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Dissolution Kinetics of Magmatic Rocks via Ultrasonic Leaching for Calcium, Magnesium and Aluminum

Mehmet Hikmet ÖZKAN, Ramazan GÜRKAN[♠], Aysun ÖZKAN,
Mehmet AKÇAY

Cumhuriyet University, Faculty of Science & Arts, Department of Chemistry, Sivas, Turkey

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ABSTRACT

Ultrasound is known to enhance solid-liquid interface reactions. This study deals with the investigation of the dissolution of quartz monzonite from magmatic rock class in hydrochloric acid of 1.0% HCl (v/v) in the presence of ultrasound. Dissolution kinetics of ultrasonic leaching for destructive analysis of a magmatic rock sample was investigated. Various dissolution kinetics parameters such as dissolution order (n), dissolution rate constant (k), initial dissolution rate (r_i) and maximum dissolution (S_{max}) were determined as the functions of the mass of sample, the grain size of sample and ultrasonication power for Ca, Mg and Al. The kinetic parameters were evaluated to reflect the quantitative aspect of the magmatic rock dissolution behavior.

Key Words: Kinetics, Ultrasonic Metal Leaching, Partial Leaching, Magmatic Rocks.

1. INTRODUCTION

Ultrasound is an increasingly used tool to enhance chemical process [1]. Unlike other new technologies such as the use of micro-waves (dipolar species), electrochemistry (conducting medium) and photochemistry (the presence of a chromophore), which require some special attribute of the system being activated in order to produce an effect, ultrasound requires only the presence of a liquid to transmit its energy. Power ultrasound enhances chemical and physical changes in a liquid medium through the generation and subsequent destruction of cavitation bubbles. Like any sound wave, ultrasound is propagated via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power, the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form; the fate of these cavities, when they collapse in succeeding compression cycles, generates the energy for chemical and mechanical effects.

In heterogeneous solid-liquid situations, the collapse of cavitation bubbles near a surface produces an unsymmetrical inrush of fluid to fill the void with the result that a liquid jet is formed, targeted at the surface. This effect increases mass and heat transfer to the surface by disruption of interfacial boundary layers. Inter-particle collisions can lead to erosion, cleaning of the solid surfaces, degassing, wetting of the particles and particle size reduction. The appearance of micro-currents, due to ultrasonic irradiation on the solid-liquid interfaces in the diffusion layer thickness, even compared with that which exists when the suspension is stirred vigorously. The cavitation effect leads to the appearance of many micro-chinks on the solid surface subjected to ultrasound. Because the diffusion speed increases, the solution goes to the bottom of the capillaries and accelerates the leaching.

In this context, ultrasonic leaching is being used in many applications to prepare different inorganic-organic samples with complicated matrix structure for analysis, and is thought to be an alternative method to conventional total dissolution techniques. It has been reported that high recoveries of organics from granular activated carbon [2], sediment [3], fly ash [4], biological materials [5], and elements from atmospheric particulate [6] and geological samples [7, 8] are possible when they are analyzed after ULM extraction. This operation requires a much shorter time than that required for other extraction procedures. Similar results may also be expected for labile (physical bound) metal fractions in atmospheric particulate and on the bio-collector sprouts as reported in previous studies on the

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[♠] Corresponding author, e-mail: rgurkan@cumhuriyet.edu.tr

physical and chemical effects of ultrasonication [9].

The kinetics models of dissolution for the elements in magmatic rocks via ultrasonic effect have received considerable attention, but no attention has been paid to those of multi-component systems. The dissolution mechanism is important for ultrasonic leaching. Therefore, kinetics parameters of dissolution, such as dissolution order (n), dissolution rate constant (k), initial dissolution rate (r_i) and maximum dissolution (S_{max}) must be calculated for the elements in magmatic rocks.

To inquire the controlled mechanism of the dissolution processes, several kinetic models are used to test experimental data. It is probable that any kinetics is likely to be global. From a system design viewpoint, a lumped analysis of dissolution rates is thus sufficient for the practical application [10].

In the interpretation of dissolution kinetics data of the type described here, it is usually accepted that a single step in the dissolution process- that is the rate-determining step- governs the overall dissolution rate of the rock. Using current models, the slowest of the following three sequential steps is expected to be rate-determining for the dissolution of a magmatic rock via ultrasonic effect [11]:

(1) External transfer: transfer of the solvent from the bulk fluid to the rock particle by molecular and convective diffusion via ultrasonic effect.

(2) Internal transfer: transfer of the solvent from the particle surface to the interior site by diffusion in the void space of the pores, by surface migration on the pore surface, or by volume diffusion.

(3) Dissolution of the rock: chemical and physical leaching including mechanical leaching of very small particles.

Dependence on step (1) is normally overcome by ultrasonic effect. It is only in the case where dissolution is very rapid, or mixing is very slow, that transport to the external rock sample surface needs to be considered as a possible rate-determining step. The majority of dissolution mechanisms proposed are generally based on step (2) as the rate-determining step, that the dissolution process is based on a diffusion-controlled model, or alternatively based on step (3), which occurs at an immeasurably fast rate. The final alternative is that the combination of steps (1) and (2) controls the rate of dissolution [11, 12].

When the rate of the chemical dissolution process (step 3) is much slower than the rate of diffusion, then the process will be chemically controlled.

A simple kinetic analysis is the first order equation in the form [13, 14].

$$\frac{dS}{dt} = k_{1,s}\left(S_{max} - S\right) \quad (1)$$

Where $k_{1,S}$ is the rate constant of first order dissolution and S_{max} denotes the maximum degree of dissolution at equilibrium. After definite integration by applying the initial conditions S = 0 at t = 0 and S = S at t = t, equation (2) becomes

$$\ln W = k_{1,s} \quad (2)$$

Where $W = S_{max}/(S_{max} - S)$.

Also, a second order equation based on dissolution equilibrium degree may be expressed in the form of:

$$\frac{dS}{dt} = k_{2,s}\left(S_{max} - S\right)^2 \quad (3)$$

Where $k_{2,s}$ is the rate constant of second order dissolution. Integrating equation (3) and applying the initial conditions, now we have

$$\frac{t}{S} = A + Bt \quad (4)$$

Where A is reciprocal of initial dissolution rate r_i or $1/k_{2,s}S_{max}^2$ and B is inverse of the degree dissolution equilibrium. If second order kinetics are applicable, the plot of t/s against t of Eq. 4 should give a linear relationship, from which S_{max}, $k_{2,s}$ and r_i can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

A third situation has been discussed at which the rate of the chemical process (step 3) is of the same magnitude as the rate of diffusion (step 1 and/or 2), and it is suggested that the diffusion-controlled system can be differentiated from chemically-controlled systems by two factors, namely solvent velocity and temperature. Habashi considers that a diffusion-controlled system is characterized by only a small dependence on temperature, while a chemically controlled system is more dependent on temperature [12].

In our previous studies, an ultrasonic leaching method for destructive analysis of magmatic rock samples was developed. Then, this method, which is called ULM, was applied for the determination of some elements in magmatic rocks by flame AAS after ultrasonic leaching [7, 8, 15]. In the present study, the dissolution kinetics of magmatic rocks via ultrasonic leaching for some elements such as calcium, magnesium and aluminum was investigated. The aim of this work is to calculate and evaluate the dissolution kinetics parameters such as dissolution order (n), dissolution rate constant (k), initial dissolution rate (r_i) and maximum dissolution (S_{max}) as the functions of the mass of sample, the grain size of sample and ultrasonication power for Ca, Mg and Al.

2. EXPERIMENTAL

2.1. The rock sample

The rock samples were collected from the province of Giresun in Northern Turkey. The rock sample was identified as quartz-monzonite by Yılmaz and Boztuğ [16]. The rock samples have been analyzed for the major and trace element compositions. The chemical analysis of the quartz-monzonite rock is as follows:

2.1.1. Major elements

SiO_2 59.02%, Al_2O_3 17.33%, TiO_2 0.53%, t-Fe_2O_3 4.43% (total iron oxide as ferric iron), MnO 0.15%, MgO 1.95%, CaO 4.04%, Na_2O 3.22%, K_2O 6.17%, P_2O_5 0.25 and LOI (loss on ignition) 0.98%, total 98.07.

2.1.2. Trace elements

Rb, 202; Sr, 622; Ba, 813; Y, 58; Zr, 2.68; Nb, 23; Th, 7.8; Co, 75; Cu, 62; V, 77; Pb, 41; Zn, 88 and Cr, <1.0 at ultra trace level in ppm. The major and minor minerals (mafic or accessory components) in the rock are plagioclase, quartz, orthoclase, biotite, opaque, apatite, ojite, chlorite, titanite and epidot, respectively. All the chemical analyses have been performed with the Rigaku 3270 E-WDS model XRF spectrometry using some USGS and CRPG rock standards for calibration at the Mineralogical-Petrographical and Geochemical Research Laboratories of the Department of Geological Engineering at Cumhuriyet University in Sivas.

2.2. Crushing, sieving, fractionating, softening step and dissolution by ultrasonic leaching

The procedures have been described in our earlier works [7, 8]. Rock sample was fractionated into five sample grain sizes and described in detail in Table 1.

Table 1. Sample grain size, sieve pore size and sieve pore ranges.

Sample grain size no	Sieve pore numbers, mm	Sieve pore range, mm
5	0.425	-0.425 + 0.250
4	0.250	-0.250 + 0.106
3	0.106	-0.106 + 0.063
2	0.063	-0.063 + 0.038
1	0.038	-0.038 + 0.000

The dissolution procedure contained a total of 720 samples which were of five different grain sizes (1, 2, 3, 4, 5) (Table 1), six different sample masses (0.0500, 0.1000, 0.2000, 0.3000, 0.4000 and 0.5000 g), eight different ultrasonication periods (5, 10, 15, 20, 30, 40, 50 and 60 minutes) and three different ultrasonic power (minimum, medium and maximum). The leaching solutions were analyzed for Ca, Mg and Al by flame atomic absorption spectrophotometer (FAAS-UNICAM 929 model) using the standard addition and calibration curve techniques. Optimum conditions were determined as grain size 1, 0.0500 g sample mass, 30 minutes ultrasonication time and maximum USP. Dissolution procedures for all samples were carried out in 25 cm^3 of %1.0 HCl solution. Recoveries of this leaching procedure were between 91-112 % for studied elements as previously reported [7, 8].

2.3. Ultrasonic power (USP) used for leaching process

The ultrasonic bath (50-60 kHz) used in this study has eight different power scales; the power ranges were defined as follows:

First scale: minimum ultrasonic power (min USP).
Fourth scale: medium ultrasonic power (med. USP).
Eighth scale: maximum ultrasonic power (max USP).

3. RESULTS AND DISCUSSION

Solubility (S) of calcium, magnesium and aluminum at the optimum conditions with sonication period is given in Figure 1. The results are given in terms of metal oxides percentages in all Figures and Tables.

The dissolved calcium, magnesium and aluminum at 0.0500 g sample mass, grain size 1 and maximum USP was increased by sonication period in the first 30 minutes and then remained constant. The constant solubility for three oxides at 30, 40, 50 and 60 minutes for each sample was used for reproducibility tests (see Figure 1). The trend was similar to other sample sizes, sample masses and ultrasonic powers.

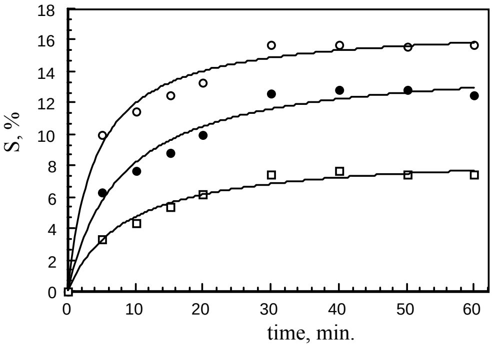

Figure 1. The plots of solubility of Ca, Mg and Al with time (at optimum conditions).

●, Ca; □, Mg; ○, Al; -, theoretical curve.
* The values of Ca and Mg concentrations have been multiplied by 3.

To test kinetics models, ln W vs. t and t / S vs. t graphs are plotted and they are shown in Figures 2 and 3 respectively.

For first order kinetics, ln (W) vs. t graph must be linear but experimental results gave a curve (Figure 2). This means that the dissolution process did not obey to the first-order kinetics law.

The graphs of solubility vs. sonication times of Ca, Mg and Al against sonication time give the hyperbolic curves (see Figure 1). Therefore, it was assumed that the dissolution process should obey the second-order kinetics law. The t / S vs. t graph were obtained and it also proves the validity of our assumption. This graph is shown in Figure.3 for Ca, Mg and Al.

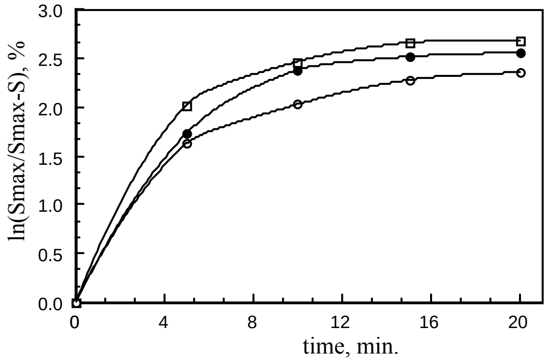

Figure 2. The graph of first order dissolution kinetics of Ca, Mg and Al (at optimum conditions).

●, Ca; □, Mg; ○, Al;

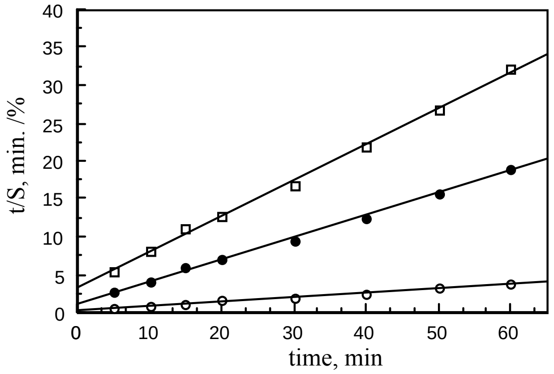

Figure 3. The graph of second order dissolution kinetics of Ca, Mg and Al (at optimum conditions), ●, Ca; □, Mg; ○, Al.

As can be seen from Figure 3, a linear increase was obtained with a correlation coefficient of $r^2 \geq 0.99$ between t / S and t. The solid lines in Figure 1 were calculated from equation 4. This result is in agreement with the experimental observations. It can be said that the dissolution process obeys the second-order kinetics law. Similar results were observed for other sample sizes, sample masses and ultrasonic powers. Thus, the dissolution process is a chemical-controlled process.

The k, r_i and S_{max} values were calculated from the slopes and intercepts of these linear plots, respectively. The kinetics parameters (k, r_i and S_{max}) and correlation coefficients of all systems for second order kinetics are tabulated for the sample mass, grain size and sonication power in Tables 2, 3 and 4, respectively.

Table 2 shows that S_{max} and r_i have significantly decreased, while k has increased by increase of sample mass for Ca, Mg and Al. Table 3 shows that S_{max} and r_i have significantly decreased, while k increases by an increase in sample grain sizes for Ca, Mg and Al. Table 4 shows that S_{max}, r_i and k have significantly increased by an increase in ultrasonic power for Ca, Mg and Al.

4. CONCLUSIONS

The dissolution kinetics of quartz monzonite rock in acidic medium (1.0%HCl, v/v) have been investigated in the presence of ultrasonic effect. We observed that the dissolution process is a chemical-controlled process for different sample sizes, sample masses and ultrasonic powers at room temperature using flame atomic absorption spectrometry. Our results suggest that the dissolution process of Ca, Mg and Al in magmatic rocks under ultrasonic effect have obeyed the second order kinetics. The reason for the use of the dissolution process combined with ultrasonic treatment is used and preferred in this study is that it is an attractive alternative method so as to avoid intensive treatments with acids, which is usually tedious and time-consuming. Metals encapsulated within rock samples can efficiently and easily be released by ultrasonic effect into the leaching environment.

In this respect, the application of sonochemical methods may introduce new analytical possibilities in preparation of environmental solid samples such as soil, rock and sediment, plant and food samples with complicated matrix to analysis, and in elucidation of dissolution reaction kinetics and mechanisms.

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Table 2. The variation in the values of S_{max}, r_i, k and r^2 with mass of samples for Ca, Mg and Al (in max USP and grain size 1).

	Ca				Mg				Al			
	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2
0.0500	3.665	0.464	3.45	0.992	2.196	0.257	5.33	0.992	16.922	4.098	1.43	0.998
0.1000	3.448	0.454	3.61	0.991	2.161	0.235	5.53	0.994	15.755	3.827	1.54	0.996
0.2000	3.233	0.429	3.85	0.996	1.945	0.238	6.29	0.993	15.639	3.553	1.77	0.997
0.3000	3.175	0.407	4.04	0.994	1.825	0.233	6.99	0.995	14.966	3.507	1.89	0.999
0.4000	3.096	0.355	4.28	0.991	1.665	0.221	8.29	0.995	14.918	3.497	2.12	0.997
0.5000	2.918	0.341	4.41	0.990	1.629	0.219	8.64	0.994	14.630	3.357	2.34	0.997

Table 3. The variation in the values of S_{max}, r_i, k and r^2 with grain sizes for Ca, Mg and Al (in max USP and 0.0500 g sample mass).

	Ca				Mg				Al			
	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2
1	3.665	0.464	3.45	0.992	2.196	0.257	5.33	0.992	16.922	4.098	1.43	0.998
2	3.321	0.459	4.44	0.994	2.053	0.225	5.43	0.991	16.865	3.496	1.53	0.996
3	2.895	0.422	6.22	0.998	1.922	0.186	5.64	0.991	16.862	2.977	2.17	0.994
4	2.339	0.349	11.87	0.999	1.439	0.154	7.43	0.994	16.331	2.467	2.25	0.990
5	1.921	0.309	16.49	0.999	1.189	0.148	10.49	0.991	15.363	2.345	3.41	0.994

Table 4. The variation in the values of S_{max}, r_i, k and r^2 with USP for Ca, Mg and Al (for sample grain size 1 and 0.0500 g sample mass).

	Ca				Mg				Al			
	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2	S_{max}	r_i	kx10^{-2}	r^2
min USP	3.359	0.355	3.14	0.990	1.953	0.235	6.06	0.993	16.754	3.129	1.15	0.996
med USP	3.478	0.396	3.22	0.990	2.089	0.239	6.19	0.991	16.766	3.900	1.39	0.998
max USP	3.665	0.464	3.45	0.992	2.196	0.257	6.33	0.992	16.922	4.098	1.43	0.998

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