Experimental study of gypsum and anhydrite dissolution due to surface flow

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ABSTRACT
An apparatus for studying the surface dissolution of soluble rocks was constructed to investigate the effect of flow velocity on the surface dissolution rate of rocks containing gypsum and anhydrite. Results reveal that the calcium concentration reaches a saturation status which is independent of the flow velocity. In addition, the presence of other soluble materials affect the rate of solubility. Another important conclusion was that the dissolution constant rate is invariable at a specified upper limit of flow velocity. A generic relation for the dissolution of materials consisting of different compositions was proposed. Finally, it was suggested that the concentration of the soluble materials can be quantified and correlated using the electrical conductivity of the solution.

RÉSUMÉ
Un appareil pour étudier la dissolution de la surface sur des roches solubles a été construit pour étudier l'effet de la vitesse d'écoulement sur le taux de dissolution en surface des roches contenant du gypse et de l'anhydrite. Les résultats révèlent que la concentration en calcium atteint un état de saturation qui est significativement indépendant de la vitesse d'écoulement. De plus, la présence d'autres matériaux solubles affecte la vitesse de solubilité. Une autre conclusion importante est que le taux constant de dissolution est invariable à une limite supérieure spécifiée de la vitesse d'écoulement. Une relation générique pour la dissolution de matériaux constitués de compositions différentes a été proposée. Enfin, il a été suggéré que la concentration des matériaux solubles peut être quantifiée et corrélée en utilisant la conductivité électrique de la solution.

1 INTRODUCTION

The dissolution of rocks is a process in which soluble minerals are dissolved by the flow of water above the surface of the rock or through the rock seams and cracks, leading to development of spaces through the rock. As a results of connections between the cracks and fissures, a conduit is formed which is augmented over time such that water flow can transport particles through it. This phenomenon when occurred in hydro-geotechnical sites, can lead to increased permeability of foundations and abutments, demolition of injection curtains, progressive and intolerable subsidence, and even loss of stability of superstructures and their eventual destruction.

Gypsum, anhydrite, halite, dolomite, and calcite are common soluble minerals widely found at shallow depths throughout the world (Craft et al., 2007; James and Kirkpatrick, 1980). Almost one-fourth of the Earth's surface is composed of gypsum and anhydrite deposits, and nearly one-tenth of them are outcrops (Ford and Williams, 1989). Wide areas of gypsum karst exist throughout the world. A detailed review of such karsts is provided by Klimchouk et al. (1996).

Different mechanisms are responsible for the dissolution of minerals. They include: dissolution of particulate materials in specific rock formations, dissolution due to flow through cracks and fissures in soluble rocks, dissolution of rocks as a result of turbulent flow above soluble rocks (e.g. in riverbeds), and finally dissolution by the laminar diffusion process prevailing at the interface of soil layers (Farid and Habibagahi, 2007).

One of the first researches on the dissolution of rocks related to the diffusion mechanisms was explained by Nernst (Nernst, 1904). Kinetics of dissolution of gypsum is found to be transport-controlled, whereas the rate of dissolution of anhydrite is controlled by both chemical and transport processes (Barton and Wilde, 1971). Moreover, the rate of dissolution may be controlled by the ratio of solution volume to solid area ($\frac{V}{A}$) (Dreybrodt, 1980).

One of the first comprehensive researches conducted on the subject of dissolution of rocks is attributed to Calcano and Alzura, who discussed the phenomenon of dissolution of sulfite rocks (Calcano and Alzura, 1967).

Liu and Nancollas considered the dissolution of fine crystals of gypsum to be a linear function of the concentration, C, and the saturated concentration (C_s) of the solution containing gypsum. They described it using the following equation:

$$\frac{dM}{dt} \propto (C_s - C) \qquad [1]$$

in which M is the mass of calcium sulfite dissolved at time t, C_s is the saturated concentration and C is the concentration at time t (Liu and Nancollas, 1971).

Fabuss et al. introduced Eq. 2 for quantifying the anhydrite dissolution (Fabuss et al. 1969):

$$\frac{dM}{dt} \propto (C_s - C)^2 \qquad [2]$$

James and Lupton carried out a comprehensive study of dissolution of gypsum and anhydrite in the foundation of

hydraulic structures. On the basis of earlier studies as well as theoretical and empirical evidence, they suggested Equations 3 and 4 for the dissolution of gypsum and anhydrite, respectively:

$$\frac{dM}{dt} = KA(C_s - C) \tag{3}$$
$$\frac{dM}{dt} = KA(C_s - C)^2 \tag{4}$$

in where K is the constant of dissolution rate per unit area, and A is the surface of calcium sulfite which is exposed to water flow (James and Lupton, 1978).

The dissolution of limestone was examined by White using Eq. 5, proposed for evaluating the constant of dissolution rate (White, 1977):

$$\frac{V}{A} \times \frac{dc}{dt} = K(C_s - C) \tag{5}$$

in which V is the volume of circulating water, dc is the differential of concentration and n is the degree of reaction.

Since gypsum karst features are quickly recognized (Klimchouk, 1996), the associated hazards in terms of environmental impacts is becoming a growing concern. Moreover, the construction of water-retaining structures requires a reliable risk assessment analysis (Ford and Williams, 1989; James, 1992; Klimchouk and Andrejchuk, 1996). To this end, it is of particular importance to understand the interaction between rock and water and how the dissolution rates of soluble ingredients can be related to the hydraulic and chemical conditions imposed.

Numerous researchers carried out experimental and numerical investigations on the factors affecting the dissolution process, including: the effects of temperature, salinity of solvent, the area exposed to fluid flow (the hole created along the axis of sample), flow velocity, and purity of the sample on the dissolution process (Christoffersen, 1976; Dreybrodt, 1988; James et al., 1981; James and Kirkpatrick, 1980; James and Lupton, 1985; Jeschke and Dreybrodt, 2002; Lebedev and Lekhov, 1990; Raines and Dewers, 1997; Rickard and Sjoeberg, 1983; Serafeimidis and Anagnostou, 2012; Shearman and Mossop, 1973; Weyl, 1958).

Past research on the solubility of rocks have been conducted either using the flow of water through a hole created in the rock sample, or by studying the dissolution of small disks of soluble rocks rotating inside the solvent fluids, with the aim that relationships for modeling the dissolution of rocks made of a pure mineral are obtained (see e. g. Al-Rawi et al., 2011; Aljubouri and Al-Kawaz, 2007; Baumann et al., 1985; Dreybrodt et al., 1996; Fisher et al., 2011; James and Lupton, 1978; Jeschke et al., 2001; Liu and Dreybrod, 1997; Raines and Dewers, 1997). However, relationships for rocks consisting of different minerals, which is the case in many real situations, are not yet presented. Moreover, in many actual conditions, water typically flows on the flat surfaces of rocks rather than through seams and cracks. Therefore, in the present study, an apparatus was constructed allowing for the water to flow above the sample surface. Using this apparatus, a number of samples composed of pure gypsum or different ratios of gypsum and anhydrite with various exposed surfaces were examined to illustrate the influence of various factors such

as flow rate on dissolution. Finally, based on results from previous research and those obtained in the current study, a general and simple relationship is proposed for the dissolution of rocks consisting of different minerals.

2   EXPERIMENTAL METHODS

2.1   Dissolution Apparatus

A photograph showing the various parts of the dissolution apparatus is shown in Figure 1. It consists of three main parts: the rock sample container, the pump and its related connections and equipment, and the tank and its equipment including the weir and piezometer. The sample is covered on its five faces but is exposed on its top surface in order to allow its exposition to only surface fluid flow.

For this purpose, a plexiglass sample container was constructed such that it ensured covering the sample on all sides except for its top surface. In order to decrease turbulence of the water flow, the inlet and outlet were designed with a slope and a perforated plate was placed at the flow entrance. Also in order to allow for the release of the air bubbles from the container, two valves were used in the inlet and outlet sections.

The sample container was reinforced and sealed using two steel frames, foam and rubber to insure stability and water tightness of the system in simple, quick and economical fashion.

In order to use the system in extended working hours, and also to prevent changes in the temperature of the circulating water, the pump and electromotor were separated. Moreover, a pressure gauge installed between the pump outlet and entrance to the container provided the pressure developed in the system.

The tank used was made of polyethylene and had a storage capacity of 120 litres. In order to measure the volume flow rate, a right-angle V-notch weir was used in conjunction with a piezometer placed at an upstream distance of 28 cm from the weir to ensure that the curvature of water surface where water level is measured is negligible (Bos, 1976). The introduction of air into the pumping system and sample container was minimized by making use of a perforated plate placed inside the tank which would reduce the flow turbulence. The discharge of the tank could be done by means of a valve connected to the tank.

2.2   Experimental Procedure

The dissolution tests can be divided into three steps: preparation of the sample and placing it in the container, performance of the tests and the final processes before the next test is conducted.

The preparation stage: the surface of the sample must be rasped to make it smooth and flat. Some silica sand is washed, dried and placed at the bottom of the container such that the rock sample will be raised to the appropriate level in order to allow for the surface flow. The sample
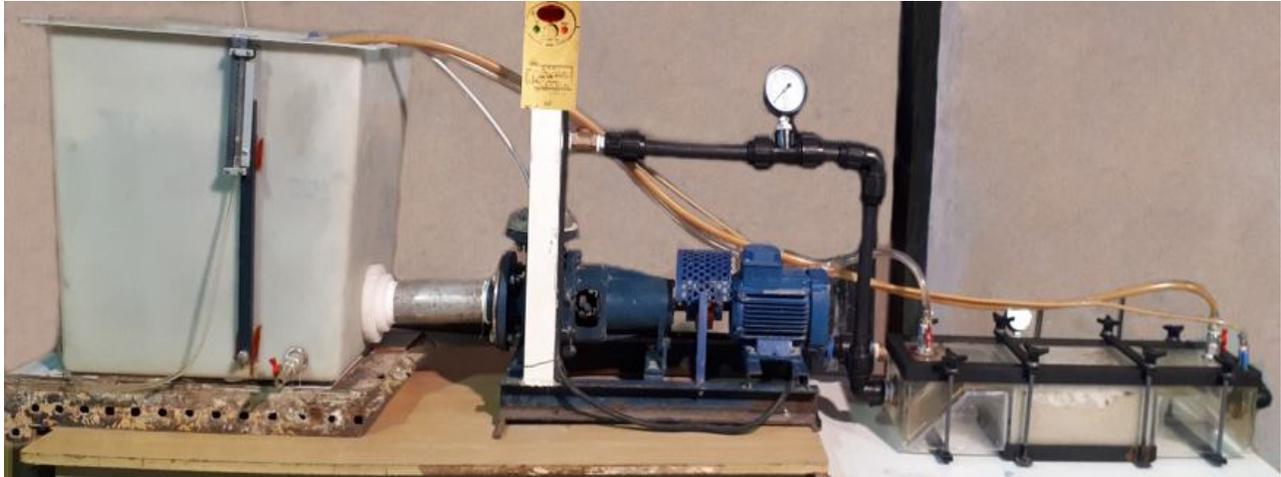
Figure 1. Dissolution apparatus of rock sample

was then sealed with silicon glue on all sides to ensure its water tightness and prevent water from flowing anywhere other than from the top of the sample. The top cover of the container was then placed and sealed using the steel frames and clamps and the sample container was then connected to the transporter pipes. Finally, the tank was filled with water and the system was ready to work.

Because large volumes of water were needed and that in many realistic conditions, considerable soluble minerals are present in the dissolving water, drinking water was used for performing the experiments. Table 1 shows a chemical analysis of the water used for the experiments. Performance of the tests: after placing the specimen and completion of preparation of the apparatus, the desired flow rate is adjusted using the piezometer and By setting the engine speed with an inverter. In order to measure the calcium concentration at any desired stage, a 100 mL sample of the water was taken at specified times for electric conductivity (EC) and titration tests. The tests were stopped when the calcium concentration reached a constant value.

The final process: When the test was completed, all parts of the apparatus were dismantled, washed and prepared for the next tests.

2.2.1 Measurement of Electrical Conductivity (EC)

Electrical conductivity (EC) is a manifestation of the amount of ions present in water. Measurement of EC is a common way to determine concentration of available ions in water. Distilled water is not electrical conductive, and an increase in dissolved ions will result in an increase in the electrical conductivity and a decrease in the electrical resistance. Considering the effect of temperature on electrical conductivity of water, the measurements must be corrected as if it were measured at a standard temperature of 25°C. According to Eq. 6, the electrical conductivity will increase about 2% for each unit increase in temperature (Sorensen and Glass, 1987).

$$EC_t = EC_{25}[1 + 0.02(t - 25)] \qquad [6]$$

The device used for the measurements of EC was equipped with an ATC (Automatic Temperature Compensation) capability. This means that the change in temperature of the water sample was corrected as if it was measured at 25°C.

Table 1. Results of drinking water chemical analysis

Composition	mg/L
Calcium	42
Magnesium	8.4
Sodium	6
Potassium	0.5
Chlorides	8
Nitrates	5
Fluorides	0.48
Nitrites	0.005
T.H[1]	190
TDS[2]	230
pH	7.7

[1]Total Hardness
[2]Total Dissolved Solids

2.2.2 Titration Test

The titration test is defined as measurement of the precise volume of a solution having a well-defined concentration, known as the standard solution, which is required for complete reaction with a specific volume of the solution with unknown concentration. The substances needed for titration tests include sodium hydroxide solution 1 M, EDTA (Ethylenediaminetetraacetic acid) solution of 0.01 M and moroxide indicator.

On each sample taken from the tank water, at least three titration tests were performed, and the mean result was reported as the calcium concentration. Measured initial calcium concentration in water was 32-48 mg/l and EC at 25°C ranged between 374-501 µS/cm.

2.2.3 In-Tank Weir Calibration

In order to determine the relationship between the head over the triangular weir installed in the tank and the flow rate, six calibration tests were performed. Two pumps were used at the entrance and exit of the tank to preserve water level at upstream and downstream of the weir. At each stage, the flow rate was controlled using valves. It is noted that in all of the tests, the distance between the water level at downstream and weir notch was more than 10 cm, which is in agreement with the criterion of Bos (1976)

In right angle V- notch weirs, the following relationship is applicable:

$$Q = CH_1^{2.5}$$ [7]

in which Q is the flow rate and H_1 is the distance between water level and bottom of the V-notch weir (Bos, 1976). Eq. 7 was fitted to the results of calibration tests and C=1.71 (R^2=0.98) was obtained.

2.3 Rock Specimens

Samples from two types of rock were used: a pure gypsum sample, obtained from the Semnan city gypsum mine (Iran); and, a gypsum, and anhydrite sample with some impurity such as limestone and dolomite, taken from the Marash dam site located 125 km southwest of Zanjan, Iran. Based on the results of XRF analyses on the samples (Table 2), the purity percentage of gypsum mine of Semnan is 99.17. Tests of composition analysis conducted on the Marash dam samples indicated that they contain nearly 54% gypsum, 37% anhydrite, and 9% other minerals, mainly consisting of Marl composition. However, due to variability in the rock samples, the gypsum and anhydrite content in test sample 5 was found to be more than test sample 6.

3 RESULTS

Table 3 summarizes the experimental results for each of the tests conducted.

3.1 Variations of Calcium Concentration with Time

Variations of calcium concentration with time for different flow velocities are shown in Figure 2. Generally, for both of the two types of samples, the increase in the flow velocity leads to a rise in the dissolution rate of soluble rock as well as a remarkable decline in the equilibrium time (time to reach saturated concentration, C_s).

In specimens with low purity, minerals other than gypsum and anhydrite also dissolve in water, affecting the dissolution rate and the maximum dissolution capacity (C_s). Comparisons between test 2 with 5, and test 3 with 6 (in which the flow velocity is the same for each pair, but the sample purity is different) reveals that purity ratio and type of impurities highly affect the dissolution trend. Also, the presence of some impurities, depending on their type (mostly "Marl type" in the present study, which does not

affect gypsum dissolution) can bring about a remarkable decline in the dissolution rate. In other words, when impurities have no major effect on dissolution (such as in the case of "Marl" in the current study), the effect of purity ratio may be seen as being approximately equivalent to the effect of the ratio of the rock surface containing soluble minerals exposed to the aqueous phase.

Also comparison between tests 5 and 6 shows that the effect of flow velocity on the dissolution rate is much more substantial compared to the purity of samples.

According to results of tests 3 and 4, it may be deduced that there exists an upper limit for the flow velocity after which the increase in the flow velocity does not contribute to increase in the dissolution rate of materials. During test 6 (with 0.65m/s flow velocity), a substantial increase in the turbidity of water was observed over the initial 48-h test period, but this was followed by a gradual reduction in turbidity as the test continued. The existence of an upper limit for flow velocity, at which K approaches a constant value, was also verified by James and Lupton (1978).

Table 2. Result of XRF analysis on rock sample

Oxide	Pure gypsum sample	Sample for 5th	Sample for 6th
	Content (%)	Content (%)	Content (%)
H_2O (LOI)[1]	20.97	22.72	25.54
NA_2O	-	0.16	0.17
MgO	0.2	0.21	0.3
Al_2O_3	-	0.59	1.32
SiO_2	-	2.3	6.9
SO_3	46.4	42.7	34.8
Cl	-	0.012	0.03
K_2O	-	0.22	0.42
CaO	32.3	30.6	29.1
MnO	-	0.097	0.19
Fe_2O_3	0.02	0.31	1.13
SrO	0.11	0.081	0.1

[1]Loss on Ignition

As dissolution continues over time, calcium concentration in water reaches a maximum value, C_s, after which water is not capable of dissolving more $CaSO_4$. The measured value of C_s for calcium obtained from pure gypsum samples was 660 mg/L which is equivalent to 2.8 g/L of gypsum. This value is in agreement with the value reported by James and Kirkpatrick (1980) which corresponded to C_s=2.5 g of gypsum per liter of distilled water at 10°C. The relatively small difference is attributed to experiment temperature and titration errors. C_s is highly dependent on factors such as temperature, type and amount of available ions in the solvent, and solubility of the other ingredients. The flow rate primarily decreases the time to reach the saturation state and has no effect on the value of C_s, however, it affects the erosion rate.

Table 3. Summary of experiment characteristics

Test No.	Type of rock	Gypsum content (%)	Q (L/min)	flow velocity (m/s)	Circulating water volume (L)	Contact area (cm^2)	Time test (hr)	Temperature range (°C)
1	gypsum	99.17	50	0.16	82	371.71	409	13-19
2	gypsum	99.17	100	0.33	95	395.69	240	19-23
3	gypsum	99.17	150	0.49	100	395.69	168	20-25
4	gypsum	99.17	200	0.65	90	371.71	120	20-28
5	gypsum, anhydrite and etc.	gypsum and anhydrite contents in the 5th sample was more than the 6th sample	100	0.33	96	357.7	240	19-23
6			150	0.49	100	381.5	153.5	21-25
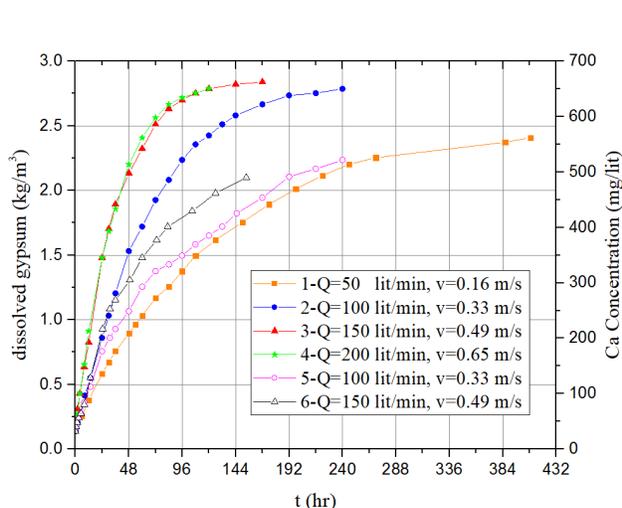
Figure 2. Variations of calcium concentration with time for different flow velocities

Figure 3. Variation of EC with time for different flow velocities

Therefore, it is recommended that the value of C_s is estimated using experiments taking into account the ambient temperature and the type and amount of the available ions in the solvent.

3.2   Variations of EC with Time

The variation of EC with time is shown in Figure 3 for the various tests and is identical to that of calcium (gypsum) concentration with time, shown in Figure 2. Presence of other soluble materials cause a gradual increase in EC as can be seen from tests 5 and 6. Over the time, the rate of change in the EC and calcium concentration reduces and the concentration approaches a constant as the water becomes saturated. The maximum value of EC obtained from experiments was about 2200 µS/cm.

Since the trend of variations of EC and calcium concentration are quite similar (Figures 2 and 3), and considering that EC measurements are much easier than conducting titration tests, the concentration of dissolved ingredients will be estimated using EC.

3.3   Variations of EC with Gypsum Concentration

In Figure 4, the variations of EC with gypsum concentration for different flow rates is shown. It can be seen that EC increases linearly with the concentration of gypsum. Table 4 provides the relationship between EC and gypsum concentration obtained from test with various flow rates. The slope of graphs related to impure samples are slightly less than the pure gypsum, mainly due to time-dependent dissolution process of other soluble materials leading to rise in the value of EC.

According to Table 4, the effect of flow rate on the EC correlation with gypsum concentration can be neglected. Therefore, measurement of EC and its substitution into Eq. 8 may provide an evaluation of gypsum concentration using A=0.0015 for pure samples. Interestingly, impure samples reveal a similar linear trend (Figure 4) but with a slightly different A value (A=0.0013 in this study).

$$C_{gyp} = A\,[EC-EC_0] \tag{8}$$
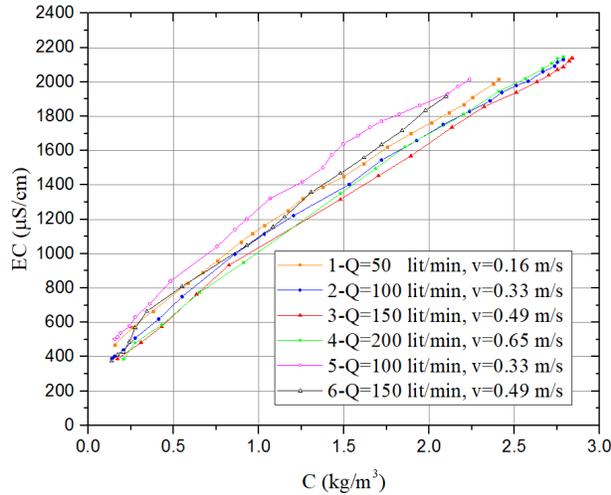
Figure 4. Variations of EC with gypsum concentration for different flow velocities

3.4 Changes in Sample Surface Appearance

Figure 5 shows the appearance of the sample before and after test 2 (flow rate of 0.33 m/s-pure gypsum), and Figure 6 shows the appearance of the sample before and after test 5 (flow rate of 0.33 m/s- gypsum plus other soluble materials).

In pure samples, the dissolution of gypsum in the surrounding areas (at the contact area between the glue and rock sample) is much more remarkable than the impure samples. Moreover, holes are observed on the surface of the pure sample, which were not present before the experiments, likely due to small seams and cracks that were present inside the sample.

In impure samples, surface obstacles (glue) have no effect on dissolution. Also, due to different strata of sample, no holes were appeared after the tests.

Table 4. Relation between EC and gypsum concentration for different flow velocities

Types of rock sample	v (m/s)	Relationship between EC & C_{gypsum}	R^{2*}
gypsum	0.16	$C_{gyp}=0.0015[EC-EC_0]$	1
gypsum	0.33	$C_{gyp}=0.0015[EC-EC_0]$	0.99
gypsum	0.49	$C_{gyp}=0.0016[EC-EC_0]$	1
gypsum	0.65	$C_{gyp}=0.0015[EC-EC_0]$	1
gypsum, anhydrite and etc.	0.33	$C_{gyp}=0.0013[EC-EC_0]$	0.99
	0.49	$C_{gyp}=0.0013[EC-EC_0]$	1

[*]Correlation Coefficient

4 CORRELATION OF THE TEST RESULTS WITH THE EQUATION OF JAMES AND LUPTON (1978)

4.1 Calculation of K for Pure Gypsum (n=1)

For modelling the dissolution process, James and Lupton (1978) proposed the differential Eq. 9:

$$\frac{dM}{dt} = KA(C_s - C)^n \qquad [9]$$

in which n is a parameter accounting for the type of soluble material, with n=1 for gypsum and n=2 for anhydrite (James and Lupton, 1978).

Considering that dM=Vdc and using n=1, they arrived at Eq. 10 below:

$$\ln\left(\frac{C_s}{C_s-C}\right) = K\frac{A}{V}t \qquad [10]$$

For the dissolution of gypsum, where V (m³) is the circulating water volume.

Figure 5. The sample before (left) and after (right) test 2 (flow rate of 0.33 m/s-pure gypsum)

Figure 6. The sample before (left) and after (right) test 5 (flow rate of 0.33 m/s- gypsum plus other soluble materials)

It should be mentioned that all experiments in the current study were conducted using drinking water. The water temperature during tests varied between 20°C and 25°C throughout the day (except test 1, which had a water temperature of 13°C to 19°C). In all of the (pure) gypsum samples, the gypsum content was the same and their exposed surfaces were also similar. Therefore, the only variable during experiments was the flow velocity, and other factors affecting dissolution such as gypsum content, solvent salinity, contact area and temperature remained the same for all the tests. Moreover, since the flow velocity does not influence C_s (Figure 2), all experiments are expected to reach the same value of saturation concentration. This value was measured to be 2.8 kg/m³ of gypsum according to the titration tests performed.

Values of K for pure gypsum samples (experiments 1 to 4) were calculated using Eq. 10, which is plotted in Figure 7 for various flow velocities in conjunction with the values reported by James and Lupton (1978) for gypsum.

An acceptable general agreement is observed between the results. Also, it can be seen that with the increase in the flow velocity, the dissolution rate increases. Another important point is that there is an upper limit for flow velocity after which K remains constant. This is in agreement with the results reported by James and Lupton (1978). Determination of the upper limit of the flow velocity, however, requires performing more experiments.
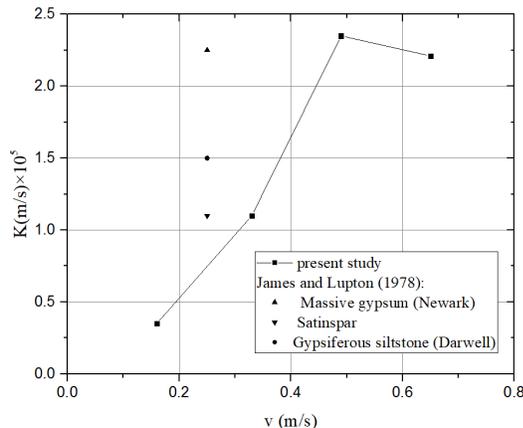
Figure 7. Variations of K with different flow velocities for experiments that performed with pure gypsum samples in conjunction with the values reported by James and Lupton (1978)

4.2   Calculation of n and K for Pure Gypsum

The values of n and K in Eq. 9 for the current experiments were calculated and the results are presented in Table 5. An important conclusion is that the power "n" in the equation for gypsum at different flow velocities is not constant and is not equal to unity either. The values of K were obtained using regression analyses in which n was also unknown. The difference between the obtained values and the values presented in section 4.1 is less than 5% indicating that K is not sensitive to the power in the equation. Due to the presence of anhydrite in samples of the Marash Dam, the value of n is greater than 1 and close to 2, which is in agreement with the results of the experiments of James and Lupton (1978) for the dissolution of anhydrite (n=2). Generally, with increasing flow velocity, the power of the equation decreases.

5   A GENERAL RELATIONSHIP FOR MODELLING THE DISSOLUTION OF GYPSUM AND ANHYDRITE

The relationship for the prediction of dissolution of gypsum and anhydrite proposed by James and Lupton (1978) has two unknown parameters, namely, n and K. As indicated before, the n value obtained for various materials and velocities is not constant Changes in the value of n leads to change in the dimension of the constant of dissolution rate (K). Hence, the exponent "n" and the dimension of the

constant "K" should be determined separately for each rock with a certain mineralogy or mineral composition. It is therefore preferable to obtain a general relationship for modeling rock dissolution in which such deficiencies do not exist.

Table 5. Values of n and K calculated using Eq. 9

Test No.	v (m/s)	K($\times 10^5$) (m/s)	K($\times 10^5$), n=1, (m/s)	n	R^2
1	0.16	0.34	0.35	1.29	0.95
2	0.33	1.15	1.1	0.71	0.95
3	0.49	2.26	2.35	0.74	0.95
4	0.65	2.24	2.21	0.66	0.82
5	0.33	0.39		1.70	0.78
6	0.49	0.61		1.53	0.54

Inspection of the variation of concentration with time indicates that among the various mathematical functions, the trend in the exponential function is closer to the trend in the variations of experimental results. The general form of the exponential functions is $y = ab^{cx} + k$, in which the power is the independent variable. Considering the trend in variations of the calcium or gypsum concentration with time, the general form of the equation the proposed for this variation is chosen to be of the form shown in Eq. 11, where C is the concentration at time t, a is the final value of concentration and b represents the rate of dissolution before equilibrium is reached.

$$C = a(1 - e^{-bt}) \qquad [11]$$

Considering the physical parameters typically used in the dissolution process, the concentration at different times takes the form shown in Eq. 12, in which C (kg/m^3) is the material concentration at time t, C_s (kg/m^3) is the saturation concentration and K (1/s) represents the constant of dissolution.

$$C = C_s(1 - e^{-Kt}) \qquad [12]$$

In Eq. 12, the power used in the dissolution equation of James and Lupton (1978) has been eliminated, and the dimension of the constant used for the dissolution rate for both gypsum and anhydrite is 1/s.

6.   VALIDATION OF THE PROPOSED RELATIONSHIP USING EXPERIMENTAL RESULTS

Considering that in the performed experiments on pure gypsum, only the flow velocity was variable and for which C_s=2.8 (kg/m^3) was obtained, the relationship for the dissolution will be of the form shown in Eq. 13. Eq. 13 is plotted in Figure 8 in conjunction with the current experimental data.

Since the temperature of water in test 1 was less than other experiments and that the temperature influences the saturated concentration, the saturated concentration in test

1 is expected to be less than 2.8 (kg/m^3). That experiment was terminated after 18 days since it didn't reach equilibrium state during this period because of the very low flow velocity.

In Figure 9, the constants of dissolution rate obtained for different flow velocities are plotted assuming C_s=2.8 (kg/m^3). Based on this figure, the increase in flow velocity results in increase in the value of K, but beyond a certainflow velocity, the increase in flow velocity has no effect on changing the value of K.

$$C = 2.8(1 - e^{-Kt})$$ [13]
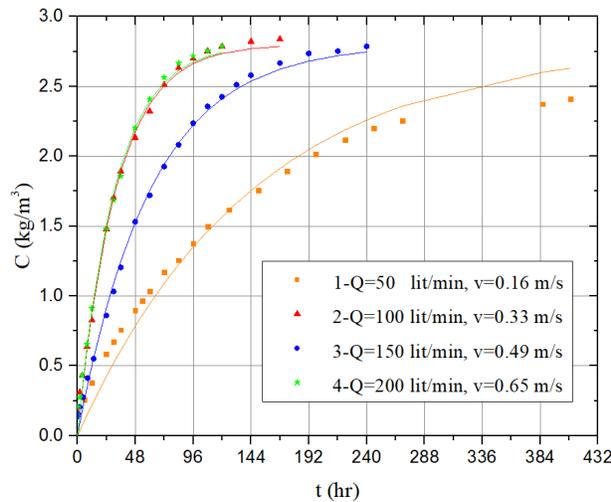
Figure 8. Curve fitting of Eq. 13 on the results of experiments performed with pure gypsum samples

7 MODELING RESULTS OF PREVIOUS STUDIES USING THE PROPOSED DISSOLUTION FUNCTION

7.1 James and Lupton (1978)

Results of the experiments reported by James and Lupton (1978) on the dissolution of gypsum and anhydrite are modeled using the current proposed Equation (Eq. 12) and the result is presented in Table 6. Comparison of test results and model relationship using Eq. 12 is shown in Figure 10 for gypsum and in Figure 11 for anhydrite.

As can be seen, the proposed relationship is in complete agreement with the results of James and Lupton (1978). Since the dimension of dissolution constant rates in the proposed equation (1/s) is not the same as those in James and Lupton (m/s for gypsum and m^4/kg.s for anhydrite), no comparison can be made regarding the dissolution rate constants between the two studies. It is noted that the constant of dissolution rate depends on various factors such as the flow velocity, temperature, type and composition of the solvent and the sample, and the area exposed to water flow. The advantage of the proposed relationship over that by James and Lupton is the elimination of an unknown parameter (n) and the unification of dissolution constant rates for both anhydrite and

gypsum, which allows the modeling of dissolution of rocks composed of both minerals.
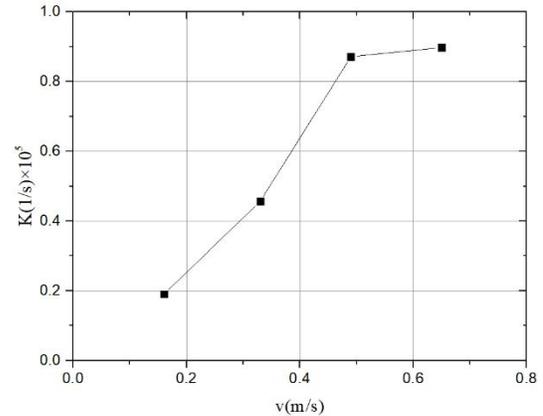
Figure 9. Variations of K with different flow velocities with C_s=2.8 (kg/m^3) for experiments that performed with pure gypsum samples

Table 6. Curve fitting of experimental results of James and Lupton (1978) with the form of Eq. 12

Sample	v (m/s)	T (°C)	C_s (kg/m^3)	K×10^5 (1/s)	R^2
gypsum	0.3	23	2.58	121	1
anhydrite	0.09	23	2.03	7.7	1
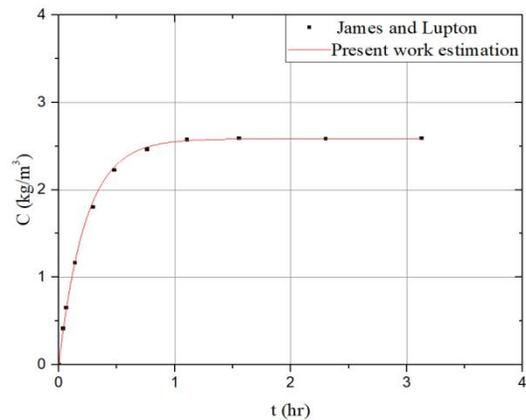
Figure 10. Curve fitting of experimental results of James and Lupton (1978) with the form of Eq. 12 for gypsum

7.2 Al-Rawi et al. (2011)

Al-Rawi et al. (2011) investigated the effects of temperature, flow velocity, solvent salinity, gypsum content, and contact area (size of the hole drilled in the sample) using a similar apparatus to that of James and Lupton (1978). Their experimental results are curve fitted

to Eq. 12 and the result is summarized in Table 7. Due to lack of reports on the experiment characteristic (circulating volume of water, exposed area to water flow and saturated concentration), the comparison with the relation proposed by James and Lupton (1978) is not possible.

The value of C_s for experiments related to effects of flow velocity, size of the drilled hole and gypsum content was taken as 2.58 (kg/m^3) (similar to the value used by James and Lupton, 1978) and for solvent salinity it was taken to be equal to 3.7 (kg/m^3) (according to graphs presented by Al-Rawi et al. (2011)). Results shown in Table 7 indicate that the proposed equation can model the variations of concentration with time very well, and can take into account effects of the various factors on the dissolution of the rock materials.
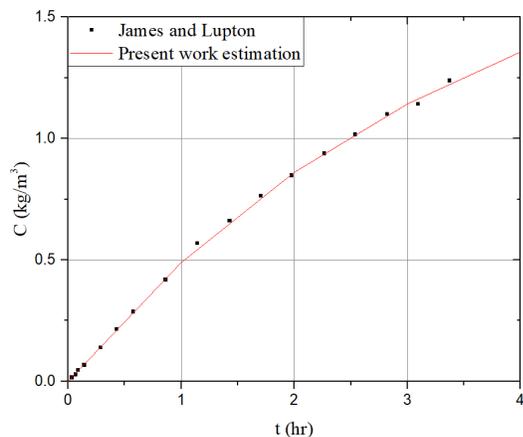
Figure 11. Curve fitting of experimental results of James and Lupton (1978) with the form of Eq. 12 for anhydrite

8   CONCLUSION

An apparatus was designed and constructed to investigate the surface dissolution process in rocks. Using gypsum and anhydrite as the archetypes of available soluble minerals, effects of flow velocity on the rate of dissolution was examined. Results validated the existence of a saturated concentration value which is independent of the flow velocity in the system. Also an upper limit for the flow velocity was obtained from the experiments beyond which the dissolution constant rate remained unchanged. Furthermore, results of titration tests exhibited a linear correlation with the measured calcium concentrations, proposing that arduous concentration experimentation may be replaced by the much simpler EC measurements. Finally, a general relationship for the dissolution of both gypsum and anhydrite was proposed, with the advantage that the   parameters needed for modeling are universal and easier to obtain in comparison with the relationships proposed in previous research.

Table 7. Curve fitting of experimental results of Al-Rawi et al. (2011) with the form of Eq. 12

a) Effect of flow velocity

Gypsum content (%)	v (m/s)	K×10^5 (1/s)	R^2
16.7	0.64	1.59	0.96
16.7	1	1.74	0.94
16.7	1.18	1.85	0.94
78.2	0.64	6.62	0.91
78.2	1	7.4	0.92
78.2	1.18	8.48	0.95

b) Effect of hole diameter

Gypsum content (%)	Hole diameter (mm)	K×10^5 (1/s)	R^2
75.1	4	6.9	0.95
75.1	6	8.73	0.91
75.1	8	13.01	0.92
82	4	8.28	0.95
82	6	11.43	0.94
82	8	20.06	0.98

c) Effect of solvent salinity (gypsum content= 84.7%, C_s=3.7 kg/m^3)

NaCl Content (%)	K×10^5 (1/s)	R^2
1	15.77	0.99
3	19.78	1
5	29.47	1

d) Effect of gypsum content

Gypsum content (%)	K×10^5 (1/s)	R^2
16.1	1.44	0.99
39.2	2.26	0.88
78.2	7.56	0.91
89.9	16.84	1

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