E.A. ABDEL-AAL*, I.A. IBRAHIM*, M.M. RASHA*, A.K. ISMAIL *

HYDROMETALLURGICAL PROCESSING OF EGYPTIAN MAGNESITE ORE FOR PRODUCTION OF MAGNESIUM SULPHATE

Egyptian magnesite ore (43.32% MgO) from the Eastern Desert was leached with aqueous sulfuric acid. The following optimum conditions of leaching were determined: ore grain size –0.5 mm, temperature 60 °C, leaching time 40 min., molar ratio of H_2SO_4 to MgO 1.075, and solid/ liquid ratio of 1:4.5. These conditions lead to recovery of about 99% MgO. The resultant liquor was partially neutralized to remove ferric oxide and optimum conditions of its purification were determined. Purified magnesium sulphate solution was then evaporated and 99.5% magnesium sulphate crystals were obtained. Block flow sheet of the process was proposed.

INTRODUCTION

Many processes have been adapted to produce magnesium sulphate from magnesites by leaching with sulphuric acid. Harry (1972) prepared magnesium sulphate suitable for magnesia production (purity 99.5% MgO) by leaching of one part of magnesite of grain size < 297 μm suspended in 2.3 parts of water with 0.99 part of 98% H_2SO_4 at 80 °C for 2 hours. The slurry was mixed with MgO in order to adjust the pH at 6–7. Bankewicz et. al. (1978) prepared magnesium sulphate from magnesite (42% MgO) of < 0.2 mm particle size by treating it with 60% H_2SO_4 at 1.65 kg acid/kg magnesite ratio under continuous stirring. A water soluble $MgSO_4$ fertilizer containing 17.4% of Mg was obtained. Shcherbakov et al. (1981) manufactured $MgSO_4 \cdot H_2O$ by treating magnesite with H_2SO_4 in the presence of $MgSO_4$ mother liquor, decreasing the corrosiveness of the medium and increasing the productivity of process by mixing magnesite with mother liquor and then adding the sulphuric acid. The pH of the reaction mixture was maintained at 7–10. Karanova et al. (1982) showed that the optimum conditions for treating magnesite refractory waste with sulphuric acid were: final pH 7.0–7.5, concentration of H_2SO_4 18–20%, reaction time 40 min., and temperature above 95 °C. The 90% of conversion of MgO was achieved.

Xi, Zhaoshen et. al. (1988) fired magnesite at 800–900 °C for 10–15 hours to MgO which was subjected to spontaneous cooling, purification, pulverization, air

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

classification, and reaction with 75% H_2SO_4 (final pH 6–9) to $MgSO_4 \cdot H_2O$. Similarly, Prakash et al. (1982) prepared $MgSO_4 \cdot 7H_2O$ from calcined waste dust magnesite by treating it with H_2SO_4.

In this study, a sample Egyptian magnesite was leached with aqueous sulphuric acid, neutralized, and filtered. Resultant filtrate was evaporated to obtain hydrated magnesium sulphate. The block flow sheet of the process is proposed.

EXPERIMENTAL

Raw material and apparatus

Magnesite sample from the Eastern Desert (Egypt) and 98% pure sulphuric 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 filtrated under vacuum in a Büchner-type filter using polypropylene cloth of 200 mesh aperture size.

Procedure

A calculated amount of magnesite was added gradually into agitated sulphuric acid solution in the reaction flask. After the desired reaction time the slurry was neutralized to pH 7–8.5 and filtered from silica, calcium sulphate, ferric oxide, and other impurities. The clear solution was analysed for MgO content and then evaporated. Resultant crystals were analysed for total MgO content. The residue was washed three times with warm water. Filtration and washing times were recorded to calculate the filtration rate. The pressure difference applied was about 500 mm Hg. The rate of filtration (in tonnes of MgO produced per square meter per day) is given by the following equation:

$$F = \frac{W \cdot 10\text{-}6}{A \cdot 10\text{-}4 \cdot 0{,}8} \cdot \frac{1}{t/86400} \ [\text{t MgO/m}^2 \cdot \text{day}]$$

where:
F – filtration rate, tonne $\text{MgO/m}^2 \cdot$ day,
W – weight of MgO in filter solution,
A – filter area, m^2,
t – filtration and washing times in seconds,
0.8 – ratio of effective filter area to total filter area.

Characterization of magnesite ore

Chemical, X-ray diffraction, thermal and sieve analyses of the magnesite ore were performed and the results are given in Tables 1–3. Table 1 shows the chemical composition of the examined sample. It contains 43.32% of MgO and low contents of CaO, SiO_2, Fe_2O_3 and Al_2O_3. Table 2 shows the X-ray diffraction of the sample which indicates that the ore contains magnesite ($MgCO_3$) as major mineral, dolomite ($CaMg(CO_3)_2$) and antigorite ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) as minor minerals. Thermal

analysis of the ore shows two endothermic reactions, one at 550 °C due to the decomposition of magnesite:

$$MgCO_3 \rightarrow MgO + CO_2$$
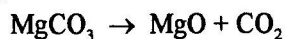
and the second at 850 °C due to the decomposition of dolomite:

$$CaCO_3 \cdot MgCO_3 \rightarrow CaO \cdot MgO + 2\ CO_2$$
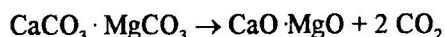
Table 1. Chemical analysis of magnesite ore

Constituent	%	Constituent	%
MgO	43.32	SO$_3$	0.24
CO$_2$	49.41	Na$_2$O	0.22
CaO	3.38	MnO$_2$	0.14
SiO$_2$	0.78	K$_2$O	0.08
Fe$_2$O$_3$	0.47	P$_2$O$_5$	0.05
Al$_2$O$_3$	0.36	Moisture	0.39
Cl	0.33	L.O.I., 1000 °C	49.75

Table 2. X-ray diffraction analysis of magnesite ore

I/I^0	d	Mineral	I/I^0	d	Mineral
16	2.881	D	7	1.520	M
100	2.750	M	10	1.500	M
17	2.507	M	6	1.440	A
9	2.340	M	7	1.420	M
6	2.200	D	11	1.360	M
49	2.104	M	12	1.340	M
6	2.060	D	5	1.250	M
15	1.946	M	4	1.160	A
8	1.790	D, M	7	1.070	M
41	1.703	M			

D – dolomite, CaMg(CO$_3$)$_2$, M – magnesite, MgCO$_3$, A – antigorite, 3MgO · 2SiO$_2$ · 2H$_2$O

Particle size distribution of the crushed ore as received is given in Table 3. It is obvious that the ore contains little (12.4%) of fine fraction (–0.5 mm). The MgO content in different fractions are similar.
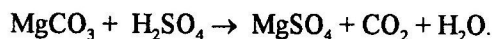
Table 3. Particle size distribution of the crushed magnesite ore

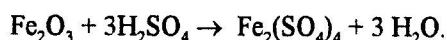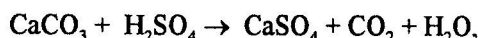| Particle size, mm	Weight, %	MgO, %
–16 + 8	21.2	43.4
–8 + 4	33.2	43.3
–4 + 2	17.9	43.2
–2 + 1	9.9	43.4
–1 +0.5	5.4	43.4
–0.5	12.4	43.3

RESULTS & DISCUSSION

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

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + CO_2 + H_2O.$$

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

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O,$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_4 + 3 H_2O.$$

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

Effect of particle size
It is well known that a 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 process and should be limited, if possible. Series of experiments were 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 °C for 30 minutes at solid/liquid ratio 1:6 g/ml with 16.7% acid solution and at stoichiometric ratio $H_2SO_4 : MgO = 1$.

Obtained 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 are given in Table 4 revealing that for leaching the optimum particle size of the magnesite ore is −0.5 mm (−35 mesh) where 78.7% MgO recovery was achieved. Further grinding of the ore to −0.335 mm particle size gives insignificant increase in MgO recovery.

Table 4. Effect of particle size on the MgO recovery
of tested magnesite

Particle size, % (−0.5 mm fraction*)	MgO recovery, %
0	62.2
25	66.4
50	70.4
75	74.0
100	78.7
100**	79.5

*The remaining was −4.0+0.5 mm fraction.
** 100% of −0.335 mm fraction.

Effect of reaction temperature

Experiments were carried out at temperature ranging from 30 to 80 °C to study the effect of temperature on both MgO recovery and filtration rate. At lower temperatures the viscosity of the liquid phase is higher which leads to a decrease in the mobility of reacting ions and consequently lowers the reaction efficiency. On the other hand, at higher temperatures excessive foam formation together with increasing of the corrosivity of sulphuric acid are encountered.

The leaching experiments were performed under the following conditions:

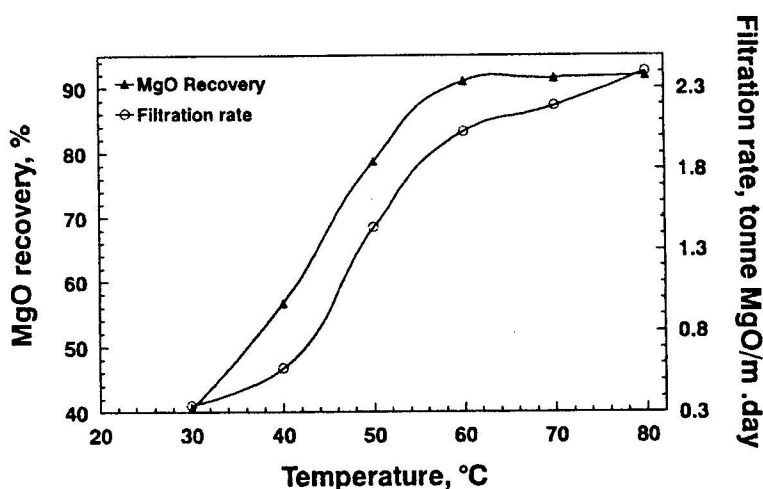|	
Particle size	100% – 0.5 mm.
Reaction time	30 min.
Solid/liquid ratio	1:6 g/ml.
Stoichiometric ratio H_2SO_4/MgO	1.0.
Acid concentration	16.7%.

Fig. 1. Effect of temperature on MgO recovery

Results are given in Fig. 1. These data reveal that the MgO recovery and filtration rate increase with increasing of temperature. The optimum temperature is 60 °C which gives 91% MgO recovery. Further increase in the temperature did not lead to a pronounced 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 (10–60 min.). Results are given in Figure 2. These results reveal that recoveries of MgO increase with the increase of reaction time. The optimum reaction time is 40 min. which gives 92.5% MgO recovery and 2.07 tonne MgO/m² day filtration rate. Increase of reaction time over 40 minutes gives no appreciable increase in MgO recovery as well as in filtration rate.
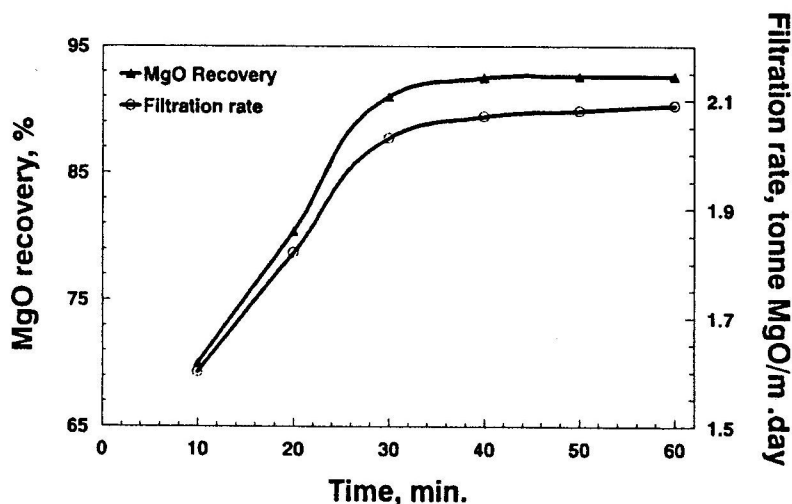
Fig. 2. Effect of time on MgO recovery and filtration rate

Effect of solid/liquid ratio

To study the effect of solid/liquid ratio on MgO recovery, experiments were carried out at solid/liquid ratio changing from 1:6 to 1:3 g/ml. Results are presented in Fig. 3. An optimum solid/liquid ratio was 1:4.5 g/ml and corresponds to 93% MgO recovery. Lower solid/liquid ratios led to diluted magnesium sulphate solution (17.7%) which subsequently required more energy to evaporate. On the other hand, at higher solid/liquid ratio, the final solution is saturated with magnesium sulphate which promotes crystallization and increases losses in filtration. Moreover, the filterability is drastically decreased due to higher viscosity of the solution. Concentration of resultant $MgSO_4$ solution is 23.2% which meets the industrial limits (23–26%) (Sololov et al. 1981, Bursa, Stanisz-Lewicka 1984).
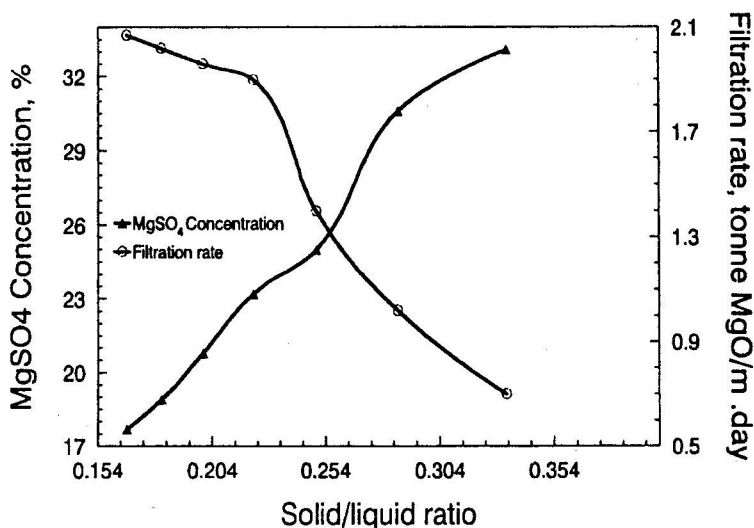

Fig. 3. Effect of solid/liquid ratio on magnesium sulfate concentration and filtration rate

Effect of sulphuric acid to magnesium oxide stoichiometric molar ratio

The effect of stoichiometric molar ratio of H_2SO_4 to MgO (S) was studied by changing this ratio from 1.00 to 1.10 under the optimum experimental conditions. Results are given in Figures 4, 5. The increase in H_2SO_4 to MgO molar ratio leads to increase of MgO recovery which reaches 98.9% at 1.075. Further increase in the stoichiometric molar ratio leads to increase of the content of free H_2SO_4 acid in the magnesium sulphate solution, and consequently, formation of

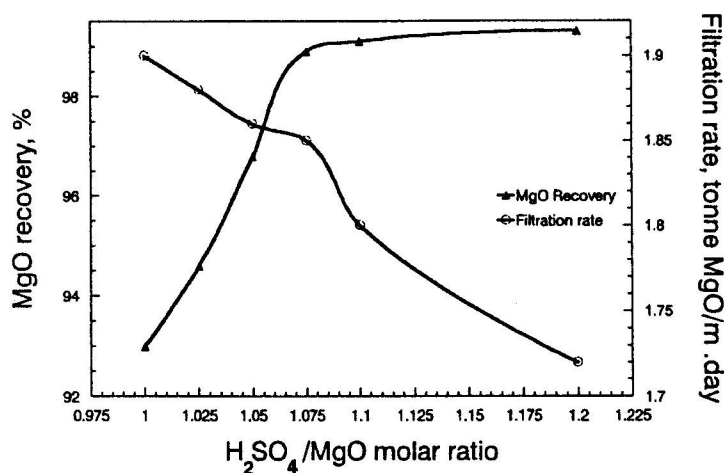Fig. 4. Effect of sulphuric to MgO
molar ratio on MgO recovery and filtration rate

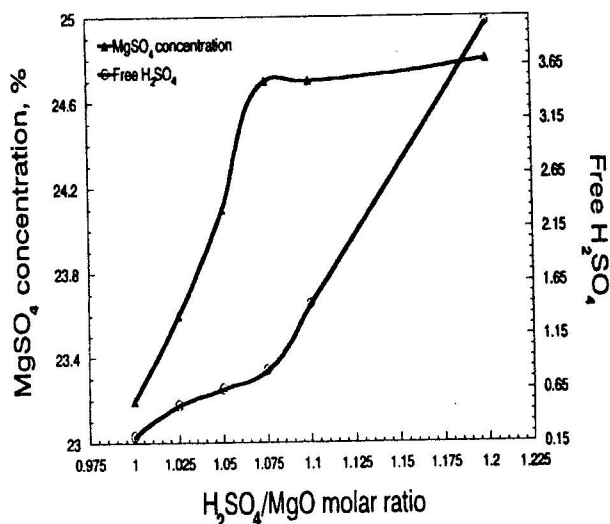Fig. 5. Effect of sulphuric acid to MgO molar ratio
on magnesium sulphate and free sulphuric acid concentrations

$MgSO_4 \cdot H_2SO_4$, $MgSO_4 \cdot H_2SO_4 \cdot 3H_2O$ and $MgSO_4 \cdot 3H_2SO_4$ compounds (*Encyclopedia...* 1969). At the optimum stoichiometry (1.075), the free sulphuric acid content is 0.82%.

Optimum of the leaching conditions

The optimum conditions and results of decomposition of the magnesite ore with sulphuric acid are summarized in Table 5. The maximum MgO recovery achieved was 98.9%.

Table 5. Optimum conditions and
results of magnesite leaching

Conditions:		
Particle size	100%	–0.5 mm
temperature, °C		60
Reaction time, min.		40
Solid/liquid ratio, g/ml		1 : 4.5
H_2SO_4 acid stoichiometry		1.075
H_2SO_4 concentration, %		23.4
Results:		
MgO recovery, %		98.90
$MgSO_4$ concentration, %		24.70
Filtration rate,		
tonne MgO/m² day		1.85
Free H_2SO_4, concentration %		0.82

Purification

Dissolved impurities (iron, aluminium and manganese) are best removed by precipitation at pH 6–8 for 10 minutes at 60 °C. Different compounds were used as additives to maintain pH within the required range. 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 $Mg(OH)_2$ (pH =10.5).Calcination of magnesite above 1000 °C leads to decrease in its chemical reactivity (Moorres 1987). Quantities of these compounds required to increase the pH are given in Table 6. Amounts of additives (expressed as fractionations of leached magnesite ore) securing the final pH from 7.0 to 8.2 :

Additive	%	Additive	%
Magnesite ore	40	Magnesium hydroxide	6
Calcined magnesite at 550 °C	10	Pure magnesium oxide	7
Calcined magnesite at 850 °C	6		

Magnesite ore calcined at 850 °C and freshly prepared magnesium hydroxide gave the best results.

Table 6. Amounts of different additives and the corresponding pH

| % Related to leached magnesite ore	pH				
	Magnesite ore	Magnesite calcined at 500 °C	Magnesite calcined at 850 °C	Magnesiumh hydroxide	Pure MgO
4.0	1.4	1.5	2.5	2.6	2.3
5.0	1.5	1.8	3.9	4.2	3.3
6.0	1.6	2.0	8.0	8.2	4.6
7.0	1.7	2.2	–	–	8.0
9.0	1.8	4.0	–	–	–
10.0	1.9	7.0	–	–	–
20.0	2.7	–	–	–	–
30.0	6.0	–	–	–	–
40.0	7.5	–	–	–	–

Quality of product and residue

The produced magnesium sulphate solution was evaporated till the specific gravity reached 1.35 g/ml, then it was cooled. The crystallized magnesium sulphate as well as the leaching residue were analysed chemically and with X-ray diffractometer. Chemical composition of both magnesium sulphate crystals and residue are given in Table 7.

Table 7. Chemical analysis of magnesium
sulphate product and of the solid residue

Constituent, %	Product	Residue
MgO	17.57	0.94
SO_3	34.86	33.12
CaO	0.08	21.75
Na_2O	0.10	0.004
K_2O	0.037	0.001
MnO_2	0.01	0.82
Fe_2O_3	0.002	3.23
Al_2O_3	0.001	2.49
SiO_2	0.001	5.31

The purity of magnesium sulphate crystals was about 99.5%, while X-ray diffraction indicated $MgSO_4 \cdot 6H_2O$ and presence of the following compounds in decreasing order of abundance:

$$CaSO_4 \cdot 2H_2O, \quad Fe_2O_3, \quad CaSO_4 \cdot 0.5H_2O.$$
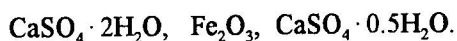
CONCLUSIONS

Leaching of Egyptian magnesite ore from the Eastern Desert with aqueous sulphuric acid was examined. Recovery of 99% of MgO was achieved under the following leaching conditions: particle size –0.5 mm, temperature 60 °C,

Ore

↓

| Crushing & Grinding |

↓

H_2SO_4

Recycled Soln. → | Leaching | → CO_2+ Vapour

↓

Calcined Magnesite → | Purification & Neutralization |

↓

Wash Water

| Filtration & Washing | → Residue

↓

| Crystallization | → Water Vapour
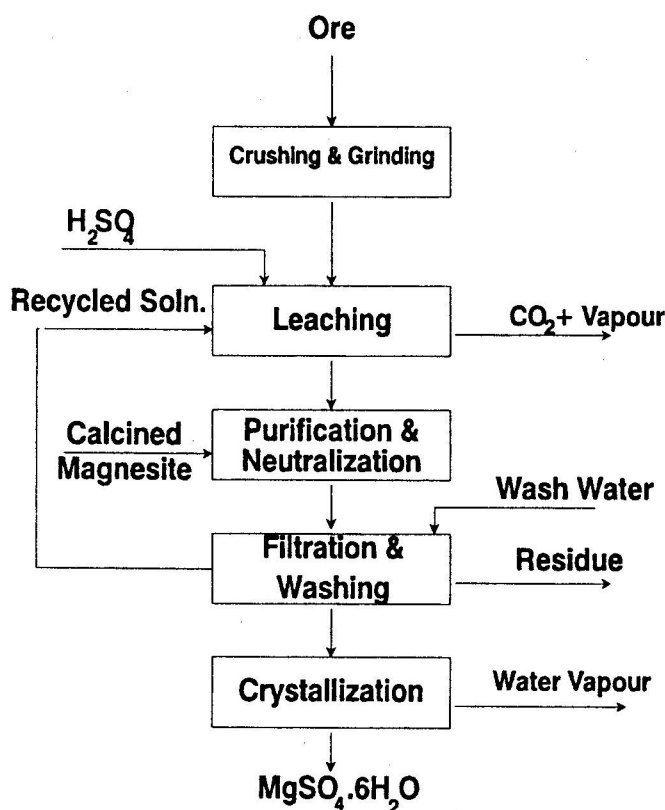
↓

$MgSO_4.6H_2O$

Fig. 6. Block flowsheet for the production of magnesium sulphate
from Egyptian magnesite ore

reaction time 40 minutes, solid/liquid ratio 1:4.5 g/ml, sulphuric acid to magnesium oxide molar ratio 1.075, and H_2SO_4 concentration 23.4%. Resultant slurry was neutralized with magnesite calcined at 850 °C to remove the impurities. Slurry was then filtered at the rate of 1.85 tonne MgO/m^2day at 500 mm Hg pressure difference. The purity of produced magnesium sulphate crystals reaches 99.5%. The process flowsheet is proposed in Fig. 6.

REFERENCES

BANKIEWICZ M., JANICZEK W., SKOWRONSKI B., GUCKI T. (1978), *Fertilizer containing in the form of soluble in water,* (Instytut Nawozów Sztucznych) Pol. Pat. 97, 938.

BURSA S., STANISZ-LEWICKA M. (1984), *Effect of temperature and concentration on reaction of magnesium carbonate and iron (II) sulfate,* (Polit. Szczec., Szczecin, Pol.), Pr. nauk. Inst. Technol. Nieorg. Nawozów Miner. PWr., 25, 171–7.

Encyclopedia of chemical technology, (1969), Kirk-Othmer, II Ed., Vol. 12 (10) Canterford.

HARRY E. (1972), (Magnesia, Cross) Gold Fields of South Africa Ltd., Ger. offen 2. 159, 973.

KARANOVA S., POPOV K., RUNEV I., SLARKOVA P., DRAGANOV S., DOICHINOVA I.,GRUEV K., BOYADZHIEVA M., LAZAROV S. (1982), *Use of magnesium refractory waste for production of magnesite sulfate* (Tsentr. Khim. Prom., Bulg.), Khim. Ind. Sofia.

MOORRES C. (1987), *Production of high grade magnesia by chemical processing routes*, Division of Mineral Chemistry CSIRO, Port Melbourne 3207 Australia, Sym. Sev. Austral. Inst. Min. Metall. Res., Dev. in Extractive Metallurgy.

PRAKASH S., and GUPTA K.N. (1982), *Commercial production of magnesium chemical from industrial waste dust and fines*, Natl. Metall. Lab. (CSIR Jamshedpur India) E. W. Chem. Eng. World, 22 (1), 39–41.

SHCHERBAKOV V.V., POLAKOV E.V., FAIRUSHIN L.KH., KAROV L.Ya.(1981), *Magnesium sulfate heptahydrate*, Chemical Plant. U.S.S.R. Patent 827, 395.

SOLOLOV L.D., KASHKAROVA O.D., SAFRYGIN Yu. S., MARAVEU A.V., ANDREEVA N.K. (1981), *Magnesium sulfate*, U.S. Patent 4, 264, 570.

XI Z., FOMING Z., SHENQING G. (1988), *Method for producing magnesium sulfate fertilizer from magnesite*, Shuomirgsha, CN 86, 105,794.

Abdel-Aal E.A., Ibrahim I.A., Rasha M.M., Ismail A.K., (1994), Hydrometalurgiczny przerób egipskiej rudy magnezytowej w celu otrzymania siarczanu magnezu, *Fizykochemiczne Problemy Mineralurgii*, 28, 165–175 (English text)

Przeprowadzono ługowania egipskiej rudy magnezytowej (43,32% MgO), wydobywanej na terenie Pustyni Wschodniej (Eastern Desert). Zastosowano roztwór kwasu siarkowego jako czynnik ługujący. Określono następujące, optymalne warunki prowadzenia procesu ługowania: uziarnienie rudy – poniżej 0.5 mm, temperatura 60 °C, czas ługowania – 40 min, stosunek molowy H_2SO_4 do MgO – 1,075, stosunek fazy stałej do ciekłej w pulpie – 1:4,5. Zastosowanie optymalnych warunków ługowania zapewnia 99% odzysku MgO. Roztwór po ługowaniu był następnie częściowo zobojętniany w celu usunięcia tlenków żelaza. Określono także optymalne parametry prowadzenia procesu oczyszczania roztworu. Po oczyszczeniu roztwór poddawano odparowaniu i krystalizacji siarczanu magnezu z wydajnością 99,5%. Zaproponowano schemat hydrometalurgicznego procesu przerobu rudy omawianą metodą.