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Leaching Kinetics of Calcined Magnesite in Ammonium Chloride Solutions

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Abstract: In this paper the kinetic of calcinated magnesite dissolution was investigated using ammonium chloride. The relation of calcinated particles dissolution was obtained in the range of 40 to 80 Celsius degrees. By investigating reactant concentration variation with time, the kinetics variable models were determined. This research showed that the reaction satisfies the shrinking-core model for spherical particles and the chemical reaction dominates the reaction rate. Assuming the validity of Arrhenius's law, the activation energy for the reaction was obtained 42.26 kJ/ mole.

Key words: Dissolution kinetic, Arrhenius's law ,Magnesite, Ammonium Chloride

INTRODUCTION

Magnesium compounds is one of the most common compounds in the earth layer, however there are impurities with magnesite such as calcium impurity but there are also the operations that helped us purify it for some other reactions that we need nowadays(wicken O.M. Duncan, L.R., 1975; J. Basselt. R.C-Denney. G.H. Jeffery and J. mendham, 1976). The magnesium compositions have a very important part in human being's life (Copp,A.N, 1992; Copp.Albert N,1990). Because the most magnesium compositions and even the pure magnesium are obtained from the magnesium oxide, it is the basic substance for the modern society. The most methods of producing magnesite oxide were the leaching of its ore by using various solvents (Demir.F, Do¨nmez, B. Cü olak, S, 2003; Demir. F,Do¨nmez, B. Okur, H. Sevim, F, 1997; Ekmekyapar, A., Ersüahan, H., Do¨nmez, B,1993) .There were a lot of ways to obtain magnesite(B. Bayrak, O. Laçin, F. Bakan and H. Saraç, 2006; F. Bakan, O. Laçin, B. Bayrak and H. Saraç, 2006; Demir, Oral Lacüin,* and Bu1nyamin Do1nmez, 2006) and leaching by using ammonium chloride have been chosen. The reaction of calcination magnesite is so important in industry nowadays (Ersahan, H., Ekmekyapar, A., Sevim. F, 1994) and the method of ammonium chloride is the base method for concentrating magnesium in the recent years and now there are several factories in the world that produce magnesium oxide with this method too.

When solid magnesium oxide is added to an aqueous solution of ammonium chloride, magnesium chloride, ammonia and water will be produced (Tkacova *et al.,* 1981; Ranjitham and Khangaonkar, 1990):

$$2NH_4Cl + Mg\ O \rightarrow MgCl_2 + 2NH_3 + H_2O \quad (1)$$

The reaction of calcinated magnesite with ammonium chloride according to Equation (1) can play an important role in extraction of the magnesium and/or in recovery of the ammonia. Good understanding of the mechanisms encountered is important for designing as well as for an efficient operation of reactors. Although, there was limited kinetic data available for an engineering analysis of this process ,it was observed that the rate of reaction (1) strongly depends on properties of the solid as well as reaction conditions of the process itself (Raschman, 2000) and different conclusions regarding the mechanism have been presented (Tkacova *et al.,* 1981; Glaser *et al.,* 1988). The obtained results from the kinetic investigations for producing high purity magnesite that was studied in these experiments can be the first step for industrializing the studied methods.

2. The experimental method:

The sample of magnesite ore was obtained from Ghalee Bid located in Zahedan .The chemical structure of this sample is brought in table 1 by standard gravimetric and volumetric methods (Furmann, N. H, 1963).

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Table 1: chemical structure of magnesite ore from Ghalee Bid

Material type	Wt%
SiO_2	6.00
Fe_2O_3	1.1
Al_2O_3	0.24
CaO	3.64
MgO	41.92
L.o.I	47.10

In this research, the obtained samples, first jabbed by cylindrical mill with mesh 14, then calcinated in three different temperatures 700, 800 and 900 for three hours in oven, after that the calcinated magnesite was jabbed and divided into the sizes of 25, 35 and more than 35 mesh.

The experiments were performed in well-mixed spherical glass batch reactor that equipped with the magnet mixer with cylinder blade length 2 centimeter and diameter of 0.5 centimeter and thermometer. The mixer race in all tests was constant equal to 600 rpm. In all steps 50 grams of samples settled in 48.2 molar ammonium chloride solutions. Each experiment required 3 hours that in each 20 minutes 5 milliliter of sample was taken. We added 3 milliliter buffer (pH=10) and then add 30 milliliters twice distillated water into the reactor, finally this solution was titrated with one normal EDTA (ethylenediamine tetraacetic acid) and of course Eriochrome black T as indicator.

2.1. The temperature effect:

The calcinated magnesite was used at 700 Celsius degree and the size 25 mesh in order to test of temperature effect. In the range 40 to 80 Celsius degrees, the 5 different temperatures were chosen: 40, 50, 60, 70 and 80 Celsius degrees. For each of them a separate test was executed and within the same method that was explained above, every 20 minutes we experimented the accidental chosen sample and then we titrated each of them. The following values were brought in the table 2. From this table, it is observed that the dissolution rate is highly sensitive to the reaction temperature.

Table 2: The temperature effect on calcinated magnesite at 700 degree Celsius and the size 25 mesh

	40 c	50 c	60 c	70 c	80 c
Time (min)	Extraction Fraction	Extraction Fraction	Extraction Fraction	Extraction Fraction	Extraction Fraction
20	0.05	0.07	0.10	0.12	0.18
40	0.08	0.11	0.17	0.23	0.31
60	0.13	0.17	0.25	0.34	0.43
80	0.16	0.21	0.32	0.41	0.5
100	0.19	0.25	0.38	0.47	0.57
120	0.24	0.30	0.43	0.52	0.61
140	0.26	0.34	0.48	0.57	0.65
160	0.29	0.38	0.52	0.6	0.67
180	0.32	0.42	0.56	0.62	0.69

2.2. the Chloride Ammonium Concentration:

This effect was investigated by four experiments. The reactor was fulled with 50 grams calcinated magnesite at 700 Celsius degree and size 25 mesh. In each experiment the temperature was constant and only the ammonium chloride concentration was changed. The concentrations were 2.48, 3.6, 4.2 and 5.0 molar, afterwards performing experiment was done and each sample was titrated and the results were shown in table 3.

Table 3: The chloride ammonium concentration effect on calcinated magnesite at 700 degree Celsius and the size 25 mesh

At T= 70 c	2.48 Molar	3.6 M	4.2 M	5 M
Time (min)	Extraction Fraction	Extraction Fraction	Extraction Fraction	Extraction Fraction
20	0.13	0.13	0.13	0.13
40	0.24	0.24	0.24	0.24
60	0.33	0.33	0.33	0.33
80	0.42	0.42	0.42	0.42
100	0.46	0.46	0.47	0.48
120	0.52	0.52	0.53	0.53
140	0.57	0.58	0.58	0.59
160	0.61	0.61	0.62	0.62
180	0.63	0.63	0.64	0.64

2.3.the Calcination Temperature:

For investigation, we calcinated some magnesite at 700, 800 and 900 Celsius degrees then experimented each of them. The size of particles was 25 mesh and the constant temperature was 70 Celsius degree also the 48.2 molar ammonium chloride was used in each experiment. First 50 grams of the calcinated magnesite were poured in the 400 milliliter ammonium chloride 2.48 molar then titration was carried out after performing like the previous ones. The results were shown in the table 4.

Table 4: The calcination temperature effect on calcinated magnesite with the size 25 mesh

	700 c	800 c	900 c
Time (min)	Extraction Fraction	Extraction Fraction	Extraction Fraction
20	0.15	0.11	0.08
40	0.22	0.20	0.15
60	0.31	0.28	0.21
80	0.40	0.33	0.28
100	0.46	0.41	0.32
120	0.51	0.45	0.39
140	0.55	0.51	0.42
160	0.59	0.52	0.47
180	0.61	0.59	0.49

2.4. The particle size:

The experiments were performed for four different particle sizes (20 mesh, 25 mesh, 35 mesh and more Than 35 mesh). The temperature was constant at 700 Celsius degree and the concentration of chloride Ammonium was also 48.2 molar. Like the last methods, performing and titration were done and the Values were shown in the table 5.

Table 5: The particle size effect on calcinated magnesite at 70 Celsius degree

At T=70 c	20 Mesh	25 Mesh	35 Mesh	> 35 Mesh
Time (min)	Extraction Fraction	Extraction Fraction	Extraction Fraction	Extraction Fraction
20	0.11	0.14	0.16	0.20
40	0.21	0.25	0.29	0.36
60	0.26	0.32	0.40	0.48
80	0.31	0.41	0.47	0.55
100	0.34	0.46	0.55	0.60
120	0.38	0.52	0.59	0.64
140	0.42	0.57	0.62	0.65
160	0.45	0.60	0.64	0.68
180	0.49	0.62	0.67	0.70

3.The Reaction Kinetic:

The dissolution kinetic was obtained by using the shrinking-core model for spherical particles. While the fluid film controls the rate of reaction, the layer resistance on the surface of a solid related such a various terms like relative velocity of solid and fluid and the particle size of solid. These terms were related in the various methods of solid and fluid contact like the packed bed and the falling of solid in the fluid bed (John Wiley and Sons Inc, O. Levenspiel, 1996). A successful reactor design for these processes depends on kinetics data strongly. In such systems, the reaction rate can be generally controlled by one of the following steps(John Wiley and Sons Inc ,O. Levenspiel,1996):

(A) Diffusion through the fluid film
(B) Diffusion through the ash
(C) Chemical reaction at the surface of the core of unreacted materials.

The experimental data have been evaluated according to the shrinking-core model. In this model:

$$A(aq) + bB(s) \rightarrow \text{Products} \quad (2)$$

If no ash layer covers the unreacted core as the reaction proceeds, there could be only two controlling steps, fluid film diffusion or chemical reaction (John Wiley and Sons Inc, O. Levenspiel, 1996). If the process is controlled by resistance of the fluid layer:

$$\frac{t}{\tau} = 1 - (1-x)^{\frac{2}{3}} \quad (3)$$

Where:

$$\tau = \frac{\rho_B y R_0^2}{2bC_{Ag}D}$$

If Eq. (2) is controlled by resistance of the chemical surface reactions, then we had:

$$\frac{t}{\tau} = 1 - (1-x)^{\frac{1}{3}} \quad (4)$$

Where:

In the calculations, it was observed that the best value of the regression coefficient clarify the rate state was for surface reaction control. The computer program and simple mathematical model also aided us analyzing the integral rate. So the only method that we should use was the shrinking-core for spherical particle and the reaction controlled the rate of reaction. To make sure about the results of these statistical analyses, graphical methods were used for testing the experimental data .These results were shown in tables and figures 1, 2 and 3 (To simplify the recognition of this part, the given values in tables were also drawn by figures 1 and 2). Attending to figure.1 and the slopes of straight lines, the apparent rate constants were obtained consequently.

Table 6: 1 - (1 - x) $^{1/3}$ vs. time at various reaction temperatures

	40 c	50 c	60 c	70 c	80 c
Time (min)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)
0	0	0	0	0	0
20	0.01	0.01	0.03	0.05	0.06
40	0.03	0.03	0.05	0.08	0.12
60	0.05	0.06	0.09	0.12	0.19
80	0.07	0.08	0.13	0.18	0.26
100	0.08	0.10	0.16	0.24	0.32
120	0.10	0.11	0.19	0.29	0.40
140	0.11	0.15	0.22	0.33	0.48
160	0.12	0.18	0.26	0.38	0.52
180	0.13	0.19	0.30	0.43	0.59

Table 7: 1 - (1 - x) $^{1/3}$ vs. time at various particle sizes

At T=70 c	20 Mesh	25 Mesh	35 Mesh	> 35 mesh
Time (min)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)	1 - (1- x)^ (1/3)
20	0.03	0.03	0.04	0.07
40	0.06	0.07	0.10	0.15
60	0.08	0.12	0.16	0.22
80	0.11	0.18	0.22	0.30
100	0.14	0.22	0.29	0.38
120	0.16	0.28	0.35	0.46
140	0.18	0.31	0.41	0.55
160	0.21	0.37	0.47	0.62
180	0.25	0.41	0.52	0.70

By finding results for the six different temperatures, the [1-(1-x)$^{1/3}$] table was given according to time of dissolution; the particle size for four different sizes also was drawn. According to these tables, it was indicated that the lines had almost constant slope and the chemical reaction controls the rate of reaction.

RESULTS AND DISCUSSION

The tables showed the relationship between temperature and rate of reaction for instance at 80 Celsius degree and time of 140 minutes, the solution of magnesite reached 96 percent while at 40 Celsius degree and time of 180 minutes it was only 43 percent approximately.

In the leaching process, it was observed that the reaction rate was sensitive to both particle size and temperature .About the relationship between the calcinated magnesite solution and calcination temperature as it was showed in its own table the partial conversion of calcinated magnesite at 700 degree Celsius was more

than 800 and 900 Celsius degrees. Through the Smithson's investigations (Palmer B.r, Nebo c.o., Rau M.F and Fuerstenan M.c , 1981) the solution of calcinated magnesite in the ammonium chloride for the samples at the temperatures less than 600 was not accomplished correctly. About the size of particles, decreasing the size increased the solution of magnesite.

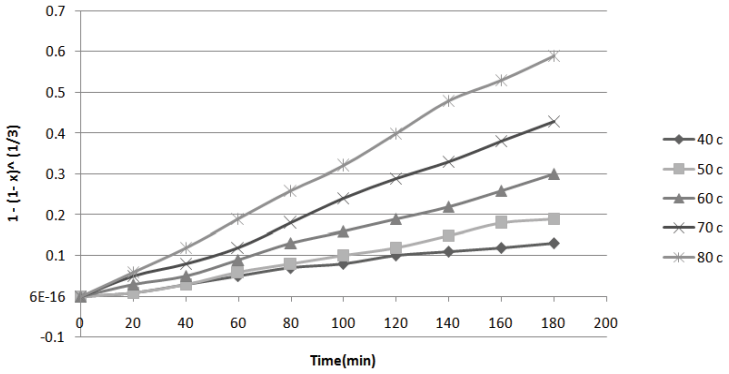

Fig. 1: 1 - (1 - x)$^{1/3}$ vs. time at various reaction temperatures

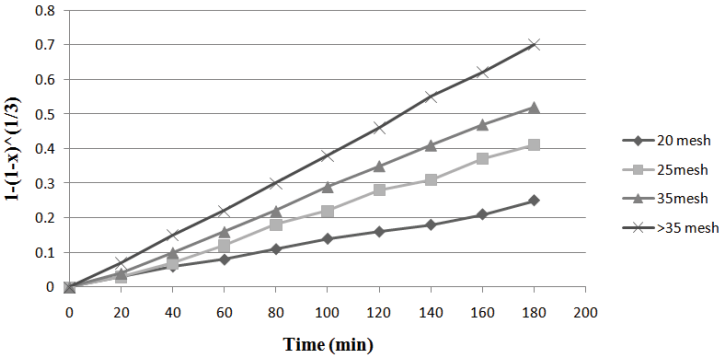

Fig. 2: 1 - (1 - x)$^{1/3}$ vs. time at various particle sizes

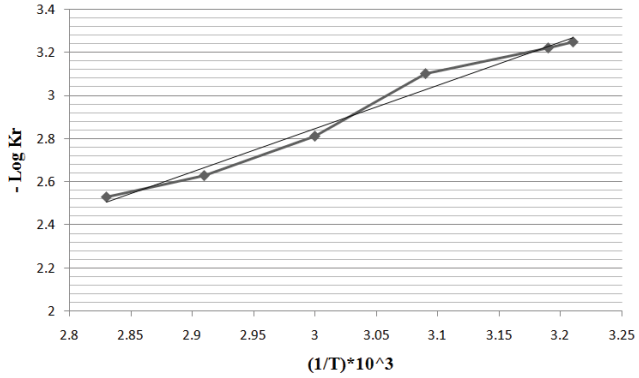

Fig. 3: Arrhenius plot for the leaching of MgO

The dissolution kinetics obeys a shrinking-core model with the surface chemical reaction as the rate-controlling step. The linear dependence of the rate constant on the inverse particle radius is proof for the proposed surface reaction of shrinking-core model. Using the Arrhenius's law:

$$k=k_0e^{-E/RT} \quad (5)$$

And also according to the graph of -log k_r versus (1/T) which was plotted for the each value of the temperature, these values were obtained:

$E = 42.26$ and $k_0 = 6113$

Also we had:

$1 - (1 - x)^{1/3} = kt$

Then we could say:

$1 - (1 - x)^{1/3} = 6113e^{-42.26/RT}t$

Conclusions:

There are the major conclusions that can be declared .Magnesium chloride is an excellent medicine that is fast acting and safe. Magnesium chloride is also very flexible in terms of methods of application as it can be nebulized, applied orally, intravenously in emergency situations. It serves as precursor to other magnesium compounds. It is however used for a variety of other applications besides the production of magnesium such as: the manufacture of textiles, paper, cements ,fireproofing agents, refrigeration brine, and dust and erosion control. Mixed with hydrated magnesium oxide, magnesium chloride forms a hard material called Sorel cement .The kinetics of the liquid-solid reaction between calcined magnesite and ammonium chloride was investigated. The main aim of this research was to study the possible effects of the reaction rate on the dissolution of calcined magnesite with ammonium chloride solutions. In the leaching process, it was observed that the reaction rate is rather sensitive to both particle size and temperature. As we said about the size of particles, decreasing the size increased the solution of magnesite. The dissolution kinetics obeys a shrinking-core model with the surface chemical reaction as the rate-controlling step. The linear dependence of the rate constant on the inverse particle radius satisfied the proposed surface reaction of shrinking-core model. The activation energy of the process was found to be 42.26 kJ mol^{-1} that approves related works (Tkacova. K, Turcaniova, L, Hocmanova, 1982).It can be expressed that because of less ammonium chloride consumption the process can be more economic and surely advantageous. This is the nontoxic and safe technique and consequently can be a significant reason for the research and development of these kinds of processes.

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