Investigation of solvent type on dissolution strength of gypsum foundations (Case study of Marash Dam)

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Abstract

In the construction of dams, geotechnical and hydrological studies are one of the most important measures before the start of the project. The presence of gypsum and anhydrite in the foundations and supports of the axis under study, concerns such as the risk of irregular settlements, dissolution of the foundation and, by its nature, instability in the foundations and supports of the dam.Dissolution of sulfate rocks proceeds by different mechanisms and at different rates compared to the dissolution of carbonate rocks [1]. For each type of stone, different factors affect the dissolution process. One of these factors is the type of solvent and its chemical composition. In this study, by conducting experiments on gypsum materials, the solubility of four types of distilled water solution, distilled water solution With one percent sodium chloride, The water sample of Marash dam and municipal water has been measured and calculated on the mentioned materials. Finally, the obtained results show the difference in the solubility of gypsum in the sample of the mentioned solutions.

Keywords: dissolution strength, gypsum materials, anhydrite, foundation, barrier, solvent.

Introduction

From ancient times the need for water has been and will be one of the main needs of human beings.With the increase of population and increasing need for water for consumption in various matters,it creates challenges for water supply. One of the ways to solve this challenge is the control of surface water by constructing dams. Experimental and theoretical results show that the presence of gypsum and anhydrite in the foundation and the selected axis of the dam, raises concerns about their dissolution over time. The solvent and the percentage of its chemical compounds affect the amount and speed of dissolution. In this research, four types of solutions have been tested on a sample of gypsum and anhydrite of Marash dam. The purpose of these experiments is to investigate the type of solvent and its chemical composition on the dissolution strength of gypsum-containing specimens. Which is located in Iran and near Zanjan province, should be studied in three types of solutions.

research method

In this research,at first, the chemical balance of gypsum and anhydrite and its chemical behaviors in the face of the solution have been briefly studied. Also, the solubility properties of gypsum and anhydrite with innovative relationship Lui & Nancollas (1971), which have been calculated, are mentioned. Dissolution (electrical conductivity and titration) is given and superficially compared with

each other. Finally, using the electrical conductivity test, the solubility of existing solvents relative to the mentioned sample (sample prepared from Marash dam containing gypsum) is investigated.

Gypsum dissolves by a simple two phase dissociation (solid and solvent):

$$CaSO_4 + 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2$$
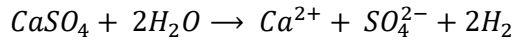
[1]

Gypsum, like $CaCO_3$ and salt, dissolves reversibly, but anhydrite does not. When anhydrite is dissolved it forms a solution of calcium sulphate which, at common temperatures and pressures, is in equilibrium with the solid phase of gypsum, but not with anhydrite. If disequilibrium of the solid-solvent system occurs, gypsum precipitates. This is due to the instability of anhydrite under normal surface and shallow sub-surface thermobaric conditions (Fig.1). The solubility of gypsum in pure water at 20°C is 2.531 g/l, or 14.7 mM/L. The dependence of the solubility of gypsum on temperature is reported by many authors (Blount & Dickson, 1973; James, 1992; Liley et ai, 1963; see Fig.2).[4]
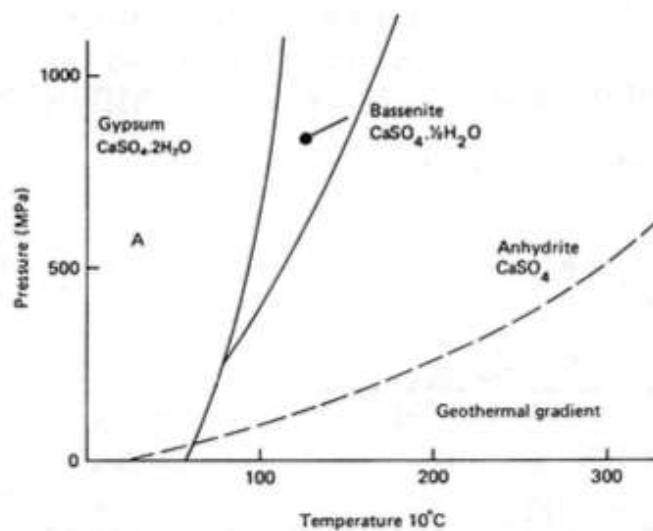

Fig.1. Equilibrium diagram for the system CaS0$_4$ - H$_2$O (after Zanbak & Arthur, 1986).

mum (about 2.66 gil) at 43°C. Cigna (1985) examined the possible effects on gypsum solubility caused by mixing waters at different temperatures. He found that when mixing equal amounts of two saturated waters (one at 10°C, and another at temperatures ranging from 40 to 100°C) the solubility in the mixture increased by between 2 and 13%. This effect may play some role in the karstification of areas with geothermal waters.

Anhydrite may be thought to lack specific solubility. This is due to its chemical instability in deep subsurface conditions (James, 1992). Some of the values presented in the literature are misleading: the actual solubility of anhydrite at ordinary temperature is equivalent to that of gypsum. When dissolved in water, anhydrite produces a solution $CaS0_4$ which eventually reaches an equilibrium concentration similar to the gypsum-water system in pure water, which is 2.00 g at 20 ° C.[1]
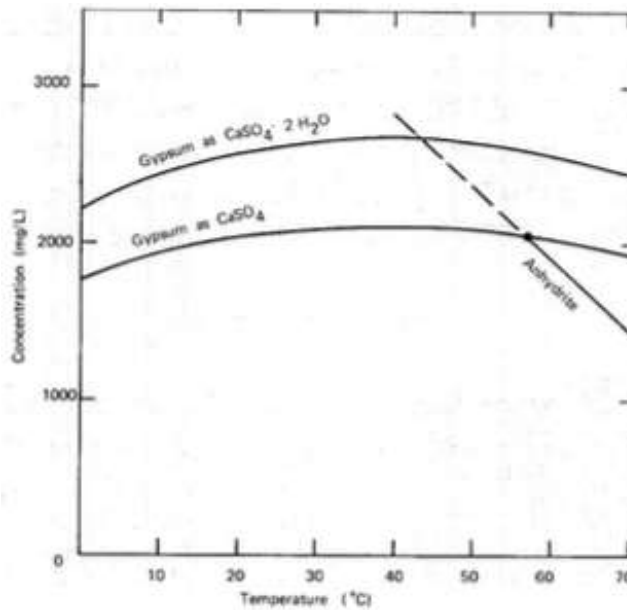
Fig. 2. Solubilitycurves for gypsum and anhy- drite based on the experimental data of Blount & Dickson (1973). The upper curve pertains to the mass loss of gypsum rock in solution. The lower curve is calculated as $CaSO_4$ and displays the invariant point at 58°C, where gypsum, anhydrite and liquid coexist (AfterWhite, 1988).[1]
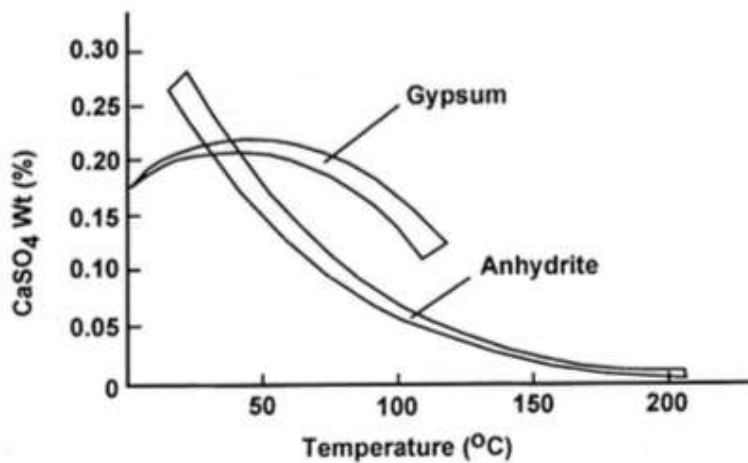

Fig. 3. Solubility of gypsum and anhydrite in water at one atmosphere pressu- re (after Zanbak & Arthur, 1986)[1]

James (1992) pointed out that anhydrite in contact with water tends towards a metastable state characterised by supersaturated solutions. These probably account for some of the high solubilities quoted for anhydrite, which range up to 3.5 g/L.

Figure 3 shows the solubility data for anhydrite and gypsum in their stability regions; this information was summarised by Zanbrak & Arthur (1986). The solubility of anhydrite is lower than that of gypsum under these pressure conditions, and decreases with increasing temperature.Pressure does not substantially affect the solubility of gypsum within common geological environments. In contrast the $CaCO_3 - CO_2 - H_2O$ system is influenced by the presence of a gas phase that makes it sensitive to pressure. The solubility of gypsum increases slightly at pressures exceeding 100 bars (Manikhin, 1966), but at depths of less than a thousand metres or so, the influence is negligible.[1]

2. Solubility properties of gypsum and anhydrite

Solubility of rock is a process that occurs with the flow of water on the rock or with the infiltration and movement of water inside the rock. The stone remains. This phenomenon will cause problems in the field of dam stability after dams. High dissolution rate with the development of cracks and fissures leads to increased permeability of the foundation.

The first people to start relatively comprehensive studies on rock solubility were Kalkano and Alzora, who in 1967 studied and discussed the solubility of sulfate rocks (gypsum and anhydrite) from an engineering perspective [2]. The researchers then studied how water seeped into the contact of calcium sulfate with other substances and how the phenomena resulting from dissolution were created and spread.

Lui and Nancolas (1971) considered the dissolution of gypsum microcrystals as a linear function of the normal dominance (C) and saturation concentration (C_s) of the gypsum-containing solution and expressed it as Equation 1:

$$\frac{dM}{dt} \propto (c_s - c) \qquad (1)$$

where in:

dM changes in mass or weight, dt changes in time, C is the initial concentration of calcium ions, C_s is the concentration of calcium ions in the saturated state.

Fabus et al. (1969) presented Equation (2) for the dissolution of anhydrite [2]:

$$\frac{dM}{dt} \propto (c_s - c)^2 \qquad (2)$$

3. The chemical composition of water

The type of water in the area consists of carbonate rocks in terms of carbonate chemical composition. Such waters are able to dissolve rocks if they are not saturated. For example, the presence of carbon dioxide significantly increases the solubility of calcium carbonate and can reach about 400 mg/l (400 ppm) [7]. This amount is 30 times more than its solubility in pure water and in these conditions the amount of carbon dioxide is more than 1320 ppm. However, if the concentration of carbon dioxide is low, the solubility of carbonates in pure water is higher [8].

4. Dissolution methods

4-1. Dissolution with conductor: A device called a conductometer is used to measure the conductivity of solutions. Each conductivity device has two identical platinum metal electrodes. The electrodes are placed in parallel in a Pyrex glass container or other durable glass. The set of these electrodes in a glass chamber is called a conductor cell. To measure the conductivity of a solution, a cell conductor is placed in that solution, and the device shows the conductivity of the solution with the appropriate voltage it sends between the electrodes.

One of the important parameters in determining the solubility of soluble materials is to change the maximum amount of soluble solvent in the solvent. Thus, a certain amount of soluble material is prepared in powder form and poured in a certain volume of solvent in stages. In each step, the soluble concentration and the number of the conductor are read until the change in the powder of the material inside the solvent does not change the number of the conductor and reaches the so-called saturation stage. µSiemens / Cm (micro Siemens per centimeter).

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Fig. 4. View of a digital conductivity meter

4-2. Titration method : Titration or titration is also called titration, [13] in chemistry is the determination of the concentration of an unknown solution by various methods. It is a common quantitative laboratory method in decomposition chemistry, used to measure the unknown concentration of an analyte. One of the best known titrations is acid and base volumetric titration. [18] Because volume measurement is so important in titration, it is also called volume analysis. A pure reagent, called a titrant or titrator, [14] is used as a suitable solution. A volume of titrant at a certain concentration reacts with a solution or analyte [15] to determine its concentration. The volume of reactant titrant is called the titrant. The purpose of a titration is to gradually and cautiously add the titrator to the solution containing the titrant until the reaction between the two is complete. And perform volumetric calculations based on it. The equivalence point in a titration occurs when the amount of titrant added is chemically exactly equal to the amount of analyte in the sample. For example, in the titration of sodium chloride with silver nitrate, the equivalence point is reached when we add one mole of silver ion for each mole of chloride ion in the sample. The point of equivalence of EDTA with calcium ions is when we add one mole of EDTA per mol of Ca. Sometimes it is more appropriate or even necessary to add the excess of the standard titrator to the analyte and then determine the excess by titration with the second standard solution. This method is called reverse titration. In this method, the equivalence point is equivalent to the point where the initial titer value is chemically equivalent to the analyte value plus the return titer value. The difference between the equivalence point and the end point of a titration is remarkable. The equivalence point of a titration is a theoretical point that cannot be determined empirically. Instead, by observing some physical changes made around the equivalence point, it can only be estimated. This physical change is called the end point. Every effort is made to ensure that the difference between the equivalence point and the end point is small. However, due to the inadequacies in physical changes and our ability to observe them, there is some difference. The volume difference between the equivalence point and the end point is called the titration error. Often an identifier is added to the solution to be titrated to create a visible physical change (end point) near the equivalence point. Large changes in the relative concentration of the analyte with the titrator occur in the equivalence point region. Concentration changes cause the detector to change its appearance. Examples of changes are: appearance or disappearance of color, discoloration, appearance or disappearance of solution turbidity. Often devices are used to detect endpoints. These devices respond to some of the properties of the solution that change significantly during titration. Examples of these devices are: voltmeter, ammeter, ohmmeter, colorimeter, temperature stability, conductivity and absorption meter.

5. Determination of maximum soluble gypsum in distilled water, Marash dam water, water with 1% sodium chloride and municipal water, by electric conduction method

5-1. One of the important parameters in determining the solubility of soluble materials (gypsum and anhydrite) is to determine the maximum soluble amount of these materials in water. The form is poured in stages and in each step the concentration of gypsum and anhydrite and the conductometer number are read until there is no change in the reading of the conductometer number. In this research, some gypsum prepared from the Marash dam site, in the mentioned solutions, with a volume of 250 cc and a temperature of 22 ° C, was poured step by step and the conductometer number was read.

5-2. To determine the maximum dissolution rate of gypsum, in a certain amount of four solutions (distilled water, distilled water and 1% sodium chloride, Marash dam water and municipal water), gradually pour powdered gypsum prepared from Marash dam and with a mixer, thoroughly It was stirred and the changes in the electrical conductivity of the water were measured by a conductivity meter (Figure 5). With increasing the amount of powder, the electrical conductivity of the solution increased, but in the end, increasing the other powder did not increase the electrical conductivity of the solution and the electrical conductivity reached a constant value. To be sure, more powder was added to the solution and stirred for several hours, but during this time the electrical conductivity of the solution remained constant, indicating that the solution had reached saturation. In this case, the measured values were recorded and diagrams of changes in electrical conductivity relative to the weight percentage of gypsum were drawn. This experiment was performed three times with the above waters (Figure 5).

A. How to pour gypsum powder

B. Electrical conductivity

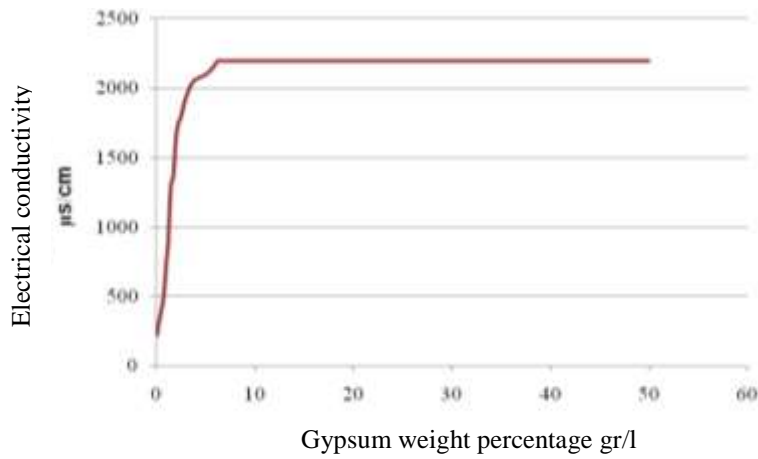**Fig. 5. Experiment to determine the maximum amount of gypsum soluble in different waters**

Gypsum weight percentage gr/l

Fig. 6. Changes in electrical conductivity versus weight percentage of gypsum in distilled water solution
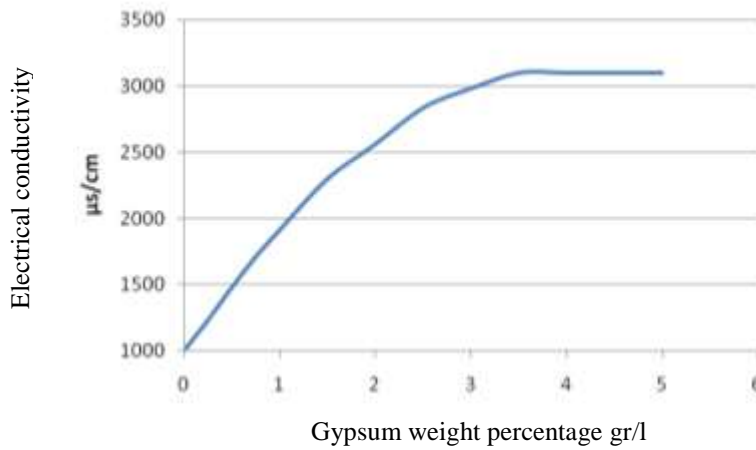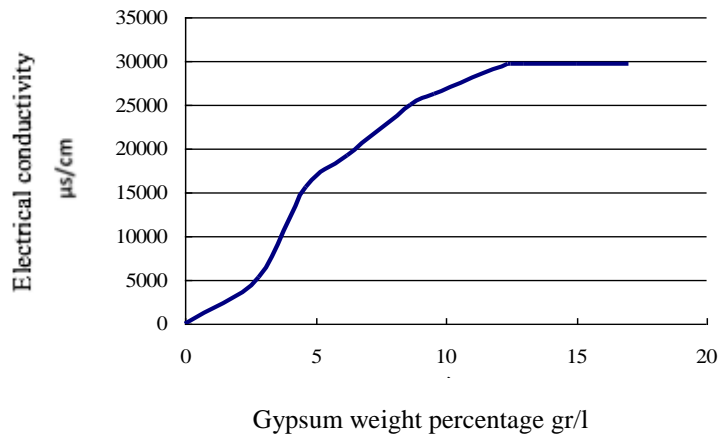

Gypsum weight percentage gr/l

Fig. 7. Changes in electrical conductivity versus weight percentage of gypsum in sediment water solution of Marash Dam

Gypsum weight percentage gr/l

Fig. 8. Changes in the electrical conductivity of gypsum versus weight percentage of gypsum in a solution of distilled water and 1% sodium chloride
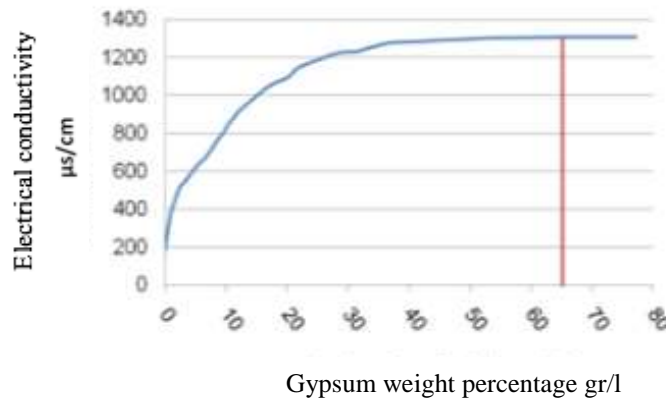

Gypsum weight percentage gr/l

Fig. 9. Changes in electrical conductivity versus weight percentage of gypsum in municipal water solution

Table 1 shows the values of maximum electrical conductivity and maximum gypsum soluble in different waters.

Table 1. Maximum electrical conductivity and maximum gypsum values

Type of solution	Maximum electrical Ec(µs/cm) conductivity	Maximum water-soluble Cs(gr/lit) gypsum
Distilled water	2200	6.25
Marash Dam Water	3100	3.5
Water with one percent sodium chloride	29750	12.5
municipal water	1310	65.2

For example, the detailed results of the maximum water-soluble gypsum test are shown in Table 2:

Table 2. test results for determining the maximum soluble gypsum in municipal water.

Maximum electrical conductivity (µs/cm)Ec	Maximum water-soluble (gr/lit)Cs	column
180	0	1
358	0.8	2
444	1.6	3

513	2.4	4
544	3.2	5
578	4	6
610	4.8	7
642	5.6	8
664	6.4	9
698	7.2	10
733	8	11
774	8.8	12
805	9.6	13
850	10.4	14
880	11.2	15
914	12	16
960	13.6	17
1004	15.2	18
1045	16.8	19
1073	18.4	20
1093	20	21
1142	21.6	22
1167	23.2	23
1190	25.2	24
1215	27.2	25
1230	29.2	26
1232	31.2	27
1250	33.2	28
1267	35.2	29
1280	37.2	30
1285	41.2	31
1293	45.2	32
1298	49.2	33
1305	53.2	34
1306	57.2	35
1308	61.2	36
1310	65.2	37
1310	69.2	38
1310	73.2	39
1310	77.2	40

Result

1. Comparing the two methods of measuring the dissolution of electrical conductivity and titration, due to greater ease and less specialized calculations in the field of chemistry, as well as accelerating the measurement and measurement, the method of electrical conductivity was used. The electrical conductivity test was performed by a conductor. The conductor battery was

placed in the desired solution and the device showed the electrical conductivity of the solution using the appropriate voltage.

2. According to the results of four experiments with different solvent and the same solute, the maximum values of water-soluble gypsum and maximum electrical conductivity are different from each other. It can be concluded that the compounds in solution affect the dissolution rate.

3. Among the four solutions mentioned during the research, the highest solubility is related to municipal water and the lowest solubility is related to the water sample of Marash dam. Due to this, the presence of ions and additives in municipal water increases the solubility of gypsum.

4. According to the curves prepared from the experiment, the changes in electrical conductivity relative to the weight percentage of gypsum in the water sample of Marash Dam compared to the other 3 solutions at low weight percentage have reached saturation. As a result, it can be assumed that the solubility capacity of this soluble sample is less than that of the mentioned solvent samples.

5. The reason for the low solubility of the Marash dam water sample compared to the other two solutions can be considered the presence of soluble ions in this sample. Also, the presence of impurities in the prepared gypsum sample can not be ignored. Distilled water is more than the water of Marash Dam.

6. In a comparative position, the maximum amount of gypsum dissolution per unit (g/l) in municipal water solution with a significant difference of the highest amount, then distilled water solution and one percent sodium chloride, in the next position of distilled water and finally Marash dam water sample. Also, the maximum electrical conductivity per unit (μSiemens / centimeter) in aqueous solution and one percent sodium chloride with a significant difference of the highest amount, then distilled water solution, is in the next position of the water sample of Marash dam and in the last place of municipal water.

7. As shown in Figure 2, as the amount of gypsum in municipal water increases, the electrical conductivity increases. Finally, this direct relationship does not continue and with further increase in the amount of these substances, the amount of electrical conductivity does not change and remains constant. This means that the maximum gypsum soluble in municipal water is equivalent to unchanged electrical conductivity, which according to The results show that the unconducted electrical conductivity is 1310 μS / cm and the equivalent concentration of calcium sulfate (soluble gypsum) is 652 g / l.

8. Finally, according to the above results, it is suggested that during the studies before the construction of dams with gypsum, with relevant tests to determine the chemical characteristics of water passing through the selected axis, the solubility of available water is measured and if reservoir topography allows, the location When the gypsum mass will be exposed to direct water flow, a clay blanket will be applied on it to prevent direct contact of this mass with water. The water entering the dam can also be saturated to significantly reduce dissolution near zero.

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