# Extraction of Magnesia from Egyptian Serpentine Ore via Reaction with Different Acids. II. Reaction with Nitric and Acetic Acids

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The results of a kinetic study of the dissolution of magnesia from Egyptian serpentine ore with nitric and acetic acids are presented. The effects on the magnesia dissolution of (a) temperature ranging from 30 to 105 °C, (b) time ranging from 2.5 min to several days, and (c) molal ratios between one of the acids and MgO in the ore ranging from 4.42 to 3.86, are presented. From the analysis of the dissolution rate on the basis of a core model, it was found that dissolution rate of MgO could be well expressed by a rate equation based on the rate-limiting step of the surface chemical reaction. The apparent activation energies were ca. 17.4 and 8.3 kcal $\mathrm{mol}^{-1}$ for nitric and acetic acid respectively.

The high activation energy of reaction with nitric acid was found to be associated with relatively higher values of activation entropy ($\Delta S^* = -19.5$ cal $\mathrm{mol}^{-1}$ $\mathrm{K}^{-1}$), whereas the relatively low activation energy of reaction with acetic acid is associated with negative values of entropy of activation ($\Delta S^* = -44.3$ cal $\mathrm{mol}^{-1}$ $\mathrm{K}^{-1}$). The values of the latter parameter indicated that their values are related to the complexing affinity of magnesium cation towards acid anion. Thus, the values of entropy of activation are the predominant factor for the reaction between the ore and studied acids.

In the present article we investigate the kinetics of reactions between roasted serpentine ore and both nitric and acetic acids at different temperatures. This is a continuation of the previous study on the reaction of the same ore with sulfuric acid.[1)]

The previous investigation by means of X-ray diffractometry and chemical analysis clarified that the ore is composed of a complex mixture of talc and different varieties of serpentine minerals.[1)] The suggested formulae of these minerals are $\mathrm{Mg_4(OH)_4(Si_4O_{10})\cdot 4H_2O}$, $\mathrm{Mg_3(OH)_4(Si_2O_5)}$, $\mathrm{Mg_{4.5}Al_{1.5}(Si_{2.5}Al_{1.5})O_{10}(OH)_8}$, $\mathrm{Mg_{4.25}Al_{1.75}(Si_{2.25}Al_{1.75})O_{10}(OH)_8}$, and $\mathrm{(Mg,Fe)_3Si_2O_5(OH)_4}$. It was found that the percentage of extraction of magnesium oxide from unroasted serpentine ore by sulfuric acid amounted to ca. 62.9, it was increased to ca. 94 as a result of roasting of the ore at 800 °C for 2 h. We suggested that the roasted ore is transformed to a mixture of $\mathrm{Mg_2SiO_4}$, $\mathrm{Mg_{1.5}Al_{0.5}O_4}$, $\mathrm{(Mg,Fe)_2SiO_4}$, MgO, $\mathrm{Fe_2O_3}$, and $\mathrm{SiO_2}$. The last mentioned compounds are more relative towards acid attack than serpentine ore.[2)] The increase in temperature of roasting of the ore leads to transformation of orthosilicates to $\mathrm{MgSiO_3}$ and $\mathrm{Mg_{0.5}Al_{0.5}Si_{0.5}Al_{0.5}O_3}$, which are less reactive towards acid attack than forsterite from one side but still more reactive than serpentine ore from the other side.[2)]

The aim of this study is to define optimum conditions which might be used in the production of acetate and nitrate of magnesium which would find wide industrial applications.[3)]

## Experimental

**Serpentine Ore.** The ore used in the present investigation is the same ore which was used in the previous work.[1)]

**Preparation of Extract Solutions.** The methods of preparation of the extract solutions which contained the soluble reactions products were described previously.[1,4)]

**Methods Of Chemical Analysis.** The methods of determination of $\mathrm{MgO, Al_2O_3, Fe_2O_3}$, and CaO in the different extract solutions were mentioned previously.[4)]

**Kinetic Measurements.** The techniques of kinetic measurements, methods of analysis and calculation, and meaning of symbols are the same as those applied to the reaction between sulfuric acid and serpentine ore.[4)]

**Chemicals.** All the chemicals used throughout the work were of analytical grade and were obtained from Merck Chemicals Company, Darmstadt, Germany. The concentrated nitric acid and glacial acetic acid were diluted to the desired concentrations for use in the different kinetic measurements.

## Results and Discussion

The effect to temperature and acid concentration on the kinetics of magnesia removal from serpentine ore is shown in Figs. 1 and 2. These were taken as representative examples for nitric and acetic acids. The percentage of magnesia released from roasted ore with different acids increases with increasing reaction time and with molal ratios between the reactants as can be seen from Figs. 1 and 2. The straight lines obtained by plotting $\ln(1-x)$ vs. time ($t$) of reaction are presented in Figs. 3 and 4, where $x$ is the fraction of magnesium oxide leached by the acid, it is calculated by dividing the weight of magnesia in the extract solution by the weight of magnesia in the quantity of roasted ore used in the experiments. The reaction was found to be pseudo-

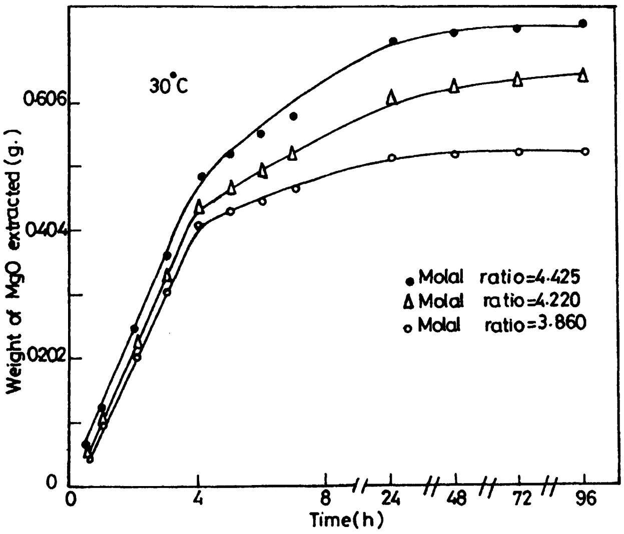

Fig. 1. Effect of molal ratio between nitric acid and magnesia in the roasted serpentine ore on the extent of release of magnesia after different duration times of the leaching at 30 °C.

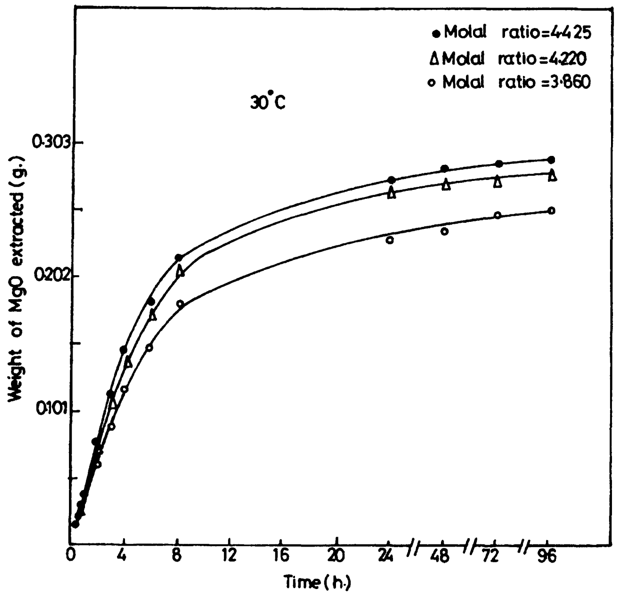

Fig. 2. Effect of molal ratio between acetic acid and magnesia in the roasted serpentine ore on the extent of release of magnesia after different duration times of the leaching at 30 °C.

first order overall for $x \leq 30\%$, with respect to the magnesia in serpentine ore. The rate constants $k_r$ were evaluated from the slopes of the least squares first order fits, as represented in Figs. 3 and 4, where they were determined according to the rate equation[5] which was expressed as $k_r = (-\text{slope}/C_H)$. The different reaction equations of the dissolution of reaction products from serpentine ore roasted at 800 °C by solutions of different acids (HL) may be expressed as follows:

$$\mathrm{Mg_{1.5}Al_{0.5}Si_{0.5}Al_{0.5}O_4 + 6HL \rightarrow 1.5MgL_2 + AlL_3 + 0.5SiO_2 + 3H_2O} \qquad (1)$$

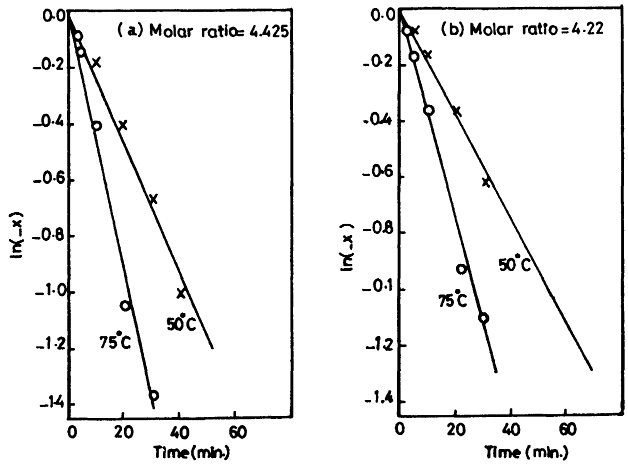

Fig. 3. Pseudo-first order plots for the reaction between nitric acid and magnesia in the roasted serpentine ore with different molal ratios at 50 and 75 °C. (a) molal ratio of $H^+/MgO = 4.425$. (b) molal ratio of $H^+/MgO = 4.22$.

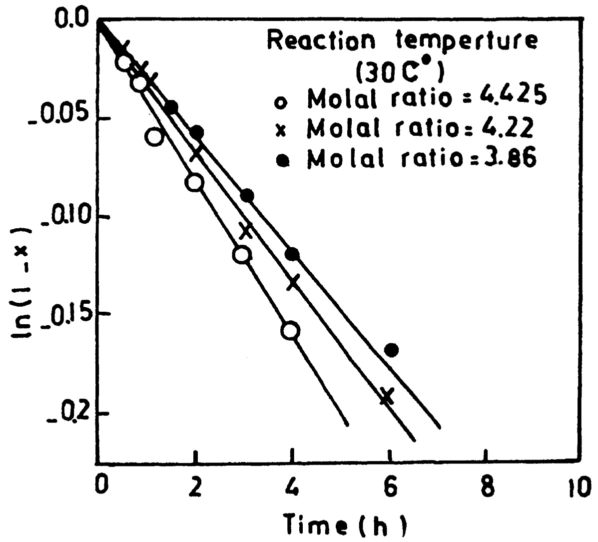

Fig. 4. Pseudo-first order plots of the reaction between acetic acid and magnesia in the roasted serpentine ore with different molal ratios at 30 °C. ○-molal ratio of $H^+/MgO = 4.425$. ×-molal ratio of $H^+/MgO = 4.22$. ●-molal ratio of $H^+/MgO = 3.86$.

$$\mathrm{(Mg,Fe)_2SiO_4 + 4HL \rightarrow 2(Mg,Fe)L_2 + SiO_2 + 2H_2O} \qquad (2)$$

$$\mathrm{Mg_2SiO_4 + 4HL \rightarrow 2MgL_2 + SiO_2 + 2H_2O} \qquad (3)$$

The dissolution reaction of the ore roasted at 1000 °C may be represented according to the following equations:

$$\mathrm{Mg_{0.5}Al_{0.5}Si_{0.5}Al_{0.5}O_3 + 4HL \rightarrow 0.5MgL_2 + AlL_3 + 0.5SiO_2 + 2H_2O} \qquad (4)$$

$$\mathrm{(Mg,Fe)SiO_3 + 2HL \rightarrow (Mg,Fe)L_2 + SiO_2 + H_2O} \qquad (5)$$

(L denotes for $NO_3^-$ or $CH_3COO^-$)

These suggestions were discussed previously in the light of structural changes of serpentine composition at different temperatures; such changes affect its reactivity towards different acids.

The leaching of serpentine ore in different acid solutions, a heterogeneous reaction, was found to follow the shrinkage core model.[6)] This model assumes that the reaction rate is controlled by one of the following three steps: diffusion of acid through a film surrounding the particle, chemical reaction on the surface of particle, and diffusion of the products back through the film. The fact that the degree of stirring of reaction mixture did not affect the dissolution rate, eliminated the need to consider the diffusion steps as the rate-limiting ones. Moreover, the dissolution rates were not zero order. Thus, the dissolution rate was most likely to be controlled by surface chemical reaction. From the values presented in Tables 1 and 2, it can be concluded that the values of rate constants for the reaction between the ore and nitric acid are higher than those for the reaction with acetic acid, although the value of energy of activation of reaction with the former acid (17.4 kcal mol$^{-1}$) are higher than that calculated for the reaction with the latter acid (8.32 kcal mol$^{-1}$) (Tables 1 and 2). This phenomenon may be attributed to the value of entropy of activation in case of nitric acid ($\Delta S^* = -19.47$ cal mol$^{-1}$ K$^{-1}$) being higher than that in case of acetic acid ($\Delta S^* = -44.3$ cal mol$^{-1}$ K$^{-1}$). This difference means that the degree of solvation of the intermediate activated complex in the case of the former acid is lower than that with the latter acid. On the basis of the foregoing discussions we postulate that the first step in the reaction is the hydroxylation of the surface of silicate, followed by protonation and anion adsorption as fast steps, whereas the desorption of metal cation–acid anion complex is considered as the latest and rate-determining step. The same mechanism was postulated by Warren and Devuyst[7,8)] for the acid dissolution of different oxides and can be represented by the following steps:

Step I (surface hydroxylation)

$$\overset{|}{\mathrm{s}}\text{–MgO} + H_2O \overset{\text{fast}}{\rightleftharpoons} \overset{|}{\mathrm{s}}\text{–Mg(OH)}_2 \qquad (6)$$

Table 1. The Values of Rate Constants, Resultant Activation Energy ($E_a$) and Entropy of Activation ($\Delta S^*$) of the Interaction between Nitric Acid and Roasted Serpentine Ore

| Temp | Molal ratio | $k_r \times 10^2$ | $E_a$ | $\Delta S^*$ |
|---|---|---|---|---|
| K | acid : ore | g mol s$^{-1}$ | kcal mol$^{-1}$ | cal mol$^{-1}$ K$^{-1}$ |
| 348 | 4.43 | 2.98 | 16.96 | -20.34 |
| 348 | 4.22 | 2.74 | 17.69 | -19.46 |
| 348 | 3.86 | 2.47 | 17.59 | -21.61 |
| 323 | 4.43 | 1.68 | 16.96 | -17.92 |
| 323 | 4.22 | 1.65 | 17.69 | -16.92 |
| 323 | 3.86 | 1.50 | 17.59 | -19.19 |
| 303 | 4.43 | 0.16 | 16.96 | -19.38 |
| 303 | 4.22 | 0.11 | 17.69 | -19.09 |
| 303 | 3.86 | 0.11 | 17.59 | -21.28 |

Mean value of $\Delta S^* = -19.47$ cal mol$^{-1}$ K$^{-1}$, Mean value of $E_a = 17.4$ kcal mol$^{-1}$.

Table 2. The Values of Rate Constants, Resultant Activation Energy ($E_a$) and Entropy of Activations ($\Delta S^*$) of the Interaction between Acetic Acid and Roasted Serpentine Ore

| Temp | Molal ratio | $k_r \times 10$ | $E_a$ | $\Delta S^*$ |
|---|---|---|---|---|
| K | acid : ore | g mol s$^{-1}$ | kcal mol$^{-1}$ | cal mol$^{-1}$ K$^{-1}$ |
| 378 | 4.43 | 6.85 | 8.39 | -44.1 |
| 378 | 4.22 | 6.14 | 8.27 | -44.6 |
| 378 | 3.86 | 4.46 | 8.35 | -45.1 |
| 348 | 4.43 | 2.58 | 8.39 | -44.0 |
| 348 | 4.22 | 2.16 | 8.27 | -44.7 |
| 348 | 3.86 | 1.64 | 8.35 | -45.0 |
| 323 | 4.43 | 1.76 | 8.39 | -42.7 |
| 323 | 4.22 | 1.67 | 8.27 | -43.2 |
| 303 | 4.43 | 0.35 | 8.39 | -44.1 |
| 303 | 4.22 | 0.33 | 8.27 | -44.6 |
| 303 | 3.86 | 0.23 | 8.35 | -44.7 |

Mean value of $\Delta S^* = -44.30$ cal mol$^{-1}$ K$^{-1}$, Mean value of $E_a = 8.30$ kcal mol$^{-1}$.

Step II (surface protonation)

$$\overset{|}{\mathrm{s}}\text{–}\mathrm{Mg(OH)_2} + 2\mathrm{H_3O^+} \overset{\text{fast}}{\rightleftharpoons} \overset{|}{\mathrm{s}}\text{–}\mathrm{Mg(OH_2{}^+)_2} + 2\mathrm{H_2O} \qquad (7)$$

Step III (anion adsorption)

$$\overset{|}{\mathrm{s}}\text{–}\mathrm{Mg(OH_2{}^+)_2} + 2\mathrm{L^-} \overset{\text{fast}}{\rightleftharpoons} \overset{|}{\mathrm{s}}\text{–}\mathrm{Mg(OH_2L)_2} \qquad (8)$$

Step IV (desorption)

$$\overset{|}{\mathrm{s}}\text{–}\mathrm{Mg(OH_2L)_2} \xrightarrow{k_r} \overset{|}{\mathrm{s}} + \mathrm{Mg(OH_2L)_2}\ (\mathrm{aq}) \qquad (9)$$

( L denotes 1/2 $SO_4{}^{-2}$, $CH_3COO^-$, $NO_3{}^-$ anions)

Steps I—III are considered to be fast and to have reached equilibrium, while the desorption Step IV is considered as a rate-determining step.

Hence it was observed that the values of rate constants depend on the complexing affinity of the acid anions towards the magnesium cation[9—13] and the degree of solvation of transition state activated complex in the reaction media. So the observed rate constants increase in the following order: acetic < sulfuric < nitric.

**Leaching of $Al_2O_3$, $Fe_2O_3$, and CaO.** The extent of leaching of the three oxides from the ore by different acids increases with increasing temperature, time and molal ratios between reactants. The highest percentages of leaching of aluminium oxide, iron oxide and calcium oxide amount to ca. 27, 35, and 45% respectively by nitric acid, whereas they amount to ca. 27 and 15% in case of leaching with acetic acid.

The observed high values of extraction of the three oxides by both acids with respect to sulfuric acid[1] may be attributed to the relatively higher solubility of acetates and nitrates over that of sulfates in the reaction media. So that the removal of such salts from the produced magnesium salts must be taken into consideration in the case of preparation of highly pure magnesium compounds. How to remove such contaminations will be published later in the form of a patent.

**Conclusions.** From the experimental conditions employed and results obtained in this investigation, we conclude that:

1- The results of leaching of magnesia from the ore by nitric and acetic acids clarified that the first order rate equations are appropriate for expressing and correlating the experimental results.

2- The relatively high values of energy of activation of magnesia depletion from the ore, which amount to 17.4 and 8.3 kcal mol$^{-1}$, indicate that the reaction does not proceed via a diffusion process, but proceeds via chemically-controlled processes on the surfaces of particles of ore.

3- The reasonably high yield of extraction of magnesia from roasted ore indicates that the ore can be exploited in preparation of magnesium nitrate and magnesium acetate with a low price, provided that the removal of impurities of aluminium, iron, and calcium is taken into consideration.

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