

E.A. ABDEL-AAL\*, M.M. RASHAD\*

## **HYDROMETALLURGICAL PROCESSING OF EGYPTIAN MAGNESITE ORE WITH NITRIC ACID**

Egyptian magnesite ore (43.32% MgO) from the Eastern Desert was leached with aqueous nitric acid and the following optimum conditions of leaching were determined: ore particle size 100% –0.5 mm, temperature 50 °C, leaching time 30 min, HNO<sub>3</sub> to MgO molar ratio 1.05, and liquid/solid ratio of 2.8:1.0 ml/g. These conditions lead to recovery of 96.2% MgO. Resultant liquor was first treated with stoichiometric amount of sulfuric acid in order to precipitate calcium ions and then was neutralized with MgO. Purified magnesium nitrate solution was evaporated and magnesium nitrate crystals of 99.7% purity were obtained. Block flowsheet of this process was proposed.

### INTRODUCTION

Many processes have been adapted to produce magnesium nitrate from magnesites by leaching with nitric acid. Marchenko (1976) treated fine grained magnesite (–0.5 mm) with 39–55% nitric acid at 10–20% excess magnesite powder. The reaction time depended on the dissolution temperature, it was 10 hours for 20–30 °C, but at 79 °C, it was only 3 hours. Al and Fe nitrates were removed from 30–40% magnesium nitrate solution by hydrolysis at 170 °C for 1 hour. Najomr (1977) showed that the calcined magnesite at 700 °C for 1 hour was dissolved in 65% HNO<sub>3</sub> while Fe<sup>2+</sup> was converted to Fe<sup>3+</sup> which was insoluble in magnesium nitrate product solution. Abrosimova (1979) showed that the recovery of MgO was increased after leaching of caustic magnesite with 40–45% nitric acid in slightly over stoichiometric ratio (105–110%). Galkin (1985) separated aluminium and iron from produced magnesium nitrate solution by neutralization with excess magnesite. Kubovy (1991) showed that the optimum temperature range for reaction of magnesite ore with nitric acid was 75–95 °C. Li (1992) determined the optimum conditions of leaching of calcined magnesite with nitric acid: particle size –325 mesh, nitric acid concentration 50%, reaction temperature 40–50 °C and reaction time 20–30 minutes.

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\* Central Metallurgical Research and Development Institute, P.O. Box 87, Helwan, Cairo, Egypt.

In this study a sample of Egyptian magnesite was leached with aqueous nitric acid, treated with stoichiometric amount of sulfuric acid, neutralized and then filtered. Resultant filtrate was evaporated to obtain hydrated magnesium nitrate.

## EXPERIMENTAL

### Raw material and apparatus

A sample of magnesite from the Eastern Desert (Egypt) and 65% pure nitric 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 the residue was decanted using cationic flocculant (Praestol 441, trade name).

### Procedure

Calculated amount of magnesite was added gradually into agitated nitric acid solution in the reaction flask. After the desired reaction time, slurry was treated with stoichiometric amount of sulfuric acid to precipitate calcium, neutralized to pH 7.0–7.5, and the solid residue impurities (silica, calcium sulphate, ferric oxide and others) were decanted by flocculation. The optimum clarification conditions were determined. The obtained solution was analyzed for MgO content and then evaporated. Resultant crystals were also analyzed for total MgO content.

### Characterization of magnesite ore

Chemical, X-ray diffraction, thermal and sieve analyses of the magnesite ore were performed and the results have been 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 its 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.

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

## RESULTS AND DISCUSSION

### Leaching

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



Moreover, nitric 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 nitric 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 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  $60$  °C for 30 minutes at liquid/solid ratio 5:1 ml/g with about 24% nitric acid concentration and at stoichiometric ratio ( $\text{HNO}_3:\text{MgO}$ ) = 1. Results given in Table 1 revealed that the optimum particle size of the magnesite ore for leaching is  $-0.5$  mm ( $-35$  mesh) where 90.5% MgO recovery was achieved. Further grinding of the ore gives insignificant increase in MgO recovery.

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

Particle size, % ( $-0.5$ mm fraction)*	MgO recovery, %
0	84.3
25	85.8
50	87.3
75	88.8
100	90.3
100**	90.7

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

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

### Effect of reaction temperature

Experiments were performed under the above optimum conditions at different temperatures ranging from  $30$  to  $80$  °C. At lower temperatures, where the viscosity of liquid phase is higher, the mobility of reacting ions is low and which leads to low the reaction rate. On the other hand, higher temperatures result in excessive foaming

formation together with increasing corrosivity of nitric acid. Results (Fig. 1) reveal that the MgO recovery increase with the temperature up to about 50 °C which gives 90.2% 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 (Fig. 2) show that the reaction of magnesite with nitric acid is a spontaneous reaction of a high rate. Practically, the recovery of MgO equal to 80.5% was obtained after 5 minutes of leaching. It is obvious that recovery of MgO increases with the increasing reaction time. The optimum reaction time is 30 minutes where 90.2% of MgO recovery is achieved. Increase of reaction time over 30 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  $\text{Mg}(\text{NO}_3)_2$  concentration, experiments were carried out at liquid/solid ratio changing from 5:1 to 2:1 ml/g. Results are presented in Fig. 3. Higher liquid/solid ratio (5:1 ml/g) leads to lower magnesium nitrate concentration (26.12%) which requires more energy to evaporate. On the other hand, at lower liquid/solid ratio (2:1 ml/g), the filtrate becomes supersaturated which results in crystallization and losses of magnesium nitrate during filtration. The optimum liquid/solid ratio is 2.8:1 ml/g which gives 91.7% MgO recovery and 37.52% of  $\text{Mg}(\text{NO}_3)_2$  in the filtrate.

### Effect of $\text{HNO}_3/\text{MgO}$ stoichiometric molar ratio

The effect of molar ratio of  $\text{HNO}_3$  to MgO on MgO recovery and  $\text{Mg}(\text{NO}_3)_2$  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  $\text{HNO}_3/\text{MgO}$  molar ratio gives an increase in MgO recovery which at the ratio of 1.05 reaches 96.2%. Further increase in this molar ratio produces an increase of free  $\text{HNO}_3$  content in magnesium nitrate solution and does not produce higher MgO recovery.

### Optimum of the leaching conditions

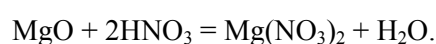
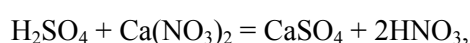
Table 2. The optimum conditions and the results of magnesite leaching

Conditions		Results	
Particle size	100% –0.5 mm	MgO recovery, %	96,20
Temperature, °C	50	$\text{Mg}(\text{NO}_3)_2$ concentration, %	39.40
Reaction time, min	30		
Liquid/solid ratio, ml/g	2,8:1		
$\text{HNO}_3$ acid stoichiometry	1.05		
$\text{HNO}_3$ concentration, %	39.98		

The optimum conditions and results of decomposition of the magnesite ore with nitric acid are summarized in Table 2. The maximum MgO recovery achieved under these conditions is 96.2%.

### Purification

Calcium ions, the major dissolved impurity are usually precipitated as sulfates using sulfuric acid (Jeny 1978, Grill et.al. 1980). The effect of sulfuric acid to calcium oxide molar ratio on the efficiency of calcium removal was studied. The free nitric acid is neutralized by increasing pH of the solution to 7.0–7.5 using pure magnesium oxide. 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
- acid concentration – 98%
- time – 10 min.

The results (Table 3) reveal that increasing H<sub>2</sub>SO<sub>4</sub>:CaO mole ratio leads to increase in the efficiency of removal calcium ions up to 95.73% at 1.0 mole ratio. Further increase in H<sub>2</sub>SO<sub>4</sub>/CaO mole ratio produces an increasing concentration of free sulfuric acid. The free nitric acid produced in the above operation is utilised with 4% magnesium oxide.

Table 3. Effect of H<sub>2</sub>SO<sub>4</sub> to CaO mole ratio on the efficiency of CaO removal

H <sub>2</sub> SO <sub>4</sub> to CaO mole ratio	Efficiency of CaO removal
0.800	86.30
0.900	90.83
1,000	94.95
1.050	95.73
1.075	95.95
1.100	96.13

## **Decantation**

The residue was separated from the magnesium nitrate solution by decantation without and with a cationic polyacrylamide flocculant.

### **Decantation without flocculant**

To determine the settling rate of the studied slurry, a series of experiments was carried out under the following conditions:

temperature – 50 °C  
slurry density – 1.335 g/ml  
pH – 7.0 – 7.5

Results given in Figs. 5, 6 reveal that the settling rate is slow. This is attributed to the repulsive forces between the particles of silica, calcium sulphate, and iron oxide which carry electronegative charges (zeta potential is  $-13.3$  at  $\text{pH} > 7$ ). The suspended particles were settled for a long time (240 minutes) of the settling rate  $6.6 \cdot 10^{-3} \text{ cm}^3/\text{sec}$  with small clarification efficiency (about 44%).

### **Decantation with flocculant**

Addition of cationic polymer (Parastol 441) was tested. The added polymer leads to collecting and wrap up particles bearing opposite charge and to formation of flocs which at high settle rate (Kenneth 1978, Laskowski et al. 1992). The effect of flocculant dose as well as of temperature on the clarification efficiency were studied.

### **Effect of flocculant dose addition**

The effect of flocculant dose on the clarification efficiency was studied in a series of experiments where amounts of added polyacrylamide (Parastol 441) were changed from 0.04 to 0.10% (related to the magnesite ore). The clarification efficiency was determined at different times (from 5 to 150 minutes). The results (Fig. 7) reveal that increasing of flocculant dose from 0.04 to 0.08% leads to increase in clarification efficiency. This is due to the neutralization of charges of colloidal particles. The optimum flocculant dose is 0.08% of magnesite weight which gives clarification efficiency of 80% after 100 minutes. Any further increase in the flocculant dose affect adversely the clarification efficiency. This could be attributed to increasing of the electrostatic repulsion forces due to maintaining excessive positively charged flocculant particles.

### Effect of temperature

A series of experiments was carried out in the temperature range from 40 to 60 °C to study the effect of temperature on the clarification efficiency (Fig. 8). The optimum temperature is 50 °C which gives clarification efficiency 80% after 100 minutes.

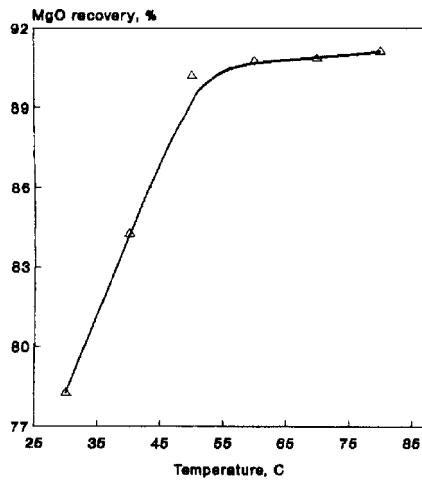


Fig. 1. Effect of temperature on MgO recovery

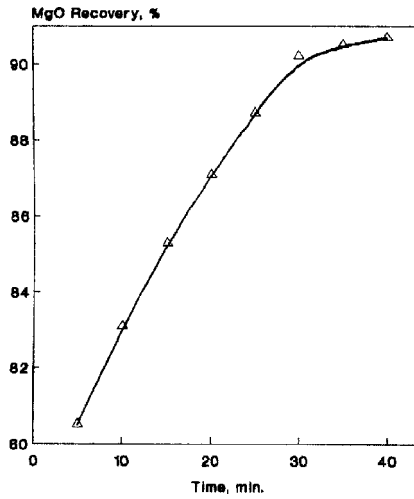


Fig. 2. Effect of time on MgO recovery

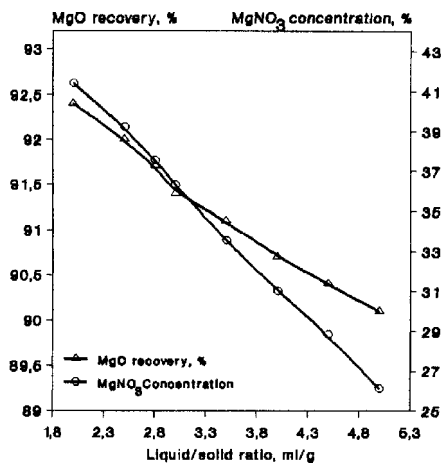


Fig. 3. Effect of liquid/solid ratio on MgO recovery and magnesium nitrate concentration

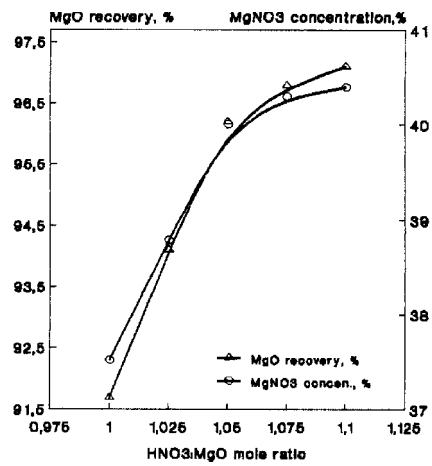


Fig. 4. Effect of HNO<sub>3</sub> : MgO mole ratio on MgO recovery and magnesium nitrate concentration

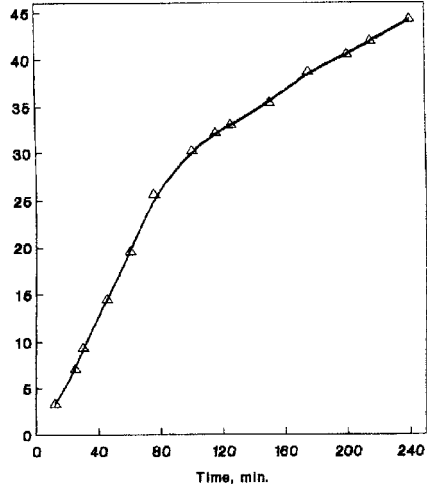


Fig. 5. Effect of time on clarification efficiency without flocculant

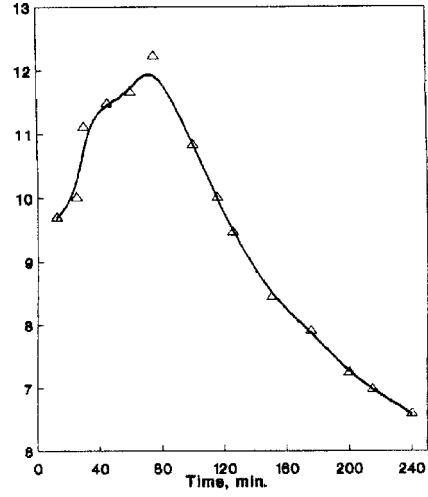


Fig. 6. Effect of time on settling rate without flocculant

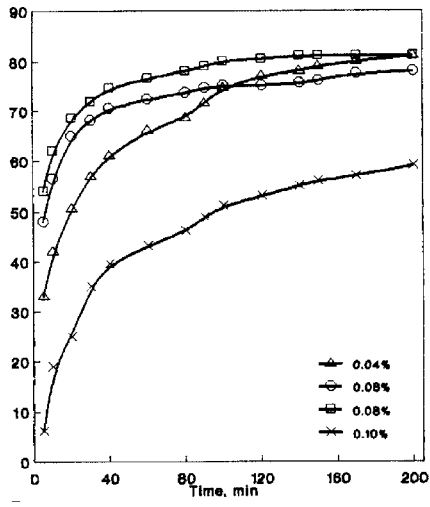


Fig. 7. Effect of flocculant dose on clarification efficiency

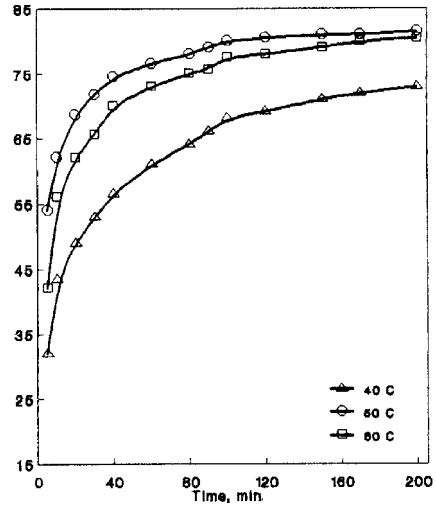


Fig. 8. Effect of temperature on clarification efficiency



### Optimisation of the decantation with flocculant

The results as well as the optimum conditions of the decantation stage with flocculant are given in Table 4.

Table 4. The optimum conditions and the results of decantation

Conditions	
Dose addition, %	0.08
Temperature, °C	50
Time, min	100
Results	
Clarification efficiency, %	80

### Quality of product

The produced magnesium nitrate solution was evaporated and magnesium nitrate hexahydrate was crystallized at room temperature. The resultant  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was analyzed (Table 5). The purity of magnesium nitrate crystals was about 99.7%

Table 5. Chemical analysis of magnesium nitrate product

Constituent	%
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99.70
CaO	0.09
$\text{SO}_3$	0.15
$\text{MnO}_2$	0.008
$\text{Fe}_2\text{O}_3$	0.001
$\text{Al}_2\text{O}_3$	nil

### CONCLUSIONS

Leaching of Egyptian magnesite ore from Eastern Desert was examined. Recovery of 96.2% MgO was achieved under the following leaching conditions: particle size 100% -0.5 mm, temperature 50 °C, reaction time 30 minutes, liquid/solid ratio 2.8:1.0 ml/g and nitric acid to magnesium oxide molar ratio 1.05. The resultant slurry was treated with  $\text{H}_2\text{SO}_4$  to precipitate calcium ions and then neutralized to remove iron,

manganese and aluminum impurities. The slurry was separated by using cationic flocculant and the clarification efficiency of 80.5%. The purity of produced magnesium nitrate crystals reached 99.7%. The proposed process flowsheet is given in Fig. 9.

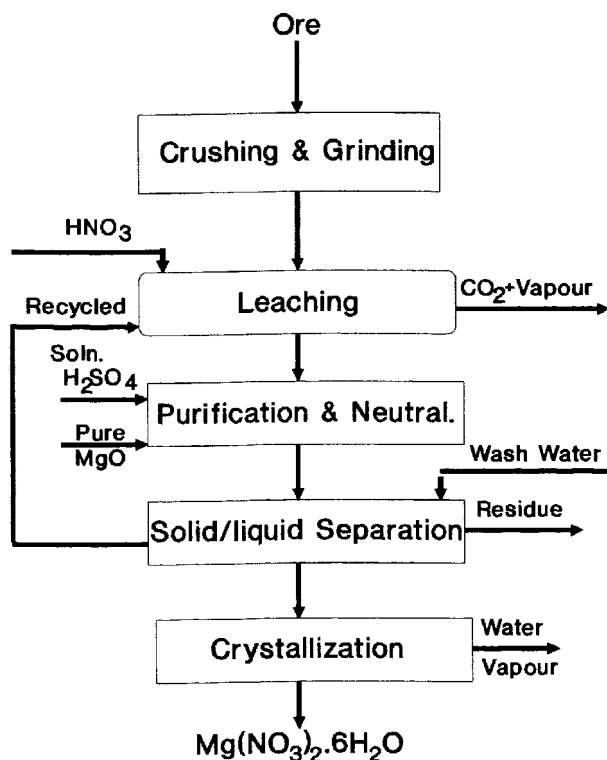


Fig. 9. Block flowsheet for production of magnesium nitrate from Egyptian magnesite ore

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**Abdel-Aal E.A., Rashad M.M.**, Hydrometalurgiczna przeróbka egipskich rud magnezytowych za pomocą kwasu azotowego. *Fizykochemiczne Problemy Mineralurgii*, 31, 7–17 ( w jęz. angielskim)

Egipska ruda magnezytowa, zawierająca 43,3% MgO, pochodząca z Pustyni Wschodniej była ługowana kwasem azotowym. Określono, że optymalne warunki ługowania to: wielkość ziarna –0.5 mm, temperatura 50 °C, czas ługowania 30 min, stosunek molowy HNO<sub>3</sub> do MgO 1,05 oraz stosunek fazy ciekłej do stałej 2,8/1 ml/g. Warunki te pozwoliły na odzyskanie 96,2% MgO. Powstający roztwór najpierw traktowano stechiometryczną ilością kwasu siarkowego w celu wydzielenia jonów wapnia w postaci osadu, a następnie neutralizowano za pomocą MgO. Otrzymany roztwór azotanu magnezu poddano odparowaniu i otrzymano krystaliczny azotan magnezu o czystości 99,7%. W pracy podano schemat przerobu badanej rudy.