

Dissolution Rate of Gypsum Under Different Environments

Zeki A. Aljubouri

*Department of Geology
College of Science
Mosul University*

Hazim A. Al-Kawaz

*Dams and Water Resources
Research Center
Mosul University*

(Received 30/11/2006 , Accepted 22/2/2007)

ABSTRACT

Dissolution rate (K) of gypsum rocks of Fat'ha Formation (Middle Miocene) was determined at three different environments; closed system, that is still water and open system, that is flowing water and river water.

In closed system, the dissolution rate is not a constant; it increases as the concentration (C) of the dissolving solution. In an open system, dissolution rate is a constant at constant flow velocity (V) and given temperature (T). It increases with an increase of either of them; however, the effect of (V) on (K) is much more pronounced than that of (T).

Published data on the value of dissolution rate (K), based on laboratory experiments, are exaggerated by a factor of (4.1) to (4.6) compared with values of the present study. This is possibly due to the fact that these data represent dissolution through fissures in gypsum rocks and being far from natural environments for gypsum dissolution.

/

() (K)
.
(K)
(K) (C)
(V) (K) (T) (V) (K)
(T) (K)
(K) (4.6) (4.1)

INTRODUCTION

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

Due to the relatively high solubility of the gypsum rocks, it is therefore important to study their rate of dissolution, among other properties, in order to be able to take the necessary measures to avoid the collapse of dam foundations. The solubility of a substance is the number of grammes dissolved in one litre of water at equilibrium, i.e. at saturation and at a given temperature. Dissolution rate is the speed at which this equilibrium is reached.

James and Lupton (1978) derived the following equation for the dissolution rate (K) for gypsum:

$$dM / dt = KA(Cs - C) \dots\dots\dots(1a)$$

$$K = dM / dt.A(Cs - C) \dots\dots\dots(1b)$$

where *M* (Kg) is the mass of calcium sulphate dissolved in time *t* (sec.), *A* (m²) is the area exposed to solution, *C_s* is the concentration of saturated solution, i.e. the solubility of gypsum (2.41 Kg/m³ at 20° C, Weast, 1974) and *C* is the concentration of calcium sulphate in solution at time *t*.

The purpose of this work is to determine the dissolution rate of gypsum at three different environments, that is, in still water, i.e. in closed system, where flow velocity is zero; in open system, that is in flowing water and in river water environments. Also to compare the results of this work with published experimental results on dissolution rate of gypsum.

METHODOLOGY

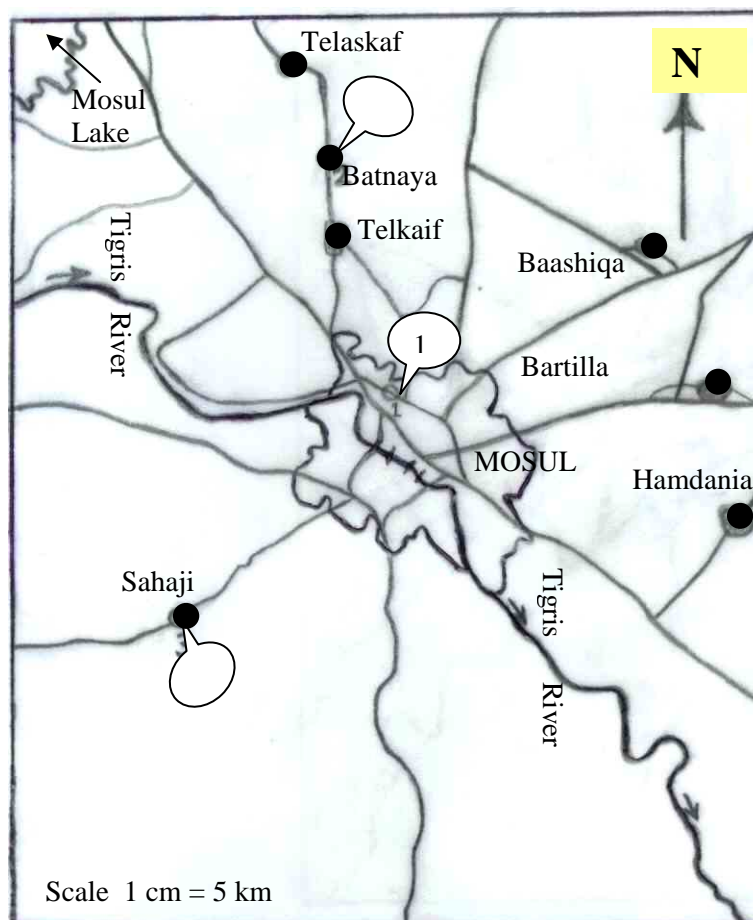
A total number of (28) gypsum samples were collected from Fat'ha Formation at three localities, Al-Araby living quarter, 7 km northwest, Batnaya village, 22 km north and Sahaji village, 18 km southwest of Mosul (Fig.1). Only (18) samples were used, the rest are being kept for future studies.

Gypsum samples were each cut into a regular cube with dimensions of (10x10x10 cm). The chips from all samples were collected, mixed and crushed to a fine powder, then sieved to pass through (250 μ). The powder was used for chemical analysis, including (H₂O⁺) determinations. The physical properties, like form, hardness, colour, lustre and streak, all conform with typical gypsum properties.

Specific gravity determinations were carried out on (20) samples and the method used was similar to Jolly's balance method, where each cube weighed in air then hanged, immersed and weighed in water. The average determined value was (2.31) very close to the published value of (2.32) for gypsum (Hurlbut and Klein, 1977, Berry et al., 1983).

Chemical analyses for the three major oxides (CaO, SO₃ and H₂O⁺) were carried out. CaO was determined volumetrically by titration the calcium ion solution in the unknown sample with 0.01M EDTA solution, using erichrome black T (EBT) indicator. SO₃ (and SO₄ in water samples) was determined gravimetrically using barium chloride (BaCl₂) for the precipitation of sulphate ions (Vogel, 1961, p.473 for CaO, p.463 for

$\text{SO}_3 \cdot \text{H}_2\text{O}^+$ was determined by heating (1 g) of powdered sample in a furnace at (300°C) for one hour and the loss in weight was converted to (H_2O^+).



Locality (1): Al-Arabi Living Quarter. Samples: 1,2,7,8,13 and 14.
 Locality (2): Batnaya. Samples: 3,4,9,10,15 and 16.
 Locality (3): Sahaji. Samples: 5,6,11,12,17 and 18.

Fig.1: Sample locations.

For the determinations of the dissociation rate (K) at different environments, three types of experiments were carried out and six gypsum cubes were used for each type. Still water (closed system) experiments were performed at home; a metal can having the dimensions of (24x24x35 cm) and a capacity of about (20) litres was used. The cube was placed on a skeletal metal stand inside the can which was filled with ordinary tap water, placed in the shade and covered. Water temperature for these and for flowing water experiments were taken three times daily and an average was used at the end of each experiment. Loss in water due to evaporation was continuously compensated so that water level remained constant. The assemblage is similar to that in figure (2), but without inlet and outlet water.

For flowing water experiments, the arrangement is shown in figure (2). Flow rate was taken every two days by monitoring the time taken to fill a bottle of (2) litres, then converting the (l/s) to (m/s) by dividing (l/s) by the area of the cross section of the cylindrical outlet pipe.

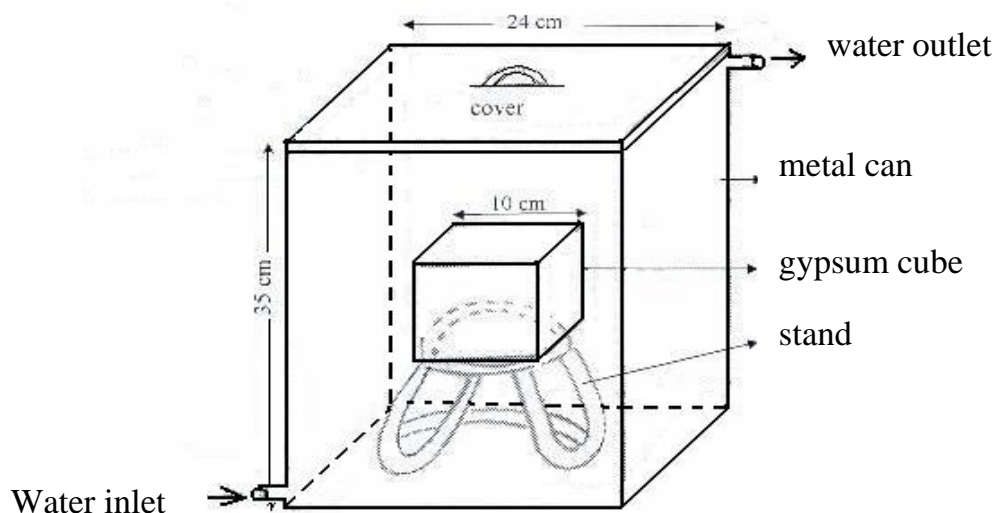


Fig.2: Perspective sketch diagram for the dissolution of gypsum cube.

For river water experiments, holes of about (2) cm in diameter were made throughout the sides of the can. The edges of its open end were bent inwards for a distance of about (4) cm and holes were made in the resulting frame. The threads of one end of a (5) m rope were made into a net through these holes, covering the open end of the can, allowing water to enter the can freely and preventing the cube from getting out. The other end of the rope was fastened to a post. The can was floating within Tigris River water and the gypsum cube inside it was freely swirling. It was noticed that there was slight variation in river water temperature with time and hence temperature recordings were taken every (10) days. Flow rate of Tigris River at the place of experiments was measured by placing a cork float in water and monitoring the time it takes to cover a distance of (100) meters.

To get the concentration (C) of the dissolving solution, at least three water samples at different intervals, were taken for each experiment and their (SO_4) contents were determined and converted to (CaSO_4). In closed system experiments, only the last concentration (C) at the end of the experiment was used since this represents the total mass dissolved (dM) in the total time (dt). In flowing and river water experiments, an average (C) was used, since there were little variations in the concentrations of the dissolving solutions.

RESULTS AND DISCUSSION

The results of chemical analyses for the major oxides, each as an average of five analyses are: CaO 32.65%; SO_3 46.21% and H_2O^+ 20.42%, giving a total of 99.28%. Normative mineralogy for these analyses (Aljubouri and Sulayman, 1996, Aljubouri and Khattab, 1997, Aljubouri, 1999, Aljubouri and Alrawas, 2006) is gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 97.57% and anhydrite CaSO_4 1.94%. It is clear that from physical properties, specific gravity and chemical analyses, the collected samples are gypsum of high purity.

The results of the three types of experiments, closed system, flowing water and river water, for the determinations of the dissolution rate of gypsum are shown in table (1). For closed system (still water) experiments (Table 1A), dissolution increases with the increase of the concentration (C) of the dissolving solution, that is with the decrease of (Cs-C), but the relationship is not linear (Fig.3). Calculations show that soon after (67)

Dissolution Rate of Gypsum Under Different

days, that is at (67.5) days, the concentration (C) reaches equilibrium, that is (Cs-C) equals zero and the value of dissolution rate (K) drops to zero.

Table 1: Dissolution rate (K) of gypsum at different environments (for symbols see equation 1).

A- STILL WATER (Closed System)						
Sample No.	dM (Kg)	dt x10 ⁶ (s)	Cs-C (Kg/m ³)	V (m/s)	K x10 ⁻⁵ (m/s)	T (°C)
1	0.0143	1.728	1.696	0	0.0081	27
2	0.0214	2.592	1.339	0	0.010	27
3	0.0286	3.456	0.982	0	0.014	27
4	0.0357	4.320	0.625	0	0.022	28
5	0.0393	4.752	0.447	0	0.031	28
6	0.0428	5.184	0.268	0	0.051	28
B- FLOWING WATER (Open System)						
Sample No.	dM (Kg)	dt x10 ⁶ (s)	Cs-C (Kg/m ³)	V (m/s)	K x10 ⁻⁵ (m/s)	T (°C)
7	0.85	2.592	2.23	0.08	0.24	24
8	1.13	3.456	2.24	0.08	0.24	24
9	1.54	3.456	2.25	0.14	0.33	25
10	1.00	2.246	2.26	0.14	0.33	25
11	1.37	2.592	2.26	0.19	0.39	26
12	1.81	3.456	2.24	0.19	0.39	26
C- RIVER WATER (Open System)						
Sample No.	dM (Kg)	dt x10 ⁶ (s)	Cs-C (Kg/m ³)	V (m/s)	K x10 ⁻⁵ (m/s)	T (°C)
13	1.17	2.160	2.20	0.24	0.41	16
14	1.39	2.592	2.18	0.24	0.41	16
15	1.72	2.592	2.21	0.30	0.50	16
16	1.15	1.728	2.20	0.30	0.51	17
17	1.64	2.160	2.30	0.34	0.55	17
18	1.96	2.592	2.30	0.34	0.55	17

Cs=2.41 Kg/m³, V=Flow velocity (m/s), Area (A)=0.06 m²

It is interesting to note that Al-Dabbagh (1989) in his study of the solubility of gypsum in a closed system and using the water of Mosul Lake as dissolving solution, found that the concentration of the solution in calcium sulphates, that is (C) after (10) days only, was (2.393 g/l). This is equal to the concentration (C) after (67) days of this study. The reason for this discrepancy is that Al-Dabbagh used for his experiment very fine gypsum powder (< 75 micron). Surface area and hence solubility increases with decreasing grain size (Krauskopf, 1967).

James and Lupton (1978), James and Kirkpatrick (1980) and Langmuir (1997) used the term "dissolution rate constant" for (K) in equation (1), however, it has been proved that in this study it is not a constant in a closed system (Table 1A). The third author gave it a value of (0.2x10⁻⁵ m/s) at (25° C) and the value estimated from James and Lupton (1978, Fig.10) and from Aljubouri and Khattab (1996, Table 2) is about (0.14 x10⁻⁵ m/s). Both values are extrapolated or estimated, that is not determined from experiments. In table (1A) the expression (dM/dt) is constant for all variations in (dM) and (dt) throughout the six experiments (samples 1 to 6). It has a value of about (8.26x10⁻⁹ Kg/s).

In the flowing water experiments, the dissolution rate (K) ranges in value for the six studied sample (7 to 12) from (0.24x10⁻⁵ m/s) to (0.39x10⁻⁵ m/s) at velocity from (0.08 m/s) to (0.19 m/s) respectively and an average temperature of (25° C, Table 1B). It is clear that dissolution rate (K) and (dM/dt) in this case are constants at constant flow velocity (V) and given temperature.

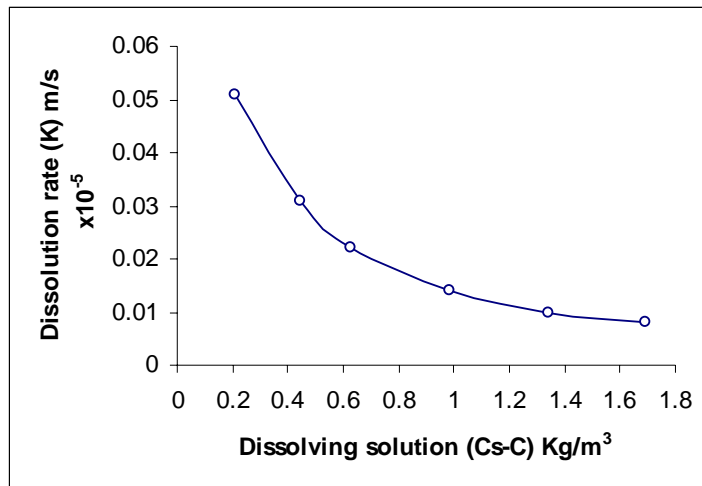


Fig. 3: Closed system. Relationship between concentration of the dissolving solution (Cs-C) and dissolution rate (K). Data from Table (1A).

In the river water experiments, the dissolution rate (K) ranges in value, for the six samples (13 to 18) from $(0.41 \times 10^{-5} \text{ m/s})$ to $(0.55 \times 10^{-5} \text{ m/s})$ at flow velocity (V) from (0.24 m/s) to (0.34 m/s) and an average temperature (16.5° C) , Table 1C). Here, again (K) and (dM/dt) are constant at constant flow velocity (V) and given temperature.

In both cases, the plot of flow velocity (V) versus dissolution rate (K) is linear, however, river water samples have lower slope than flowing water samples (Fig.4). This is because the temperature of river water is lower by about (9° C) than the flowing water (Table 1B and C) and dissolution rate (K) is proportional to flow velocity (V) and temperature (T).

The equation for (K) at different (V) and (T) deduced from table (1) is:

$$K \times 10^{-5} (\text{m/s}) = 1.353V + 0.005T + 0.015 \dots \dots \dots (2)$$

From this equation, it is clear that the effect of flow velocity on (K) is much more pronounced than the effect of (T). Calculations prove that for each (1° C) change in temperature (T) there is only change of $(0.006 \times 10^{-5} \text{ m/s})$ in (K); on the other hand, for each (0.1 m/s) change in (V), there is a change of $(0.15 \times 10^{-5} \text{ m/s})$ in (K).

The determined values for (K) in table (1 B and C) for flowing and river waters are all much lower than the published values by James and Lupton (1978), James and Kirkpatrick (1980) and Langmuir (1997) for the same or similar (V) and (T). For example James and Lupton (Opt. cit.) gives a value for the "dissolution rate constant" (K) of $(1.4 \times 10^{-5} \text{ m/s})$ at flow velocity (V) of (0.15 m/s) and temperature (T) of (23° C) . Using equation (2), the value is $(0.33 \times 10^{-5} \text{ m/s})$ for this study.

In table (2) in James and Lupton (1978) and table (2) in Aljubouri and Khattab (1997), the equation for dissolution rate (K) at different (V) and (T) is:

$$K \times 10^{-5} (\text{m/s}) = 8.614V + 0.105T - 2.28 \dots \dots \dots (3)$$

Using this equation for the calculations of (K) of the present study for samples (7 to 18) in table (1 B and C), the value obtained for (K) in the flowing water and river water are bigger, on an average by a factor of (4.6) and (4.1) respectively than those obtained in the present study and shown in table (1).

Using equation (3) for sample (18) as an example, the value of (K) is $(2.43 \times 10^{-5} \text{ m/s})$ instead of $(0.55 \times 10^{-5} \text{ m/s})$, which means that either (dM) in table (1 C)

should be (8.7 Kg) instead of (1.96 Kg), or (dt) would be (6.8) days instead of (30) days and these figures are very unrealistic, if not impossible.

Using ionic strength (I) for the calculation of dissolution rate (K), the following equation (Langmuir, 1997, p.71) is used:

$$K / K_o = 1 + 2.2\sqrt{I} \dots\dots\dots(4)$$

where (K_o) is the dissolution rate at zero ionic strength (1.5×10^{-5} m/s) at (V) of (0.14 m/s) and (T) of (23° C) (James and Lupton, 1978, Table 4, p.260). Langmuir (1997) gave the relationship between ionic strength (I) and obtained conductivity (EC) as:

$$I = 1.7 \times 10^{-5} \cdot EC \dots\dots\dots(5)$$

On the other hand, the relationship between (SO_4) concentration (Y) and electrical conductivity (EC, X) (Al-Nuaimi et al., 2006) is:

$$Y(SO_4) = 1.1829X(EC) - 517.1 \dots\dots\dots(6)$$

From this equation (SO_4) calculated ($= C \times 0.7056 \text{ Kg/m}^3$) as an average from table (1 B and C) is converted to (EC), then using equation (5), the (EC) is converted to (I) and in this case the value of (I) is (930×10^{-5} mos/cm). Using equation (4), dissolution rate (K) can be calculated, with a value of (1.82×10^{-5} m/s) instead of (0.33×10^{-5} m/s) as worked out from equation (2). It is also high compared with values for river water in table (1 B and C).

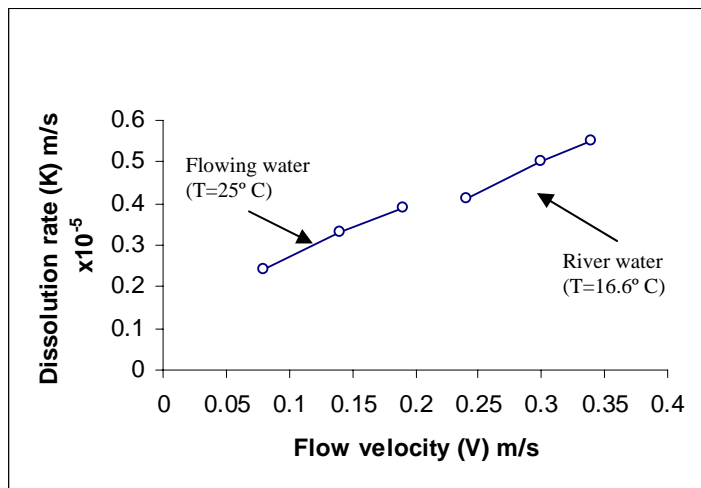


Fig. 4: Open system. Relationship between flow velocity (V) and dissolution rate (K). Data from Table (1B,C).

The most likely explanation for this rather large discrepancy for the value of (K) between the published data and present study is that the experiments of James and Lupton (1978) for the determinations of (K) were far from being natural environments. Distilled water was made to pass through a hole having a diameter of (2.5 mm) in a core of gypsum with a length of about (10 cm). Present study experiments involved the immersion of gypsum cube either in flowing water which is a good simulation of natural environments or in river water which is a real natural environments.

In fact, James and Lupton (Opt. cit.) experiments could be applied to fissures in gypsum rocks where and according to James and Kirkpatrick (1980) the dissolution rate (K) starts to increase rapidly when water flows through fissures having diameter of about (2.4 mm) in gypsum rocks.

CONCLUSIONS

The present study concludes:

1. Dissolution rate (K) for gypsum in a closed system is not a constant; it increases as the concentration (C) of the dissolving solution.
2. In an open system, dissolution rate is constant at a constant flow velocity (V) and given temperature (T), it increases with an increase of flow velocity (V) or temperature (T), however, the effect of (V) is much more pronounced than that of (T).
3. Published data on dissolution rate (K) are exaggerated by a factor of (4.1) to (4.6) compared with values of the present study. At flow velocity (V) of (0.15 m/s) and temperature (T) of (23° C) the dissolution rate (K) and according to these data is (1.4×10^{-5} m/s) instead of (0.33×10^{-5} m/s) in the present study. The most likely explanation is that these data represent experiments being far from natural environments but could be applied to fissures in gypsum rocks.

REFERENCES

- Al-Dabbagh, S.M., 1989. The dissolution of gypsum and anhydrite in closed system. Confidential, GS 18, DWRRC, University of Mosul, Iraq. (In Arabic).
- Aljubouri, Z.A., 1999. The effect of weathering on gypsum rocks (Middle Miocene) from west Butma area, Northern Iraq. Raf. Jour. Sci., Vol.10, No.1, pp.62-74.
- Aljubouri, Z.A. and Alrawas, A.M.S., 2006. Mineralogy and petrography of technical plaster and local juss. Iraqi Jour. Earth Sci., Vol.6, No.1, pp.1-11.
- Aljubouri, Z.A. and Khattab, S.I.A., 1997. The dissolution of calcium sulphate rocks below the foundation of large hydraulic structure. Raf. Jour. Sci., Vol.8, No.1, pp.63-73
- Aljubouri, Z.A. and Sulayman, M.D., 1996. Mineralogy and geochemistry of gypsum rocks of Al-Fat'ha Formation at west Butma area, northern Iraq. Raf. Jour. Sci., Vol.7, No.1, pp.114-128.
- Al-Nuaimi, H.J., Al-Abbasi, M.W. and Khattab, M.F., 2006. Hydrogeochemical and sedimentological study of Al-Khosar estuary, Mosul City, Northern Iraq, (In Arabic, In press).
- Berry, L.G., Mason, B. and Dietrich, R.V., 1983. Mineralogy. Freeman and Company, San Francisco. USA, 561p.
- Hurlbut, C.S.Jr. and Klein, C., 1977. Manual of mineralogy (after James D. Dana), 14th Edition, Wiley and Sons, New York, USA, 532p.
- James, A.N. and Kirkpatrick, I.M., 1980. Design of foundations of dams containing soluble rocks and soils. Quat. J. Enging. Geol., London, Vol.13, pp.189-198.
- James, A.N. and Lupton, A.R.R., 1978. Gypsum and anhydrite in foundations of hydraulic structures. Geotechnique, Vol.28, No.3, pp.149-272.
- Krauskopf, K.B., 1967. Introduction to geochemistry. McGraw-Hill Book Company, New York, 721p.
- Langmuir, D., 1997. Aqueous environmental geochemistry. Prentice Hall, New Jersey, USA, 600p.
- Vogel, A.I., 1961. Quantitative inorganic analyses. Longman, London, 1216p., (CaO, p.473, SO₃, p.463).