Hydrometallurgical processing of serpentine ore

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Abstract. Serpentine ore from the Eastern Desert of Egypt was leached with aqueous hydrochloric acid. Experimental statistical design program (ESD) was applied to study the influence of different variables on leaching efficiency (reaction temperature, leaching time and Hydrochloric acid (HCl) to Magnesium oxide (MgO) molar ratio (stoichiometry) where the liquid/solid ratio of 5:1 ml/g was maintained constant along the experiments. The mathematical model and the different contours (curves generated from ESD) were discussed. The results showed that, all the studied parameters are effective. The results have been collected at a 3-D cube showed that at high levels of parameters (4 hrs , 95 ºC and 1.6 S), the Magnesium oxide recovery was about 96.5%, while Magnesium oxide recovery was 67.1% at the low levels (2 hrs, 65 ºC and 1.4 Stoichiometry (S).

1. Introduction
Serpentine, [Mg₃Si₂O₅(OH)₄], a hydrated magnesium silicate, is abundant mineral all over the world. Egypt has serpentine resources. The serpentine sample in this study is characterized by high contents of magnesium and silica (36.8% SiO₂) as well as low calcium and aluminum contents. Moreover, important quantities of nickel (0.4 % NiO) and chromium (0.4 % Cr₂O₃) are also present in the ore.

This mineral has been utilized in various applications, such as fertilizer production, soil amelioration, extraction of amorphous silicate, carbon sequestration, extraction of pure magnesium compounds and silica production, refractories [1-9]. Magnesium metal has wide range of applications in our life. It is manufactured by electrolysis of molten anhydrous magnesium chloride [10, 11]. So, production of magnesium chloride salts and other magnesium compounds from serpentine have great interest due to various applications in different industries. Magnesium has high chemical reactivity and always present as compounds in nature e.g. minerals and salts [12].

Production of magnesium compounds depends mainly on extraction of magnesium minerals using different mineral acids from serpentine or other ores such as magnesite [13-17] and dolomite [18]. Serpentine ore is widespread all over the world. Serpentine minerals include three minerals namely chrysotile, lizardite, and antigorite, all of which have similar compositions based on the presence of the main nucleus Mg₃Si₂O₅(OH)₄, and differ slightly in the degree of substitution of Mg by Fe and Al [19].

The main commercially occurrences of serpentine ores in the world are in Canada, U.S.S.R and Africa [20]. In addition, serpentine ores are widely spread at different regions in Egypt, namely, in the Eastern Desert (Barrameya, along the Quift-Quseir road, Wadi Gabel El-Rubshi) [21-23].
2. Experimental

2.1. Raw materials and apparatus
A sample of serpentine ore from the Eastern Desert (Egypt) and 36% pure hydrochloric acid were used. The reaction was performed in a 500 ml round bottom flask fixed in water bath that adjusted to the required temperature. Reaction mixture was agitated at a rate of 500 rpm. and then filtered under vacuum in a Buchner-type filter using polypropylene filter cloth of 200 mesh aperture size.

2.2. Characterization
Powdered samples (100 % -200 mesh) was analyzed using X-ray powder diffraction (XRD), Bruker AXS diffractometer (D8-ADVANCE) with Cu Kα radiation, operating at 40 kV and 10 mA. The diffraction data were recorded for 20 values between 4° and 70° and the scanning rate was 0.5° min⁻¹. Types of the phases in the samples were identified using the X-ray powder data file, published by the American Standard for Testing Material (ASTM). Scanning Electron Microscope, JEOL instrument (Japan) model JSM-5410 was used for sample imaging.

Philips X-ray fluorescence (XRF) Spectrometer was applied for determining the chemical composition of the ore.

2.3. Procedure
Calculated amount of serpentine was added gradually into agitated hydrochloric acid solution in the reaction flask. After the desired reaction time, slurry was filtered and washed with warm water from silica and other insoluble materials. The filtrate was analyzed for MgO and CaO contents and then evaporated. Resultant crystals were analyzed for total MgO content. The residue was washed two times with warm water.

An experimental Box–Behnken design was used to study the interaction of the following variables (leaching time, reaction temperature and HCl:MgO stoichiometry) that affects the leaching of serpentine ore.

The applied variables are: reaction time in hours (2, 3, 4), reaction temperature, °C (65, 80, 95) and stoichiometry (1.4, 1.5, 1.6).

The filtration fundamentals are obtained by applying Darcy's equation. The filtration characteristics of magnesium chloride solution from un dissolved silica and other components are expressed by the filtration rate, the specific cake resistance and the specific filtering medium resistance. High efficiency of the filtration operation is achieved when the filtration rate is maximum whereas cake resistance and filtering medium resistance are minimum. The basis of the filtration study is the correlation derived from Darcy’s equation which is given as follows:

\[
\frac{dV}{d\theta} = \frac{G_e \Delta P A^2}{\mu \alpha \omega \cdot V + V_e} \quad (1)
\]

where:
V - Volume of filtrate at the time used, cm³
\( \theta \) - Filtration time, sec
\( V_e \) - Equivalent volume of filtering medium which is defined as the volume of filtration corresponding to fictitious weight of cake that causes resistance equal to the effective filter medium resistance.
Specific Cake Resistance (\( \alpha \)), cm/g
Equivalent Volume of Filtering Medium (\( V_e \)), cm³
Pressure difference in g/cm² (\( \Delta P \) cm Hg x 2.54 x13.32)
Viscosity of Filtrate at 90 °C (\( \mu \)), Poise
Weight of Solids per Unit Volume of Slurry \((\omega)\), g/cm\(^3\)
Gravitational constant \((G_c)\)

The reciprocal of the above equation gives:

\[
\frac{d\theta}{dV} = \frac{\alpha \mu \omega}{A^2 \Delta P G_c} (V + \omega)
\]  
(2)

Which represents an equation of a straight line when \(\Delta \theta / \Delta V\) is plotted against \(V\). The calculations of the filtration data comprise the following:

Experimental data of \(V\) and \(\theta\),
Viscosity, calculated from the rate of flow of the filtrate compared with that of water at the same temperature (poise),
Pressure difference in g/cm\(^2\) (\(\Delta P\) inch Hg \times 2.54 \times 13.32),

Plotting \(V\) against \(\Delta \theta / \Delta V\) and calculated the slope (sec/cm\(^3\)),

Specific cake resistance, \(\alpha\) from the conversion:

\[
\alpha = \text{slope} \times A^2 \times G_c \times \frac{\Delta P}{\mu} \times \frac{1}{W} \times \frac{1}{\Delta \theta} \text{cm/g}
\]  
(3)

Equivalent volume of filtering medium, \(V_e\):

\[
V_e = \frac{\text{interceptor}_\text{slope}}{\text{poise}} \text{ cm}^3
\]

Filtering medium resistance, \(R\) from the conversion:

\[
R = \frac{\alpha W}{A} \times V_e \text{ cm}^{-1}
\]  
(4)

Filtration rate at \(V = \alpha \text{ cm}^3\) \(\frac{dV_e}{d\theta}\) from the conversion:

\[
\frac{dV_e}{d\theta} = \frac{G_c \Delta P A^2}{\mu \alpha W} \times \frac{1}{\alpha + \frac{V_e A}{\omega}} \text{ cm}^3/\text{sec}
\]  
(5)

The following filtration conditions were applied:
Type of filter: Laboratory Buchner Type Funnel
Diameter of filter: 9.5 cm
Filter area: 70.9 cm\(^2\)
Pressure difference: 550 mm .Hg
Type of filter cloth: Single layer polypropylene
Temperature of slurry: 90 °C
Density of slurry: 1.2 g/ml

For calculating the filtration rate, the slurry is poured in the Buchner Funnel while suction is applied and the rate is determined from the volume accumulating in the receiver in the time required to all the liquid to be sucked and the surface of cake becomes dry.
3. Results and discussion

3.1. Characterisation of the ore

Mineralogical composition

As stated earlier this was accomplished using XRD. Figure 1 shows the pattern obtained. It shows that the major mineral is antigorite \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\).

![X-ray diffraction pattern](image)

**Figure 1.** XRD patterns of serpentine ore (*Antigorite).

Chemical composition

As subjected to XRF analysis, the chemical composition of the ore was shown in Table 1. The serpentine sample in this study is characterized by high contents of Magnesium (35.8 % \(\text{MgO}\)) and Silica (36.8% \(\text{SiO}_2\)), low calcium content (3.8 %) and low aluminum content (0.4 % \(\text{Al}_2\text{O}_3\)). Moreover, an important quantity of nickel (0.4 % \(\text{NiO}\)) and chromium (0.4 % \(\text{Cr}_2\text{O}_3\)) is also present in Egyptian serpentine ore.

**Table 1.** Chemical composition of serpentine ore.

| Component | Concentration, % | Component | Concentration, % |
|-----------|------------------|-----------|------------------|
| \(\text{SiO}_2\) | 36.80 | \(\text{ZnO}\) | 0.091 |
| \(\text{MgO}\) | 35.80 | \(\text{SO}_3\) | 0.031 |
| \(\text{Fe}_2\text{O}_3\) | 7.64 | \(\text{Co}_3\text{O}_4\) | 0.026 |
| \(\text{CaO}\) | 3.81 | \(\text{SrO}\) | 0.015 |
| \(\text{NiO}\) | 0.441 | \(\text{P}_2\text{O}_5\) | 0.008 |
| \(\text{Al}_2\text{O}_3\) | 0.381 | \(\text{CuO}\) | 0.007 |
| \(\text{Cr}_2\text{O}_3\) | 0.361 | \(\text{LOI}*\) | 14.40 |
| \(\text{MnO}\) | 0.163 | | |

\(\text{LOI}^*: \text{Loss on Ignition at 1000 °C}\).
3.2. Statistical experimental design

An experimental Box–Behnken design [24] was used to study the effect of some variables (reaction time, reaction temperature and stoichiometry) on the leaching of serpentine ore (% recovery of MgO). The design-matrix of different runs, 17 experiments, as well as the levels of each factor are shown in Table 2. The applied variables were: reaction time in hours (2, 3, 4), reaction temperature ºC (65, 80, 95) and stoichiometry (1.4, 1.5, 1.6).

Table 2. Experimental Box Behnken Design with 3 levels and 3 variables

| Run | Factor 1  | Factor 2  | Factor 3  |
|-----|-----------|-----------|-----------|
|     | A: Time, hr | B: Temperature, ºC | C: Stoichiometry |
| 1   | -1        | +1        | 0         |
| 2   | 0         | -1        | -1        |
| 3   | 0         | +1        | +1        |
| 4   | -1        | 0         | -1        |
| 5   | 0         | 0         | 0         |
| 6   | 0         | -1        | +1        |
| 7   | +1        | 0         | +1        |
| 8   | +1        | +1        | 0         |
| 9   | -1        | 0         | +1        |
| 10  | -1        | -1        | 0         |
| 11  | +1        | 0         | -1        |
| 12  | +1        | -1        | 0         |
| 13  | 0         | +1        | -1        |
| 14  | 0         | 0         | 0         |
| 15  | 0         | 0         | 0         |
| 16  | 0         | 0         | 0         |
| 17  | 0         | 0         | 0         |

| Levels          |
|-----------------|
| Variables       | -1 | 0 | +1 |
| Reaction Time, hr | 2  | 3 | 4  |
| Reaction Temperature, ºC | 65 | 80 | 95 |
| Stoichiometry   | 1.4 | 1.5 | 1.6 |

Magnesium oxide recovery was the response used for evaluation and comparing experimental results. Box–Behnken experimental design for the variables is shown in Table 3. Plots of the response (% recovery of MgO) surface contours and the best predictive models for estimate of the response variables were developed. The Box–Behnken design in Table 3 can fit the following model [24] following a second order polynomial function by which correlation between studied factors and response was generated.

\[ E(y) = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} X_i X_j \]  

(6)
where \( y \) is the estimate of the response variable and \( X_i \)'s are the values of independent variables [reaction time, reaction temperature and concentration] those are known for each experimental run. The parameters \( \beta_0, \beta_1 \) and \( \beta_{ij} \) are the regression parameters.

Software package, Design-Expert 6.1, Stat-Ease, Inc., Minneapolis, USA, was used for regression analysis of experimental data and to plot response surface. Analysis of variance (ANOVA) was used to estimate the statistical parameters. The extent of fitting the experimental results to the polynomial model equation was expressed by the determination coefficient, \( R^2 \). F-test was used to estimate the significance of all terms in the polynomial equation within 95% confidence interval.

### 3.3. Leaching

Leaching is based on the decomposition of the serpentine with hydrochloric acid according to the following equation:

\[
6 \text{HCl} + \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow 3\text{MgCl}_2 + 2\text{SiO}_2 + 5\text{H}_2\text{O} \tag{7}
\]

Moreover, hydrochloric acid reacts with some impurities e.g. \( \text{CaC}_0_3, \text{Fe}_2\text{O}_3, \ldots \) etc.

The obtained results of magnesium oxide recovery for each run are represented in table 3. It can be seen from this table that all the studied factors are significant regarding the magnesium oxide recovery. The statistical design data showed that the standard deviation was 4.73. The good predictability of the models can be indicated by correlation coefficient \( R^2 \) of 0.9032.

The correlation between the magnesium oxide recovery and the process parameters (reaction time, reaction temperature and stoichiometry) is shown in the following model that is generated from experimental data in table 3:

\[
\text{Magnesium Oxide Recovery, } \% = 24.61 + 1.98A + 1.46B + 0.11C - 9.67A^2 - 0.05C^2 - 0.04AB - 5.17B^2 - 0.04BC \tag{8}
\]

where \( A \) is the reaction time (hour), \( B \) is the reaction temperature (°C) and \( C \) is the stoichiometry. The estimated values of magnesium oxide recovery using the above model are calculated. The experimental results are presented in table 3. These values are confirming the agreement of the generated previous model with the experimental results.
Table 3. Magnesium Oxide Recovery according to the experimental statistical design conditions.

| Run | Factor 1: Time (hours) | Factor 2: Temperature (°C) | Factor 3: Stoichiometry | Response 1: MgO Recovery % |
|-----|------------------------|--------------------------|------------------------|--------------------------|
| 1   | 2                      | 95                       | 1.5                    | 87.1                     |
| 2   | 3                      | 65                       | 1.4                    | 67.1                     |
| 3   | 3                      | 95                       | 1.6                    | 94.5                     |
| 4   | 2                      | 80                       | 1.4                    | 79.4                     |
| 5   | 3                      | 80                       | 1.5                    | 88.2                     |
| 6   | 3                      | 65                       | 1.6                    | 71.8                     |
| 7   | 4                      | 80                       | 1.6                    | 90.7                     |
| 8   | 4                      | 95                       | 1.5                    | 96.5                     |
| 9   | 2                      | 80                       | 1.6                    | 82.3                     |
| 10  | 2                      | 65                       | 1.5                    | 69.3                     |
| 11  | 4                      | 80                       | 1.4                    | 86.3                     |
| 12  | 4                      | 65                       | 1.5                    | 78.9                     |
| 13  | 3                      | 95                       | 1.4                    | 89.2                     |
| 14  | 3                      | 80                       | 1.5                    | 88.3                     |
| 15  | 3                      | 80                       | 1.5                    | 88.5                     |
| 16  | 3                      | 80                       | 1.5                    | 88.2                     |
| 17  | 3                      | 80                       | 1.5                    | 88.7                     |

Figure 2 shows the relation between the effect of reaction time and stoichiometry on magnesium oxide recovery at different temperatures: figure 2.a at 65°C, figure 2.b at 80°C and figure 2.c at 95°C. These results showed that, the MgO recovery increases with increasing the reaction temperature. The optimum temperature is 95 °C which gives 96.5% MgO recovery. Further increase of the reaction temperature gave no increase in MgO recovery. At low reaction temperature, the viscosity of liquid phase is higher that leads to a decrease in the mobility of reacting ions and consequently lowers the reaction rate. On the other hand, higher temperatures result in excessive foam formation together with increasing corrosively of hydrochloric acid.

Figure 3 shows the effect of Temperature and stoichiometry at different leaching times (figure 3.a for 2 hr, figure 3.b for 3 hr and figure 3.c for 4 hr). Results reveal that the reaction of serpentine with hydrochloric acid is a spontaneous reaction of a high rate. It is obvious that recovery of MgO increases with the increasing reaction time. The optimum reaction time is 4 hours where 96.5% of MgO recovery is achieved. Increase of reaction time over 4 hours gives no appreciable increase in MgO recovery.
Figure 2. Effect of reaction time (hour) and stoichiometry on magnesium oxide recovery at different temperatures: figure 2.a at 65°C, figure 2.b at 80°C and figure 2.c at 95°C.
Figure 3. Effect of temperature and stoichiometry for different leaching times (figure 3.a: 2 hr, figure 3.b: 3 hr and figure 3.c: 4 hr).

Figure 4 shows the effect of leaching time and temperature at different stoichiometry. The achieved results reveal that, with increase in HCl : MgO molar ratio leads to MgO recovery increase. MgO recovery at molar ratio of 1.6 goes up to 98.5%. Further increase in the molar ratio produces an increase of free HCl content in magnesium chloride solution and does not lead to MgO recovery increase.
Figure 4. Effect of leaching times and temperatures at different stoichiometry (figure 4.a: 1.4, figure 4.b: 1.5 and figure 4.c: 1.6).

All the experimental data has been collected at the 3-D cube as shown in figure 5. This cube show that the highest magnesium oxide recovery of 96.5% can be obtained at the highest levels of parameters. The smallest magnesium oxide recovery of about 63.9% was obtained at the lowest levels of parameters. Decreasing any of the main variables lead to the decrease of magnesium oxide recovery.
Figure 5. 3-D Plot for all the experimental data for leaching of serpentine ore.

3.4. Optimum conditions for the leaching

The optimum conditions and results of decomposition of the serpentine ore with HCl are summarized in Table 4. The maximum MgO recovery achieved is 96.5%.

Table 4. Optimum conditions and results of serpentine leaching.

| Conditions                  | Values, %       | Results                  | Values, % |
|-----------------------------|-----------------|--------------------------|-----------|
| Particle size, Mesh         | 86 % -200       | MgO Recovery             | 96.5      |
| Temperature, °C             | 95              |
| Reaction time, hr           | 4               |
| Liquid / Solid Ratio, ml/g  | 4 : 1           |
| HCl Concentration, %        | 12.07           |
| Stoichiometry               | 1.6             |

3.5. Solid liquid separation

The filtration data are tabulated in Table 5. The filtration characteristics of magnesium chloride slurry are determined by deriving the values of slope, intersection and equivalent volume from the curve shown in Figure 6. The slope and intersection were calculated. The viscosity, specific gravity of slurry and weight of solids per unit volume of slurry were determined experimentally. From these data in the afore-mentioned substituting equations, the filtration characteristics were obtained and given in Table 6. The main factors affecting the filtration rate is the viscosity of slurry, viscosity of the solution, insoluble residue thickness as well as the applied pressure difference.
Table 5. Filtration Data of Magnesium Chloride solution from Precipitated Silica.

| Volume (V), cm³ | Time (θ), sec | ▲ V | ▲ θ | ▲ θ/▲ V |
|----------------|---------------|-----|-----|---------|
| 5              | 3             | 5   | 3   | 0.6     |
| 10             | 7             | 5   | 4   | 0.8     |
| 15             | 12            | 5   | 5   | 1.0     |
| 20             | 18            | 5   | 6   | 1.2     |
| 25             | 26            | 5   | 8   | 1.6     |
| 30             | 35            | 5   | 9   | 1.8     |
| 35             | 45            | 5   | 10  | 2.0     |

Figure 6. ▲ θ/▲ V Versus Volume.

Table 6. Filtration Characteristics of Magnesium Chloride solution from Precipitated Silica.

| Item                                      | Value          |
|-------------------------------------------|----------------|
| Slope, sec/cm³                            | 0.0486         |
| Intersection, sec/cm³                     | 0.3143         |
| Specific Cake Resistance (α), cm/g        | 2.9X10⁹        |
| Equivalent Volume of Filtering Medium (Vₑ), cm³ | 6.5            |
| Filtering Medium Resistance (R), cm⁻¹     | 2.3X10⁸        |
| Filtration Rate dV_max/dθ, ml/min.        | 36             |
| Filtration Time, sec                      | 35             |
| Viscosity of Filtrate at 90 °C, Poise     | 0.02           |
| Specific Gravity of Slurry, g/cm³         | 1.2            |
| Weight of Solids per Unit Volume of Slurry (W), g/cm³ | 0.2            |
4. Conclusions

Egyptian Serpentine ore from the Eastern Desert Area was leached with aqueous hydrochloric acid. Box–Behnken experimental statistical design is applied to study the influence of different parameters on leaching process. The liquid/solid ratio of 5:1 ml/g was applied. The mathematical model was generated. The results showed that, all the studied parameters of reaction temperature, reaction time and stoichiometry are effective. The results are presented as a 3-D cube. These results reveal that, high magnesium oxide recovery of about 96.5% was achieved at reaction time of 4 hours, reaction temperature of 95 ºC and HCl : MgO stoichiometry of 1.5. On the other hand, the recovery of magnesium oxide was 67.1% at low parameters levels (3 hours reaction time, 65 ºC reaction temperature and 1.4 HCl : MgO stoichiometry). Magnesium chloride slurry was filtered to separate the clear solution from insoluble residues using vacuum filtration technique (horizontal pan filter). The achieved filtration rate of magnesium chloride solution is 36 mL/min under pressure difference of 550 cm².Hg.

5. References

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