Dissolution Rate Constant of Carbonates under Natural Environments

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Abstract

Dissolution rate constant (K) of carbonates was determined by immersing a total of eight carbonate samples of Pila Spi Formation(Middle-Upper Eocene, 3 samples) and Fat'ha Formation (Middle Miocene, 5 samples) in Tigris River for a period of (8) months. Due to their very high dolomite contents, the Pila Spi samples did not show any detectable loss of weight and thus their dissolution rate constant (K) could not be determined. The dissolution rate constant (K) of Fat'ha samples was in the range from ($0.24x10^{-5}$ m/s) to ($0.56x10^{-5}$ m/s) with an average of ($0.39x10^{-5}$ m/s). It has been observed that dissolution rate constant (K) increases with an increase in calcite (decrease in dolomite). On the other hand, there is an inverse relationship between dissolution rate constant (K) and the insoluble residue (I.R.).

Introduction

Limestones or carbonates, among other soluble minerals like gypsum and anhydrite, constitute parts of foundations of several dams throughout the world. In Iraq Limestones exist in the foundations of the Mosul Dam, as part of rhythmic sediments including in addition to limestones, gypsum, anhydrite and marls, belonging to the Fat'ha Formation (Middle Miocene).

Although the solubility of limestone (0.015 Kg/m^3) which is here considered to consist exclusively of calcium carbonate, is much lower than that of gypsum (2.41 Kg/m^3, at 20º C; Weast, 1970; James and Kirkpatrick, 1980), however, it is important to study its rate of dissolution among other properties, in order to be able to take the necessary measurements to avoid the collapse of dam foundations.

James and Lupton (1978) derived the following equation for the dissolution rate constant of gypsum and limestone:

$dM/dt = KA (C_s – C)$ ………. (1a)
$K = dM/dt A (C_s – C)$ ……… (1b)

Where M (Kg) is the mass of calcium carbonate dissolved in time t (sec); A (m^2) is the area exposed to solution; C_s is the concentration of the saturated solution, i.e. the solubility of limestone (0.015 Kg/m^3) and C (Kg/m^3) is the concentration of calcium carbonate in the dissolving solution at time t.The purpose of this work is to determine dissolution rate constant of carbonates in Tigris River (natural environment) and to compare the results of this work with published experimental results on dissolution rate constant of limestone and dolomite.

Methodology

A total number of (12) samples were collected from an outcrop exposed by a road cutting, near Zawita town (65) kilometers north of Mosul (Fig.1), where Fat'ha Formation (Middle Miocene) conformably lies on Pila Spi Formation (Middle-Upper Eocene). Because of the little variations in the lithology of the Pila Spi Formation (Aljawadi, 1978), four samples representing the formation were collected from the same thick massive bed. On the contrary, the eight samples representing the limestone of Fat'ha Formation were collected from different levels within the rhythmic sequence of marl, gypsum and carbonates.

For the dissolution experiment, only eight samples were used. The other four (one from Pila Spi and three from Fat'ha) were kept as spares. Samples were cut into different shapes, according to the available original specimen. Five samples (1,2,4,5 and 6) were roughly cut into cubes;sample (3) was a parallelogram; sample(7)was a cylinder and sample (8) was irregular in shape.

Each sample was drilled right through; a wire was passed through it and the two ends of the wire were fastened to a water intake pipe of a nearby water treatment plant. The samples were immersed in river water at depth of about (2 m) at a distance of about (15 m) away from the river bank. All samples (except sample 7) were immersed for a period of (8) months (244 days), from (5.12.2007) to (5.8.2008). Sample (7) was replaced by another because it was accidentally snapped off by fisher men.

Water temperature was recorded twice every month and an average was taken. Flow velocity of Tigris River at the place of experiment was measured three times at different time intervals by placing a cork float in water and monitoring the time it took to cover a distance of (200) meters. At the end of experiment, it was observed that Pila Spi samples (1 to 3) did not lose any detectable weight, due possibly to their high magnesium (high dolomite) contents which was confirmed by chemical analyses (Table 3). Sample characteristics including the formation, dimension, original weight, and some remarks on the hand specimens are given in Table (1).

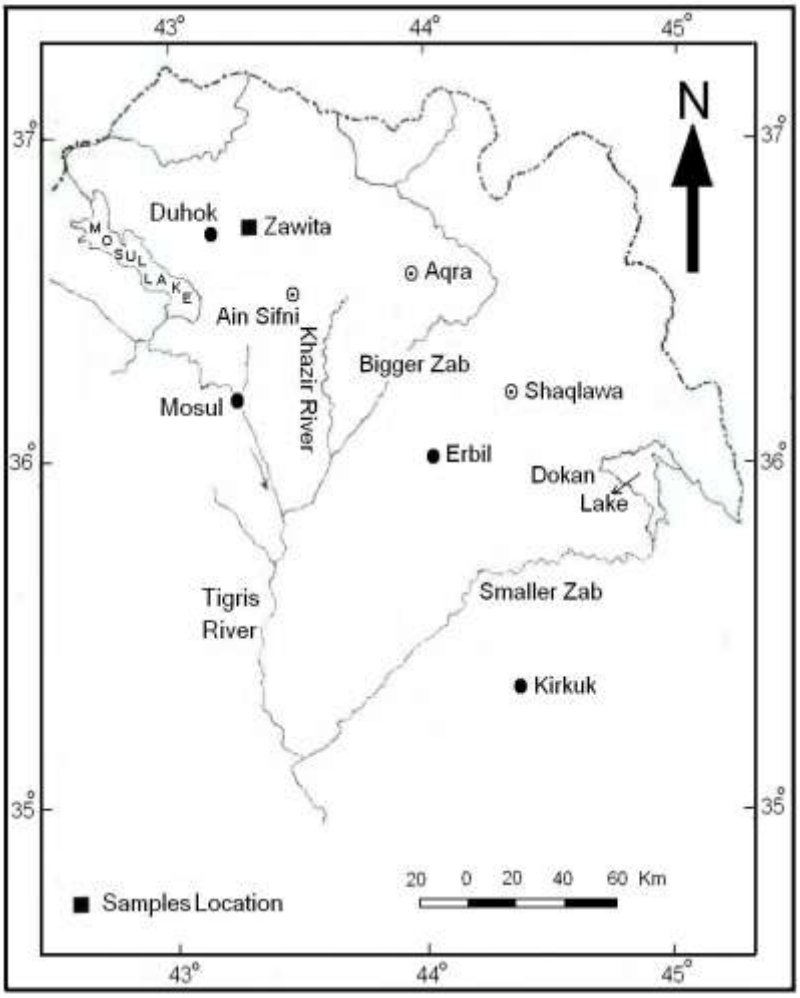

Fig.1: Samples location

Table 1: Characteristics of the studied samples.

S.N.	Formation	Dimensions (cm)	Weight (g)	Remarks
1	Pila Spi	7.0x7.2x7.4	805	Hard, massive dolostone
2	Pila Spi	7.0x7.1x7.3	855	Hard, massive dolostone
3	Pila Spi	7.4x10x18	2970	Hard, massive dolostone
4	Fat'ha	6.2x6.8x6.8	670	Highly ssiliferous limestone
5	Fat'ha	5.8x6.8x7.0	605	Highly fossiliferous limestone
6	Fat'ha	6.0x7.0x7.0	750	Fossiliferous limestone
7	Fat'ha	9.4x10.5	1660	Fossiliferous limestone
8	Fat'ha	Irregular	2335	Fossiliferous limestone

Four river water samples at the place of the experiment ; the first sample at the beginning, two in the middle and the last at the end of experiment, were collected and analyzed at Mosul Dam laboratory for their ion constituents and an average was taken. Table (2) shows ranges and averages of cations and anions, as well as electrical conductivity (EC), pH, total dissolved solids (TDS), flow velocity and tepmerature of Tigris River water at place of experiment.

Table2: Tigris River water analyses, given as ranges and averages of dissolved species, flow velocity and temperature at the studied locality.

	Range	Average	All cations and anions are in (mg/l) or (ppm)
EC (µmos/cm)	380-400	391	
pH	8.1-8.3	8.2	
Ca	56-86	73	
Mg	26-34	30	
Na	7-9	8	
K	5-8	6	
Cl	14-18	16	
SO_4	105-109	107	
CO_3	51-103	72	
HCO_3	210-249	235	
TDS	257-333	300	
Flow velocity m/s	0.74-0.95	0.83	
Temperature °C	10-14	12	

Chemical analyses (CaO, MgO, CO_2 and I.R.) were carried out at the Department of Geology, University of Mosul. CaO and MgO were volumetrically determined by titrating their solution with (0.01 M) EDTA and using erichrome black T indicator. However, two titrations of the unknown sample solutions were carried out. In the first, the pH of the sample solution must be between (12) and (13). At this pH, only calcium ions in the solution are exchanged for sodium in the EDTA and thus calcium only is titrated and determined. In the second titration, the pH of the sample solution must be (10) and at this pH both (Ca and Mg) ions are exchanged for sodium in the EDTA. The difference between second and first burette readings gives (Mg) concentration (Vogel, 1961; Abawi and Hasan, 1990).

Carbon dioxide (CO_2) was determined by carefully adding a known weight of the sample solution to a known weight of (10% HCl) and the weight (sample +acid) is taken affter effervescence has ceased, i.e. when all (CO_2) is driven off. The loss in weight is the weight of (CO_2). The experiment is monitored by using a standard or ANALAR $CaCO_3$.(Dhannoun, etal., 1988)

Insoluble residue (I.R.) was determined by dissolving (10g) of the powdered sample in (10%) hydrochloric acid and then filtering, drying and weighing the undissolved part of the sample (Majeed, 1983).

The results of chemical analyses of all samples are given in Table (3).

Table 3: Chemical compositions and mineral phases of the studied samples.

S.N.	MgO	CaO	CO2	I.R.	Total	Calcite%	Dolomite%
1	15.19	36.38	44.79	3.38	99.74	27.13	69.47
2	18.36	32.66	45.22	3.24	99.48	12.66	83.97
3	18.93	31.75	45.57	3.27	99.52	9.63	86.57
Samples: 1, 2 and 3 Pila Spi; Samples: 4,5,6,7, and 8 Fat'ha						Av. 16.47	Av. 80.00
4	6.88	41.74	40.07	10.78	99.47	57.42	31.47
5	7.03	40.29	39.40	13.16	99.88	54.45	32.16
6	5.82	43.43	39.96	10.02	99.23	63.06	26.62
7	4.94	45.05	40.55	8.90	99.44	69.14	22.60
8	1.36	11.20	9.07	77.55	99.18	16.62	6.22
Av. excluding sample (8)						Av. 60.77	Av. 28.21

Previous Studies

James and Kirkpatrick (1980) determined the dissolution rate constant (K) for an almost pure limestone sample (97.90% calcite). They used the same apparatus used for gypsum in (James and Lupton, 1980). A limestone core sample having a diameter of (28 mm) and a length of about (100 mm) was drilled right through, and the resulting hole has a diameter of (2.5 mm). Distilled water was allowed to pass through the hole for a period of up to (3) hours and the concentration of calcium ions in water was determined by atomic absorption spectrometer (AAS). Temperature was between (5) and (23 °C). Flow velocity was from (0.05) to (0.75 m/s). A value of dissolution rate constant (K) at (10 °C) and flow velocity of (0.05 m/s) was ($0.4x10^{-5}$ m/s).

Letterman (1995) determined the dissolution rate constant (K) for limestone samples containing variable amounts of dolomite and insoluble residue (I.R). In his experiment a limestone disc with a diameter of about (3 cm) and a thickness of (3 mm) was glued to a metal disc attached to a rotating shaft at a speed ranging from (200) to (1200 rpm). The whole assembly was immersed in a tank containing deionized water. The concentration of calcium and magnesium in the water (due to dissolution of the rotating limestone disc) was measured with time by (AAS). Water temperature was between (5) and (25 °C) and the time of experiment was up to (1.6) hours. Dissolution rate constant for a sample (B) at (12 °C) and (600 rpm) was ($0.84x10^{-5}$ m/s). The sample consists of (calcite 92%, dolomite 4% and I.R. 4%).

Al-kattan, et al, (2002) determined the dissolution rate constant (K) for Calcite at acidic condition and at 25Cº in the presence of Na PO_3 and $MgCl_2$.

Alarrajy (2008) determined the dissolution rate constant (K) for a limestone sample of Fat'ha Formation (Middle Miocene). A core sample having a diameter of about (6.5 cm) and a length of (13 cm) was fixed inside a cylindrical cell and a drinking (tap) water was allowed to pass on its surface at a flow velocity between (0.05) and (1.75 m/s) at three different temperatures (25, 40 and 60 °C). The time of experiment was one hour. The dissolution rate constant (K) was rather high, ranging from ($8.23x10^{-5}$) to ($57.36x10^{-5}$ m/s). At a flow velocity of (0.5 m/s) and a temperature of (25 °C) the value of (K) was ($39.25x10^{-5}$ m/s).

Factors Affecting The Dissolution Rate Constant (K)

The important factors that affect the dissolution rate constant (K) of limestone and calcium sulphate rocks (gypsum and anhydrite) are: the concentration of calcium ions in solution; the pH; the temperature; the time (t) which represents the duration of dissolution process on the sample, and lastly the flow velocity of the dissolving solution.

The concentration of calcium ions (m Ca^{2++}) in solution is expressed in (mmol/Kg) and the higher the pH of the solution, the lower is the (m Ca^{2++}), that is calcite reaches saturation state at low concentrations of calcium ions and higher pH. The higher the (CO_2) pressure the higher the (m Ca^{2++}) concentrations.

Using the equation of (Langmuir, 1977, p.198): [$mCa^{2++}=9.057x\ (pCO_2)^{0.3613}$], it is possible to calculate the (pCO_2). In the present study, the concentration of Ca^{2+} ions for calcite is (28 ppm) and equals to (0.7 mmole/Kg). This gives a value for (pCO_2) of ($10^{-3.46}$) which is practically equals to (CO_2) pressure ($10^{-3.5}$ bar) at atmospheric pressure of one bar.

At this CO_2 pressure and (m Ca^{2++}) concentration of (0.7 mmole/Kg), and according to (Langmuir, 1997, Fig.6-6, p.202), the saturation pH of calcite is about (8.3). This means that and ignoring other factors (time and flow velocity) calcite in Tigris River water of the present study (pH=8.2) is near saturation.

James and Lupton (1978), James and Kirkpatrick (1980), Letterman (1995), Aljubouri and Al-Kawaz (2007) and Alarrajy (2008), all noted a direct relationship between temperature of the dissolving solution and dissolution rate constant (K). However, temperature is only important when dissolution experiments are carried out at variable or wide range of temperatures. In the present study the range of temperature of river water was rather narrow (10-14 °C) and therefore its effect is rather limited. It only serves for comparison with other works.

The longer the time (t, sec), the more mass (dm) is dissolved. This is important in the case when the concentration of the solution for calcite (m Ca^{2++}) is near saturation. In this case the dissolution rate is rather slow and requires longer time to reach a measurable weight loss. This is exactly what happened in the present study. The experiment required (8) months for the loss of only (19 g, 1.4%) as an average from a mass of (1.38 Kg) for samples (4 to 7) (Tables 1 and 4).

Perhaps, the most important factor affecting the dissolution rate constant (K) is the flow velocity (V, m/s). Regarding the effect of temperature on the value of (K), all the mentioned workers, also observed a direct relationship between flow velocity and the dissolution rate constant (K). However, Aljubouri and Al-Kawaz (2007) and Alarrajy (2008) stated that the effect of flow velocity on (K) is much more pronounced than that of temperature.

It must be emphasized that it is rather difficult to compare values of (K) obtained from different experiments by different authors, since the whole experimental model in each case is different leading to different values of dissolution rate constant (K).

Discussion

Dolomite in Table (3) was calculated by converting all MgO to dolomite; (Dolomite%=MgOx4.5733). Calcite was then calculated after subtracting (CaO) in dolomite from total (CaO) and converting the remaining to calcite (Calcite%= CaOx1.7848) (Aljubouri, 1972). To determine (C) in equation (1), the concentration of calcium carbonate ($CaCO_3$) in the dissolving solution, HCO_3 or CO_3 concentrations in river water analysis (Table 2) could not be used, since both give higher values of ($CaCO_3$) than that given by (C_s), i.e. (C_s-C) will be negative. The reason is the dissolved carbon dioxide in water which increases the values of HCO_3 and CO_3 (James and Kirkpatrick, 1980; Langmuir, 1997). In this case, the concentration of calcium in Table (2) must be used. But first the equivalent calcium for SO_4 is calculated, subtracted from total calcium and the remaining is converted to $CaCO_3$. This gives value of (C) of (0.007 Kg/m^3) and (C_s-C) becomes (0.008 Kg/m^3). The dissolution rate constant (K, m/s) could then be calculated and is given in Table (4).

Table 4: Dissolution rate constant (K, m/s) of the studied samples.

S.N.	dM (Kg)	dt (sec)	Area (m^2)	C_s - C	K (m/s)
1	n.d.	$21.88x10^6$	0.0311	0.008	--
2	n.d.	$21.88x10^6$	0.03053	0.008	--

3	n.d.	$21.88x10^6$	0.0784	0.008	--
4	0.015	$21.88x10^6$	0.0265	0.008	0.33
5	0.010	$21.88x10^6$	0.0247	0.008	0.24
6	0.020	$21.88x10^6$	0.0266	0.008	0.44
7	0.030	$13.65x10^6$	0.030	0.008	0.56
8	0.055	$21.88x10^6$	0.055	0.008	0.59

C_s = 0.015 Kg/m^3; C = 0.007 Kg/m^3; Flow velocity = 0.83 m/s; pH = 8.2;
n.d. = not detected.T=12 ^{o}C

Pila Spi samples (1 to 3) did not exhibit any measurable loss after immersion for eight months. This is due to their high (MgO) or dolomite content which averages at (80%) (Table 3). This suggestion is confirmed by Fat'ha samples (4 to 7) where dissolution rate constant (K) increases with calcite content from (0.24x10^{-5} m/s) to (0.56x10^{-5} m/s) with increasing calcite from (54.45%) to (68.14) (Tables 3 and 4). This is in agreement with the findings of Letterman (1995, p.48).

The plot of (calcite%) versus (dissolution rate constant K) gives a good linear relationship (Fig.2) with the following equation:

Y (K) = 0.02183 X,(calcite%) – 0.9575 (Intercept C) ……….(2)

So that, the value of (K) could be predicted from knowing calcite or dolomite percentages or from (MgO%).

The insoluble residue (I.R.) of Fat'ha samples (4 to 7) gives an inverse relationship with the dissolution rate constant (K) though the relationship is not so linear (Fig.3). This is also in agreement with Letterman (1995). The equation for this relationship is:

Y (K) = - 0.075 x (I.R.) + 1.229 ……….(3)

Fig.2: Relationship between calcite content and dissolution rate constant (K) (Data from Tables 3 and 4).

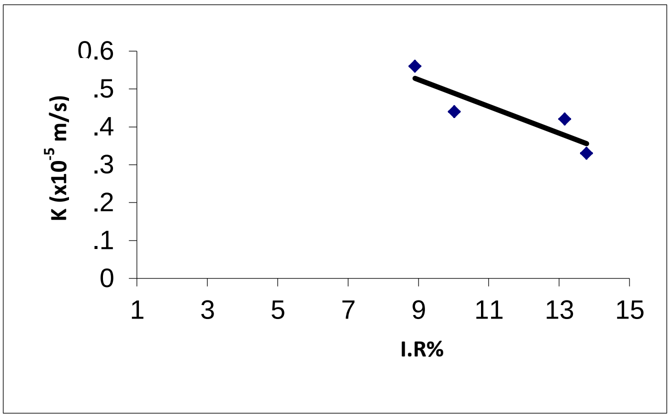

Fig.3: Relationship between insoluble residue (I.R) and dissolution rate constant (K) (Data from Tables 3 and 4).

The not so high linearity of the relationship is possibly due to the different proportions of quartz and clay minerals which both constitute the bulk of the insoluble residue. It could be assumed that a sample with relatively high quartz content which is highly resistant to weathering and erosion would give lower value of dissolution rate constant (K).

Sample (8) with highest dissolution rate constant (K) of (0.59x10^{-5} m/s) has the lowest calcite content (16.62%) and the highest insoluble residue (77.15%) and can not be plotted on figure (2). This sample is obviously not a carbonate; it is more likely to be a marl. The high value of (K) (0.59x 10^{-5}m/s) is not only due to dissolution since the amount of calcite is very small; it is due to relatively high erodibility of the marl (clayey materials) subjected to running water (erodibility is the resistance of a material, a soil or a marl, to detachment and transport; Atawoo and Heerasing, 1997.

The values of dissolution rate constant (K) of the present study range from (0.24×10^{-5} m/s, sample 5) to (0.56×10^{-5} m/s, sample 7) (sample 8 is excluded), with an average of (0.39×10^{-5} m/s) which is very close to that given by James and Kirkpatrick (1980) of (0.4×10^{-5} m/s). However, flow velocity of the present study (0.83 m/s) is much higher than that in James and Kirkpatrick (opt. cit.) of (0.05 m/s). Temperature of water of present study was (12º C) as an average, close to that of the authors (10º C). The other important difference is the chemical composition of the limestone. Calcite percent of the present study, as an average is (60.77%, Table 3). On the other hand, calcite percent in James and Kirkpatrick (opt. cit.) is (97.85), that is it is almost a pure calcite. As it has been stated earlier, the higher the calcite, the higher the dissolution rate constant (Fig.2). It is perhaps that this high calcite percent makes up for the low flow velocity of the experiment..

Conclusions

1. Carbonate samples with high dolomite contents (about 80%) do not exhibit any detectable dissolution. On the other hand, samples with low dolomite, high calcite (60% average) have a dissolution rate constant (K) of about (0.39×10^{-5} m/s). This value is very close to that of James and Kirkpatrick (1980) of (0.4×10^{-5} m/s).
2. It has been proved that dissolution rate constant (K) increases with increasing calcite or decreasing dolomite and decreases with increasing amount of insoluble residue.

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ثابت معدل ذوبان الكاربونات في البيئة الطبيعية

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الملخص

تم حساب ثابت معدل ذوبان الكاربونات (K) لثمانية نماذج تابعة لتكوين البلاسبي (الايوسين الاوسط–الاعلى، 3 نماذج) وتكوين فتحة (المايوسين الاوسط، 5 نماذج)، وذلك بغمر هذه النماذج في مياه نهر دجلة لفترة (8) اشهر. وتم ملاحظة ان نماذج تكوين البلاسبي الثلاثة لم تظهر أي فقدان محسوس في الوزن بسبب وجود الدولومايت، وعليه لم يكن بالامكان قياس ثابت معدل الذوبان (K). ان قيمة ثابت معدل الذوبان (K) لنماذج تكوين الفتحة الخمسة تقع ضمن المدى من ($0.24x10^{-5}$ m/s)والى($0.56x10^{-5}$ m/s) وقد لوحظ بأن ثابت معدل الذوبان (K) يزداد بازدياد نسبة الكلسايت (نقصان الدولومايت) في نماذج الدراسة. ومن جهة اخرى هناك علاقة عكسية بين ثابت معدل الذوبان (K) ونسبة الفضالة غير الذائبة (.I.R).