Effect of Dissolved Sodium Chloride Content in Water on The Dissolution of Gypseous Rock (Case Study; Chamshir Dam Reservoir, SW Iran)

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Abstract: Solubility amounts of gypsum are variable in the presence of water containing dissolved salts, especially sodium chloride (NaCl). In this paper, a study of gypsum dissolution in chloride saline water under controlled laboratory conditions using circulation apparatus is presented. The aim is to understand the influence amount of dissolved NaCl variables on amount and rate of gypsum dissolution. The rock samples were obtained from the proposed Chamshir dam site located approximately 20km to the southeast of Gachsaran city. The results showed that the amount of gypsum dissolution increases with increasing the dissolved NaCl in the water (up to 7.76 gr/lit when the amount of dissolved NaCl is 100 gr/lit). But with increasing the NaCl to greater than this amount, the gypsum dissolution amount decreases again. At the other hand, gypsum dissolution rate constant, contrary to its dissolution amount, decreases with increasing the amount of dissolved NaCl in water (up to 0.158×10^(-5) m/s when the amount of dissolved NaCl is 100 gr/lit) and then increases again.

Key words: Gypsum, Sodium chloride, Amount of dissolution, Dissolution rate constant

INTRODUCTION

Geotechnical engineers are faced to the severe problems when constructing hydraulic structures such as dams on gypseous soils or rocks. The problem of water leakage through soluble bedrock is the most important subject in constructing of such dams. Excessive leakage may lead to defects in the structural performance of the rock layer supporting the hydraulic structure. Several researchers agreed that the dissolution of gypsum or anhydrite can manifest itself in different ways causing the development and generation of leakage paths (i.e., enlarging fissures and accelerating seepage flows resulting in gaps and caverns), increasing permeability of granular zones, deterioration of foundations (attacking concrete grouts) and finally the progressive and intolerable settlements (Calcano and Aizura, 1967; James and Lupton, 1978; James and Kirkpatrick, 1980).

There are more several agents which can increase dissolution of gypseous rocks in dam reservoirs. Chloride saline water is one of these agents. The studies by James and Lupton (1978) showed that increasing the chloride salinity of the solvent has a great influence on the amount of gypsum dissolution. This is because of high solubility potential of sodium chloride (NaCl) than those of gypsum. Of course, increasing in the amount of gypsum dissolution with increasing in water salinity occurs until a definite level and after reaching to saturation state (equilibrium state), dissolution will stop. After this stage, the return (i.e. precipitation of gypsum) reaction occurs with increasing of water salinity (Ford and Williams, 2007). So far, several researchers have studied the influence of ions upon dissolution of materials (Elena-Ramos et al., 2011; Ukawa, 2006; Erdogdu, 2004; Oelkers, 1994).

The study area in this paper is Chamshir dam reservoir that located in the southwest of Iran; about 20 km southeast of Gachsaran city with coordinates of 50° 52' 36" E and 30° 10' 59" N (Fig. 1). The dam is now under study and has been designed as a concrete dam (Gravity-Arc dam); height of 155 meters and the useful volume of reservoir is 1.8 milliards cubic meters. Most parts of the dam reservoir are covered by evaporative deposits. Since, chloride saline water (due to salt rocks dissolution) can increase dissolution of gypsum rocks in contact with dam reservoir water; therefore, the aim of the present paper is study of effect of dissolved NaCl amount in water on the gypsum dissolution.

Geological setting:

According to the geological map of Ghachsaran region (Setudehnja and OB-Perry, 1966) (Fig. 1), geological formations in study area from oldest to youngest are Gachsaran (Early Miocene), Mishan (Early-Middle Miocene), Aghajari (Miocene-Late Pliocene), Bakhtiari (Late Pliocene- Pleistocene) and alluvial sediments. Chamshir dam reservoir is located on Gachsaran, Mishan and Aghajari formations. The oldest
outcrop in the reservoir belongs to Gachsaran formation. In the typical section adopted from oil drillings cores in the Khuzestan area (Fig. 2), this formation includes of 7 members as follows: first member: alternation of thick anhydrite, limestone and shale with 40 m thickness. Second member: thick salt layer, anhydrite with thin layers of limestone with 115 m thickness. Third member: thick anhydrite with salt to 347m thickness. Fourth member: thick salt layer with marl, gray limestone and anhydrite with 290m thickness. Fifth member: red and gray marl with alternation of gypsum with 324m thickness. Sixth member: alternation of anhydrite (or gypsum), salt, red marl and limestone layers with 258m thickness. Seventh member: alternation of gypsum, gray marl and limestone with thickness of 139 m. According to the field observations, in this area, members 5, 6 and 7 of Gachsaran formation are in contact with dam reservoir. Mishan formation which is isocline with Gachsaran formation, covers west to southwest of dam and form the Chamshir dam axis. Aghajari formation has formed small parts of reservoir, has the more outcrop in southwest of reservoir and consists of sandstone, siltstone, conglomerate and gypsum marl.

The study area is in Zagros Folded Zone or External Zagros, based on Stocklin classification (1968) and Simply Folded Zone based on Berberian classification (1995). Compaction due to tectonics forces of Zagros Folded Zone, created some faults and little and large over thrusts with NW-SE trend in the study area among which Dezr Soleyman Thrust (DST) and Chamshir fault zone are the most important ones (Fig. 1). The thrust related fractures which lead to development of the several chloride saline springs in the dam reservoir, are suitable location for water leakage after dam impounding.

**Fig. 1:** Geological map of study area (modified Gachsaran geological map, 1:100,000, Iranian Oil Operating Companies (IOOC), 1966)

**Experimental Work:**

**Material Used:**

The material used in this study was gypseous rock samples, obtained from Chamshir dam reservoir in south-west Iran. The study has been carried out on thin sections of gypsum rocks procured from the Gachsaran formation of Iran (Fig. 3a). The rocks is essentially composed of single crystals of gypsum, but minor fraction of carbonated micritic veins is present also (maximum 10%). The micritic veins are composed of microcrystalline calcite. The occurrence of the microcrystalline materials, occupying some preferential flow paths, can be related to early diagenesis. Most of the rocks are relatively fresh while the rest show slight discoloration on their surfaces and are described as being slightly weathered. Also, the XRD analysis of a representative gypseous rock sample showed that gypsum is main mineral and micrite is accessory mineral (Fig. 3b).
Experimental Setup:
The idea of the proposed setup was in accordance with the testing technique suggested by James and Lupton (1978). Ghobadi (1985) made a circulation apparatus borrowed from James and Lupton (1978) which we modified and improved it to achieve better results. The process basically involves the dissolution of gypsueos rock due to the flow of water on the rock samples surface. The dissolution circulation apparatus which used for tests (Fig. 4) comprised of a large water reservoir (100×50×50 cm). A pump with 0.5 Hp, circulate water in the reservoir. A digital device which linked to a CO₂ capsule keeps water pH constant as automatically. Also, this apparatus has fridge, heater and thermostat systems.
Sample Preparation and Experimental Method:
A great number of block samples, taken from different locations of the study area, were collected. They were then transported to the Rock Mechanics Laboratory of Engineering geology Department of Bu-Ali-Sina University in Hamedan city. The 40-50 mm long gypsumous rock samples with a 57 mm diameter was prepared using a mechanical cutter. The ends of the sample were trimmed parallel to each other. These samples were prepared and weighted separately for each of cycles. Also, its dimensions were measured with 0.01 mm accurate. Furthermore, in order to more accurate comparison, we tried that total area of samples which were in contact with water being similar in all cycles. Table 1 shows the physico-chemical characteristics of used water in the tests. After preparing the cylindrical rock samples and locating it base inside the bath, the bath was filled with urban. Because of excessive water used by circulation apparatus, we used urban water instead of pure water. In all cycles, the water volume in reservoir was 70 liters and water temperature was adjusted equate to 10 C°. CO₂-enriched water is injected at constant flow rate in the water reservoir with a pressure equal to 0.2 bar. Specimens of the circulating water were taken for the analysis throughout the time period of testing (about 4 hours).

**Determination of Gypsum Content in the Water:**
To analyze the dissolved calcium sulphate in water and to illustrate a relationship between gypsum dissolution and time, a method (gypsum by precipitation with acetone “quantitative”) was used for such purpose. The method is in accordance to (Diagnosis and improvement of saline and alkali soils), (U. S. D. A., 1954).

**Table 1:** Major ions chemical composition of used water in the test.

<table>
<thead>
<tr>
<th>Physicochemical characteristics</th>
<th>Cations (mg/l)</th>
<th>Anions (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH EC (µS/cm) TDS (mg/l)</td>
<td>K⁺ Na⁺ Mg⁺ Ca⁺ SO₄⁻ Cl⁻ HCO₃⁻ NO₃⁻</td>
<td></td>
</tr>
<tr>
<td>7.25 757 484.50</td>
<td>2.30 25.00 9.24 92.70 46.70 44.00 283.00 31.70</td>
<td></td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**

**Effect of Sodium Chloride Content on the Amount of Dissolution:**
According to the Table 2 and figure 5 data, dissolution of gypsum in water increases with increases in the amount of dissolved NaCl until cycle 4. In this cycle, the amount of gypsum dissolution is max while the amount of dissolved NaCl is 100 gr/lit. After this stage, the amount of gypsum dissolution decreases with increasing the amount of dissolved NaCl. This is because of ionic strength phenomenon. As NaCl solubility is higher than gypsum, gypsum reaches to saturation state with delay than natural conditions (when it is in contact with very low salinity water). Therefore, added NaCl to water disturbs thermodynamic conditions and solubility of gypsum also increases with increasing the potential of water solubility. But in equilibrium state, solubility of gypsum ceases with increasing NaCl and return reaction occurs.

Therefore, it can be noted that increasing the chloride salinity of the solvent (using low percentages of NaCl additives) has a great influence on the amount of gypsum dissolution, and further increase in the chloride...
salinity exhibited a greater increase in the amount of dissolution when compared with the lower salinity concentration.

Contrary to the laboratory conditions, the water in the dam reservoir has low salinity and studies show that its initial NaCl is near to the NaCl amount of cycle 1 (Torabi-Kaveh, 2011). This is because of small outcrops of salt layers in the study area. Thus it seems that in this state reach to the 2-4 cycles is far from reality in laboratory. But according to studies carried out by Torabi-Kaveh (2011) on the Dez Koh Soleyman thrust (Darbeh gorge), there are several springs with average chloride salinity more than 30000 mg/lit in the study area and it is expected that its discharge increases after dam impounding. Therefore, reaching to the subsequent laboratory cycles (especially cycle 2) is not unexpected after dam impounding.

Table 2: Test results of gypsum dissolution in the water at different amounts of NaCl.

<table>
<thead>
<tr>
<th>No. of cycle</th>
<th>Amount of dissolve NaCl (gr/lit)</th>
<th>Section surface of samples (A) (m²)</th>
<th>Number of sampling</th>
<th>Mass loss of samples (Kg)</th>
<th>Temperature (°C)</th>
<th>Water volume in circulation (m³)</th>
<th>pH</th>
<th>Time of saturation (hr)</th>
<th>Primary concentration of CaSO₄ 2H₂O (C) (gr/lit)</th>
<th>Saturation concentration (Cₛ) (gr/lit)</th>
<th>Dissolution rate constant (K) (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.04</td>
<td>0.225337</td>
<td>11</td>
<td>0.1934</td>
<td>10</td>
<td>70 × 10⁻⁴</td>
<td>7.6</td>
<td>44</td>
<td>0.426</td>
<td>2.67</td>
<td>0.240</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.227766</td>
<td>15</td>
<td>0.4052</td>
<td>10</td>
<td>70 × 10⁻⁴</td>
<td>7.4</td>
<td>44</td>
<td>0.426</td>
<td>5.51</td>
<td>0.221</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>0.223525</td>
<td>17</td>
<td>0.4087</td>
<td>10</td>
<td>70 × 10⁻⁴</td>
<td>7.4</td>
<td>44</td>
<td>0.426</td>
<td>6.23</td>
<td>0.199</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.226821</td>
<td>11</td>
<td>0.4167</td>
<td>10</td>
<td>70 × 10⁻⁴</td>
<td>7.4</td>
<td>44</td>
<td>0.426</td>
<td>7.76</td>
<td>0.158</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>0.222876</td>
<td>11</td>
<td>0.3891</td>
<td>10</td>
<td>70 × 10⁻⁴</td>
<td>7.4</td>
<td>44</td>
<td>0.426</td>
<td>6.92</td>
<td>0.171</td>
</tr>
</tbody>
</table>

Fig. 5: Variation of gypsum dissolution amount vs. amount of dissolved NaCl in the water.

**Effect of Sodium Chloride Content on the Dissolution Rate Constant:**

According to the obtained data, the dissolution rate constant is determined by James and Lupton (1978) equation (Equation 1):

\[
\frac{dM}{dt} = KA (C_s - C)
\]

(1)

Where

The quantity dM/dt is the rate of mass loss from a solid surface of area A. K is a constant representing the combined diffusion properties of the boundary layer and diffusing species; (Cₛ – C) is the subsaturation concentration or local solution potential. Cₛ is the concentration of dissolved substance in a saturated solution and has a value depending upon the chemical composition of water.

Regarding to the data in Table 2 and figure 6, the concentration difference between solvent ions and ions in boundary layer is high because of low amounts of dissolved NaCl and gypsum in cycle 1. Thus, ion exchange rate between solvent ions and samples is high at diffusion boundary layer. But from cycle 1 to cycle 4 with increasing of dissolved NaCl, the concentration difference between solvent ions and ions in boundary layer decreases and consequently dissolution constant rate of gypsum will decrease. As cycle 4 has lowest dissolution
constant rate ($K = 0.158 \times 10^{-5} \text{ m/s}$). But after cycle 4, relative increasing of concentration difference between solvent ions and ions in diffusion boundary layer leads to relative increasing in dissolution rate of gypsum, because increasing of dissolution rate constant in comparison to natural conditions (where amount of NaCl and in general water salinity is low) show a decrease. Another important point is that relative increasing of dissolution rate constant occurs in the system is false, because gypsum dissolution is stopped thermodynamically and with increasing in the amount of dissolved NaCl in water, gypsum will precipitate. In general, because the conditions of cycle 1 is near to reality it is expected that dissolution rate constant will high after dam impounding, but as mentioned above, this value decreases with increasing of gypsum dissolution amount.

![Fig. 6: Variation of dissolution rate constant (K) of gypsum vs. amount of dissolved NaCl in the water.](image)

**Conclusion:**

Results show that the effect of dissolved NaCl in the tested range (0.04-120 gr/lit) leads to a significant difference in the amount and rate of gypsum dissolution. As concluded in the literature, increasing of the solvent chloride salinity, increases the gypsum dissolution due to increase in the ionic strength that increases the amount of gypsum dissolution since it tends to compress the boundary layer and hence decreases the dissolution rate constant until cycle 4. But after cycle 4, increasing in the amount of dissolved NaCl in water leads to decreasing in the amount of gypsum samples dissolution and consequently relative increases in the dissolution rate constant, because the gypsum dissolution is stopped thermodynamically and increasing in the amount of dissolved NaCl causes to occurrence of the return reaction (i.e. gypsum precipitation).

Since the chloride salinity of the Zuhreh River water (dam reservoir water) is low than chloride salinity water (in the cycles of 2-5), its effect on the amount and rate of gypsum dissolution would be similar to first cycle. But with increasing in the salinity of water due to the addition of saline springs, reaching to the condition of the subsequent laboratory cycles, especially cycle 2, is not unexpected.

**REFERENCES**


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