

## Research Article

# A Study of Analytical Solution for the Special Dissolution Rate Model of Rock Salt

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Received 24 November 2016; Revised 3 March 2017; Accepted 16 May 2017; Published 8 June 2017

Academic Editor: Ying Li

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By calculating the concentration distributions of rock salt solutions at the boundary layer, an ordinary differential equation for describing a special dissolution rate model of rock salt under the assumption of an instantaneous diffusion process was established to investigate the dissolution mechanism of rock salt under transient but stable conditions. The ordinary differential equation was then solved mathematically to give an analytical solution and related expressions for the dissolved radius and solution concentration. Thereafter, the analytical solution was fitted with transient dissolution test data of rock salt to provide the dissolution parameters at different flow rates, and the physical meaning of the analytical formula was also discussed. Finally, the influential factors of the analytical formula were investigated. There was approximately a linear relationship between the dissolution parameters and the flow rate. The effects of the dissolution area and initial volume of the solution on the dissolution rate equation of rock salt were computationally investigated. The results showed that the present analytical solution gives a good description of the dissolution mechanism of rock salt under some special conditions, which may provide a primary theoretical basis and an analytical way to investigate the dissolution characteristics of rock salt.

## 1. Introduction

Rock salt is produced under special natural conditions and contains minerals such as sodium, potassium, and magnesium sulfate, carbonate, and chloride. Its formation is completed under certain physico-geographical conditions depending on the persistent work of saturated multisource salt brine in a long geological time: the development process from salt crystallization to salt precipitation and then to salt accumulation, the evolution process of thousands or millions of years, and subsequent coverage protection. Exploitation of underground rock salt has a history of over 1000 years. Rock salt is often used as a medium for underground storage of petroleum, gas, and nuclear waste. This is because compared with other rocks it has the following five major advantages: (1) very low permeability ( $K < 10^{-20} \text{ m}^2$ ); (2) a strong creeping property, which enables fissure self-repair and storage

pressure self-adaptation of rock salt; (3) a good trapping property (because underground rock salt caverns are located at the water-resisting layer) without contaminating the groundwater; (4) low costs for cavern leaching by dissolution compared with other rocks, including granite, mudstone, and basalt; and (5) absorbability of harmful nuclear radiation (a suitable medium for nuclear waste storage) and water solubility that supports convenient and economical construction of rock salt caverns (an ideal choice for deep burying of nuclear waste and the storage of petroleum and gas).

Rock salt caverns are leached by dissolution; specifically fresh water infuses on the ground and salt brine is discharged from the shaft mouth so that caverns of certain shapes and sizes are formed. Liang et al. [1] developed a coupling theory for the effects of dissolution and seepage and the mass transfer and mechanical properties of rock salt. Fairchild et al. [2] completed a field-test study of the dissolution characteristics

of NaCl, and they found a positive correlation between the dissolution rate and the surface area of exposure. Weisbrod et al. [3] studied the effects of the composition, flow rate, and gravity of rock salt on its dissolution process. With a numerical method and based on a field survey, Zidane et al. [4] analyzed and calculated land subsidence resulting from rock salt dissolution. Yang et al. [5] investigated the risks of gas storage in bedded rock salt caverns. In an experiment, Alkattan et al. [6] investigated the dissolution characteristics of rock salt. Using a numerical method, Chen and Liu [7] discussed the evolution of the porosity and concentration of porous media during transmission. Rezaei et al. [8] attempted to establish a fluid transport model for calcite in a mixed area of tap water and salt water. Finneran and Morse [9] focused on the dissolution kinetics of calcite in salt water.

It should be pointed out that, in recent years, extensive studies have been conducted to investigate the chemical dissolution of porous rocks [10–15], for which the dissolution of rock salt only belongs to a special case. The theoretical and numerical results of these studies have clearly demonstrated that the dissolution of porous rocks is controlled by the coupling of the following processes: solute diffusion, pore-fluid flow, and specific chemical dissolution type. Although the chemical dissolution of porous rock is almost transient (i.e., time-dependent), the dissolution surface, which is commonly represented by the so-called dissolution front, can be in either a stable state or an unstable state, depending on both the Zhao number and the critical Zhao number of the dissolution system [10–21]. The existing studies have also demonstrated that many factors, such as mineral dissolution ratios [16], mechanical dispersion [17], medium/fluid compressibility [12, 18], reactive surfaces of particles [19], temperature effect [20, 21], and the permeability-porosity relationships [22], can affect the morphological evolution of reaction fronts within porous rocks in the field of the emerging computational geosciences [23]. As a result, the first monograph on this topic was published in the world [24], indicating that a complete theoretical framework has been successfully established on the chemical dissolution-front instability in porous media. In addition, such studies have been extended to investigate physical dissolution of porous media associated with groundwater pollution and contaminant site clean-up problems [25–28].

Despite the above-mentioned achievements in this particular research field, there is a lack of systematic investigation on an analytical solution for the dissolution rate equation of rock salt, so that more in-depth study is required. In the present study, we established an ordinary differential equation for the special dissolution rate model of rock salt under the assumption of instantaneous diffusion process. We then solved the equation mathematically to give an analytical solution and fitted the analytical solution using the results of a transient dissolution test to produce the dissolution parameters of the rock salt dissolution model when the dissolution surface is in a stable state. Finally, we calculated and analyzed the influential factors of the equation. This study provides a theoretical basis for understanding the dissolution mechanism of rock salt dissolution model under some special conditions.

## 2. Dissolution Mechanism of Rock Salt

**2.1. Diffusion in Solution.** The dissolution of rock salt is a process where rock salt molecules diffuse in water. Diffusion is caused by a gradient of the chemical potential, where molecules diffuse from the high-concentration zone to the low-concentration zone by their own thermal motion and eventually reach an approximate balance. Diffusion occurs even in the absence of macroscopic flow of the fluid. Diffusion can be described by Fick's first law: the diffusion rate is directly proportional to the concentration gradient. The diffusion flux is defined as the flux passing through the unit-area reference surface per unit time, and it can be expressed as a first-order partial differential equation:

$$J = -D \frac{\partial C}{\partial \mathbf{n}}, \quad (1)$$

where  $J$  is the diffusion flux ( $\text{g}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ ), namely, the mass flow of a substance passing through the unit area vertical to the normal direction,  $C$  is the substance concentration ( $\text{g}\cdot\text{cm}^{-3}$ ), namely, the amount of substance per unit volume, and  $D$  is the diffusion coefficient ( $\text{cm}^2\cdot\text{min}^{-1}$ ). The diffusion coefficient of solutes is generally related to the solvent and temperature, but, in certain cases, it can also be the function of rock porosity [22–25].

**2.2. Dissolution Boundary Layer.** During fluid transport for cavern leaching by dissolution, there is a dissolution boundary layer on the internal wall surface of the cavern, where the mass exchange between the solvent and rock salt (the dissolution process of rock salt) is completed.

Based on the study of Durie and Jessen [29], the concentration distribution profile at the salt dissolution boundary layer has a parabolic shape. The concentration distribution at the dissolution boundary layer can be expressed by the following equation:

$$C - C_1 = (C_0 - C_1) \left(1 - \frac{z}{\delta}\right)^2, \quad (2)$$

where  $C_0$  is the concentration of the solution at the wall surface of rock salt,  $C_1$  is the average concentration of the solution outside the boundary layer,  $C$  is the concentration of the solution in the boundary layer,  $\delta$  is the thickness of the boundary layer, and  $z$  is the distance from the wall surface of rock salt (cm).

The concentration distribution profile of the rock salt solution in the dissolution boundary layer is shown in Figure 1.

**2.3. Dissolution Rate Equation of Rock Salt.** Some researchers [30, 31] proposed that the dissolution rate equation of rock salt can be established according to the mass balance principle:

$$\frac{dR}{dt} = -\frac{D}{\rho_s} \left. \frac{\partial C}{\partial \mathbf{n}} \right|_{\Gamma_1}, \quad (3)$$

where  $R$  is the dissolved radius (cm),  $t$  is the dissolution time (min),  $D$  is the diffusion coefficient ( $\text{cm}^2\cdot\text{min}^{-1}$ ),  $\rho_s$  is

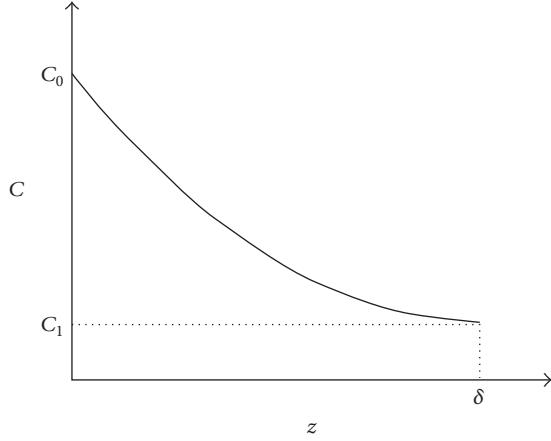


FIGURE 1: Concentration distribution profile of rock salt solution in the dissolution boundary layer. The horizontal axis is the distance from the wall surface of rock salt in the normal direction ( $\delta$ ) and the vertical axis is the concentration ( $C$ ).

the density of rock salt ( $\text{g}\cdot\text{cm}^{-3}$ ),  $C$  is the concentration of the rock salt solution ( $\text{g}\cdot\text{cm}^{-3}$ ),  $\partial C/\partial n$  is the concentration gradient of the rock salt surface, and  $\Gamma_1$  is the dissolution surface.

If it is assumed that the diffusion rate is very quick, the following equation can be derived from (2):

$$\frac{\partial C}{\partial z} = -\frac{2}{\delta} (C_0 - C_1) \left(1 - \frac{z}{\delta}\right), \quad (4)$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=0} = -\frac{2}{\delta} (C_0 - C_1), \quad (5)$$

$$\left.\frac{\partial C}{\partial n}\right|_{z=0} = -\frac{2}{\delta} (C_0 - C_1). \quad (6)$$

It is generally believed that the concentration of the wall is the saturation concentration in the solution mining process of rock salt, so that we can get

$$C|_{z=0} = C_0 = C_s. \quad (7)$$

$C_1$  is a time-dependent parameter, so that, under the assumption of  $C_1 = C_t$ , the following equation can be obtained:

$$\left.\frac{\partial C}{\partial n}\right|_{z=0} = -\frac{2}{\delta} (C_s - C_t). \quad (8)$$

Consequently, we can get

$$\left.\frac{\partial C}{\partial n}\right|_{\Gamma_1} = -\frac{2}{\delta} (C_s - C_t), \quad (9)$$

where  $C_s$  is the saturated concentration of the rock salt solution ( $\text{g}\cdot\text{cm}^{-3}$ ) and  $C_t$  is the concentration of the rock salt solution at time  $t$  ( $\text{g}\cdot\text{cm}^{-3}$ ).

Substituting (9) into (3) gives the following equation:

$$\frac{dR}{dt} = \frac{2D}{\delta\rho_s} (C_s - C_t). \quad (10)$$

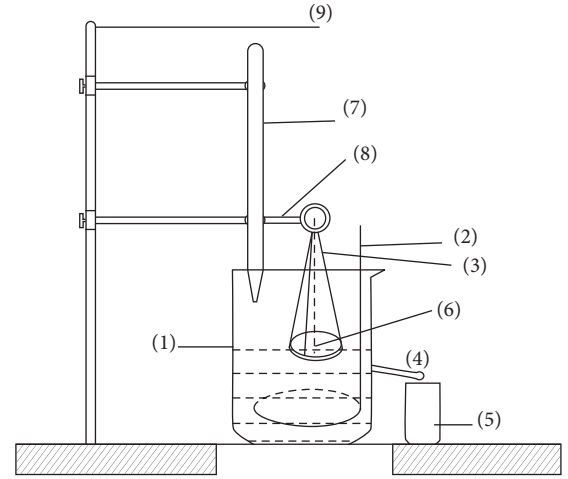


FIGURE 2: Schematic diagram of the transient dissolution instrument. (1) Glass beaker. (2) Stirrer rod. (3) Sample hanging rope. (4) Brine overflow tube. (5) Beaker. (6) Rock salt sample. (7) Fresh water infusion tube. (8) Clamp stand. (9) Iron support.

This equation is an ordinary differential equation for describing the dissolution rate of rock salt.

The dissolution characteristics of rock salt in Changshan area [32, 33] have been systematically investigated with the instrument shown in Figure 2. The experimental procedure was as follows. (1) During dissolution, the salt dissolution surface was parallel to the water level in the dissolution vessel, and the other dissolution surfaces were sealed with paraffin. (2) The flow rate was controlled by the knob of the resin column (the flow rate was adjusted in place before the experiment). (3) Slow stirring was frequently performed during the experiment to eliminate the effect of the concentration gradient, a small water sample was removed from the dissolution vessel at a certain interval, and the concentration of the salt solution in the test sample was then measured.

Because there was a very low flow rate in the brine overflow tube,  $C_t$  in the above experiment can be calculated using the following equation:

$$C_t = \frac{m}{V + Qt} = \frac{\rho_s AR}{V + Qt}, \quad (11)$$

where  $m$  is the dissolved mass at time  $t$  (g),  $A$  is the dissolution area ( $\text{cm}^2$ ),  $V$  is the initial volume of the solution ( $\text{cm}^3$ ),  $Q$  is the flow rate ( $\text{cm}^3\cdot\text{min}^{-1}$ ), and the other symbols are as defined above.

Substituting (11) into (10) and under the initial condition  $R = 0$  at  $t = 0$  gives the ordinary differential equation:

$$\frac{dR}{dt} = \frac{2D}{\delta\rho_s} \left(C_s - \frac{\rho_s AR}{V + Qt}\right), \quad (12)$$

$$R|_{t=0} = 0.$$

TABLE I: Results of transient dissolution tests of rock salt.

Dissolution time (min)	Flow rate ( $Q = 2 \text{ cm}^3 \text{ min}^{-1}$ ) Solution concentration ( $\text{g dm}^{-3}$ )	Dissolution time (min)	Flow rate ( $Q = 5 \text{ cm}^3 \text{ min}^{-1}$ ) Solution concentration ( $\text{g dm}^{-3}$ )	Dissolution time (min)	Flow rate ( $Q = 9 \text{ cm}^3 \text{ min}^{-1}$ ) Solution concentration ( $\text{g dm}^{-3}$ )
5	13.692	6	17.609	5	15.936
10	25.082	11	30.088	8	24.722
15	34.706	16	40.976	12	35.636
23	47.342	23	54.081	20	55.097
30	56.312	33	69.469	30	75.791
40	66.692	43	81.940	35	84.903
50	74.985	59	97.624	45	101.109
70	87.406	73	108.309	50	108.348
		88	117.552	60	121.383

The equation for a first-order linear ordinary differential equation ( $y' + p(x)y = q(x)$ ) is

$$y = \left[ \int q(x) e^{\int p(x)dx} dx + \text{constant} \right] e^{-\int p(x)dx}, \quad (13)$$

where constant is the constant term in the analytic solution, which depends on the conditions.

With (13) and the known conditions, (12) can be solved to give an analytical solution, and then  $R$  and  $C_t$  at time  $t$  can be calculated by

$$R = \frac{2DC_s}{\delta\rho_s} \frac{1}{2DA/\delta + Q} (V + Qt) \cdot \left( 1 - \left( \frac{V}{V + Qt} \right)^{1+2DA/\delta Q} \right), \quad (14)$$

$$C_t = \frac{\rho_s AR}{V + Qt} = C_s \frac{2DA}{\delta} \cdot \frac{1}{2DA/\delta + Q} \left( 1 - \left( \frac{V}{V + Qt} \right)^{1+2DA/\delta Q} \right).$$

### 3. Validation of the Analytical Formula for Transient Dissolution

The concentration of a rock salt solution experiment [32, 33] has been measured at different time points with the different flow rates ( $Q$ ), as shown in Figure 3 and Table 1. Figure 3 shows that the larger  $Q$  value, the higher concentration of the rock salt solution at the same time point, suggesting that dissolution of rock salt accelerates as  $Q$  increases.

The following test parameters have been reported [32, 33]:  $C_s = 295 \text{ g}\cdot\text{dm}^{-3}$ ,  $\rho_s = 2.10 \text{ g}\cdot\text{cm}^{-3}$ ,  $A = 78.54 \text{ cm}^2$ , and  $V = 500 \text{ cm}^3$ . The fitting of the test data was performed using (9). At  $Q = 2, 5, \text{ and } 9 \text{ cm}^3 \text{ min}^{-1}$ ,  $D/\delta = 0.02327, 0.03570, \text{ and } 0.05382 \text{ cm min}^{-1}$ , respectively, which shows that the dissolution parameters of rock salt are augmented and dissolution of rock salt accelerates as the flow rate ( $Q$ ) increases. The corresponding correlation coefficients are

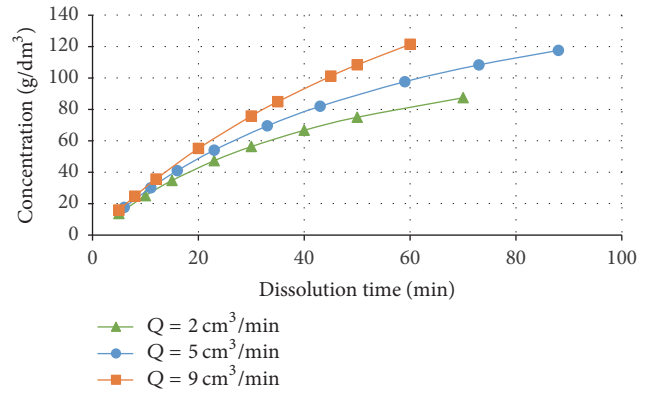


FIGURE 3: Transient dissolution test curve of rock salt.

0.9947, 0.9997, and 0.9923. The fitting results are shown in Figures 4–6.

## 4. Physical Meaning and Influential Factors of the Analytical Formula

4.1. *Physical Meaning of the Analytical Formula.* The equation for  $C_t$  can be derived from (14):

$$C_t = \frac{\rho_s AR}{V + Qt} = C_s \frac{1}{1 + Q/(2DA/\delta)} \cdot \left( 1 - \left( \frac{1}{1 + (Q/V)t} \right)^{1+2DA/\delta Q} \right), \quad (15)$$

where  $C_s(1/(1 + Q/(2DA/\delta)))$  represents the concentration of the rock salt solution at dissolution time  $t \rightarrow \infty$  and  $Q/V$  represents the dissolution rate of rock salt (the slope of the concentration curve). When the initial volume of solution is constant, the higher the flow rate, the higher the dissolution rate of rock salt.

After the test parameters were substituted into (14), the concentrations of the rock salt solutions at dissolution

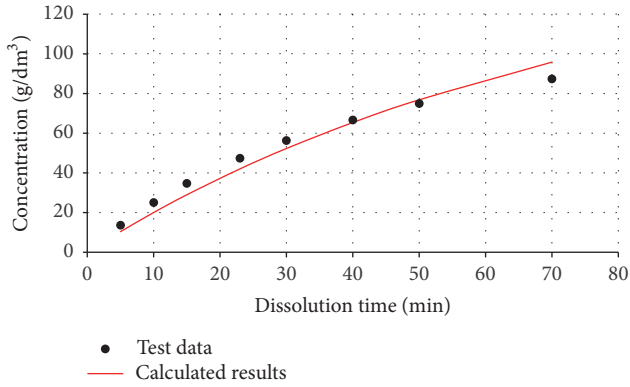


FIGURE 4: Comparison of the calculated results and test data of the transient dissolution of rock salt at  $Q = 2 \text{ cm}^3 \text{ min}^{-1}$ .

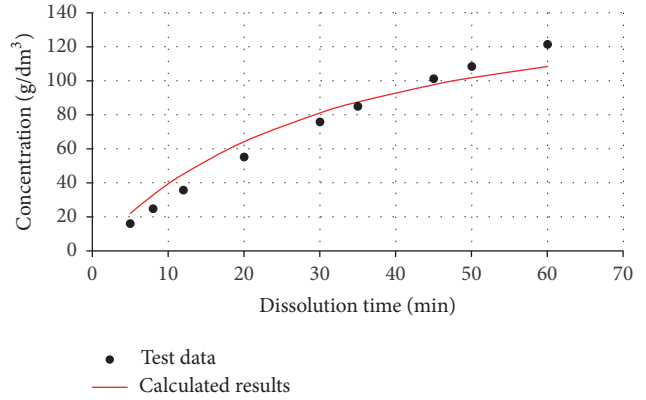


FIGURE 6: Comparison of the calculated results and test data of the transient dissolution of rock salt at  $Q = 9 \text{ cm}^3 \text{ min}^{-1}$ .

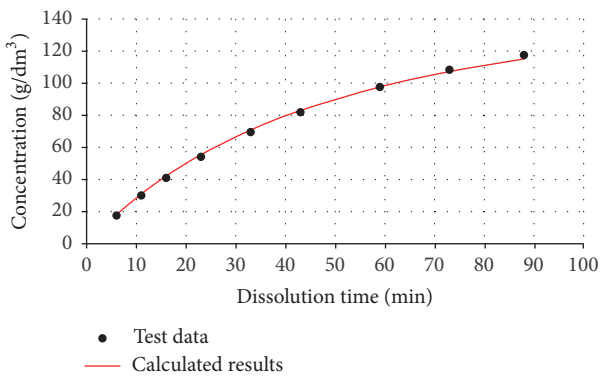


FIGURE 5: Comparison of the calculated results and test data of the transient dissolution of rock salt at  $Q = 5 \text{ cm}^3 \text{ min}^{-1}$ .

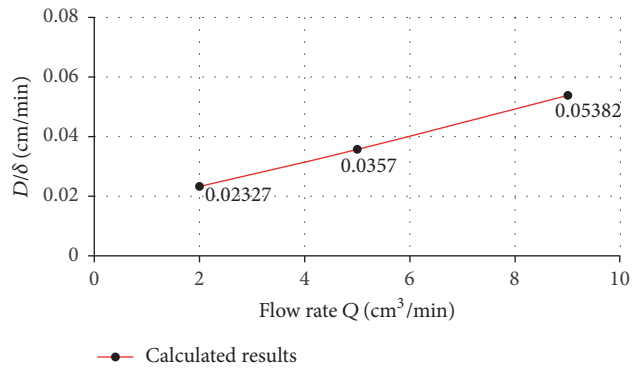


FIGURE 7: Dissolution parameter ( $D/\delta$ ) of rock salt at different flow rates ( $Q$ ).

time  $t \rightarrow \infty$  were  $0.646C_s$  ( $190.667 \text{ g}\cdot\text{dm}^{-3}$ ),  $0.529C_s$  ( $155.944 \text{ g}\cdot\text{dm}^{-3}$ ), and  $0.484C_s$  ( $142.885 \text{ g}\cdot\text{dm}^{-3}$ ) at  $Q = 2, 5,$  and  $9 \text{ cm}^3 \text{ min}^{-1}$ , respectively. The corresponding dissolution rates of rock salt are  $0.004, 0.01,$  and  $0.018 \text{ min}^{-1}$ .

#### 4.2. Influential Factors of the Analytical Formula

4.2.1. *Effect of  $D/\delta$  Parameter.* In Section 3,  $D/\delta$  values at ( $Q$ ) = 2, 5, and  $9 \text{ cm}^3 \text{ min}^{-1}$  were 0.02327, 0.03570, and  $0.05382 \text{ cm min}^{-1}$ , respectively, as shown in Figure 7. It was found that  $D/\delta$  gradually increases with increasing of  $Q$ , and an approximately linear correlation is obtained by fitting with the equation  $D/\delta = 0.00437Q + 0.01427$  (correlation coefficient 0.9996).

4.2.2. *Effect of the Dissolution Area.* Assuming that the other parameters were constant, the effect of changing the dissolution area ( $A$ ) was investigated with the following parameters:  $Q = 2 \text{ cm}^3 \text{ min}^{-1}$ ,  $D/\delta = 0.02327 \text{ cm min}^{-1}$ ,  $C_s = 295 \text{ g}\cdot\text{dm}^{-3}$ ,  $\rho_s = 2.10 \text{ g}\cdot\text{cm}^{-3}$ ,  $V = 500 \text{ cm}^3$ , and  $A = 10, 30, 50, 100, 200,$  and  $300 \text{ cm}^2$ . The calculated results are shown in Figures 8 and 9. These figures suggest that when  $A$  increases,  $R$  gradually decreases while  $C_t$  increases. This is because when the initial volume of solution ( $V$ ) is constant,  $R$  and  $C_s$  are directly proportional to the difference

between  $C_s$  and  $C_t$  ( $C_s - C_t$ ). As  $A$  increases,  $C_t$  increases, resulting in a progressive decrease of  $R$  (5). When  $A$  is very low,  $R$  and  $C_t$  show an approximately linear correlation with the dissolution time. If  $A$  is gradually increased to  $100 \text{ cm}^2$ , there is a nonlinear relationship between  $R$  or  $C_t$  and the dissolution time.

4.2.3. *Effect of the Initial Volume.* Assuming that the other parameters were constant, the effect of the initial volume ( $V$ ) of the rock salt solution was investigated with the following parameters:  $Q = 2 \text{ cm}^3 \text{ min}^{-1}$ ,  $D/\delta = 0.02327 \text{ cm min}^{-1}$ ,  $C_s = 295 \text{ g}\cdot\text{dm}^{-3}$ ,  $\rho_s = 2.10 \text{ g}\cdot\text{cm}^{-3}$ ,  $A = 78.54 \text{ cm}^2$ , and  $V = 100, 300, 500, 1000,$  and  $2000 \text{ cm}^3$ . The calculated results are shown in Figures 10 and 11. These figures reveal that with augmentation of  $V$ ,  $R$  gradually increases while  $C_t$  decreases. This is because when the dissolution area is constant, the larger the volume, the lower the concentration of rock salt. According to (5),  $R$  is directly proportional to  $C_s - C_t$ .  $C_t$  decreases with increasing  $V$ , leading to a gradual increase of  $R$ . Furthermore, when  $V$  is very low,  $R$  and  $C_t$  have a nonlinear correlation with the dissolution time. When  $V$  is progressively increased to  $1000 \text{ cm}^3$ , there is an approximately linear relationship between  $R$  or  $C_t$  and the dissolution time.

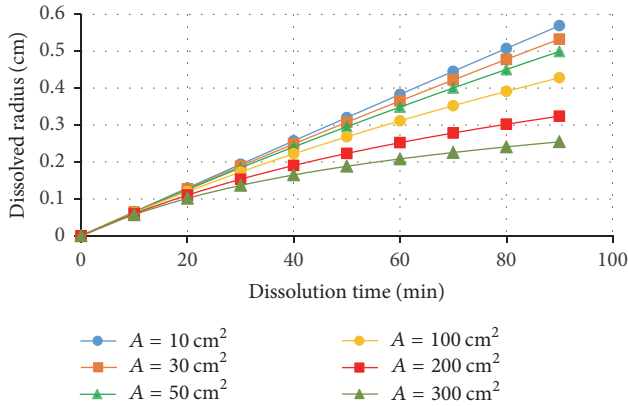


FIGURE 8: Change of the dissolved radius with dissolution time for different dissolution areas ( $A$ ).

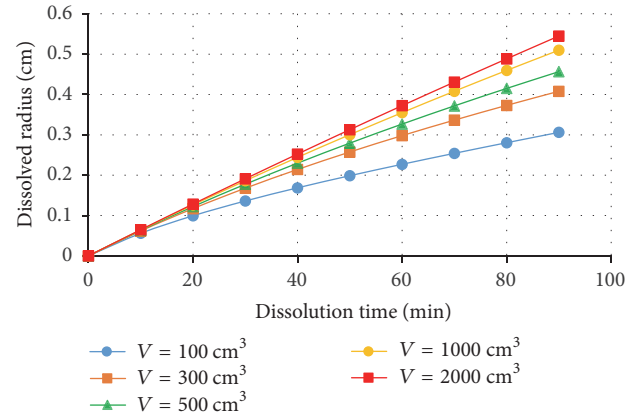


FIGURE 10: Change of the dissolved radius with dissolution time for different initial volumes ( $V$ ).

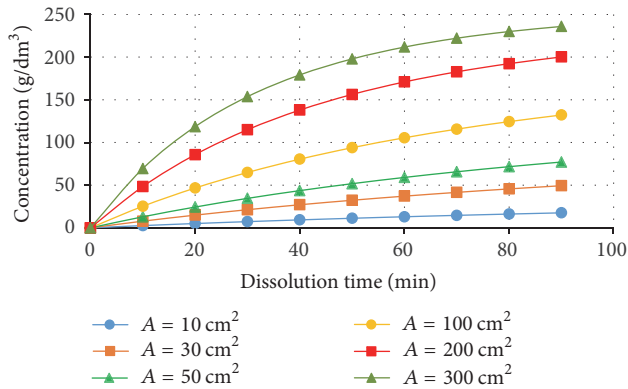


FIGURE 9: Change of the concentration of rock salt with dissolution time for different dissolution areas ( $A$ ).

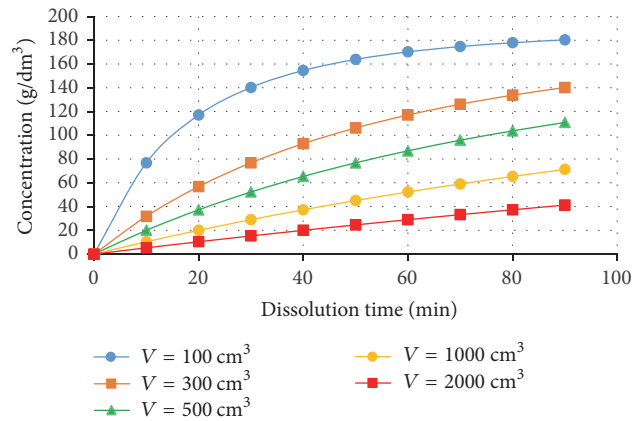


FIGURE 11: Change of the concentration of rock salt with dissolution time for different initial volumes ( $V$ ).

## 5. Conclusion

An analytical solution for the dissolution rate equation of rock salt under the assumption of an instantaneous diffusion process and its influential factors were investigated. The following conclusions can be drawn from this study.

(1) An ordinary differential equation for the dissolution rate of rock salt was established by calculating the concentration distribution of rock salt at the boundary layer. It was then solved mathematically to give an analytical solution. Thereafter, the analytic solution was used to fit transient dissolution test data of rock salt. The fitting results show that, at flow rates of 2, 5, and 9  $\text{cm}^3 \text{min}^{-1}$ , the transient dissolution parameters are 0.02327, 0.03570, and 0.05382  $\text{cm min}^{-1}$ , respectively.

(2) The physical meaning of the analytical formula for the dissolution rate of rock salt was discussed. The analytical formula partly represents the concentration of that rock salt solution at the dissolution time  $t \rightarrow \infty$  and partly represents the dissolution rate of rock salt. This study demonstrates that when the initial volume of the rock salt solution is constant, the larger the flow rate, the higher the dissolution rate of rock salt.

(3) The influential factors of the analytical formula were investigated. The results showed that there is an approximately linear relationship between the dissolution parameter ( $D/\delta$ ) and the flow rate ( $Q$ ):  $D/\delta = 0.00437Q + 0.01427$  (correlation coefficient 0.9996). The changes of the dissolved radius and concentration of rock salt with dissolution time for different dissolution areas and different initial volumes were also calculated using the analytical formula.

(4) The results of this study can provide the basic parameters for the leaching of rock salt caverns and also a theoretical reference for the transient dissolution of rock salt.

It must be pointed out that chemical dissolution of porous rocks including rock salt is a very complicated scientific problem [10–24]. The dissolution surface that is commonly represented by the dissolution front can exist in either a stable state or an unstable state, depending on the coupled behavior among the solute diffusion, pore-fluid flow, and chemical reaction type in the whole dissolution system [34]. This indicates that this study still has certain limitations, which should be improved in the future research.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

This study is supported by the Scientific Research Foundation of Fujian University of Technology (Grant no. GY-Z160051), the Fujian Provincial Natural Science Foundation Projects (Grants nos. 2013J01170, 2015J05090, 2016J01205, and 2017J05070), and the National Natural Science Foundation of China (Grant no. 51508097); the authors gratefully acknowledge these supports.

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