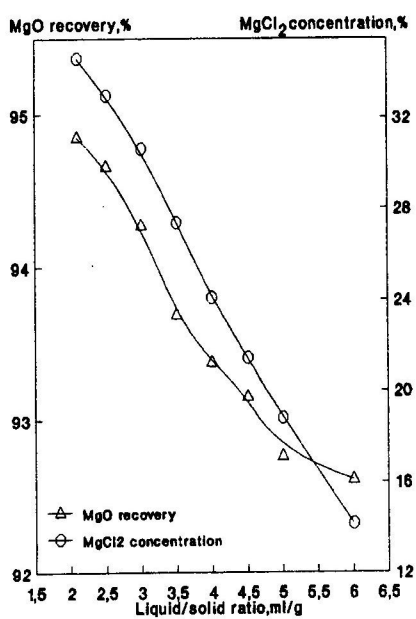


Fig. 3. Effect of liquid/solid ratio on MgO recovery and magnesium chloride concentration

### Effect of HCl/MgO stoichiometric molar ratio

The effect of molar ratio of HCl to MgO on MgO recovery and  $\text{MgCl}_2$  concentration was studied by changing this ratio from 1.00 to 1.10 under the optimum experimental conditions. Results are given in Fig. 4. The increase in HCl/MgO molar ratio leads to increase of MgO recovery which at ratio 1.06 reaches 99.1%. Further increase in this molar ratio produces an increase of free HCl content in magnesium chloride solution and does not produce an increase in MgO recovery.

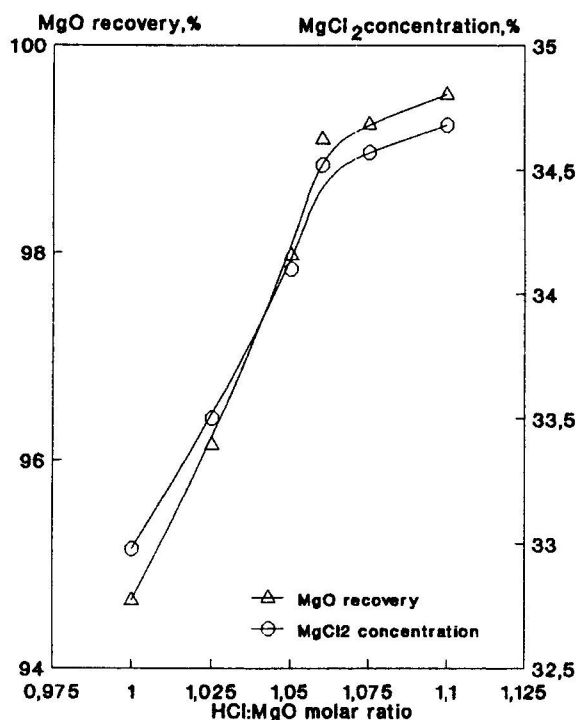


Fig. 4. Effect of HCl/MgO mole ratio on MgO recovery and  $\text{MgCl}_2$  concentration

### Optimum of the leaching conditions

The optimum conditions and results of decomposition of the magnesite ore with HCl are summarised in Table 2. The maximum MgO recovery achieved is 99.10%.

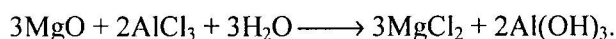
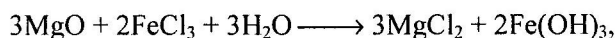
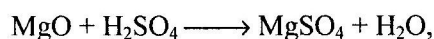
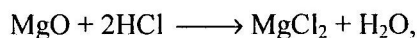
### Purification

Calcium ions, the major dissolved impurity are precipitated as sulphates using sulphuric acid, Jeny (1978) and Grill et. al. (1980). The effect of sulphuric acid to calcium oxide molar ratio on calcium removal efficiency was studied. Other dissolved impurities like iron, aluminium and manganese are removed by precipitation at pH

Table 2. Optimum conditions and results of magnesite leaching

Conditions:	
Particle size	100%–0.5 mm
Temperature, °C	60
Reaction time, min	15
Liquid/solid ratio, ml/g	2.5:1
HCl acid stoichiometry	1.06
HCl concentration, %	18
Results:	
MgO recovery, %	99.10
MgCl <sub>2</sub> cocentration, %	34.52

7.0–7.5 for 10 minutes at 60 °C by addition of various additives. These were chemically pure magnesium oxide (pH of its slurry was 10.4), magnesite (pH 9.2), magnesite calcined at 550 °C (pH 10.2), magnesite calcined at 850 °C (pH 10.4) and freshly prepared magnesium hydroxide (pH 10.5). The main reactions in this stage are:



## REMOVAL OF CALCIUM

### Effect of H<sub>2</sub>SO<sub>4</sub>/CaO mole ratio

Experiments were carried out to study the effect of H<sub>2</sub>SO<sub>4</sub>/CaO mole ratio on the efficiency of calcium removal under the following conditions:

Temperature: ambient, time: 10 min, acid concentration: 98%.

The results (Table 3) reveal that increasing H<sub>2</sub>SO<sub>4</sub>:CaO mole ratio leads to increasing removal efficiency of calcium ions up to 93.3% at 1.1 mole ratio. Increasing H<sub>2</sub>SO<sub>4</sub>/CaO mole ratio higher than the optimum value leads to increasing concentrations of free sulphuric acid.

Table 3. Effect of  $\text{H}_2\text{SO}_4:\text{CaO}$  mole ratio on efficiency of CaO removal

$\text{H}_2\text{SO}_4:\text{CaO}$ mole ratio	Efficiency of CaO removal, %
1.000	79.30
1.025	84.83
1.050	88.95
1.075	91.73
1.100	93.30
1.125	93.63

#### Removal of iron, aluminium and manganese

Iron, aluminium and manganese are removed by adding one of the following materials: pure magnesium oxide, calcined magnesite at 550 °C, calcined magnesite at 850 °C, and freshly prepared magnesium hydroxide securing the final pH from 7.0–8.2. The added amount is 4% of the amount of leached magnesite ore. The total efficiency of purification is 97.4%.

#### Filtration

The filtration rate of  $\text{MgCl}_2$  solution is 2.18 tonne  $\text{MgO}/\text{m}^2$  per day under the following conditions: pressure difference – 600 mm Hg, cake thickness– 8 mm, type of filter cloth – polypropylene, slurry temperature – 60 °C.

Table 4. Chemical analysis of magnesium chloride product

Constituent	%
MgO	19.74
$\text{Cl}^-$	34.92
CaO	0.09
$\text{SO}_3$	0.15
$\text{MnO}_2$	0.008
$\text{Fe}_2\text{O}_3$	0.001
$\text{Al}_2\text{O}_3$	0.001

#### Quality of product

The produced magnesium chloride was evaporated till the specific gravity of the solution reached 1.45 g/ml. The solution was cooled and magnesium chloride hexahydrate was crystallized. The resultant  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was analysed (Table 4). The purity of magnesium chloride crystals was about 99.5% with total dissolved impurities content 0.25%.



## CONCLUSIONS

Leaching of Egyptian magnesite ore from Eastern Desert was examined. Recovery of 99.1% MgO was achieved under the following leaching conditions: particle size 100% -0.5 mm, temperature 60 °C, reaction time 15 minutes, liquid/solid ratio 2.5:1

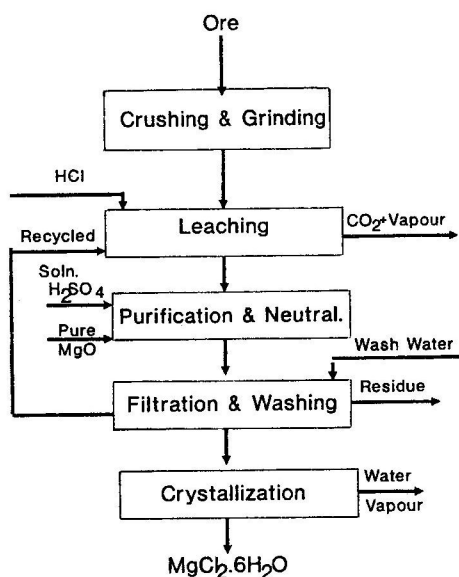


Fig. 5. Block flowsheet for production of magnesium chloride from Egyptian magnesite ore

ml/g and hydrochloric acid to magnesium oxide molar ratio 1.06. The resultant slurry was treated with  $\text{H}_2\text{SO}_4$  to precipitate calcium ions then neutralized to remove iron, manganese and aluminium impurities. The slurry was then filtered at the rate of 2.18 tonne  $\text{MgO}/\text{m}^2\cdot\text{day}$  at 600 mm Hg pressure difference. The purity of produced magnesium chloride crystals reaches 99.5%. The proposed process flowsheet is given in Fig. 5.

## REFERENCES

- ABDEL-AAL E.A., IBRAHIM I.A., RASHAD M.M., ISMAIL A.K. (1994), *Hydrometallurgical processing of Egyptian magnesite ore for production of magnesium sulphate*, *Fizykochemiczne Problemy Mineralurgii*, 28, 165–175.
- Encyclopaedia of chemical technology* (1969), Kirk–Othmer, II Ed., Vol. 12 (10) Canterford.
- GRILL M., GROHMANN H. (1980), *Large scale recovery of high purity magnesium oxide*, *Veitscher Magnesitwerke Austrian* 78, 3, 328.
- HARRIS G.B., PEACY J., MONETTE S. (1988), *Manufacture of concentrated magnesium chloride for production of magnesium*, Pamour Inc., Braz. Pedido PI BR 87, 02, 745.
- HORAK V., SPACEK V., SOUKUP V. (1974), *Recovery of magnesium chloride solution*, *Czech* 155, 586.

- JENY J., JEDLICKA H., BOROCLY P., GON S., DIEFT F. (1976), *Pure MgO*, Ruthmer Indsriearglage A-G Brom. Pedido 75, 099.
- JENY J. (1975), *Removal of calcium from acidic salt solutions*, Ruthmer Engineering G.m.b.H, Ger. Offen 2, 638, 123.
- MEJDAL G., MARCUSSEON J.B., TRETEN K.W. (1990), *Preparation of high purity  $MgCl_2$  by leaching of magnesium minerals with HCl for Mg manufacture*, Norsk Hydro A/S Fr. Demande FR2, 648, 126.
- PERTL I.A. (1973), *Magnesium oxide manufacture from magnesite*, Österreichish Amerikanische Magnesite A-G, Ger. Offen 2, 137, 373.
- SEN GUPTA D.K., MUKHERJEE S.K. (1984), *Extraction of chemical grade magnesium from Jhiroli magnesite*, J. Mines. Met. Fuels 32 (4-5), 185-8.
- YA D., WANG C., LI J. (1990), *Production of boric acid and magnesium chloride from boromagnesite by hydrochloric acid salting out process*, Huben Research Institute of Chemistry Faming Zhuanli Shenqing Gongkai Shumingshu, CN 1, 042, 884.

**Abdel-Aal E.A., Ibrahim I.A., Rashad M.M., Ismail A.K.**, Hydrometalurgiczna przeróbka egipskich rud magnezytowych, *Fizykochemiczne Problemy Mineralurgii*, 30, 207-216 (w jęz. angielskim).

Ługowano za pomocą 32% roztworu kwasu solnego rudę magnezytową z Pustyni Wschodniej zawierającą 43% MgO. Określono, że optymalne warunki procesu to: wielkość ziarn -0,5 mm, temperatura 60 °C, czas ługowania 15 minut, stosunek molowy HCl do MgO 1,06 oraz stosunek fazy ciekłej do stałej jak 2,5:1 ml/g. Warunki te pozwoliły na odzyskanie około 99,1% MgO. Otrzymany w wyniku ługowania roztwór traktowano obliczoną ilością kwasu siarkowego w celu wytrącenia jonów wapnia a następnie roztwór neutralizowano w celu usunięcia jonów żelaza. Określono także optymalne warunki tej operacji. Oczyszczony roztwór chlorku magnezu poddano odparowaniu i otrzymano krystaliczny  $MgCl_2$  o czystości 99,5%. W pracy proponowano blokowy schemat przerobu badanych rud.