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Technical Conference Paper

Experimental Characterization of Temperature Dependence of Salt Dissolution Rate

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Abstract

The dissolution rate of salt walls is a crucial parameter in developing models of salt wall evolution during formation and operation of the salt caverns that make up the U.S. Strategic Petroleum Reserve. Several series of experiments were performed to quantify the relation between salt dissolution and the temperature, salinity, and flow velocity of the brine in contact with the salt. The experiments used a continuous flow facility to expose the walls of cylindrical salt samples to brines over a range of temperatures (24 to 50°C), salinities (0 to 90% of saturation), and velocities (0.4 to 4 cm/s). Both pressed salt and salt core samples were tested. The mass loss per unit time was measured, in addition to changes in the density of the flowing brine, while monitoring the brine temperature and flowrate. The data show that under these low velocity, laminar conditions the flow speed is not a dominant parameter. Statistical analysis of the data provides an empirical relation between salt dissolution rate, brine saturation and brine temperature. In addition, both the present work and prior work in the literature show that the dissolution rate is affected by salt surface roughness characteristics. The effect of roughness could not be quantified in the present work, but differences in dissolution rates between salt samples with "smooth" and "rough" dissolution were clear. A review of the existing literature is provided as well as a comparison of the current data to those in the literature. Suggestions for future work include more carefully controlled roughness experiments and extension of flows into the turbulent regime.

Key words: Salt Dissolution Experiments, Caverns for Liquid Storage, Salt Properties, Strategic Petroleum Reserve.

Introduction

The U.S. Strategic Petroleum Reserve (SPR) is made up of a system of 62 salt caverns located at four different sites along the Texas and Louisiana gulf coast. The SPR is the world's largest emergency supply of petroleum with the capacity to hold 727 million barrels of oil, which at 100 USD/barrel equates to a total value of almost 73 billion dollars. The salt caverns are solution mined to roughly cylindrical geometries with a total height of about 610 m (2000 feet) and average diameter of about 61 m (200 feet). Once the caverns are formed, they are filled with crude oil, which floats on top of saturated brine left over from the dissolution process. During oil draw down, raw water (surface water that is unsaturated with respect to NaCl) is injected into this brine layer so that the oil is forced out the top where it is sent to market. This injection of raw water leads to further dissolution of the cavern walls and a change in cavern geometry. Due to the extremely high monetary value of the contents of the caverns, its importance to national security, and the need for safe and environmentally responsible facility operations, a thorough understanding of changing cavern geometry and the resulting cavern integrity is paramount. Currently the computer models that predict changes in cavern geometry can provide reasonable approximations to these changes when calibrated against actual sonar data taken from one of the caverns. This calibration is performed by adjusting certain scaling factors that change the dissolution rate of salt until the model prediction matches the sonar data. While this method does provide a very close approximation, it is desirable to obtain an empirical relation for dissolution rate to improve the model's predictive ability, robustness and accuracy. Of particular interest here is how water temperature affects the dissolution rate. Historical practice at SPR has been to simulate temperature at the numerical code default, which is 75°F. That may have been an adequate assumption when the caverns were developed 30 years ago and all the fluid in the cavern was recently introduced from surface facilities, but current operations that inject small amounts of water into large, warm brine pools show that the operative brine temperatures are ~90-120°F in the cavern while active dissolution is taking place. This laboratory study seeks to separate the effects of temperature from other drivers and quantify them in a dissolution rate expression relevant to the lab scale. If sufficient temperature sensitivity is observed in the lab, further study will be undertaken to explore how these compare with the temperature correction function in the numerical model and whether these effects are observed at the cavern scale.

Literature Review

Several papers have been published regarding the dissolution rates of salts as a function of different factors including salt type, flow rate, solution salinity and temperature. This section attempts to provide a brief summary of the work performed and the key results obtained. Interested readers are directed to the original papers for more information.

This question was initially investigated by Durie and Jessen (1964). Their experimental setup consisted of a cylindrical test section in which a cylindrical salt core sample was placed and centered coaxially to the test section. Samples were then subjected to laminar flow of pure water or unsaturated brine through the annular gap between the outer surface of the salt core and the internal surface of the test section. Tests were carried out at room temperature of 23.8°C (74.8°F) and at brine salinities ranging from 0 to 4 mols/liter or 0 to 73.5% NaCl saturation. Durie and Jessen observed that the salt surface developed significant irregularities during the dissolution process. This observation motivated them to calculate both an average dissolution rate of the sample and an initial dissolution rate. The average dissolution rate was calculated as the total volume of salt lost divided by the dissolution period. The initial dissolution rate was the rate at which the sample was calculated to dissolve during the early stages of dissolution, when the salt surface was still smooth. They found that the average dissolution rate was approximately 2-4.7 times faster than the initial dissolution rate, indicating an increase in surface area of 2-4.7 times the original value caused by roughening.

Saberian (1976) related the dissolution rate to the flow rate of fresh water over the salt surface, with average velocity over the salt surface ranging from 0 to 40 cm/s. He produced an empirical relation between flow velocity in cm/s and dissolution rate in cc/cm^2/min:

$$\text{Dissolution Rate} = C1 + C_2V + C_3V^2 + C_4V^3 + C_5V^4$$

where.

$C_1 = 2.2709 \times 10^{-2}$

$C_2 = -8.8188 \times 10^{-4}$

$C_3 = 1.4519 \times 10^{-4}$

$C_4 = -2.5186 \times 10^{-6}$

$C_5 = 1.1076 \times 10^{-8}$

His data and empirical fit show that below flow velocities of 5 cm/s, dissolution rate is not affected by flow rate. Saberian (1983) quantified dissolution rates of core salt from the Grand Saline and Hockley Domes as a function of brine temperature and salinity, and developed an empirical relation for dissolution rate as a function of temperature and salinity based on the data. In this 1983 study, however, brine was not actively flowed over the surface, instead the sample was simply submerged in a brine solution and natural convection occurred Additionally, Saberian only calculated the average dissolution rate of the samples and did not attempt to calculate an initial dissolution rate for a smooth surface as was done by Durie and Jessen. The Saberian (1983) empirical relation is given as:

$$\dot{m}_T = 0.000803(1.2019-\rho)^{1.42}T^{1.3}\exp\left[0.00039\left(\frac{\rho-1}{1.2019-\rho}\right)\Delta T\right]$$

where the dissolution rate $\dot{m}_T$ has units of cc/cm^2/min, ρ is the brine specific gravity, and T is the temperature in degrees Fahrenheit. A discussion of the comparison of the present results to the Saberian data and empirical fit is included later in this paper as well as a discussion of the differing dissolution mechanisms.

Charnavel et al. (2006a,b) suspended salt core and salt lick machined samples in a tank and monitored the natural convection mass loss as a function of the temperature of the fresh water surrounding the samples. They found dissolution rates of salt cores were 1.5 times faster than that of salt licks, but both were lower than those found by Saberian (1983), possibly due to differences in experimental procedure. They found excellent repeatability of salt lick dissolution, better than that of salt cores that sometimes contained insoluble layers. They also found that the orientation of the suspended samples affected the dissolution rate, with a vertically suspended cylindrical sample dissolving more uniformly and better fitting their assumed shape for analysis.

Kruglov and Maljukov (1997) did not perform dissolution tests, but discussed how surface roughness and surface irregularities increase the effective surface area that contributes to dissolution. They measured micron-to-millimeter scale features on salt surfaces and determined that the actual surface area is 1.5 to 5 times the surface area of the same geometry with an assumed smooth surface. The importance of this work and its relation to the present results are discussed later in this paper. Table 1 summarizes the experimental scope of the cited literature on dissolution rate.

Table 1. Summary of prior salt dissolution tests.

	Salinity Range [%Saturation]	Temperature Range [°C]	Surface Conditions [Rough/Smooth]	Salt Type	Flow Conditions
Durie & Jessen (1964)	0-73.5	23.8	Both	Core	Laminar flow through an annular gap
Saberian (1976)	0	23.8	Rough	Core	Upward flow through annular gap. Laminar to turbulent.
Saberian (1983)	0-94.5	4.4 – 65.5	Rough	Core	Natural convection in a tank
Charnavel et al. (2006a,b)	0	22-52	Rough	Core and Lick	Natural convection in a tank

Salt Sample Selection

In the initial exploratory experiments, salt cores taken from the Egan natural gas storage field (Acadia Parish, LA) and salt cores machined from pressed salt blocks (United Salt Ranch House Solar Salt Blocks) were used. Both types of samples exhibited varying behavior during dissolution. Some samples would maintain a smooth surface during the dissolution process and others would become roughened and irregular, forming “craters” as sometimes seen by Charnavel et al. (2006b). Figure 1 shows samples cut from a pressed salt block dissolving in a “smooth” (left) and a “rough” (right) manner. Both samples were dissolved in 75% saturated brine at 24°C (75.2°F) for one hour with similar brine flow characteristics, yet exhibit markedly different surface characteristics. Because of this variance in dissolution mechanism, it was impossible to make meaningful conclusions from the data in early tests. To control this variable, all salt samples used to acquire the data presented in this paper were cut from pressed salt blocks from the same lot. This measure proved effective, as no samples exhibited “rough” dissolution in the experiments presented here.

While the crystalline structure of the pressed salt samples used in this work is not analogous to that of samples taken from a naturally occurring salt dome, the two samples are chemically equivalent. Preliminary comparisons showed that salt cores from the Egan storage facility dissolved 1.5 to 2 times faster than the machined salt cylinders used in these tests . Charnavel et al. (2006b) noted that “real salt cores” dissolve 1.5 times faster than “salt lick cores” (as used in the present work). Further work is proposed later in this paper to relate the dissolution rate of these salt block samples to in situ dissolution cases.

It is the authors' opinion that the dissolution characteristics of halite salt are best understood by initially studying these cases of "smooth" dissolution. When samples develop surfaces of varying roughness, a variable is introduced that is hard to measure or control during a dissolution experiment. As discussed in the literature review, neither Durie and Jessen nor Saberian ever quantified the effects that roughness had on the effective surface area. Both authors noted the effects that this roughness had on dissolution, but a detailed study of surface topology and the resulting increase in surface area was never performed. Because of this, we felt the best methodology for the present work would be to first understand the dissolution behavior of smooth cases, where there is a controlled and well defined surface area. We will later extend the work to address roughened cases in a quantitative manner, rather than qualitative as has been done in the past. Additionally, pressed salt licks are routinely used as a replacement for cores in many laboratories because of their wider availability, so a further understanding of the validity of this substitution is also valuable.

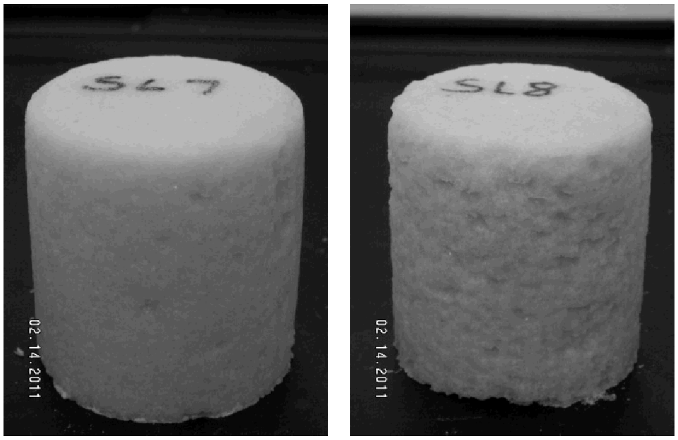

Figure 1. Example showing how different samples can exhibit different surface characteristics under similar dissolution conditions (75% saturated NaCl solution, 24°C). Flow past left sample had mean gap velocity of 0.27 cm/s, while that on right was 0.14 cm/s.

Experimental Setup

The main experimental test section consisted of a Lexan tube with a 8.9 cm (3.5 inch) inner diameter. A 7.6 cm (3 inch) diameter Lexan cylindrical post was mounted coaxially inside the Lexan tube. Salt samples were mounted vertically inside the Lexan tube, held in between the upper and lower Lexan posts, as shown in Figure 2. Brine was fed to the test section via a constant head tank located 3.66 m (12 ft.) above the test section. The flow rate was controlled by an orifice mounted directly below the test section, and the desired flow rate was achieved by selecting the appropriate orifice. In the experiment, brine flowed from the constant head tank, through a flow meter, through the annular gap of the test section and out the orifice into a collection pan. From the collection pan, the brine was pumped back to the main supply tank, and from there back to the constant head tank. A schematic of the experimental apparatus is shown in Figure 3. In runs where the brine temperature was greater than room temperature, a heater was immersed in the supply tank and used to maintain the brine at the desired temperature. All tanks and piping were insulated to minimize temperature changes during each experiment.

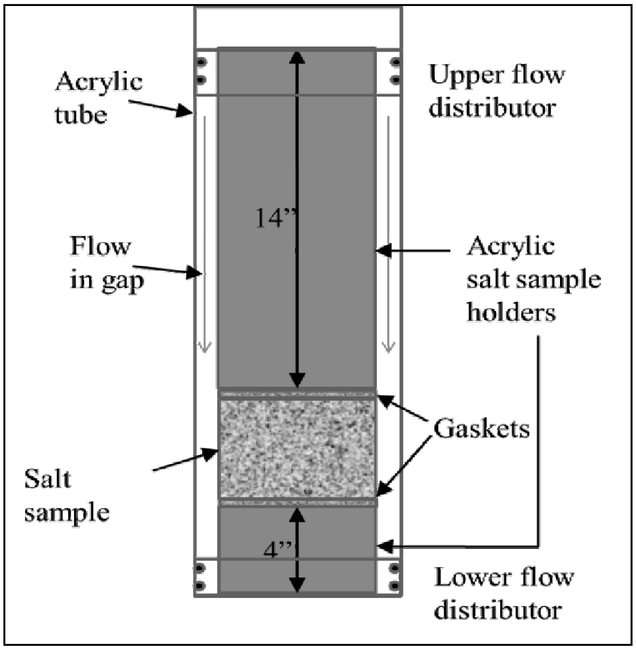

Figure 2. Test section showing salt sample held between Lexan posts, and the annular brine flow along the sample walls.

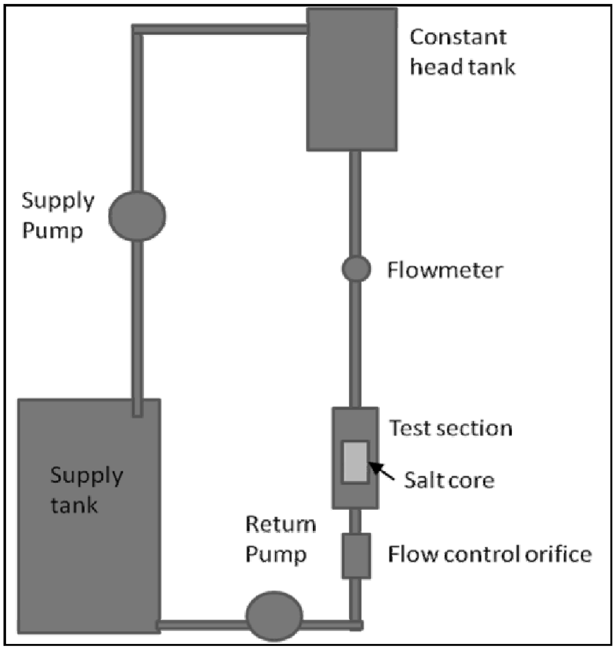

Figure 3. Overall schematic of the experimental apparatus. Flow is from the supply tank to the head tank, with a gravity-driven flow from the head tank through the test section. A submersible heater in the supply tank was used to set and maintain the test temperature.

Procedure

To perform a test, a salt sample (nominally 7.6 cm (3") diameter, 7.6 cm (3") long) was dried in a dry-air-purged oven at 40°C (104°F) for at least three days. Its mass and volume were measured using a Mettler PM-4000 digital balance (0.01 gram accuracy) and dial calipers. The sample was then mounted in the test section, which was backfilled with saturated brine. The sample was allowed to soak in the saturated brine for one hour before starting the test so that any air trapped in the sample could escape. While the sample was soaking, the brine solution to be used in the test was brought up to the desired temperature using a heater immersed in the supply tank, and a bypass flow was used to bring the entire test apparatus up to the test temperature. The salinity level of the brine was measured using a digital densitometer (Anton Paar DMA 35)**.**

Once the sample had soaked for an hour, the test was started and the start time was recorded. During the test, the temperature of the test solution was monitored with three thermocouples: one located in the supply tank, one located in the constant head tank, and one located at the top of the test section. Additionally, brine saturation was monitored by taking density samples at evenly spaced time intervals throughout the duration of the test, and flow rate was measured by a flow meter located between the constant head tank and the test section. The test was allowed to run until approximately 10% of the sample had dissolved at which time the test was stopped, the time was recorded, and the sample was removed and dried in the dry-air-purged oven at 40°C (104°F) similar to the initial drying conditions until the mass leveled out at a constant value, indicating no further water mass remained in the sample. The sample mass loss was then determined by weighing with the same Mettler balance, and converted to a volumetric loss by applying the measured dry sample density. The dissolution rate was reported as the volume of salt lost per unit surface area of the sample per unit time the sample was immersed. The brine temperature for the experiment was reported as the average temperature recorded by the thermocouple located at the top of the test section and the average salinity was calculated from the average of the flowing brine density readings taken during the test. The ratio of the mass flow rate of water to the dissolution rate of the salt sample was large enough that there was never any appreciable change in salinity across the test section. The flow rate was calculated as the average flow rate recorded by the flow meter.

Discussion

Dissolution as a Function of Flow Rate

Durie and Jessen (1964) as well as Saberian (1976) reported that as long as the flow was laminar, flow rate had no effect on dissolution rate. This observation was corroborated by the data collected in these experiments, which had a maximum gap velocity of 3.782 cm/s, which gives a gap Reynolds number of 505. Because it was demonstrated that flow rate had no effect on salt dissolution rate in the laminar range, the empirical correlation developed below does not include flow rate as a variable, so it is only intended to be applicable for laminar flow conditions.

Establishing an Empirical Relation between Dissolution Rate, Salinity, and Temperature

A quadratic least squares regression was performed on the data to establish an empirical relation between temperature, salinity and dissolution rate and the relation is plotted in Figure 4. The surface shown in the figure fits the data with an R-squared value of 0.99. Figure 5 shows the fits along with the present data for approximately constant saturation levels. Figure 6 shows the current data plotted against the empirical relation proposed by Saberian (1976), showing that Saberian measured dissolution rates were approximately 2-3 times higher than those found in the present work. The authors hypothesize that this discrepancy is predominantly due to surface roughness, as the data in this work was taken only from smoothly dissolving samples and Saberian used only roughened samples.

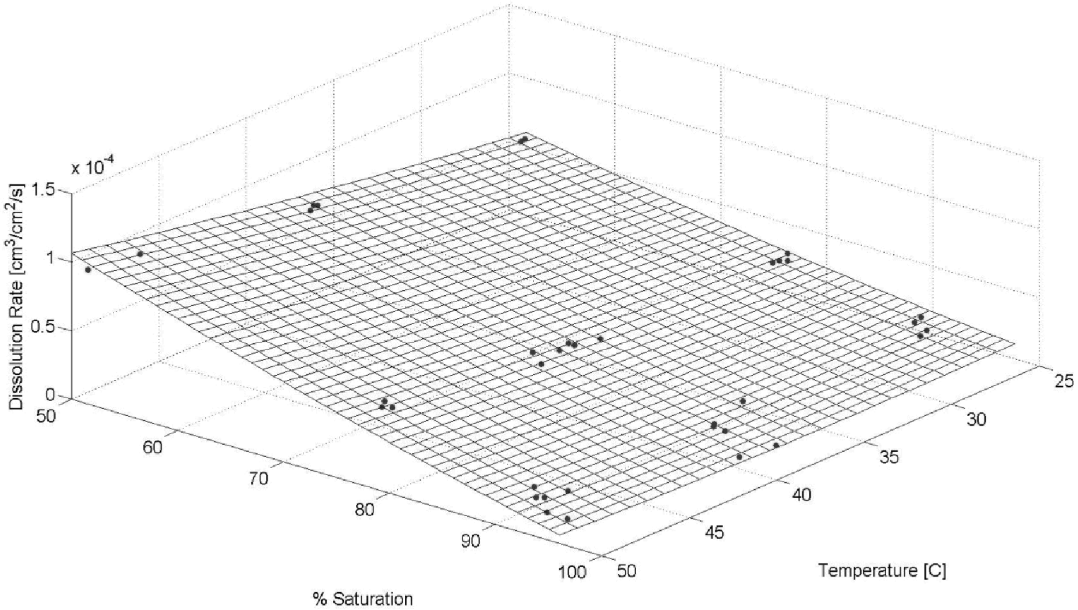

Figure 4. Experimental data with surface of best fit.

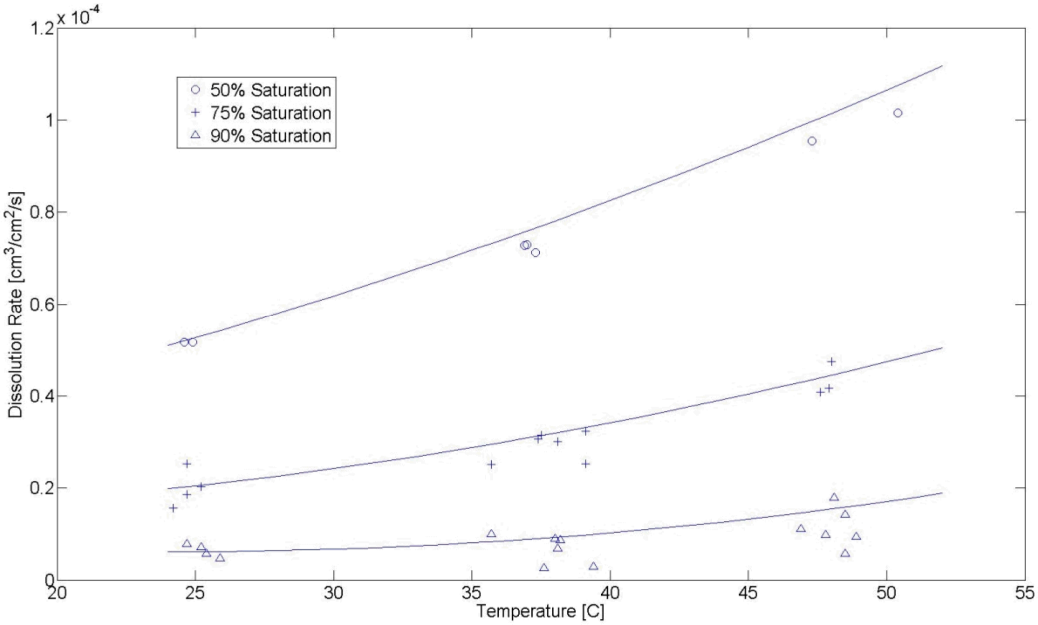

Figure 5. Present experimental data with lines of constant saturation.

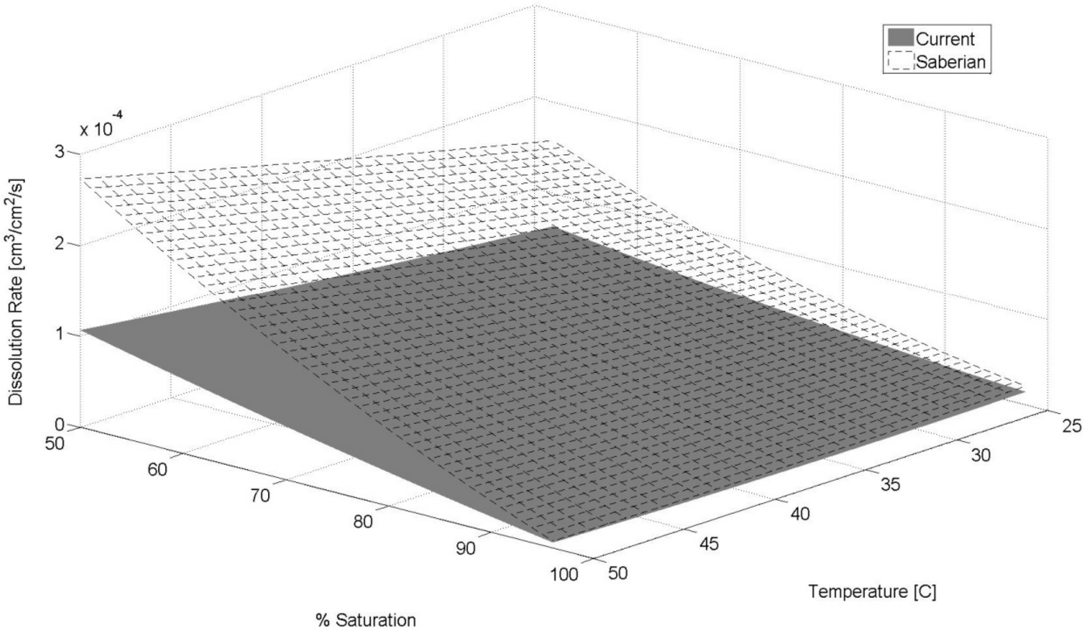

Figure 6. Comparison of the current data to the relation proposed by Saberian (1976).

In order to make our empirical relation obtained from smoothly dissolving salt blocks more applicable to *in situ* dissolution, we included a multiplicative coefficient to the equation we obtained from the least squares regression. This roughness coefficient, c_r, is equal to 1 for a smooth surface and can be scaled up to match the surface of best fit to data when the salt surface is not smooth. With this roughness coefficient, the final empirical relation proposed is:

$$R_d = [a_0T^2 + a_1S^2 + a_2TS + a_3T + a_4S + a_5]c_r$$

Where:

R_d= Dissolution rate (cc/cm^2/s)	a_0 = 1.647e-8
T =Temperature (°C)	a_1 = 8.425e-9
S = Salinity (% Saturation)	a_2 = -4.293e-8
c_r= Roughness Constant	a_3 = 3.064e-6
	a_4 = -1.269e-6
	a_5 = 6.185e-5

Shown in Figure 7 is the quadratic surface of best fit with a roughness coefficient c_r=2.57 fitted to the salt core data obtained by Saberian. Graphically, it can be seen in Figure 7 that this provides an excellent fit to the data. The R^2 value for this fit is 0.98, implying excellent correlation and demonstrating the ability of this relation to be applied to a wide array of data. According to our hypothesis, this indicates that the roughness observed in the samples used by Saberian increases the effective surface area by 2.57 times its original value. The hypothesis is supported by the work of Kruglov and Maljukov (1997) who suggested increases in effective surface area due to roughness in the range of 1.5 to 5 times the original smooth surface value.

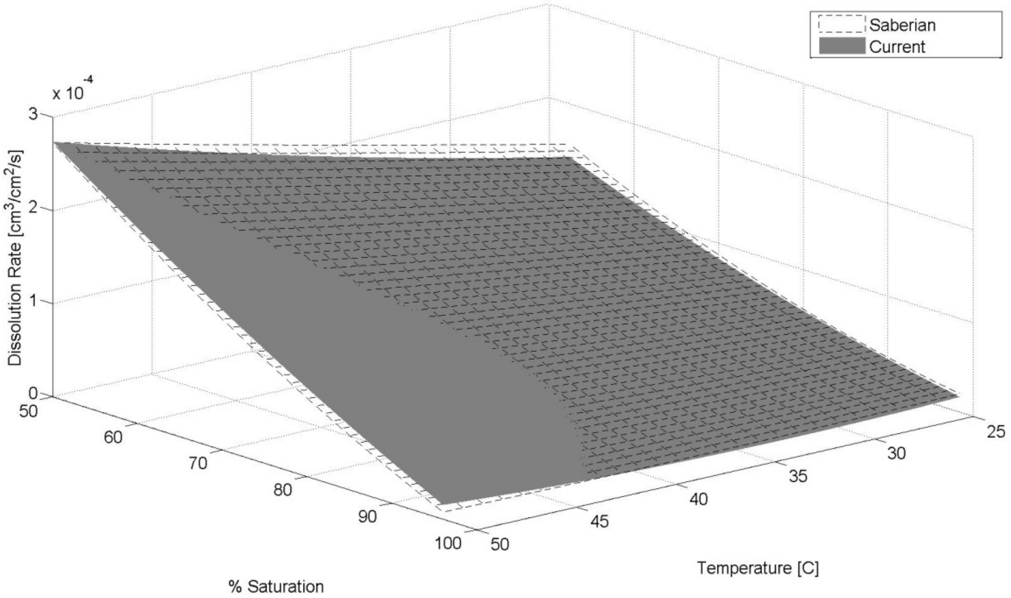

Figure 7. Comparison of present rough wall dissolution formula with data of Saberian (1983).

Application to Dissolution Modeling at SPR

While the project does not have in-situ measurements of raw water temperature and salinity in close vicinity to the salt walls, it does have ample data for the brine withdrawal stream. The cavern leaching patterns suggest that the brine is typically well-mixed, and the authors believe that the withdrawal stream is likely representative of cavern brine between injection and withdrawal depths. Brine temperatures of 25-50°C and saturations of >90% saturation encompass most of the normal operating range for SPR cavern leaching. Figure 8 shows the curves of the dependence of dissolution rate on temperature at both 90% and 95% saturation generated by the empirical relation proposed earlier for a smooth surface (c_r=1). These data show that there is a strong dependence of dissolution rate on brine temperature under conditions representative of those found in SPR caverns. Further work must be done to explore how this relation acquired in the laboratory matches fdata for SPR salt cores as well as for cavern-scale leaching operations where temperature data are available.

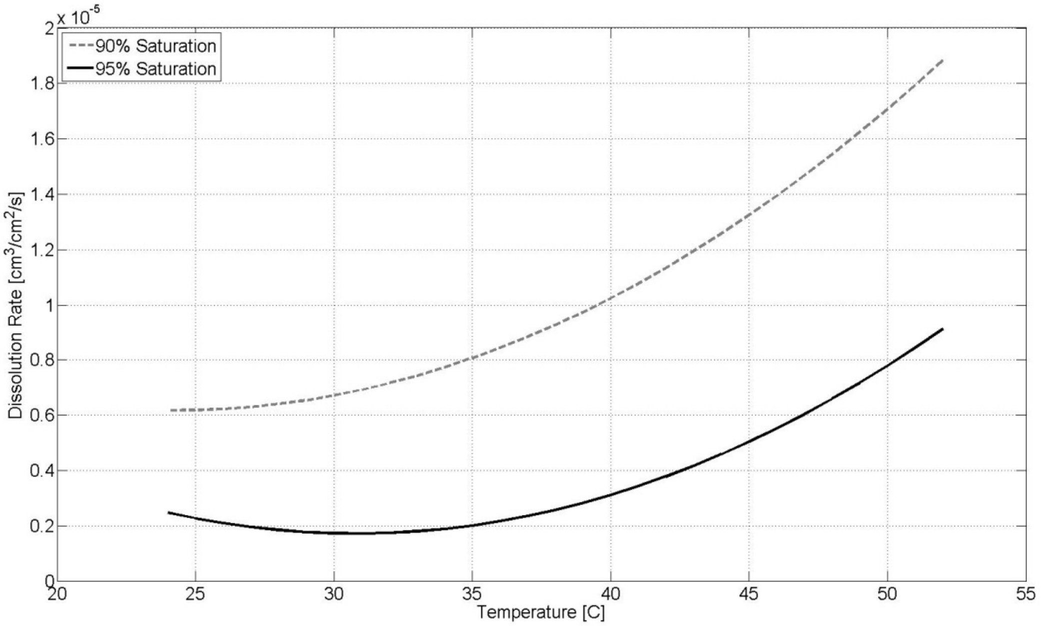

Figure 8. Dependence of dissolution rate on temperature at two NaCl saturation levels. Note that the local minimum in the 95% saturation line is an artifact of the surface fitting.

Future Work

Leaching experiments performed to date focused on several important parameters, namely:

1. The effect of brine concentration on dissolution rates
2. The effect of brine temperature on dissolution rates
3. To a lesser extent, the effect of brine flow velocity on dissolution rates

A correlation has been developed to predict dissolution rate as a function of brine concentration and temperature, with a roughness multiplier that increases dissolution by 2.57 times when the dissolving surface becomes rough. Brine velocity is not included in the correlation because it does not seem to control dissolution so long as the velocity is low enough to be within the laminar range.

Planned future experiments are intended to focus on the effect of surface roughness on dissolution rate. This investigation will be done by carefully machining the surface of the salt block samples prior to the dissolution experiments, and optically profiling the post-test surfaces to get a better measure of the increase in surface area due to roughening during dissolution. The expected range of surface area increase will be within reasonable bounds, around 1.5 to 5 times the smooth surface area (Kruglov and Maljukov, 1997). In addition, we propose to perform experiments with higher brine velocity to extend into turbulent flow regimes. This will require upgrading the current gravity-fed flow loop to include active pumping to average velocities in the 10-30 cm/s range, where measurable increase in dissolution is expected (Saberian, 1976).

The SPR solution mining code SANSMIC contains a temperature adjustment function for dissolution rate, though it has historically been left at a fixed value with an input T = 75°F. Any calibration has been affected by adjusting other parameters. The origin of the temperature adjustment function is not cited in the code documentation. The authors intend to explore the temperature function more closely in light of the laboratory results and temperature sensitivities shown here.

Acknowledgements

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