

## Article

# Characterizing the Dissolution Rate of CO<sub>2</sub>-Brine in Porous Media under Gaseous and Supercritical Conditions

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**Abstract:** The CO<sub>2</sub>-brine dissolution homogenizes the distribution of residual CO<sub>2</sub> and reduces the leakage risk in the saline aquifer. As a key parameter to immobilize the free CO<sub>2</sub>, the dissolution rate of CO<sub>2</sub>-brine could be accelerated through mechanisms like diffusion and dispersion, which are affected by the subsurface condition, pore structure, and background hydrological flow. This study contributed the calculated dissolution rates of both gaseous and supercritical CO<sub>2</sub> during brine imbibition at a pore-scale. The flow development and distribution in porous media during dynamic dissolution were imaged in two-dimensional visualization using X-ray microtomography. The fingerings branching and expansion resulted in greater dissolution rates of supercritical CO<sub>2</sub> with high contact between phases, while the brine bypassed the clusters of gaseous CO<sub>2</sub> with a slower dissolution and longer duration due to the isolated bubbles. The dissolution rate of supercritical CO<sub>2</sub> was about two or three orders of magnitude greater than that of gaseous CO<sub>2</sub>, while the value distributions both spanned about four orders of magnitude. The dissolution rates of gaseous CO<sub>2</sub> increased with porosity, but the relationship was the opposite for supercritical CO<sub>2</sub>. CO<sub>2</sub> saturation and the Reynolds number were analyzed to characterize the different impacts on gaseous and supercritical CO<sub>2</sub> at different dissolution periods.

**Keywords:** porous media; CO<sub>2</sub> storage; dissolution rate; heterogeneity; micro-computed tomography

## 1. Introduction

The residual and solubility trapping of CO<sub>2</sub> in the saline aquifer maximize the storage capacity and ensure the reservoir integrity of CO<sub>2</sub> sequestration [1]. After CO<sub>2</sub> is injected into target reservoirs, it migrates in permeable rock under a supercritical state and dissolves into brine to form carbonic acid [2]. The dissolution process reduces the risk of CO<sub>2</sub> leakage through the caprock of the reservoir due to the upward movement of the CO<sub>2</sub> plume under the buoyancy effect [3]. The dissolution rate of CO<sub>2</sub>-brine, which represents the mass transfer process, serves as an important parameter to immobilize the free-phase CO<sub>2</sub>.

The major driving force of the dissolution rate is the partitioning non-equilibrium concentration and is controlled by the interfacial and environmental conditions in the porous media [4]. If the pore space is occupied by the brine with high CO<sub>2</sub> concentrations, the dissolution rates will be reduced, increasing the time spans of the CO<sub>2</sub> precipitation from hundreds to thousands of years. Depending on

the stage of CO<sub>2</sub> sequestration and the physical properties of the saline aquifers, diffusion, advection, and convection can occur during the mass transport [5]. Through these mechanisms, the CO<sub>2</sub> near the two-phase interface is dissolved and transported away. Then, further fresh brine imbibes into the in situ pores and sequentially makes contact with free-phase CO<sub>2</sub>, accelerating the dissolution process.

To determine the dissolution rate of the injected CO<sub>2</sub>, scaling analysis based on simulation and experiments of the convective mixing and non-equilibrium imbibition have been applied to characterize the effect of convection and diffusion [6–8]. In previous studies, the dissolution process was widely investigated between the non-wetting phase (air/non-aqueous phase liquid) and the nearby wetting phase (water/brine) in porous media. For the observation focused on a single pore or a cluster and connected pore throats, the dissolution is dominated by molecular diffusion and mass transfer at the CO<sub>2</sub>–water interfacial area [9]. Besides, in a 2-D model, the observed convection and dissolution rates are mainly an effect of dispersion due to the transport velocity of the solvent phase.

Dynamic measurement of the dissolution process is necessary to determine the potential impacts of the above mechanisms on the dissolution rate. During the CO<sub>2</sub> dissolution, brine saturated with CO<sub>2</sub> will be removed more effectively from the CO<sub>2</sub>-brine interface and more unsaturated brine comes into contact with the CO<sub>2</sub>. This process will be affected by the actual formation environment, including the reservoir temperature and pressure, flow development, heterogeneity, pore structure, and gas distribution [10]. In addition, the flow rate of the brine in the aquifer could be regarded as constant, while in the background, the flow CO<sub>2</sub> plume pushes the in situ brine to move forward at different flow rates. Thus, different CO<sub>2</sub> injection rates will result in the various dissolution rates of CO<sub>2</sub> at the field scale. Despite its recognized importance, measurement of the accurate dissolution rate of CO<sub>2</sub> into brine in realistic subsurface conditions is challenging due to the difficulty of conducting large-scale numerical simulations and experiments with reservoir complexity [11–13].

As the depth of target reservoir increases, CO<sub>2</sub> turns into the supercritical state because temperature and pressure surpass the critical point of the gas. In this state, compared to gaseous CO<sub>2</sub>, supercritical CO<sub>2</sub> exhibits unique characteristics such as a high density, low viscosity, and high diffusivity and solubility. However, the studies of the effect of CO<sub>2</sub> phase state on dissolution rate are insufficient. For a given CO<sub>2</sub> droplet, the dissolution rate depends on the gas pressure and the fluid pair composition in the aquifer [14], while the dissolution rate of the CO<sub>2</sub> plume is sensitive to the density distribution inside the underground layer [15]. In the deep saline aquifer, the migration of denser fluid enhances CO<sub>2</sub> dissolution and brings in the trapping mechanism of density-driven convection between the gas plume and the CO<sub>2</sub>-saturated brine. Meanwhile, higher diffusivity generally supports solubility trapping [16]. When the CO<sub>2</sub>-brine system is strongly dispersive, more CO<sub>2</sub> will dissolve into the brine, and the dissolution process will be accelerated [17]. As the CO<sub>2</sub> solubility is enhanced under a supercritical state, it is expected that increasing pressure in deeper aquifers can greatly promote the solubility of CO<sub>2</sub> in aqueous solution [18]. Therefore, an adequate reservoir condition is important to reduce the time span of solubility trapping and will increase storage security [19].

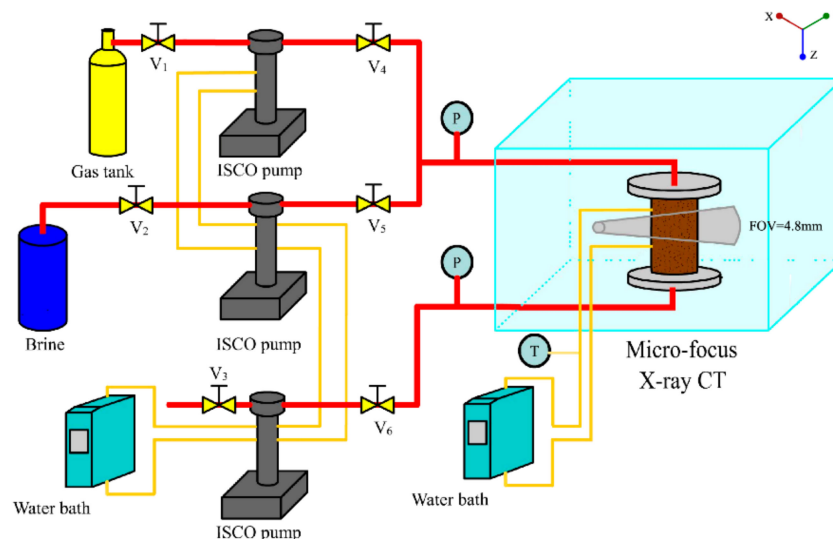
In this study, we performed comparison experiments to measure the dissolution rate of gaseous and supercritical CO<sub>2</sub> in brine in brine-saturated porous media. The sand-filling core was pre-saturated with supercritical CO<sub>2</sub>, followed by the brine injection, to dynamically characterize the two-phase dissolution. The process was reproduced with gaseous CO<sub>2</sub> to quantify the impact of the phase state on the dissolution rate. The micro-computed tomography (micro-CT) was applied to observe and measure the dynamic CO<sub>2</sub>-brine dissolution, and visualized the flow development and distribution at different periods of CO<sub>2</sub> dissolution under supercritical and gaseous states. The CO<sub>2</sub> dissolution rates were analyzed with the porosity, CO<sub>2</sub> saturation, and the Reynolds number of the injected brine since the factors mainly contribute to the two-phase dissolution during the flow development in heterogeneous porous media.

## 2. Materials and Methods

### 2.1. Experimental Material and Performance

The porous media was un-consolidated glass beads (average particle diameter of 0.35–0.45 mm, As-one, Inc., Osaka-shi, Japan) packed in the vertical sand-pack holder. To simulate the reservoir condition, the temperature and pressure were maintained at 40 °C and 8 MPa, and CO<sub>2</sub> was under a supercritical state. The condition corresponds to the depth of 800 m for a typical geological reservoir. Also at room T&P conditions (25 °C and 0.1 MPa), CO<sub>2</sub> under a gaseous state was injected into the holder as the non-wetting phase for comparisons. The brine we employed in the experiments contained 3 mass % of NaCl (Analytical reagent AR, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China) to simulate the subsurface salinity. Additionally, potassium iodide (KI, Analytical reagent AR, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China) was dissolved in the brine as a contrast agent to enhance the contrast between brine and gas in the CT images, and the KI concentration was 6 mass %.

The experimental setup is shown in Figure 1. It consisted of a micro-X-ray CT scanner (InspeXio SMX-225CT, Shimadzu, Kyoto, Japan), syringe pumps, core holder, and temperature system. Three syringe pumps (260D, Teledyne ISCO Inc., Lincoln, NE, USA) were used in this system. Two syringe pumps injected brine and gas into the porous media and another syringe pump controlled the back pressure to keep the pressure stabilized throughout the experiments. The packed bed was 32 mm in length and 6 mm in diameter. A simple holder was fabricated from PEEK and stainless steel. The thickness of its wall was 3 mm. By using water-warmed temperature jackets, the temperature of the three syringe pumps was kept at the configured temperature, and an electric heating tape was used to control the temperature of core holder. The core holder, syringe pumps, and experimental pipelines were all wrapped in heat insulation cotton.



**Figure 1.** Experimental apparatus. The syringe pumps, ISCO pumps, were used as injection pumps and back pressure pump. The micro-computed tomography (Micro-focus X-ray CT) was configured under the same parameters between different sets of experiments. The length of the FOV (field of view) of the packed beads was 4.8 mm.

### 2.2. Experimental Produce

Porous media was filled into the holder that was dried and vacuumed for a long time. CO<sub>2</sub> was injected into the system at a relatively low flow rate. When the temperature and pressure were kept stable for 2 h, the porosity and the original CO<sub>2</sub> distribution were acquired with the CO<sub>2</sub> saturated scan. Then, brine without saturated CO<sub>2</sub> was injected downward into the holder, and the flow rate remained

constant at 0.04 mL/min. Series of CT scans were conducted during these injections. Since the brine injection and the CT scan were performed simultaneously, the non-wetting phase could be changed dynamically, and CO<sub>2</sub> was constantly dissolved into the brine flow. Each experiment was run for several hours until the variation in the CO<sub>2</sub> saturation was less than 1%. We obtained 308 slice images with a cross-sectional area of 512 × 512 pixels for each slice, and the thickness of each slice was 16 µm. The length of the FOV (field of view) was 4.8 mm and located at the middle-upper part of the holder to prevent the end effect and allow the fluid flow to fully develop. In these experiments, scanning was performed at 90 kV and 50 µA. The spatial resolution was 16 µm/voxel.

### 3. Results and Discussion

In our experiments, the unsaturated brine was injected into the CO<sub>2</sub>-saturated core at a Darcy velocity of 2.04 m/d. With similar core characteristics, the injection flow rate was much lower than the velocities in the dissolution experiment in the literature [9]. Therefore, the dissolution mechanism dominated during the brine imbibition and CO<sub>2</sub> gradually dissolved in the pore space as the brine injection continued.

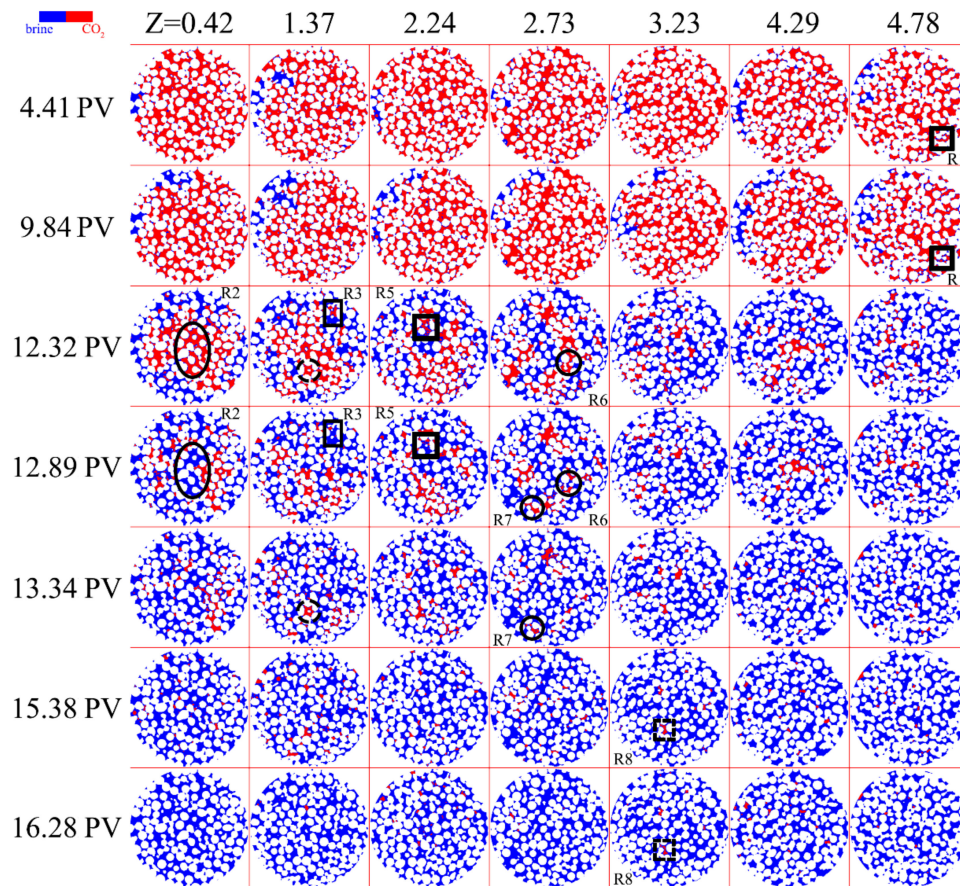
#### 3.1. Pore-Scale CO<sub>2</sub> Dissolution and Flow Development

The time-lapse images of CO<sub>2</sub>-brine dissolution were rendered for selected slices, as shown in Figure 2. It is demonstrated that the overall dissolution rates are sensitive to the aqueous flow field, which was affected by the CO<sub>2</sub> distribution and the resulting reductions in relative permeability [20,21]. In the first few pore volumes (PV), the brine invaded along the side of the core and formed a continuous flow path. With the continuous injection of brine, the flow path expanded radially and stretched to the surrounding pores. The flow development in the downward imbibition was severely affected by the gravity effect, and flow bypassing occurred. A small amount of brine intruded into other areas of the core and formed film flow on the surface of the wetting porous media. The film water and corner flow in the former PV resulted in the swelling of thin film within pores and subsequent fragmentation of CO<sub>2</sub> droplets (shown in Figure 2 R1). The water flow between CO<sub>2</sub> bubbles and pore walls was found to affect the CO<sub>2</sub> dissolution rate [22]. In this period, the dissolution rate was controlled by the extension of the flow path. The fundamental reason for this is that further dissolution based on flow development was hindered by the pore structure under the gravity effect. The critical time of the dissolution rates was observed to be extremely sensitive to the position and size of the heterogeneous region, suggesting the disruption of the pore structure to the phase equilibrium [23].

The dissolution expansion was initiated at about 9.48 PV, and the duration was about 3 PVs. The brine began to invade the pores in the center of the core and formed multiple fingerings. With the branching and expansion of the fingerings, the large CO<sub>2</sub> cluster dissolved rapidly in the brine, significantly enhancing the CO<sub>2</sub> dissolution rate (shown in Figure 2 R2). Dissolution fingering may occur at CO<sub>2</sub>-brine interfaces because of instabilities in CO<sub>2</sub> saturation and flow development during dissolution, as observed in a homogeneous pore network [24] and heterogeneous porous media [25]. High contact between the injected brine and the CO<sub>2</sub> surface (i.e., low bypassing) resulted in a greater CO<sub>2</sub> dissolution rate (shown in Figure 2 R3). Particularly for supercritical CO<sub>2</sub> under larger buoyancy forces, the faster growth of perturbations existed over time, which can provoke a more complicated structure of fingers and also more CO<sub>2</sub> dissolution into brine [17]. In contrast, the CO<sub>2</sub> bubbles located parallel to the flow direction led to more bypass trapping and lower average effluent concentrations [26]. The CO<sub>2</sub> bubbles, which were bound by the bypass flow, generally had low connectivity to the surrounding brine, or were isolated in the large pores through the connected pore throats (shown in Figure 2 R4). The flow bypassing was found to restrain the dissolution rate in experiments with CO<sub>2</sub> confined to the central region in the sand-filling core. Simultaneously, the brine that already occupied some corners of the pore gradually filled the pore space owing to the diffusion of the CO<sub>2</sub> in the brine (shown in Figure 2 R5). When the brine filled the upstream pores, some of the downstream bubbles happened to snap-off, and the detached part then rapidly dissolved (shown



in Figure 2 R6 and R7). The flow development and the diffusion and the coupled water flow and dissolution at the pore scale enhanced the dissolution rate at the pore-network scale, shortening the total depletion time of CO<sub>2</sub> [9,27].

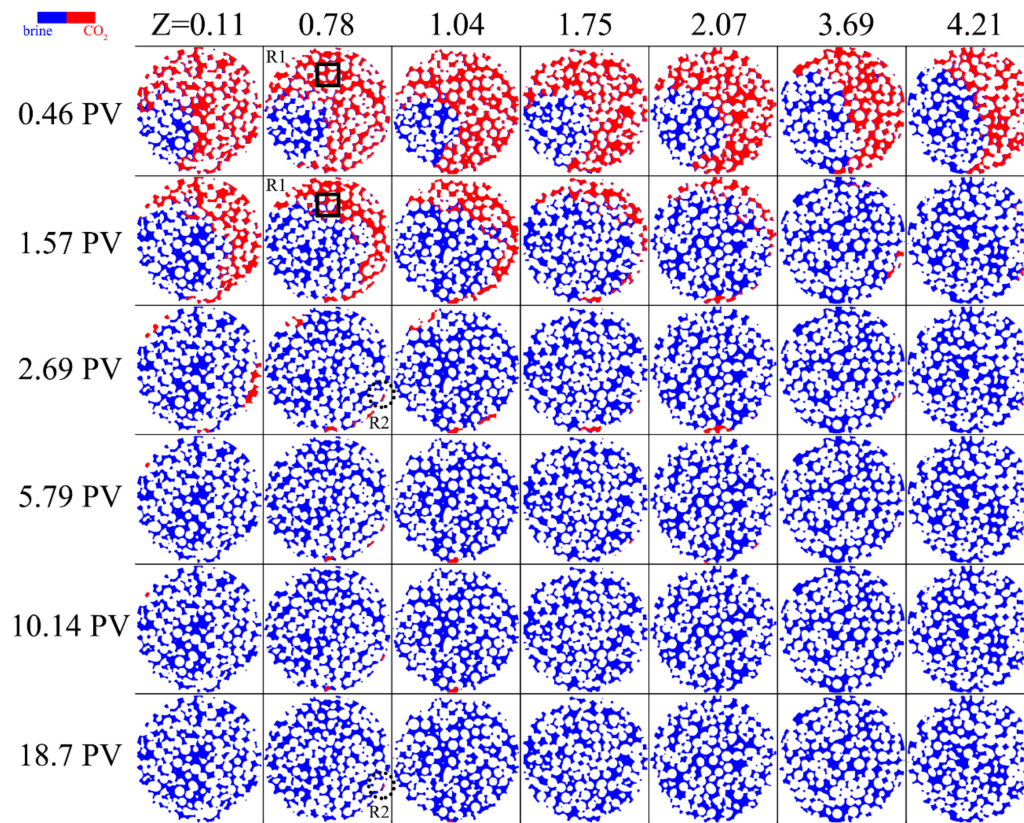


**Figure 2.** Time-lapse images of the supercritical CO<sub>2</sub> (red) at different positions for 0.04 mL/min. The position of the image along the vertical direction of the brine injection is short as Z, which is also the distance from the inlet.

After the major CO<sub>2</sub> bulk dissolved, the remaining CO<sub>2</sub> bubbles were trapped in the unconnected pores. The effect of the diffusion mechanism on the dissolution rate was enhanced during this period. CO<sub>2</sub> clusters trapped in the large pores were split by brine and changed in size and shape (shown in Figure 2 R8). The newly isolated CO<sub>2</sub> singlet existed for 1–3 PV, while the bubbles that inherited from the period of rapid dissolution expansion sometimes persisted for more than 4 PV. These isolated bubbles reduced the overall CO<sub>2</sub> dissolution rate and prolonged the duration of complete CO<sub>2</sub> dissolution.

For brine imbibition in porous media saturated with gaseous CO<sub>2</sub>, the dissolution process was sustained for longer due to the residue of small bubbles. The flow development was limited, and a major priority path formed. The duration of gaseous CO<sub>2</sub> dissolution expansion was almost the same as supercritical CO<sub>2</sub>. However, the density difference between gaseous CO<sub>2</sub> and the brine is over two orders of magnitude smaller than the case in supercritical CO<sub>2</sub>. This leads to the brine imbibition being more concentrated in the porous media, directly restricting the number of the fingering. Figure 3 intuitively shows the consequence of this. Along part of the holder wall, the brine formed the priority path under the gravity effect, which occurred during the cross-sectional expansion. It is observed that the brine imbibition mainly occurred at the center of the core, and the time node when the CO<sub>2</sub> bulk began to dissolve occurred much earlier than for the supercritical CO<sub>2</sub>.

The thin-film flow led to the snap-off of the bubble connected in large pore clusters (shown in Figure 3 R1). Within 2 PVs, the dissolution expanded along the flow paths with rapid CO<sub>2</sub> dissolution in the brine. However, characteristics of flow development indicated that brine tended to avoid the gaseous CO<sub>2</sub> clusters, implying lower dissolution rates and less probability of dissolution events. In the previous study, imbibition of unsaturated brine was more focused and had a lower sweep efficiency [9]. Taking the efficiency into account, the comparison of our results indicates that the supercritical CO<sub>2</sub> demonstrates its superiority to improve the trapping efficiency of CO<sub>2</sub> sequestration during the imbibition. The brine failed to invade into some pores at the corner of the core, and the isolated bubble sometimes existed for more than 16 PV (shown in Figure 3 R2). The gaseous CO<sub>2</sub> singlet significantly prolonged the duration of the dissolution, which is harmful to the trapping security of the CO<sub>2</sub> sequestration.



**Figure 3.** Time-lapse images of gaseous CO<sub>2</sub> (red) at different positions for 0.04 mL/min.

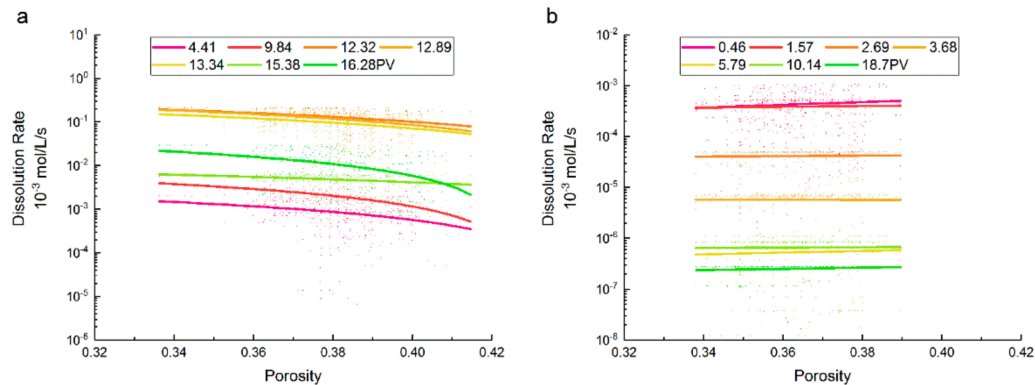
### 3.2. Porosity and Saturation Influence

The dissolution rate of CO<sub>2</sub> is defined as the CO<sub>2</sub> molar flux, which acts as an important indicator of the residual and solubility trapping mechanism [6]. The CO<sub>2</sub> dissolution is controlled by both diffusion and dispersion mechanisms, but the CO<sub>2</sub> dispersivity is commonly one to two orders of magnitude greater than the molecular diffusion coefficient. When brine imbibes to contact with CO<sub>2</sub>, the dispersion between CO<sub>2</sub> and brine dominates and therefore the dissolution rate of this period is increased. As both dispersion and diffusion are active under a supercritical state, the dissolution rate follows the analogous definition of the pseudo-diffusion coefficient (Dps) which can be used for quantification of the dissolution rate of CO<sub>2</sub> in water [28]. In the case of the dissolution in porous media, it was calculated based on the rate of loss of CO<sub>2</sub> from the CO<sub>2</sub> phase,

$$Dps(x, t) = \frac{C(0, t)}{\Delta t} - \frac{\rho_g * \Delta \theta * \Delta x}{\Delta t^2 * U} \quad (1)$$

where  $Dps(x, t)$  is the  $CO_2$  dissolution rate,  $C(0, t)$  is the concentration of  $CO_2$  at the inlet of the core,  $\Delta t$  is the time interval of each CT scan,  $\rho_g$  is the  $CO_2$  density,  $\Delta\theta$  is the difference of  $CO_2$  volume fraction,  $U$  is the Darcy flux, and  $\Delta x$  is the distance of brine imbibition below the inlet of the core.

The dissolution rate values at different PVs and their correlations with porosity are shown in Figure 4. The dissolution rate of supercritical  $CO_2$  was about two or three orders of magnitude greater than that of gaseous  $CO_2$ , indicating the prominent properties of the supercritical  $CO_2$  during the dissolution process. In addition, the value distribution of the dissolution rate of  $CO_2$  under the supercritical state was similar to that of gaseous  $CO_2$  and spanned about four orders of magnitude. The dissolution rate of supercritical  $CO_2$  increased as the flow path of the brine gradually expanded, and decreased as the isolated bubbles gradually dissolved due to the diffusion mechanism. By contrast, the dissolution rate of gaseous  $CO_2$  dropped rapidly, and the value differences were approximately one order of magnitude at different PVs. This can be attributed to the difference in the critical time of dissolution expansion. In the cases of supercritical and gaseous  $CO_2$ , the dissolution rate was maintained at a relatively large value during the domination of the dissolution expansion, and changed slightly with brine injection. Then, the dissolution rate of gaseous  $CO_2$  decreased more dramatically because of the diverse number of residual  $CO_2$  bubbles. The features correspond to the flow development which is shown in Figures 2 and 3.



**Figure 4.**  $CO_2$  dissolution rate vs. porosity at different injection PVs for (a) supercritical  $CO_2$  and (b) gaseous  $CO_2$ .

The porosity was defined by the following equation, as given in [29],

$$\varphi = \frac{Vc}{V} \quad (2)$$

where  $\varphi$  is the porosity,  $Vc$  is the void space in the pore structure, and  $V$  is the volume of the core sample. In our experiments, an adequate threshold was chosen to extract the pore space from the original CT images. The porosity profiles were generated from the CT scans of the dry core.

The dissolution rate of supercritical  $CO_2$  decreased as porosity increased, and this trend increased with the increment of porosity. Simultaneously, the relatively small dissolution rate, which was located in the region of large porosity, decreased faster, and the descending trends between PVs had significant differences. In the previous study, a larger porosity heterogeneity may have led to more significant changes to the dissolution rate [30], while a simple relationship between the  $CO_2$ -brine dissolution rate and cross-sectional area of adjoining pores would therefore not necessarily be expected [31]. This also proves the more active solubility of supercritical  $CO_2$ .

The dissolution rate of gaseous  $CO_2$  gradually increased with porosity, which showed no obvious effect on the variation of the dissolution rate. For both gaseous and supercritical  $CO_2$ , no observable correlation existed between the ranges of the  $CO_2$  dissolution rate and porosity at different PVs. However, when the porosity was between 0.36 and 0.38, the value ranges of dissolution rates under a

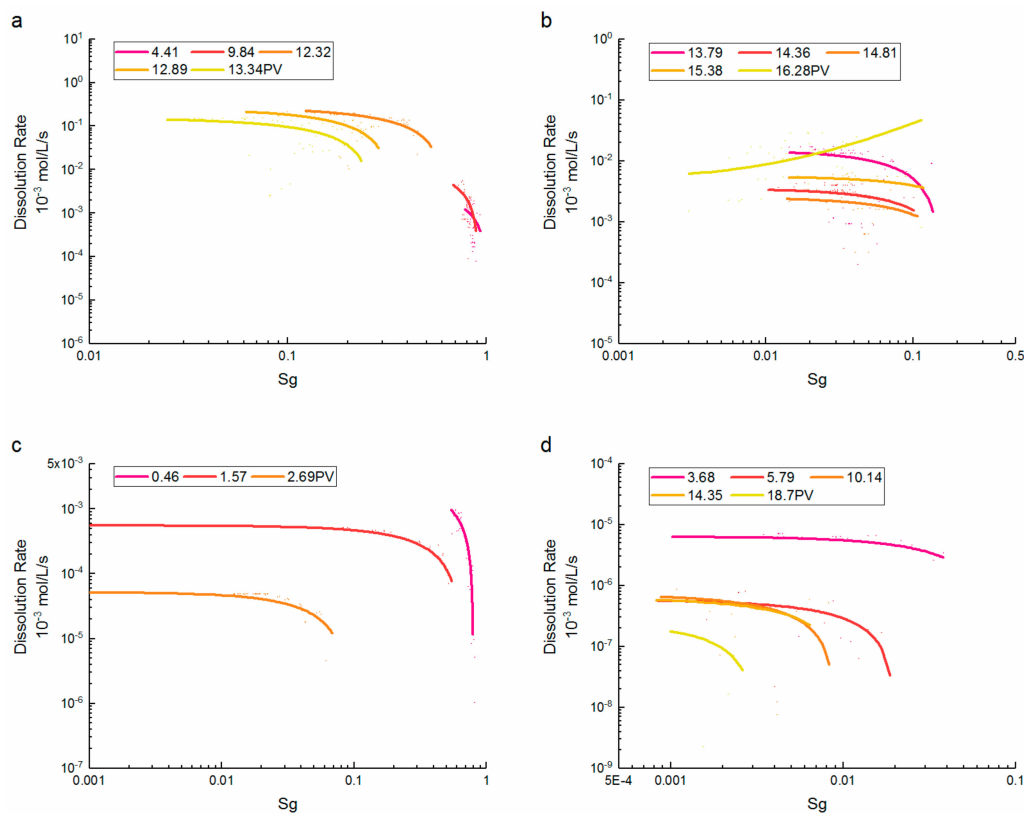


supercritical state were greater. It is suggested that pore-size distribution will affect the dissolution rate, which is another mechanism identified for trapping as varying solubility is applicable [32].

In previous studies, CO<sub>2</sub> saturation and the CO<sub>2</sub> reduction rate originating from the CO<sub>2</sub> dissolution are generally used to calculate the CO<sub>2</sub> capacity and trapping efficiency, respectively [1,10]. By using numerical analysis and resistivity monitoring, the computation of CO<sub>2</sub> saturation could be conducted. Also, the saturation could be indirectly obtained by isotope or acoustic data with accessible cost and convenient technicalities. The CO<sub>2</sub> saturation could be expressed as shown in Equation (3), based on the definition of porosity,

$$S_g = \frac{V_g}{\varphi} \quad (3)$$

where  $S_g$  is the CO<sub>2</sub> saturation,  $V_g$  is the volume of CO<sub>2</sub> phase, and  $\varphi$  is the porosity. As the CO<sub>2</sub> saturation increased, almost all CO<sub>2</sub> dissolution rates had slight variations. Consequently, after the saturation exceeded a certain threshold, the dissolution rate plummeted severely, which even varied from one to two orders of magnitude at the same PV. At high CO<sub>2</sub> saturations, concentration gradients were near zero because of the low velocities and prolonged contact with CO<sub>2</sub>. This further reduced the active mass transfer from high saturation regions and illustrates the important role of low to medium saturations [20]. The plots of dissolution rate vs. saturation in Figure 5 were divided into two categories due to the significant differences of value ranges at different PVs, and the threshold of saturation was chosen as 0.1.



**Figure 5.** CO<sub>2</sub> dissolution rate vs. CO<sub>2</sub> saturation at different injection PVs for (a,b) supercritical CO<sub>2</sub> and (c,d) gaseous CO<sub>2</sub>.

The dissolution rate of supercritical CO<sub>2</sub> increased with the saturation decreased, which was obviously reversed with the brine injection. The dissolution rate remained less than  $6 \times 10^{-6}$  mol/L/s before the brine formed multiple fingerings and increased rapidly with the saturation reduction. The observed growth in the CO<sub>2</sub> dissolution rate as the CO<sub>2</sub> saturation declined has been attributed to the creation of new water-flow paths as CO<sub>2</sub> was dissolved [33,34]. When CO<sub>2</sub> saturation was less than



0.5, the dissolution rate increased by two order of magnitude. At higher saturations, the dissolution rate may reduce by an order of magnitude, and the inverse correlation of the dissolution rate with the saturation remained invariant at a certain PV. This is because the smaller bubbles have higher dissolution rates than larger clusters [35]. In the saturations between 0.1 and 0.01, the correlations between the dissolution rate and saturation were inverted at later PVs. Subsequently, the dissolution rate was maintained at a relatively large level without monotonic decreasing with brine injection at the end of the dissolution process. Only a few bubble clusters remained in porous media, as shown in Figure 2. This suggests that the CO<sub>2</sub> dissolution rate is more vulnerable to being controlled by the location and quantity of the dissolution events. The distribution of the CO<sub>2</sub> phase and its contact area with the brine do influence the concentration gradient (driving force) at the CO<sub>2</sub>-brine interface which, in turn, influences the dissolution rate [36,37]. The pore-scale variations of the flow field were found to significantly affect the dissolution rate of individual CO<sub>2</sub> bubbles, especially at low CO<sub>2</sub> saturations [38].

For gaseous CO<sub>2</sub>, the dissolution rate was inversely proportional to CO<sub>2</sub> saturation. At higher saturations, the dissolution rate was relatively large. A smaller size of an initial CO<sub>2</sub> cluster will lead to more rapid dissolution [39]. The dissolution rate increased rapidly with the saturation reduction due to the rapid extension of the flow path with the brine injection. This indicates that entrapped CO<sub>2</sub> can result in preferential flow, flow paths can change with time as CO<sub>2</sub> dissolved, and the size and distribution of CO<sub>2</sub> bubbles at early PVs of imbibition affected the degree to which flow bypassing occurs. The relationships between the dissolution rate and saturation were close to supercritical CO<sub>2</sub> after saturations were less than 0.5. Meanwhile, when the saturations were between 0.001 and 0.1, the dissolution rates of CO<sub>2</sub> were dispersed between different saturations with differences of one to two orders of magnitude. It is reported that CO<sub>2</sub> dissolution rates are sensitive to pore scale variations in the size, shape, and spatial distribution of CO<sub>2</sub> bubbles [34]. In the period of residual bubble dissolution (especially at saturations less than 0.01), the dissolution rates were greater at the same PV if the bubbles in the porous media were smaller.

### 3.3. Reynolds Number-Dissolution Rate Relationships

The flow regime is characterized through the dimensionless number, the Reynolds number, which represents the ratio of the inertial force to the viscous force [40]. The equation of Re is written in the formula of,

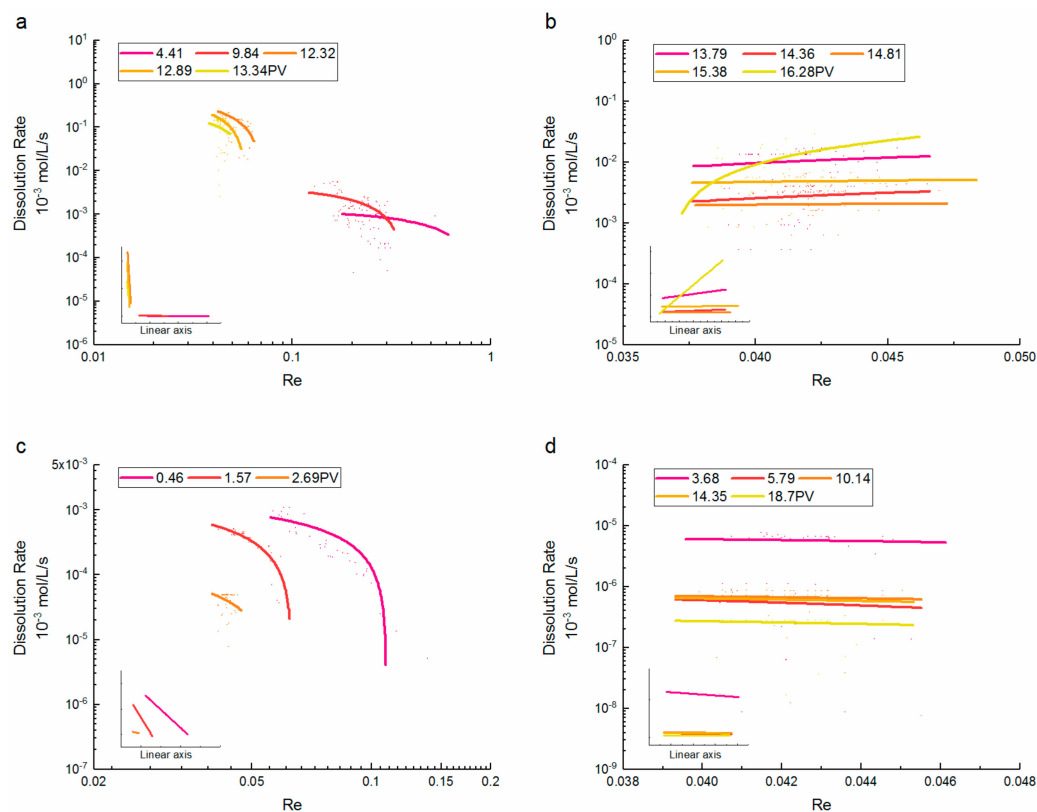
$$Re = \frac{\rho_w * U * L}{\mu_w} \quad (4)$$

where  $\rho_w$  is the density of the brine,  $U$  is the Darcy velocity,  $L$  is the characteristic length, and  $\mu_w$  is the viscosity of the brine. The Darcy velocity is proportional to the Reynolds number because the brine properties and the characteristic length are constant in the experiments. It is expected that the Darcy velocity will be affected by the saturation and the porosity at the pore scale. The Re was calculated for each position along the core since the geometry of the porous media is varied along the injection direction. In our experiments, the Re ranges from 0.001 to 1, which corresponds to laminar flows, so that the flow process was dominated by the viscous force [39].

In Figure 6, the order of the dissolution rate and the relevant range of Re varied widely at different PVs. Therefore, we adopt similar methods as the diagrams of the saturation–dissolution rate to distinguish the character of the dissolution rate when the Re distributions were concentrated in the later period of CO<sub>2</sub> dissolution. The corresponding linear relationships are presented visually in the insets.

In the early period of the supercritical CO<sub>2</sub> dissolution, the dissolution rate decreased with the increase of Re, and the relationship was reversed as most bubbles were dissolved. When the Re was greater than 0.1, the dissolution rate of supercritical CO<sub>2</sub> was relatively very small. This indicated that compared with the injection flow rate, the flow development critically determines the CO<sub>2</sub> dissolution in porous media. During the dissolution expansion, the dissolution rate increased rapidly

as the  $Re$  decreased, and the differences at different  $Re$  values were about one order of magnitude. The dissolution rates between solute and brine are highly variable in aquifers and depend on the flow rate of brine in the aquifer [41]. When buoyancy forces are preponderant (low injection flow rate), the dissolution rate increases with the distance of the brine imbibition, whereas a uniform dissolution could be observed at a high injection flow rate [42]. In the later period of dissolution, the  $Re$  was not greater than 0.01 at the same PV, but remained the order of magnitude similar to those in the early period of dissolution. In former studies, the highest dissolution rates were achieved during the injection and shortly after the injection periods, when  $CO_2$  was still mobile and distributed over many pores before it settled underneath the caprock. The dissolution rate gradually increased with the  $Re$ , and the trend was not significantly correlated with the injected PV. This is similar to the process of phase equilibrium of  $CO_2$ -brine in laminar flow. It is concluded that there is hardly any difference in dissolution rates between injection into a hydrostatic and a hydrodynamic aquifer, but with larger background flux, the dissolution rate may be higher [43]. Meanwhile, for  $CO_2$  droplets, the dissolution rate increases with the flow velocity of brine, which is proportional to the  $Re$  [39].



**Figure 6.**  $CO_2$  dissolution rate at different Reynolds numbers for (a,b) supercritical  $CO_2$  and (c,d) gaseous  $CO_2$ .

When the  $Re$  was between 0.05 and 0.2, the dissolution rate of gaseous  $CO_2$  significantly decreased with the increase of  $Re$ , and the dissolution rates were different by about two orders of magnitude at the same PV. Many bubbles resisted the accelerated dissolution; however, the overall dissolution rate for the  $CO_2$  plume decreased with time because less  $CO_2$  mass was associated with the dissolution [9]. The former studies showed that the initial dissolution rate constant depends on  $Re$ , the molecular diffusivity of  $CO_2$  in water, and the mean pore size [44]. Thus, in certain cases with the combination of the influence factors, an increase in the flow rate resulted in no increase or a decrease in the dissolution rate [45]. The distribution of  $Re$  shrunk with the brine injection, and such a tendency was suspended with the decline of  $Re$ . In contrast with the case of supercritical  $CO_2$ , the dissolution rate decreased

slightly at larger  $Re$  values in the later period of dissolution, whereas the differences in the dissolution rate between  $Re$  were inconspicuous.

#### 4. Conclusions

The dissolution of the supercritical  $CO_2$  in groundwater, which is referred to as  $CO_2$  solubility trapping, is an important trapping mechanism of  $CO_2$  geological storage in the deep aquifer. Considering the diffusion and dispersion of the  $CO_2$  migration, an accurate measurement of the dissolution rate of  $CO_2$ -brine at the pore scale is necessary to evaluate the dissolution process in the reservoir. In this study, the pore-scale dissolution rate during brine imbibition was calculated for both supercritical and gaseous  $CO_2$  using X-ray computed microtomography. Also, we verified the different impacts of the porosity and saturation and the Reynolds number on both supercritical and gaseous  $CO_2$ . The key novelties of the presented results in this study are summarized as:

- For flow development under a supercritical  $CO_2$  state, high contact between the brine and  $CO_2$  resulted in a greater  $CO_2$  dissolution rate, while the flow bypassing restrained the dissolution rate with  $CO_2$  confined to the central region. The detached part of the bubbles which happened to snap-off rapidly dissolved. The isolated bubbles reduced the overall  $CO_2$  dissolution rate and prolonged the depletion time due to the slow diffusion. For gaseous  $CO_2$ , the flow development was limited due to the greater density difference, implying lower dissolution rates and a lower probability of dissolution events. The isolated gaseous  $CO_2$  existed for much longer and significantly prolonged the duration of the dissolution.
- The dissolution rate of supercritical  $CO_2$  was about two or three orders of magnitude greater than that of gaseous  $CO_2$ , while the value distributions both spanned about four orders of magnitude. The dissolution rate of gaseous  $CO_2$  decreased more dramatically because of the diverse number of residual  $CO_2$  bubbles.
- The dissolution rate of supercritical  $CO_2$  decreased as the porosity increased, and this trend increased with the increment of porosity. The dissolution rate of gaseous  $CO_2$  gradually increased with porosity, which showed no obvious effect on the variation of the dissolution rate. When the porosity is between 0.36 and 0.38, the value ranges of dissolution rates under a supercritical state were greater.
- At high  $CO_2$  saturation, the dissolution rate of supercritical  $CO_2$  increased rapidly with the saturation reduction. At low  $CO_2$  saturation, the correlation between the dissolution rate and saturation was inverted at later PVs, and was controlled by the location and quantity of the dissolution events. By contrast, the dissolution rate of gaseous  $CO_2$  remained inversely proportional to the saturation. However, the relationships were close to supercritical  $CO_2$  after saturations were less than 0.5.
- During the dissolution expansion, the dissolution rate of supercritical  $CO_2$  increased rapidly as the  $Re$  decreased, and the differences between  $Re$  were about one order of magnitude. At later PVs, the dissolution rate gradually increased with the  $Re$ , and the trend was not correlated with the injected PV. By contrast, the dissolution rate of gaseous  $CO_2$  significantly decreased with the increase of  $Re$ . As most  $CO_2$  was dissolved, the dissolution rate decreased slightly at larger  $Re$  values, whereas the differences between  $Re$  were inconspicuous.

Measurements from this study provided the relationship between parameters in the pore-scale flow regime. It is not evident that an upscaling simulation may readily import the dissolution rate results of this study to reservoirs. Also note that the effects of salinity and wettability on the  $CO_2$ -brine dissolution process remain pertinent in porous media, which deserves further investigations.

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**Author Contributions:** Bohao Wu conducted the experiments, analyzed the results, and drafted the manuscript. Xingbo Li, Yu Liu, and Lanlan Jiang conceived the experiments and reviewed the manuscript. Ying Teng, Pengfei Lv, and Tingting Luo designed and assisted the experiments. Jianan Zheng and Dayong Wang contributed materials.

**Conflicts of Interest:** We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Characterizing dissolution rate of CO<sub>2</sub>-brine in porous media under gaseous and supercritical conditions”.

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