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POSSIBILITY OF UTILIZING EGYPTIAN DOLOMITE ORES FOR PRODUCTION OF MAGNESIUM OXIDE BY ACID LEACHING

Egyptian dolomite ores from Gebel Ataqa, Suez and Khaboba, Sinai deposits were leached with nitric acid and ammoniated to produce magnesium hydroxide which was next calcined to magnesium oxide. Calcium and ammonium nitrates containing about 19%N were obtained as a by-product which can be used as a fertilizer. The temperatures of reaction were 60 and 55 °C, times of reaction were 2.5 and 2.0 hours, and mole ratios of nitric acid to calcium and magnesium oxides were 1.10 and 1.05 for the Gebel Ataqa and Khaboba ores, respectively. The particle size of both ores was –0.5 mm. The yield of the reaction was near 100% for both dolomite samples. The purity of the produced MgO was about 98%.

INTRODUCTION

The majority of the basic refractory materials consumed in Egypt is imported. The locally produced refractory materials are manufactured from imported dead-burned magnesite because of inavailability of suitable domestic deposits containing high enough content of magnesite. Therefore, the utilisation of dolomite ores, available in Egypt in economic amounts, for the production of MgO used for refractories could be beneficial for the national economy (Girgis 1991).

Many processes have been adapted to recover magnesia from dolomites. Baran et al. 1961 have prepared magnesium oxide (95–98%) from dolomite using nitric acid. The process involved control of both temperature and pH to remove impurities. Calcinated dolomite was added to the nitric acid solution slowly to precipitate magnesium hydroxide while calcium nitrate solution was obtained as a by-product (Beverini 1966). Magnesium hydroxide can also be precipitated by ammonium hydroxide or ammonia gas. The precipitate, after filtration and washing, was calcined at 350–400 °C to give MgO. The filtrate containing $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 was either evaporated to produce fertilizer containing 25%N or neutralized with NH_3 and carbonated to get pharmaceutical grade CaCO_3 . The filtrate could also be used as liquid fertilizers (Plasil 1983).

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In this paper Egyptian dolomite was leached with nitric acid, then partially neutralized, and centrifuged. The obtained filtrates were ammoniated and the precipitated magnesium hydroxides were filtered, washed, and calcined.

EXPERIMENTAL

Raw materials and apparatus

Dolomite samples from the Gebel Ataq, Suez and Khaboba, Sinai deposits were supplied by El-Nasr Company for Refractories and Ceramic (SORNAGA). Pure nitric acid containing 58% HNO_3 was used in this study as the leaching agent. The reaction between dolomite samples and nitric acid was performed in a 500 ml round bottom flask placed in a thermostatically controlled water bath. The slurry was mechanically agitated at a rate of 500 r.p.m. The precipitated magnesium hydroxide was filtered and washed under vacuum in a Buchner-type filter using polypropylene filter cloth of 200 mesh size.

Procedure

The predetermine the amount of dolomite ore was added gradually with constant agitation to the nitric acid solution in the reaction vessel. After the elapse of the reaction time, the slurry was partially ammoniated adding ammonium hydroxide solution to pH 8.5 and centrifuged to remove silica, ferric hydroxide, and insolubles. The clear solution was analysed for MgO and CaO contents, then the solution was further ammoniated to pH 11.5 for precipitation of magnesium hydroxide which was filtered and washed three times. The filtrate was evaporated and the produced solid was dried and analyzed for total N content.

In industry, the filtration rate is expressed as tonnage of MgO produced per square meter per day. So, the same expression is used to express the filtration rate applying the following equation:

$$\text{Filtration rate} = C \cdot 40.32 \cdot F / (T \cdot 58.32)$$

Where:

C – weight of dry magnesium hydroxide cake, g

$\frac{40.32}{58.32}$ – chemical factor for converting $\text{Mg}(\text{OH})_2$ to MgO

F – filtration rate factor related to effective filter area in m^2 and conversion of g to tonne and seconds to days

T – total times of filtration, washings and drying in seconds.

RESULTS

I. Characterisation of dolomite ores

Chemical and sieve analyses of the dolomite ore samples from the Gebel Ataqa, Suez and Khaboba, Sinai areas were performed and given in Tables 1 and 2. From Table 1, it is obvious that Suez dolomite contains more MgO (21.6%) than Sinai dolomite (17.5%). In addition, Suez dolomite contains low level of impurities such as Fe_2O_3 and SiO_2 . Table 2 shows the particle size distributions of the crushed ores. The results reveal that the Suez and Sinai dolomite ores contain 13.8 and 11.1% of fine fraction (-0.5 mm), respectively.

Table 1. Chemical analyses of the tested dolomite ores

Component, %	Dolomite ore from	
	Gebel Ataqa, Suez	Khaboba, Sinai
CaO	29.40	28.10
MgO	21.60	17.50
Fe_2O_3	0.27	0.81
Al_2O_3	0.10	0.11
SiO_2	0.31	11.15
CO_2	46.70	41.20
Moisture	0.41	0.77
L.O.I., 1000°C	46.90	41.50

Table 2. Sieve analyses of the crushed dolomite ores

Particle size		Suez dolomite			Sinai dolomite		
Mesh*	mm	Wt.%	CaO%	MgO%	Wt.%	CaO%	MgO%
—	$-9.52+7.93$	15.3	29.6	21.9	18.1	28.5	17.8
—	$-7.93+6.35$	12.9	29.5	21.7	14.4	28.4	17.8
-3+4	$-6.35+4.76$	16.7	29.5	21.7	18.4	28.2	17.7
-4+10	$-4.76+2.00$	20.8	29.4	21.5	25.1	27.2	17.2
-10+18	$-2.00+1.00$	11.4	29.3	21.3	7.8	28.0	17.3
-18+35	$-1.00+0.50$	9.1	29.2	21.5	5.1	28.0	17.2
-35	-0.50	13.8	29.2	21.5	11.1	27.9	17.2

* ASTM standard

Table 3. Effect of particle size on CaO and MgO recoveries of tested dolomites

Conditions:

Reaction temperature, °C: 50

Reaction time, min.: 30

HNO₃ to CaO+MgO ratio: 1.0Concentration of HNO₃, %: 58

Particle size		Recovery, %			
		Suez dolomite		Sinai dolomite	
Mesh	mm	CaO	MgO	CaO	MgO
3 + 4	-6.35 + 4.76	71.8	69.6	71.3	69.2
-4 + 10	-4.76 + 2.00	75.7	72.4	74.9	71.9
-10 + 18	-2.00 + 1.00	79.4	77.1	78.8	76.8
-18 + 35	-1.00 + 0.50	82.1	80.5	81.7	80.3
-35	- 0.50	85.2	83.7	84.5	83.6

II. Leaching

Leaching is based on decomposition of the tested dolomites with nitric acid according to the following reaction :



Nitric acid also reacts with some impurities which are present in dolomites. The main factors which affect leaching are: particle size, reaction temperature, reaction time and stoichiometric ratio of nitric acid to CaO and MgO in the ore. These factors were systematically studied on the laboratory scale.

II.1. Effect of particle size

A series of experiments was carried out using different particle sizes of each dolomite ore ranging from about +4.76 mm to -0.5 mm. The experiments were conducted at 50 °C for 30 minutes with 58% HNO₃ and the stoichiometric ratio of HNO₃ to CaO + MgO was as 1:1.

The products obtained were analysed to determine the content of CaO and MgO. Reference was made to the original CaO and MgO in the ores to calculate the CaO and MgO recoveries. The results obtained are given in Table 3. The results show that CaO and MgO recoveries increase with decreasing particle size. This is due to the increase of the number of fine ore particles with higher surface area. The results show that the suitable particle of dolomite ores is - 0.50 mm (-35 mesh) which corresponds to 85.2% and 83.7% CaO recoveries and 84.5% and 83.6% MgO recoveries for the Suez and Sinai ores, respectively.

Table 4. Effect of temperature on CaO and MgO recoveries of the tested dolomites

Conditions:

Particle size: 100% –0.5mm

Reaction time, min.: 30

HNO₃ to CaO+MgO ratio: 1.0Concentration of HNO₃, %: 58

Temperature, °C	Recovery, %			
	Suez dolomite		Sinai dolomite	
	CaO	MgO	CaO	MgO
50	85.2	83.7	84.5	83.6
55	87.5	86.6	87.4	86.0
60	98.3	88.1	87.8	86.5
65	89.7	88.4	88.1	86.9
70	90.0	88.7	88.4	87.1

II.2. Effect of reaction temperature

A series of experiments was carried out in the temperature range of 50–70 °C to study the effect of temperature on CaO and MgO recoveries. Lower temperatures increase viscosity and hence decrease reactant ions mobility, and thus lower reaction efficiencies are expected. Higher temperatures lead to the increase of the corrosivity of nitric acid and consequently, high corrosion rate of the industrial units is encountered. The obtained results are given in Table 4. These results reveal that, the CaO and MgO recoveries increase with the increase of temperature. Suitable temperatures are 60 °C and 55 °C for Suez and Sinai dolomites, respectively.

II.3. Effect of reaction time

To study the effect of reaction time on CaO and MgO recoveries, a series of experiments was carried out at the same conditions mentioned above except 60 °C and 55 °C temperatures for Suez and Sinai dolomites, respectively, for different periods of time (0.5–3.0 hours). The obtained results are given in Table 5. The results reveal that the CaO and MgO recoveries increase with the increase of reaction time. The suitable reaction times are 2.5 and 2.0 hours for Suez and Sinai dolomites, respectively. The increase of the reaction time to 3 hours does not profoundly increase the CaO or MgO recovery (max. 0.5% increase).

II.4. Effect of nitric acid to CaO+MgO ratio

The effect of nitric acid to CaO and MgO ratio in the dolomite ores was studied by carrying out a series of experiments in which the ratio of HNO₃: CaO +

Table 5. Effect of reaction time on CaO and MgO recoveries of the tested dolomites

Conditions:

Particle size: 100% -0.5mm

 HNO_3 to CaO+MgO ratio:1.0Concentration of HNO_3 , %: 58

Reaction time,hr	Recovery, %			
	Suez dolomite at 60 °C		Sinai Dolomite at 55 °C	
	CaO	MgO	CaO	MgO
0.5	89.3	88.1	87.4	86.0
1.0	92.0	90.9	91.9	90.4
1.5	94.7	93.6	95.6	93.8
2.0	96.8	96.1	98.8	98.7
2.5	98.2	98.0	99.1	99.0
3.0	98.4	98.1	99.3	99.2

MgO varies from 1.00 to 1.20. The obtained results are given in Table 6. The results reveal that the increase of HNO_3 acid stoichiometry leads to increase of CaO and MgO recoveries reaching 99.8% and 99.7% for Suez dolomite at 1.10 ratio and 99.6% and 99.4% for Sinai dolomite at 1.05 ratio, respectively. The increase of the stoichiometry to 1.20 has no significant effect on the CaO and MgO

Table 6. Effect of HNO_3 acid stoichiometry on CaO and MgO recoveries of the tested dolomites

Conditions:

Particle size: 100% - 0.5mm

Concentration of HNO_3 : 58%

Suez dolomite

Sinai dolomite

Reaction temperature :

60 °C

55 °C

Reaction time :

2.5 hour

2.0 hours

Stoichiometry*	Recovery, %			
	Suez dolomite		Sinai dolomite	
	CaO	MgO	CaO	MgO
1.00	98.2	98.0	98.8	98.7
1.05	99.1	98.9	99.6	99.4
1.10	99.8	99.7	99.7	99.6
1.15	99.9	99.8	99.7	99.6
1.20	99.9	99.9	99.8	99.6

* Mole ratio of HNO_3 acid to total CaO and MgO.

Table 7. Optimum conditions of HNO_3 acid leaching

Conditions and results	Value	
	Suez dolomite	Sinai dolomite
Particle size	100% – 0.5 mm	100% – 0.5 mm
Temperature, °C	60	55
Reaction time, hr	2.5	2.0
HNO_3 acid stoichiometry	1.10	1.05
CaO recovery	99.8%	99.6%
MgO recovery	99.7%	99.4%

recovery. It is worth mentioning that the reaction efficiency is 100% and there are some CaO and MgO losses in the residue.

II.5. Leaching parameters

The conditions and the obtained results for decomposition of the dolomite ores with nitric acid are summarized in Table 7. The obtained CaO and MgO recoveries are 99.8% and 99.7% for Suez dolomite and 99.6% and 99.4% for Sinai dolomite, respectively.

III. Filtration

After leaching, the slurry was partially neutralized to pH 8.5 using ammonia solution (25%) and then centrifuged to remove ferric hydroxide, silica, and insoluble materials. The percentage of solids removed was about 1.5% and 13% for Suez and Sinai dolomites, respectively. The clear liquors are ammoniated to pH 11.5 for precipitation of $\text{Mg}(\text{OH})_2$. The precipitates were filtered and washed three times. The following filtration and washing conditions were applied:

Type of filter: Buchner-type funnel	Diameter of filter: 7.4 cm
Filter area: 43 cm^2	Filter cloth: Polypropylene
Aperture of filter cloth: 200 mesh	Temperature of slurry: 50 °C
Temperature of wash water: 50 °C	Washing: 3 times
Number of filter cloth layers: 2	Volume of wash water: 100 ml

III.1 Effect of cake thickness

A series of filtration runs was carried out at different cake thicknesses of produced magnesium hydroxide slurries. The pressure difference applied was 500 mm Hg.

The results obtained are given in Table 8. The results reveal that filtration rates of magnesium hydroxide slurries produced from Suez and Sinai dolomites are 0.7 and 0.5 tonne $\text{MgO}/\text{m}^2/\text{day}$ at 15 mm cake thickness. A high filtration rate

Table 8. Effect of cake thickness on filtration rates of Suez and Sinai slurries

Conditions:

Pressure difference: 500 mm Hg

Cake thickness mm	Filtration rate, tonne MgO/m ² /day		%CaO in dry cake*	
	Suez dolomite	Sinai dolomite	Suez dolomite	Sinai dolomite
5	1.1	0.9	2.0	2.3
10	0.9	0.7	1.4	1.6
15	0.7	0.5	0.8	1.1
20	0.5	0.3	0.7	1.1
25	0.4	0.2	0.7	1.0

* After calcination at 400°C

using Suez dolomite is related to low CaO/MgO ratio in the ore (1.36 compared with 1.61 in Sinai dolomite). The dissolved calcium nitrate increases the viscosity of the solution and hence decreases its filtrability (Cate 1970). The viscosity of Suez and Sinai filtrates is 5.6 and 7.2 cP at 35 °C. Lower cake thickness results in cracking and channeling of the cake which offer a preferential passage to the wash water without efficient washing. Consequently, the percentage of CaO remaining in the magnesium hydroxide cake increases at lower cake thickness.

III.2. Effect of pressure difference

Two series of filtration runs were carried out under different pressure differences for Suez and Sinai dolomites. The applied pressure difference ranged from 500 to 600 mm Hg. The results obtained are graphically represented in the Figure 1. The results reveal that the filtration rate is a linear function of the applied pressure difference for the two samples. This means that the formed cakes are practically incompressible under the applied conditions. The achieved optimal pressure difference is 600 mm Hg which gives the highest filtration rates (1.0 and 0.85 tonne

Table 9. Multi-stage washing of Suez and Sinai magnesium hydroxide cakes

Washing stage	%CaO in cake*		Washing efficiency,%	
	Suez dolomite	Sinai dolomite	Suez dolomite	Sinai dolomite
1	2.5	2.9	75	74
2	1.4	1.7	86	85
3	0.7	0.9	93	92
4	0.6	0.8	94	93
5	0.5	0.7	95	94

* After calcination at 400 °C

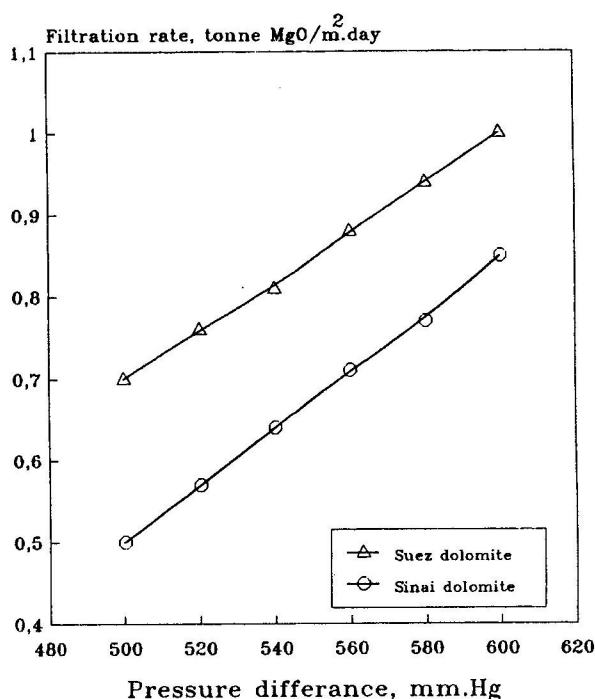


Figure 1. Effects of pressure difference on filtration rates of Suez and Sinai magnesim hydroxide slurries

MgO/m² day for Suez and Sinai dolomites, respectively. Higher pressure difference (> 600 mm Hg) results in boiling the filtrate. The percentage of CaO retained in the Suez and Sinai calcinated magnesium hydroxide samples is 0.7 and 0.9%, respectively.

III.3. Effect of washing stages

Five successive washing stages were separately applied on both samples. The results obtained are given in Table 9. The results show that the two dolomite samples behave similarly during the washing stages. It is clear that the 4th and 5th washing stages did not lead to significant washing out of the residual CaO, therefore, it is sufficient to wash the cake only three times.

IV. Quality of Products

The produced magnesium hydroxide samples were calcined at 400 °C for two hours and chemically analyzed. The results are given in Table 10 and compared with the specifications of MgO used in refractories (Morsi 1985). The results show that, the specifications of produced MgO samples are within the industrial limits. Also, the spent liquors containing calcium and ammonium nitrates were concen-

Table 10. Chemical analyses of magnesium oxide samples compared with the industrial limits

Constituent, %	MgO produced		Industrial limits*
	Suez dolomite	Sinai dolomite	
MgO	98.4	97.8	> 93
CaO	0.7	0.9	< 2.24
Fe ₂ O ₃	0.08	0.18	< 1.72
Al ₂ O ₃	0.19	0.20	—

* For refractories (Morsi, 1985).

trated by evaporation and crystallized by cooling. The obtained samples were chemically analyzed for total N. The total nitrogen percentages in produced fertilizers are 19.4 and 18.5 from Suez and Sinai dolomites, respectively.

CONCLUSION

Leaching of Suez and Sinai dolomites with nitric acid was applied. The leaching conditions are temperature 60 °C and 55 °C, reaction time 2.5 hr and 2.0 hr and nitric acid stoichiometry 1.10 and 1.05 for Suez and Sinai dolomites, respectively. Recovery values of about 99% were achieved. The produced Suez and Sinai magnesium hydroxide samples were filtered at rate of 1.00 and 0.85 tonne MgO/m²/day, respectively. The purity of produced MgO is about 98% which is suitable for refractories.

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Abdel-Aal E. A., Możliwości wykorzystania egipskich rud dolomitowych do produkcji tlenku magnezu ługowaniem kwaśnym, *Fizykochemiczne Problemy Mineralurgii*, 29, 55–65 (English text)

Rudy dolomitowe z Suezu (Gebel Ataqa) oraz z Synaju (Khaboba) były ługowane kwasem azotowym i amoniakiem w celu uzyskania wodorotlenku magnezu, który był następnie kalcynowany do tlenku. Jako półprodukty otrzymano azotany wapnia i amonu zawierające około 19% azotu, które mogą być użyte jako nawozy sztuczne. Temperatura reakcji wynosiła 60 i 55 stopni Celsjusza, a czas reakcji wynosił 2,5 i 2 godziny. Stosunki molowe kwasu azotowego do tlenków wapnia i magnezu były odpowiednio 1.10 i 1.05 dla surowców z Gebel Ataqa i Khaboba, a rozmiar ziarn w obu rudach był –0.5 mm. Wydajność reakcji była bliska 100% dla obu próbek dolomitowych. Czystość otrzymanego MgO wynosiła 98%.