Extraction of Magnesia from Egyptian Serpentine Ore via Reaction with Different Acids. I. Reaction with Sulfuric Acid

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The present study is concerned with the effectiveness of use of local Egyptian serpentine ore for production of magnesium sulfate. An investigation of the ore composition was carried out by means of X-ray diffractometry and chemical analysis. The reaction of sulfuric acid with the ore was studied at different leach parameters under laboratory conditions for the uncalcined and calcined ore. The dissolution rate constants of magnesia were determined by the analysis of the experimental data. The resultant activation energy of reaction between the acid and the studied ore was lower than the values reported previously. This result is discussed in terms of structural changes of serpentine during the calcination of ore which may affect its reactivity towards acids. The high yield of magnesia extraction from the ore emphasizes the possibility of exploitation of the ore in the preparation of sulfate salt with a lower price.

Although many studies have been carried out on the acid leaching of serpentine ore[1—3] there is no information in the literature about the exploitation of the Egyptian ore for the preparation of magnesium compounds. Such a situation leads to importation of these compounds and requires considerable foreign exchange expenses. Therefore the present investigation was carried out in the hope of providing useful guidance when considering the application of sulfuric acid for production of magnesium sulfate from local ore. A second paper will describe the important details for reactions of nitric and acetic acids with the ore at different conditions, with the goal of preparation of their corresponding salts.

Experimental

Serpentine Ore. The representative sample of the ore used in the present study was obtained from Parrameya location, eastern desert (Egypt). The provided quantity (ca. 50 kg) was sampled according to the usual method of sampling[4] and pulverized in a ball mill. The fraction containing particle sizes of 100—250 μm was collected by screening. This fraction was subjected to chemical analysis after drying at 110 °C for about 3 h. The chemical analysis of the serpentine sample:

Constituent:	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	L.O.I. (Loss on ignition)
Content (%):	39.89	4.96	4.09	2.33	36.28	12.08

Reagents: All the chemicals used were of analytical grade and obtained from Merck Chemicals Company, Darmstadt, Germany. The concentrated sulfuric acid was diluted to the desired concentration for use in the different kinetic measurements.

Preparation of Extract Solution: The pulp obtained by leaching the sample with sulfuric acid solution was filtered off and the leach residue was washed with distilled water. The common filtrate was concentrated to a standard volume (500 ml). Suitable aliquots were taken for quantitative determination of magnesium, calcium, aluminium, and iron by the methods described previously.[5]

Methods of Chemical Analysis. The contents of Al_2O_3, CaO, MgO, and SiO_2 in serpentine ore and in the leach solutions were determined according to the methods described previously.[5]

Effect of Roasting Temperature on Magnesia Extraction from the Ore. The suitable conditions for optimum extraction of magnesia, alumina, and iron oxide from roasted ore were determined by studying the effect of roasting time and temperature on the extent of extraction. Variable weights of the roasted and unroasted ore# were refluxed with 100 ml of 3 M H_2SO_4 (1 M=1 mol dm^{-3}) at boiling temperature, for different times, so as to maintain the molar ratio between the acid and magnesium oxide in the roasted ore at 3 : 1. The suspension of the reaction products was immediately filtered after the desired reaction time. The residue was washed thoroughly with distilled water several times. The combined filtrates were completed to 500 ml in a standard measuring flask. Suitable volumes of the filtrate were taken for determination of magnesia, alumina and iron oxide according the methods of analysis described previously.[5]

The fraction of MgO extracted (x) was calculated by dividing the weight of magnesia in the leach solution by the weight of magnesia in the quantity of roasted or unroasted ore used in the experiment. The same method of calculation was applied for the determination of the CaO, Fe_2O_3, and Al_2O_3.

Kinetic Measurements. A certain weight (2.4725 g) of the ore roasted at 800 °C for 2 h was refluxed with different volumes of 3 M sulfuric acid at 30, 50, and 75 °C. The molal ratios between hydrogen ions and magnesia in the ore were 4.73, 4.22, and 3.86. The reaction times varied between a few minutes and days according to molal ratios between reactants and reaction temperature.

Order, Rate and Thermodynamic Parameters of Reaction.

#The percentages of magnesia in serpentine ore roasted at different temperatures were determined according to the method described previously.[5]

The dissolution process was analyzed by the pseudo-first order kinetic equation where the rate of MgO dissolution (k_r) was determined from the following equation:[6)]

$$k_r = -(\text{slope})/C_H \tag{1}$$

The slopes of the straight lines were obtained from the plot of $\ln(1-x)$ against time (t) and calculated by using of the least square methods, Here C_H is the molal concentration of hydrogen ions. The values of activation energy (E_a), were calculated according to a method of calculation mentioned previously.[7)]

Results and Discussion

The X-ray diffraction patterns of serpentine ore (Fig. 1) under investigation clarify that it is composed of a complex mixture of different varieties of serpentine minerals of empirical formulae, $Mg_4(OH)_4(Si_4O_{10})\cdot 4H_2O$ or $Mg_3[Si_2O_5](OH)_4$, in addition to talc ($Mg_3Si_4O_{10}(OH)_2$). The presence of both Al_2O_3 and Fe_2O_3 in the ore with reasonable quantities gives an indication of the presence of significant substitutions of Si^{4+} by Al^{3+} and Mg^{2+} by Fe^{2+}, Fe^{3+} or Al^{3+}. This hypothesis was confirmed from the appearance of characteristic 'd' spacing of two varieties of aluminium serpentine: $Mg_{4.5}Al_{1.5}(Si_{2.5}Al_{1.5})O_{10}(OH)_8$ and $Mg_{4.25}Al_{1.75}(Si_{2.25}Al_{1.75})O_{10}(OH)_8$, and iron-substituted antigorite $(Mg, Fe)_3(Si_2O_5)(OH)_4$ (Fig. 1).

During leaching of the ore samples with the acid, the outer (MgOH) layers are stripped away and decomposition proceeds with production of sulfates of magnesium, aluminium, and iron in addition to amorphous silica as an in soluble residue. MgO leach efficiency was rather poor and amounts to 62.77% under the studied experimental conditions (Table 1).

The relatively low percentage of extraction of magnesium oxide from unroasted serpentine ore led us to determine the lowest temperature suitable for roasting the ore at which the maximum extraction of magnesia could be achieved. Such a result is likely to throw some light on the ore constituents and their transformation to other compounds by the roasting at different temperatures up to 1300 °C. The ore constituting minerals such as chrysotile, antigorite, aluminian-serpentine, and talc etc. are transformed to other compounds upon heating to relatively high temperatures (Fig. 1). The thermal decomposition of serpentine follows a two-stage sequence of dihydroxylation and breakdown. The mechanism of decomposition has been studied by a number of workers.[8—13)] The dehydroxylation takes place at 600—780 °C and at 800—850 °C, where the anhydride breaks down in a sharp transformation to forsterite and silica.

$$Mg_3[Si_2O_5][OH]_4 \xrightarrow{600-780\,^\circ C} Mg_3Si_2O_7\,(\mathbf{I}) + 2H_2O \tag{2}$$

$$\mathbf{I} \xrightarrow{800-850\,^\circ C} MgSi_2O_5 + 2MgO \tag{3}$$

$$2\cdot\mathbf{I} \xrightarrow{850-1000\,^\circ C} 3Mg_2SiO_4\,(\mathbf{II}) + SiO_2\,(\mathbf{III}) \tag{4}$$

The forsterite is well crystallized and persists together with the silica up to 1000 °C, but above this temperature some enstatite is formed.

Table 1. Effect of Time and Temperature of Roasting on the Extraction of MgO, Al_2O_3, and Fe_2O_3 from Variable Amounts of Unroasted and Roasted Ore with 100 ml of 3 M H_2SO_4 (Molar Ratio between the Acid and Magnesia in the Ore=3 : 1)

Temp	Time	MgO extracted /g		
°C	h	MgO	Al_2O_3	Fe_2O_3
30	-	2.49	0.097	0.076
550	1	3.052	0.1298	0.0775
550	2	3.036	0.1375	0.0775
550	3	3.056	0.1490	0.0775
600	1	3.161	0.1358	0.0775
600	2	3.157	0.1490	0.0775
600	3	3.294	0.1578	0.0775
700	1	3.366	0.1127	0.0884
700	2	3.351	0.1578	0.1297
700	3	3.362	0.1441	0.1075
800	1	3.376	0.1149	0.0952
800	2	3.387	0.1804	0.0712
800	3	3.383	0.1666	0.9160
900	1	3.264	0.0946	0.0775
900	2	3.236	0.0879	0.0680
900	3	3.246	0.0830	0.0725
1000	1	3.084	0.0879	0.0775
1000	2	3.077	0.0814	0.0753
1000	3	3.076	0.0814	0.0744

$$3\cdot\mathbf{II} + \mathbf{III} \xrightarrow{t>1000\,^\circ C} 2\cdot\mathbf{II} + Mg_2Si_2O_6 \tag{5}$$

By analogy, the thermal decomposition of the ore under investigation can be represented by the following equations:

$$Mg_{4.5}Al_{1.5}Si_{2.5}Al_{1.5}O_{10}(OH)_8 \xrightarrow{600-750\,^\circ C} Mg_{4.5}Al_{1.5}Si_{2.5}Al_{1.5}O_{14}\,(\mathbf{V}) + 4H_2O \tag{6}$$

$$(Mg, Fe)_3Si_2O_5(OH)_4 \xrightarrow{600-750\,^\circ C} (Mg, Fe)_3Si_2O_7\,(\mathbf{VI}) + 2H_2O \tag{7}$$

$$\mathbf{V} \xrightarrow{800-850\,^\circ C} 1.66(Mg_{0.5}Al_{0.5})Si_{1.5}Al_{0.5}O_5\,(\mathbf{VII}) + 3.67MgO + 0.67Al_2O_3 \tag{8}$$

$$\mathbf{VI} \xrightarrow{800-850\,^\circ C} (Mg_{0.5}, Fe_{0.5})_2Si_2O_5\,(\mathbf{VIII}) + 2MgO + Fe_2O_3 \tag{9}$$

$$\mathbf{V} \xrightarrow{850-1000\,^\circ C} 3(Mg_{1.5}, Al_{0.5})Si_{0.5}Al_{0.5}O_4\,(\mathbf{IX}) + \mathbf{III} \tag{10}$$

$$2\cdot\mathbf{VI} \xrightarrow{850-1000\,^\circ C} 3(Mg, Fe)_2SiO_4\,(\mathbf{X}) + \mathbf{III} \tag{11}$$

$$\mathbf{IX}+3\cdot\mathbf{III} \xrightarrow{t\geq 1000^\circ C} 3(Mg_{0.5}.Al_{0.5})Si_{0.5}Al_{0.5}O_3\,(\mathbf{XI})+3MgSiO_3\,(\mathbf{XII}) \tag{12}$$

$$3\cdot\mathbf{X}+\mathbf{III} \xrightarrow{t\geq 1000\,^\circ C} 2(Mg, Fe)_2SiO_4(\mathbf{X})+2(Mg, Fe)SiO_3(\mathbf{XIII}) \tag{13}$$

The presence of aluminium and/or iron substituted forsterite as well as enstatite was indicated from the shifts

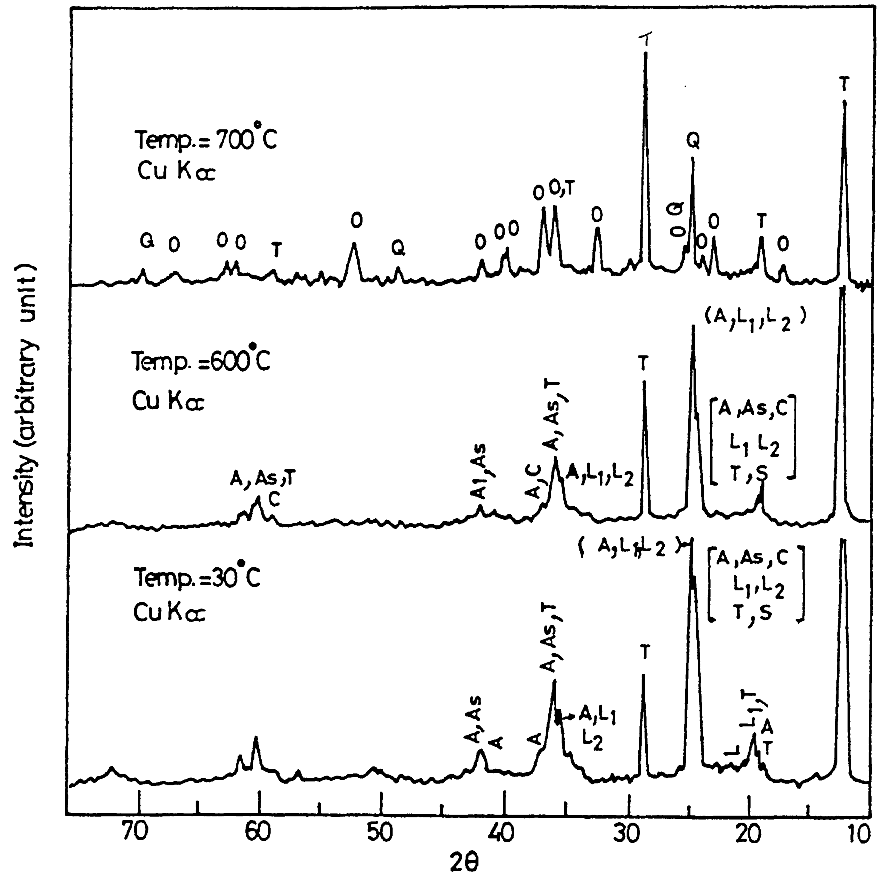

Fig. 1. X-Ray diffraction patterns of unroasted serpentine ore and ore roasted at 600 and 700 °C for 2 h (measured by using Cu *Kα* irradiation and nickel filter) Where A, A_s, C, S = Antigorite, Antigorite serpentine, Clinocrysotile, serpentine (6-layers ortho); L1, L2 = Aluminian serpentine = $Mg_{4.25}Al_{1.75}(Si_{2.25}Al_{1.75})O_{10}(OH)_8$, $Mg_{4.5}Al_{1.5}(Si_{2.5}Al_{1.5})O_{10}(OH)_8$; Tale (T) = $Mg_3Si_4O_{10}(OH)_2$; Olivine (o) = $(Mg,Fe)_2SiO_4$ and α-Quartz (Q) = SiO_2.

in their characteristic "*d*" spacing values[##] (Figs. 1 and 2). The formation of Al_2O_3 and Fe_2O_3 as suggested in Eqs. 8 and 9 was indicated from the presence of their characteristic 'd' spacing[##] of the samples heated at 1300 °C, where both oxides can be found in a well-crystallized form (Fig. 2).

On the basis of these findings, we discuss the factors which affect the values of extraction of magnesia, alumina and iron oxide from the ore by sulfuric acid. In general the values of their extraction (Table 1) increase with increasing roasting temperatures due to the dehydroxylation of the ore and formation of four-fold coordinated magnesium, aluminium, and iron, which are more susceptible towards acid attack than six-fold coordinated ions. The complete transformation of different magnesium hydroxide silicate species (serpentine ore) to aluminium and/or iron-substituted forsterite in addition to oxides of aluminium, magnesium and iron, is reached at 800 °C (Fig. 2). This transformation leads to an increase of the percentages of extraction of the different oxides mentioned before as soluble sulfates to maximal values by raising the roasting temperature to 800 °C. This phenomenon can be attributed to the reactivity of orthosilicates (Mg_2SiO_4) being relatively higher than that of sheet silicates such as serpentine ($Mg_3Si_2O_5(OH)_4$).[14)] At temperatures higher than 800 °C, forsterite is reacted with silica and transformed to less reactive enstatite, $MgSiO_3$ (chain silicate)[14)] which is accompanied by a decrease in magnesia extraction. At such elevated temperatures, some parts of aluminium and iron oxides may reunite with silica and/or magnesia, whereas the rest of both oxides transformed to more crystalline forms. These phenomena lead to a decrease in their values of extraction from decomposition products of serpentine at temperatures higher than 800 °C, as can be seen from Table 1 and Fig. 2. The incomplete extraction of magnesia from the ore at optimal conditions may be attributed to the presence of the talc as one of constituents of the ore. This hypothesis is based on the experimental results which clarified that the extraction of magnesium oxide from tale ore roasted at 800—000 °C did not exceed 11—18% efficiency.

On the basis of the results presented in Table 1, it can be seen that the optimal conditions for roasting of Parrameya serpentine ore were achieved by its calcination at 800 °C for 2 h. Therefore, the kinetic studies on the reaction between

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[##] The characteristic "*d*" spacing values of the minerals in the ore and thermal decomposition products were taken from their ASTM cards.

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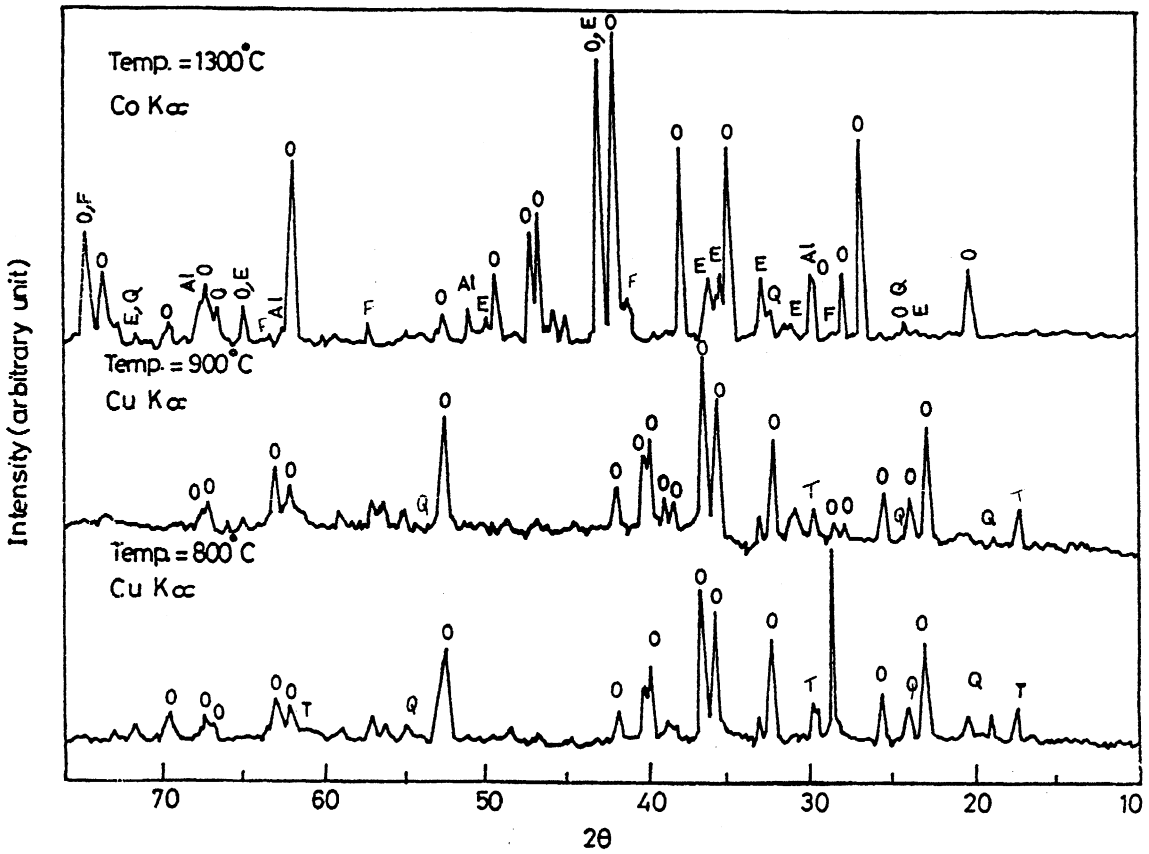

Fig. 2. X-Ray diffraction patterns of ore roasted at 800 and 900 °C for 2 h (measured by using Cu *Kα* irradiation and nickel filter) and at 1300 °C for 24 h (measured by using Co *Kα* irradiation and iron filter) where Al, F, Q, E, O, and T=α-Al_2O_3;Fe_2O_3;α-Quartz (SiO_2); Enstatite, (Mg, $Fe)_2SiO_3$; Olivine, (Mg, $Fe)_2SiO_4$, and Talc, $Mg_3Si_4O_{10}(OH)_2$, respectively.

sulfuric acid and the ore were carried out on the ore roasted at the experimental conditions mentioned before.

Kinetics of Reaction between Sulfuric Acid and the Ore. The leach efficiency of magnesia from calcined serpentine ore with sulfuric acid increased by increasing of temperature, duration time of reaction, and molal ratios between the reactants, as can be seen from Figs. 3 and 4, which were taken as representative examples. The results of extraction of magnesia from the ore indicated that the reaction rate equations based on the concept of first order equations against MgO content in the sample are mathematically appropriate for expressing and correlating the experimental results. The rates of reactions were measured by the methods described previously.[5,6] As can be seen from Fig. 5 the plots of ln $(1-x)$ vs. time are precisely linear for $x \leq 20\%$ of the reaction efficiency with sulfuric acid at working temperatures (30, 50, and 75 °C). The reaction was found to be pseudo-first-order overall, with respect to magnesium oxide content in the calcined serpentine ore. The rate constants (k_r) were calculated from the slopes of the least squares first order fits as represented in Fig. 5. The computed values of activation energies presented in Table 2, which amount to 8.52 kcal mol^{-1}, were less than reported ones,[1,3,12] which amounted to 12, 17, and 16 kcal mol^{-1}.[1,3,15] This result may be attributed to the difference between the structure of serpentine ore under investigation and that of the serpentine ore studied by other inves-

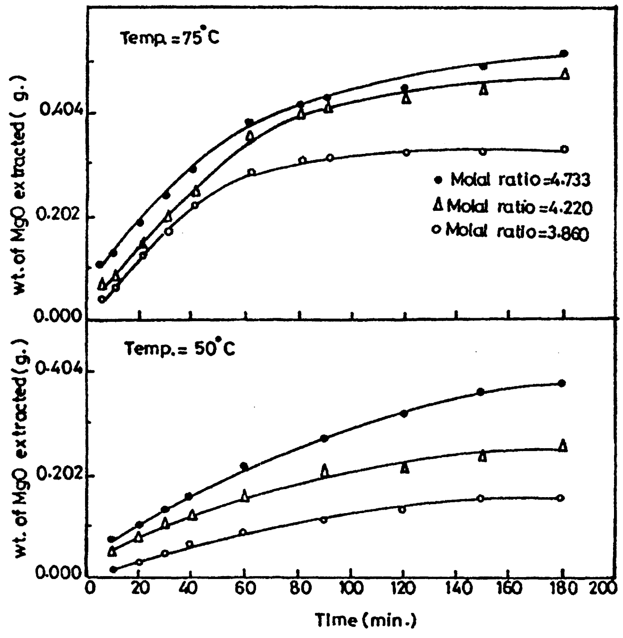

Fig. 3. Effect of molal ratio between sulfuric acid and magnesia in the roasted serpentine ore on the extant of release of magnesia from the ore after different duration times of the leaching at 75 and 50 °C.

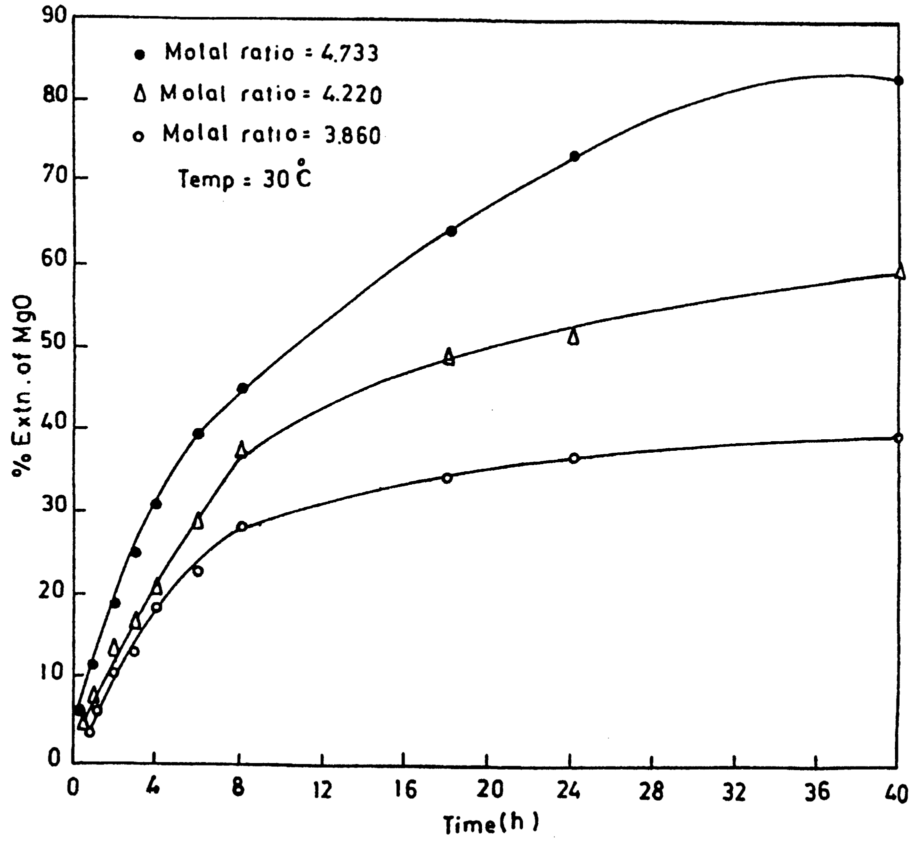

Fig. 4. Effect of molal ratio between sulfuric acid and magnesia in the roasted serpentine ore on the extant of release of magnesia from the ore after different duration times of the leaching at 30 °C.

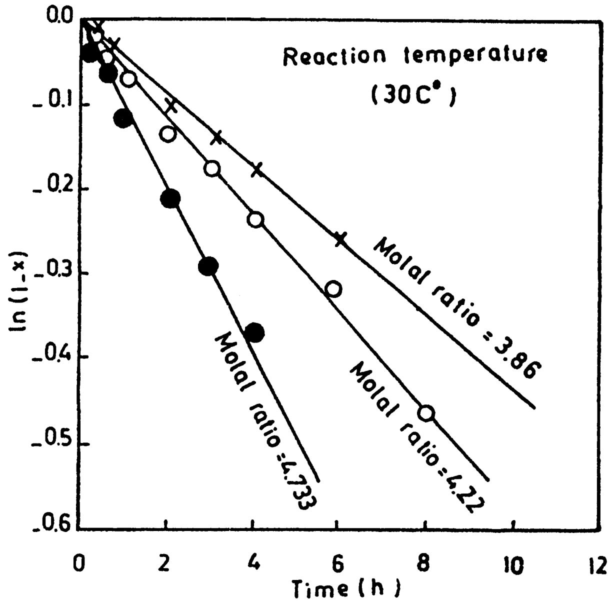

Fig. 5. Pseudo-first order plots for the reaction between sulfuric acid and magnesia in the roasted serpentine ore with different molal ratios at 30 °C. ×: molal ratio of H^+/MgO= 3.86. ○: molal ratio of H^+/MgO=4.22. ●: molal ratio of H^+/MgO=4.73.

Table 2. The Values of Rate Constants, Resultant Activation Energy (E_a), and Entropy of Activation (ΔS^*) of the Interaction between Sulfuric Acid and Roasted Serpentine Ore

Temp	Molal ratio	$k_r \times 10^2$	E_a	ΔS^*
K	(acid:ore)	$\mathrm{g\,mol\,h^{-1}}$	$\mathrm{kcal\,mol^{-1}}$	$\mathrm{cal\,mol^{-1}\,K^{-1}}$
378	4.73	10.75	8.25	43.60
378	4.22	10.46	8.38	43.30
378	3.86	9.78	8.95	41.94
348	4.73	8.26	8.25	42.10
348	4.22	4.65	8.38	42.85
348	3.86	3.60	8.95	41.72
323	4.73	2.33	8.25	42.63
323	4.22	1.54	8.38	42.95
323	3.86	1.08	8.95	41.97
303	4.43	0.79	8.25	42.98
303	4.22	0.65	8.38	42.95
303	3.86	0.59	8.95	41.22

Mean value of $\Delta S^* = -42.52\ \mathrm{cal\,mol^{-1}\,K^{-1}}$. Mean value of $E_a = 8.52\ \mathrm{kcal\,mol^{-1}}$.

tigators. The presence of significant quantities of aluminian serpentine such as $Mg_{4.5}Al_{1.5}Si_{2.5}Al_{1.5}O_{10}(OH)_8$, and iron substituted serpentine, such as $(Mg, Fe)_3Si_2O_5(OH)_4$, led to an increase in the susceptibility towards acid attack, due to the weakening in the three dimensional silicate network.[16] In other words, the fraction of tetrahedral sites occupied by aluminium increase the possibility of decomposition of framework silicates. Generally speaking, the bonds between aluminium, iron, and oxygen are weaker than those between silicon and oxygen and thus show more susceptibility towards acid attack as is the case of the serpentine ore under investigation.[17,18] The value of the activation energy, F_a, is considered as an important parameter for determining the mechanism of heterogeneous reactions. According to Glasstone et al.,[19] transport-controlled reactions have activation energies ranging from 1.9 to 6 kcal mol^{-1}, whereas that characteristic for a chemical process is considerably higher. It therefore, follows from the E_a value that the rate of dissolution of magnesia in sulfuric acid solutions was controlled by a chemical reaction on the surface of the particle.

Leaching of Al_2O_3, Fe_2O_3, and CaO. The extent of leaching of different oxides by sulfuric acid increase with increasing duration time of reaction and molal ratios between reactants at different temperatures. The highest percentages of leaching amount to ca. 8.0 and ca. 12% for aluminium oxide and iron oxide respectively. The resultant iron and aluminium sulfates produced as a result of reaction between the acid and the roasted ore are stable in acidic solution, whereas both salts are transformed to sparingly soluble basic sulfates or insoluble hydroxides by increasing of pH to ca. 3.0 and 5.0 respectively. Therefore the highest percentages of leaching of aluminium and iron from the ore were achieved in cases where an excess of unreacted acid was present in the reaction products.

The extent of leaching of CaO depends primarily on the solubility product of sparingly soluble calcium sulfate, which in turn depends on both pH of extraction solution and quantities of sulfates of aluminium, iron, and magnesium sulfate dissolved in it. The range of its leaching varied between 1.4—9.6% of the amount of CaO found in the ore.

The high yield of extraction of magnesia which amounted to ca. 94% from the ore which was roasted at a relatively, not high, temperature (800 °C) for a short time (3 h), makes it possible to utilize the ore in preparation of magnesium sulfate with a conpetitive price in comparison with the cost of its preparation from domestic dolomite or magnesitic dolomite, which have relatively lower percentages of magnesia (<36%) and need to be roasted before preparation of the salt. The removal of aluminium and iron from the sulfate solution resulted from the interaction of the ore with the acid, industrially useful compounds improve the economics of the process. The descriptive methods of purification of the magnesium sulfate to remove significant quantities of undersirable ions such as aluminium, iron, and calcium in the extract solution will be published later in the form of a patent.

Conclusions. 1. The roasting temperature of the ore has a significant effect on the percentage of magnesia extracted from the ore by sulfuric acid.

2. The resultant apparent activation energy for the extraction of magnesia from the ore by the acid which amounts to 8.52 kcal mol^{-1} indicates that the chemically-controlled processes on the surface of the particle are the rate limiting step.

3. The high yield of extraction of magnesia, which is higher than 90% for the optimal parameters of the process, emphasizes the possibility of exploitation of the ore in the preparation of magnesium sulfate with a competitive price.

4. The presence of significant quantities of undesirable ions such as aluminium, iron and calcium in the extract solutions must be taken into consideration during the preparation of pure magnesium sulfate from serpentine ore, according to the methods which will be published later in form of patent.

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