Pore Structure Characterization of Indiana Limestone and Pink Dolomite from Pore Network Reconstructions

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Abstract — Carbon sequestration in deep underground saline aquifers holds significant promise for reducing atmospheric carbon dioxide emissions (CO_2). However, challenges remain in predicting the long term migration of injected CO_2 . Addressing these challenges requires an understanding of pore-scale transport of CO_2 within existing brine-filled geological reservoirs. Studies on the transport of fluids through geological porous media have predominantly focused on oil-bearing formations such as sandstone. However, few studies have considered pore-scale transport within limestone and other carbonate formations, which are found in potential storage sites. In this work, high-resolution micro-Computed Tomography (microCT) was used to obtain pore-scale structural information of two model carbonates: Indiana Limestone and Pink Dolomite. A modified watershed algorithm was applied to extract pore network from the reconstructed microCT volumetric images of rock samples and compile a list of pore-scale characteristics from the extracted networks. These include statistical distributions of pore size and radius, pore-pore separation, throat radius, and network coordination. Finally, invasion percolation algorithms were applied to determine saturation-pressure curves for the rock samples. The statistical distributions were comparable to literature values for the Indiana Limestone. This served as validation for the network extraction approach for Pink Dolomite, which has not been considered previously. Based on the connectivity and the pore-pore separation, formations such as Pink Dolomite may present suitable storage sites for carbon storage. The pore structural distributions and saturation curves obtained in this study can be used to inform core- and reservoir-scale modeling and experimental studies of sequestration feasibility.

Résumé — Caractérisation de la structure de pore de l'Indiana limestone de calcaire et de Pink dolomite provenant des reconstitutions de réseaux de pores — La séquestration du carbone dans les aquifères salins profonds souterrains est très prometteuse pour la réduction des émissions de dioxyde de carbone (CO_2) dans l'atmosphère. Cependant, des problèmes demeurent dans la prédiction de la migration à long terme du CO_2 injecté. Relever ces défis nécessite une compréhension du transport de CO_2 à l'échelle du pore dans des réservoirs géologiques existants remplis de saumure. Les études sur le transport des fluides en milieu poreux géologique ont principalement porté sur les formations oléagineuses telles que le grès. Cependant, peu d'études ont

examiné les transports à l'échelle du pore dans le calcaire et d'autres formations carbonatées, qui se trouvent dans des sites de stockage potentiels. Dans ce travail, la micro-tomographie (microCT) à haute résolution a été utilisée pour obtenir de l'information structurale à l'échelle du pore de deux exemples de formations carbonatées : *Indiana limestone* et *Pink dolomite*. Un algorithme *watershed* a été appliqué pour extraire les réseaux de pores des images microCT volumétriques reconstruits des spécimens de roche et pour compiler une liste de caractéristiques pores des réseaux extraits. Il s'agit notamment de distributions statistiques de la taille et du rayon des pores, la séparation entres pores, le rayon des gorges, et la coordination du réseau. Enfin, des invasions de percolation ont été appliquées pour déterminer les courbes de saturation pression pour les exemples de roches. Les distributions statistiques sont comparables aux valeurs de la littérature pour l'*Indiana limestone*. Cela a servi de validation à l'approche d'extraction de réseau pour *Pink dolomite*, qui n'a pas été précédemment examinée. Basées sur la connectivité et la séparation entre pores, les formations telles que *Pink dolomite* peuvent présenter des sites de stockage appropriés pour le stockage du CO₂. Les distributions de structure des pores et des courbes de saturation obtenue dans cette étude peuvent être utilisées pour informer et renseigner la modélisation à l'échelle du réservoir et les études expérimentales de faisabilité de a séquestration.

INTRODUCTION

Storage of carbon dioxide (CO₂) in underground geological formations is recognized as a promising method for reducing greenhouse gas emissions from concentrated sources, such as coal power plants or oil refineries [1]. This process entails the injection of CO₂ into high-permeability, deep underground saline aquifers (greater than 800 m below surface [2]). Once underground, the upwards migration of the CO₂ is arrested by low-permeability caprock formations (stratigraphic trapping), ensuring the perpetual sequestering of the stored CO₂.

While the general mechanisms of sequestered CO₂ transport underground is well characterized, challenges remain in estimating the storage capacity of geological formations and the long-term security of injected carbon within the porous rocks [3-5]. Reservoir scale analyses can estimate the macroscopic migration of carbon dioxide within the geologic formation [6]. However, these studies require estimates of pore-scale transport properties of the rock as inputs [7, 8]. Determination of transport parameters within pores requires detailed micro-scale studies of the detailed rock structure, which in turn can be used to calculate:

- i) how CO₂ will flood the rock and interact with *in situ* brine;
- ii) the long-term stability of trapped carbon [9].

The pore- and micro-scale transport properties of sandstone reservoirs have been well characterized in the petrophysics literature [10-13], as sandstones contain a large portion of global petroleum reserves [10]. Recently, carbonate saline aquifers have been identified as suitable carbon dioxide sequestration sites due to their high porosity, effective stratigraphic trapping, and global abundance [14, 15]. However, in contrast to sandstones, the complex

microstructure of carbonates [16] requires a more in-depth investigation before their pore-scale transport can be known.

Limestone and dolomite form the main mineralogical components of carbonate saline aquifers [17]. Although bulk transport properties of many limestones [18] and dolomites [19] are known, a detailed examination of the microstructure of Pink Dolomite and Indiana Limestone is necessary to establish a robust methodology for characterizing carbonate geology and assessing potential storage sites in North America [3, 20].

A number of experimental techniques exist for microstructural characterization of carbonates [12, 21-31]. These include thin-section analysis [23], Scanning Electron Microscopy (SEM) [23, 24], focused ion beam-SEM [25], and mercury intrusion porosimetry [12, 21, 26, 27]. However, these techniques are destructive, so downstream or repeat measurements are impossible. Additionally, results obtained from multiple techniques must be averaged across many samples.

In contrast, X-ray microCT, is a non-destructive technique for volumetric characterization, which has been used extensively to image porous materials in three-dimensions [28-30]. MicroCT facilitates subsequent analyses, including pore space extraction used to determine the characteristics of the pore microstructure. With this technique the porosity can be estimated directly from a binary volumetric image of the sample [22]. The volumetric images can be used directly in pore-scale flow simulations and compared to experimental studies.

The experimental techniques mentioned are required to determine the micro-structure of the rock that is inaccessible from a larger scale examination. The micro-structural volumetric images are used as inputs to modeling studies, which yield pore-scale transport parameters such as permeability.

One modeling technique that has gained popularity in recent years is Pore Network Modeling (PNM), which involves a coarse-graining of a sample's void space so that it can be efficiently analyzed numerically [22, 32–37]. Techniques for extracting pore network models from digital microCT images were pioneered by Oren *et al.* [38].

A pore network model consists of a system of pores and connecting throats, whereby the detailed void space geometry obtained from microCT imaging is represented using simplified shapes [39]. Gharbi and Blunt [40] and Bijeljic *et al.* [41] performed PNM on a variety of sandstones and carbonates, and reported average pore-scale properties such as porosity, pore volume, radius and coordination number for one sample of each rock type explored. Youssef *et al.* [42] used microCT of carbonate and sandstone reservoir rocks to extract microporosity properties and to build a dual-porosity pore network model of the imaged rocks. Dual-porosity concerns for both Pink Dolomite and Indiana Limestone are considered in [43]; however, in this study we consider only the pore geometries accessible using microCT.

The present work expands on previous studies of the pore network structure of carbonates [40, 41] by performing detailed pore network extractions on multiple samples for two carbonates: Indiana Limestone and Pink Dolomite. Because Indiana Limestone has been considered previously, it can serve as a validation for the extraction and analysis methods used here. To the best of the authors' knowledge, this is the first comprehensive study of Pink Dolomite. Since dolomites form geologically under similar conditions to limestones, dolomites are of interest for CO₂ capture and storage projects. Indiana Limestone and Pink Dolomite reasonably represent the porosity and permeability conditions identified for sequestration in the Alberta basin [20] and can be taken as representative model carbonates.

The pore extraction used in this study was a modified watershed algorithm [44], which built on existing studies of geologic materials [45–48] by enhancing the tessellation process to account for overlapping pores. Watershed methods were first used for geologic samples by Thompson *et al.* [49] and Sheppard *et al.* [50]. From the network

extractions, full statistical distributions of pore size, radius and coordination number were reported, as well as throat radius and length. Full statistical distributions are required when constructing stochastic pore networks to generate a large simulation dataset. Finally, invasion percolation simulations were performed to explore the saturation behavior of the extracted networks. The geometry distributions presented here can be used as inputs for pore- and core-scale numerical studies for CO₂ storage in carbonate formations and for upscaled geometric inputs for reservoir-scale simulations. This will provide a basis for determining optimal properties for storage in carbonate-based formations.

1 METHODOLOGY

The porous microstructure of two common carbonates, Indiana Limestone and Pink Dolomite, were examined. These rocks were selected as representative model carbonates for carbon storage activities in carbonate formations in the Alberta Basin of Western Canada, which is a proposed high intensity storage site [3]. Physical samples from this region could not be obtained due to property and licensing rights, so Indiana Limestone and Pink Dolomite were chosen to approximate porosity and permeability conditions identified for sequestration in the Alberta basin [20]. All core samples were obtained from *Kocurek Industries* (Caldwell, TX, USA). Their porosity and permeability as identified by the supplier are summarized in Table 1.

Attempts were made to verify the reported porosity using pycnometry; however, the small sample dimensions led to unreliable and inconsistent results. Similarly, a porosity estimate based on gravimetric techniques (weight and density calculations to estimate the void volume) was impossible because of the irregular dimensions of the samples. Each sample formed a cylinder with an irregular elliptical cross-section. Measurement errors in the evaluated volume led to large errors in the porosity. Attempts to machine a precise dimension were unsuccessful due to the low material hardness of both Indiana Limestone and Pink Dolomite, which crumbled when machined.

TABLE 1

Summary of the core properties obtained from *Kocurek Industries* indicating the permeability, and porosity of Indiana Limestone and Pink Dolomite

Geologic material	Supplier	Formation and location	Brine permeability (milli-Darcy)	Gas permeability (milli-Darcy)	Porosity (%)
Indiana Limestone	<i>Kocurek Inc.</i>	Bedford, Indiana, USA	70	200	19
Pink Dolomite	<i>Kocurek Inc.</i>	Edwards Plateau, Texas, USA	50	94	29

TABLE 2

Summary of the sample sizes, voxel resolutions and dimensions of Indiana Limestone and Pink Dolomite. The voltage and currents reported were those used for collecting the microCT data

	Sample	Approx. dimensions (mm)		Voltage (kV)	Current (μ A)	Voxel resolution (μ m)
		Cylinder, before cropping (diameter, height)	Block, after cropping			
Indiana Limestone	#1	6, 8.5	$4.4 \times 3.6 \times 7.7$	120	90	11.07
	#2	6, 6.5	$3.6 \times 4.3 \times 5.0$	135	60	8.3
	#3	6, 9.0	$3.3 \times 3.0 \times 6.6$	135	60	8.3
	#4	6, 8.5	$3.8 \times 3.9 \times 5.8$	135	60	8.3
Pink Dolomite	#1	6, 8.5	$4.5 \times 3.7 \times 6.0$	120	60	8.3
	#2	6, 8.0	$4.2 \times 3.8 \times 5.3$	120	60	7.5
	#3	6, 9.0	$3.7 \times 3.5 \times 6.3$	120	60	7.5
	#4	6, 7.0	$3.4 \times 3.5 \times 4.5$	120	60	7.5

1.1 MicroCT

Prior to scanning, each rock core was sectioned into four cylindrical samples ($1 \text{ cm} \times 0.6 \text{ } \varnothing \text{ cm}$) using a dremel. Four samples each of Indiana Limestone and Pink Dolomite were studied using microCT. The sample volumes were at least 66.5 mm^3 for the Indiana Limestone, and 53.5 mm^3 for the Pink Dolomite, which enabled detection of macro-pores within the samples, and could facilitate future investigations of permeability on the same samples [51].

MicroCT imaging was performed using a GE Phoenix v|tome|x s equipped with a 180 kV/15 W high-power nanofocus X-ray tube (General Electric, CT, USA). Each sample was firmly affixed to the rotating table using hot-melt glue. To minimize beam hardening and ring artefacts, a 5 mm copper filter was used between the X-ray beam source and the sample. Any edge effects due to beam hardening were minimized during image processing, as described in Section 1.3, below. Voxel resolutions between $7.5\text{--}11.1 \text{ } \mu\text{m}^3/\text{voxel}$ were used¹. Table 2 summarizes the settings, resolutions, and size of each scan. The microCT voltage and current were set to obtain the broadest normalized histogram, which guided the use of a 5 mm copper filter. Each sample scan took approximately three hours. The angle offset was set to zero. Each dataset contained 1440 images, obtained at 0.25° intervals.

The datos|x image acquisition software system [52] was used to calibrate the device prior to scanning, and employed a pixel correction mask to minimize hotspots on the detector.

The datos|x software was also used to reconstruct the scanned images following the scan.

1.2 Mineral Characterization

X-ray fluorescence spectroscopy was used to determine the mineral composition of the rock. This method provides the relative amount of each mineralogical component within the material [53, 54], and was conducted with a Philips PW2404 X-ray fluorescence spectrometer (Philips Corporation, Amsterdam, The Netherlands). The samples were individually ground to a fine powder using a ceramic mortar and pestle, then pelletized and placed in the sample holder for analysis. The mineral composition determines the surface tension and contact angle values used to calculate the capillary entry pressures for the invasion percolation, discussed below.

1.3 Imaging Processing

The volumetric images were processed in three stages: a) cropping, b) filtering, and c) binary thresholding, as outlined schematically in Figure 1. The image stacks were cropped (Tab. 2) to a cubic volume to facilitate analysis and ensure any edge damage due to cutting was removed from the image. The cropped image stacks were processed with a hybrid 3D median filter (4 voxel-sided cube; implemented in Fiji [55]) to remove residual noise and mitigate edge effects due to beam hardening [28–30]. The cropped and filtered microCT image stacks were then converted to

¹ A voxel is the smallest unit of a 3D image, compared to a pixel, the smallest unit of a 2D image.

Figure 1

Schematic showing rock sample data processing and binarization methodology. Example sample shown is Pink Dolomite.

binary, black and white images using Otsu's thresholding method [56].

1.4 Pore-Scale Properties

To describe the microstructure of the pore space, the porosity, pore size, pore radius, throat radius, pore coordination number, and pore-to-pore distance were obtained. In this study, the following definitions are used:

- porosity is the void fraction of the sample, including connected and unconnected pores;
- pore size is the total digitally voxelized volume of each pore identified during pore network extraction;
- pore radius refers to the radius of the maximal inscribed sphere in each pore;
- throat radius is the radius of the minimal cross-sectional circle connecting two adjacent pores;
- coordination number identifies the number of adjacent pores connected to a given pore, and represents the connectivity of the pore space;
- pore-to-pore distance is the shortest void space path length between two pore centers, through the connecting throat.

1.5 Pore Extraction

Pore network models are simplified network diagrams representing the geometry and connectivity of the void space of a porous material. This method has been used extensively in geology to investigate the pore morphology of rock structures and to predict mesoscale fluid invasion patterns through the pore structure [34, 36, 57, 58].

In voxel-based pore extraction approaches, a maximal sphere is inscribed around each void voxel, wherein the sphere radius is the shortest distance between the voxel location and the solid wall [59]. A connected line normal to the solid wall of the largest such radii defines the skeleton of the topological network, for both pores and throats [60-64].

While these methods are effective in producing an accurate network model of the material, they are computationally expensive for the resolution available from 3D imaging techniques. Considerable improvements have been made in reducing computation time with the watershed algorithm [46, 48, 65, 66]. This technique segments the void structure based on how water would fill the wetting volume [67], and then applies Voronoi tessellations [68] to locate the pore bodies within the total volume. A main advantage of the watershed algorithm is that it is computationally faster than maximal sphere techniques.

In a study by Hinebaugh and Bazylak [44], a novel pore network extraction technique was developed using the watershed algorithm, which builds on existing studies that use the watershed algorithm for geologic materials. In this enhanced version, the Voronoi tessellation was improved by accounting for overlapping pores, ensuring consistent throat lengths and trapped air phases were accounted for.

In this study, the enhanced watershed technique [44] was used to segment the void spaces of the Indiana Limestone and Pink Dolomite samples into a topological network of spherical pores (nodes) and cylindrical throats. From the extracted pore network, statistical parameters (pore size, pore radius, throat radius, pore coordination number, and pore-to-pore distance) describing the geological core samples were extracted and invasion studies were performed. The cropped images contained between 100 and 200 million voxels.

1.6 Invasion Percolation

Invasion percolation simulations were performed on each extracted network to determine saturation-capillary pressure curves for the core samples. The invasion percolations were performed using an algorithm developed in-house [16] based on the Washburn equation [69]. This describes the capillary pressure P_c required to invade a pore:

$$P_c = \frac{2\gamma}{r} \cos \alpha \quad (1)$$

where γ is the surface tension, r is the radius of the cylindrical throat, and α is the contact angle.

For the invasion percolation simulations, all external boundary pores were initially filled with mercury [22]. The pressure was incrementally increased until it overcame the entry pressure of an interface throat. Once this occurred, the volumes of the connected pore, and any subsequent connected pores and throats with lower capillary pressures, were filled. This process was repeated until all accessible pores were filled.

2 RESULTS AND DISCUSSION

Figure 2 shows sample 2D slices before processing and 3D representations of fully cropped and thresholded pore space for Indiana Limestone (a, c) and Pink Dolomite (b, d). As can be seen from a visual inspection of Figure 2, Indiana Limestone had a lower porosity, larger and more sparse pores, and higher pore coordination number than Pink Dolomite. Pink Dolomite's pores are more evenly

Figure 2

MicroCT data cross-section of Indiana Limestone a); and Pink Dolomite b) at 8.3 μm and 7.5 μm resolution, respectively. The diameter of the cores in a) and b) are approximately 6 mm. The 3D volumes of c) Indiana Limestone and d) Pink Dolomite show the microporosity and heterogeneity of the samples. The 3D images c, d) were generated using the 3D Viewer plugin in Fiji [55, 71].

TABLE 3
X-ray fluorescence results for the Indiana Limestone and Pink Dolomite samples

Indiana Limestone		Pink Dolomite	
Chemical compound	Atomic weight (%)	Chemical compound	Atomic weight (%)
CaCO ₃	98.577	CaCO ₃	99.391
MgO	0.560	K ₂ O	0.140
SiO ₂	0.352	MgO	0.136
FeO	0.143	Cl	0.104
Al ₂ O ₃	0.117	SiO ₂	0.091
K ₂ O	0.077	FeO	0.070
Cl	0.064	Al ₂ O ₃	0.034
S	0.048	Sr	0.016
Na ₂ O	0.031	S	0.012
Sr	0.021	P ₂ O ₅	0.007
P ₂ O ₅	0.010	–	–

distributed throughout the material. This qualitative evaluation of Indiana Limestone is consistent with previous studies of this rock [40]. As stated above, this work represents the first micro-structural evaluation of Pink Dolomite. These comparisons are discussed in detail below.

2.1 Mineral Composition

The mineral compositions of Indiana Limestone and Pink Dolomite were 98.6% and 99.4%, calcite (CaCO₃) by weight percent, respectively, determined using X-ray fluorescence spectroscopy. Table 3 shows the detailed chemical composition of the rocks. The mineral composition of Indiana Limestone is consistent with literature values for bulk mineral composition [18]. To the best of our knowledge, this is the first report in the literature of the mineral structure for Pink Dolomite. Since both rocks were primarily calcite, a single contact angle of 140° could be used in the invasion percolation studies presented below [23].

2.2 Porosity

For this and the following sections, Table 4 displays a comparison between the pore-scale properties of Indiana Limestone and Pink Dolomite, determined from the pore network extraction. Table 5 further compares the results obtained for Indiana Limestone in this study to similar studies.

TABLE 4
Pore structure distributions (mean and standard deviation) determined for Indiana Limestone and Pink Dolomite

Pore structure features	Indiana Limestone	Pink Dolomite
Porosity (%)	12 ± 2	26 ± 9
Pore size (μm ³)	(20 ± 3) × 10 ³	(7.3 ± 0.2) × 10 ³
Pore radius (μm)	31 ± 2	21 ± 2
Throat radius (μm)	22 ± 1	13.6 ± 0.4
Coordination number	2.6 ± 0.2	1.9 ± 0.1
Pore-to-pore distance (μm)	137 ± 8	95 ± 7

TABLE 5
Pore space distributions of Indiana Limestone compared to literature values

Parameter	This study	Gharbi and Blunt [40]
# of samples	4	1
Porosity (%)	12 ± 2	13.05
Number of voxels	~450 ³ -530 ³	330 ³
Voxel resolution (μm)	8.3, 11.1	7.7
Physical sample volume after cropping (mm ³)	66.5-123.4	16.41
Mean pore size (μm ³)	(20 ± 3) × 10 ³	–
Mean pore radius (μm)	22 ± 1	10.17
Mean pore coordination number	2.6 ± 0.2	2.97
Number of pores	9 615-17 960	5 653
Number of throats	5 603-11 879	8 539

The porosity for the Indiana Limestone samples was (12 ± 2)%, which is lower than the sample provider's reported porosity of 19% by a significant margin. The precise explanation for the discrepancy between the provider's and our porosity measurements is unclear, and may be due to differences in the methodologies performed. However, the porosity found in this study matched closely with that reported by other researchers, 11% [41] and 13.05% [40].

The porosity of the Pink Dolomite samples was (26 ± 9)%. The standard deviation for the Pink Dolomite

Figure 3

Greyscale slices of the microCT image stacks show significant differences among the Pink Dolomite samples. Figures 3a-d are the Pink Dolomite samples 1-4, respectively. In b), the large pore is circled in white. In c), a primarily solid region is highlighted with a white box. The length bar is applicable to Figure 3a-d.

porosity was large compared to Indiana Limestone. This can be attributed to the heterogeneity observed in the Pink Dolomite (Fig. 3). In Figure 3b, a large pore (circled feature) resulted in a higher porosity and in Figure 3c, a region with high material fraction (box) led to a lower porosity. Large spatial heterogeneities within individual Pink Dolomite samples contributed to the observed variability in the porosity.

2.3 Pore Size Distributions

Figure 4 shows the pore size distributions for all pores and only the connected pores, for both rock types. For connected pores in each network, Indiana Limestone had a mean pore size of $(20 \pm 3) \times 10^3 \mu\text{m}^3$, while for Pink Dolomite, it was $(7.3 \pm 0.2) \times 10^3 \mu\text{m}^3$. A connected pore is one that is connected *via* a throat to another pore and

Figure 4

Pore size distributions for a) Indiana Limestone, and b) the associated lognormal fit to the distributions. Grey signifies all pores, and black represents the connected pores only. Pore size distribution for c) Pink Dolomite with d) the associated lognormal fit to the distributions. Note that the means and variances reported are for the lognormal distributions.

Figure 5

Pore radius distributions of the connected pores of the Indiana Limestone a) and Pink Dolomite b) samples.

their distributions are presented in Section 2.5. In the extracted pore network models of both rock types, pores with a single voxel radius were exclusively unconnected and represented between 30-50% (count) of all pores. Unconnected pores in the extracted network are likely a result from resolution limits. In this study, the microCT resolution was sufficient to observe the macropores of the carbonates. However, since carbonates have pores well below the resolution of microCT, these could not be captured in the pore network model of the investigated samples. An analysis of that type would require sub-micron resolution imaging, so a complete evaluation of the unconnected pores is beyond the scope of this paper. The macroscopic parameters determined for these important carbonate samples provide the detail and statistical distributions for pore-to-core upscaling, and serve as a baseline for higher-resolution imaging studies.

2.4 Pore and Throat Radius

The mean pore radius of Indiana Limestone was $(31 \pm 2) \mu\text{m}$, and for Pink Dolomite it was $(21 \pm 1) \mu\text{m}$, as shown in Figure 5. There is more variability in pore radius between the Indiana Limestone samples, which is likely due to the larger and irregularly shaped pores for this rock. From a visual inspection, the Pink Dolomite pores are more regularly shaped.

The pore radii for the Indiana Limestone samples can be compared to other studies [40]. The extraction technique in

this work found pore radii up to three times higher than previous studies (Tab. 5). A possible explanation for this deviation lies in the definition of a pore used by those authors. In that study [40], a pore was defined as the maximum circle inscribed within a triangle, and a throat as the connection between the pores [57]. In this study, the pore radius was defined by the maximally inscribed sphere, which can lead to larger radii. By comparison, Zhu *et al.* [31] performed thin-section analyses of Indiana Limestone and found pore radii in the range $(35-50) \mu\text{m}$, which is in the range of the present study ($\bar{r}_{\text{pore}} = 31 \mu\text{m}$). The agreement between the thin-section analysis method [31] and this study demonstrates that the modified watershed technique can capture physical rock pore spaces.

The mean throat radius of Indiana Limestone was $(22 \pm 1) \mu\text{m}$. The mean throat radius for Pink Dolomite was $(13.6 \pm 0.4) \mu\text{m}$. Representative pore and throat interfaces for Indiana Limestone and Pink Dolomite, shown in Figure 6, illustrate that the pores and throats are indeed larger for Indiana Limestone than Pink Dolomite. As mentioned above, to the best of the author's knowledge, this is the first characterization of Pink Dolomite pore and throat radius distributions.

Figure 6

Indiana Limestone a) and Pink Dolomite b) binary 2D microCT images of the pore space. Black is void space and white is solid. The green circles represent the maximal inscribed sphere (the 2D inscribed circles are presented for illustrative purposes only). The constrictions between green circles represent throats. The length bar in a) is applicable to both a) and b).

2.5 Coordination Number

The coordination number indicates the number of connections between each throat. Pore coordination number distributions are shown in Figure 7 and reveal that mean coordination of Indiana Limestone was 2.6 ± 0.2 , for connected pores. This value is close to the literature value of 2.97 [40], as shown in Table 5. For the Pink Dolomite, the mean coordination number was determined to be 1.9 ± 0.1 . The actual range of the coordination for Pink Dolomite, from 1 to 30, was larger than Indiana Limestone, which ranged from 1 to 20.

2.6 Pore-to-Pore Distance

The pore-to-pore distance for Indiana Limestone was $(137 \pm 8) \mu\text{m}$. For Pink Dolomite, the pore-to-pore distance was $(95 \pm 7) \mu\text{m}$. This result is expected, since the Indiana Limestone pores were larger and more irregular than those of Pink Dolomite. Pore-to-pore distance is a suitable indicator of throat length, which could be used along with the throat radius to calculate the hydraulic conductance of throats. The hydraulic conductance could in turn be used to estimate the absolute and relative permeabilities of the sample; however, this is an involved exercise and is beyond the scope of this paper.

2.7 Invasion Percolation

Invasion percolation simulations were performed on one extracted network each of Indiana Limestone and Pink Dolomite. Figure 8 shows the saturation-capillary pressure curves for the pore networks. Capillary entry pressures were calculated from the Washburn equation (Eq. 1), with a contact angle of 140° and surface tension of 0.480 N/m used for a calcite and mercury interface [70], based on the mineral composition shown in Table 3.

From this analysis, this sample of Indiana Limestone has a lower barrier to filling than the Pink Dolomite, although both had similar final saturations, as a fraction of their total pore sizes. The final saturation is the highest saturation value on the capillary pressure *versus* volume saturation curves [16]. Multiphase saturations, residual trapping, and contrast saturation curves for different invading fluids could be included in future work, though these important aspects are outside of the current scope of work.

The Indiana Limestone curve (in dashed dark grey) has a value of 61%, while the Pink Dolomite curve (in grey) has a value of 65% saturation. This indicates that both samples show a substantial fraction of their pore size accessible for injected carbon dioxide. The pressure limits at 0.69 kPa for Pink Dolomite and 0.62 kPa for Indiana Limestone were due to the voxel size and the minimum detectable throat radii.

Figure 7

Pore coordination number distributions for the Indiana Limestone a) and Pink Dolomite b) samples.

Figure 8

Capillary pressure *versus* saturation curves from invasion percolation results for Indiana Limestone (in dashed black) and Pink Dolomite (in grey). The figure highlights the increasing region, while the inset shows the full curve.

In future studies, higher resolution microCT will be performed in order to capture the minimum throat radii of the carbonates. As well, in future analyses, we will develop a comprehensive model to include both drainage and imbibition, which will allow us to explore CO₂ trapping in carbonates.

CONCLUSIONS

In this study, the mesoscale structures and geometries of two carbonate rocks obtained by microCT imaging were evaluated to consider their suitability as potential carbon storage sites.

An enhanced watershed algorithm reported previously [44] was used to segment the void space of the rocks into topological pore network models. Using this method, series of pore-scale geometric parameter distributions for two model carbonate rock samples representative of possible carbon storage sites in Western Canada have been presented. Gaussian and lognormal statistical distributions (mean and standard deviations) for porosity, pore size and radii, throat radii, coordination number, and pore-to-pore distance have been determined for Indiana Limestone and Pink Dolomite.

The quantities presented here for the porosity (Indiana Limestone: 12%; Pink Dolomite: 26%) and the coordination number (Indiana Limestone: 2.6; Pink Dolomite: 1.9) compared well to reported literature values [40]. The pore radii values (Indiana Limestone: 31 μm ; Pink Dolomite: 21 μm) were twice as large; however, this is likely due to the definition of a pore, and not to the imaging method or the extraction technique.

This study has also reported distributions for throat radii (Indiana Limestone: 22 μm ; Pink Dolomite: 14 μm) and length (Indiana Limestone: 137 μm ; Pink Dolomite: 95 μm), which have not been previously reported. To the best of our knowledge, this is also the first report of these geometric properties for Pink Dolomite. The primary contribution from this work is the full distribution of the microstructure characterizations. In future studies, the invasion percolation will be further developed to include multiphase flow, and the processes that would occur (such as mineralization) in a CO₂ injection well.

These geometric considerations are all important in predicting the permeability and for determining which rock is more suitable for carbon storage. However, all these

properties would need to be combined in a comprehensive model of flow in the porous rock. For example, coordination number, surface wettabilities, pore aspect ratio etc. would also be important considerations for modeling residual trapping, though it is outside the scope of this work.

Invasion percolation simulations were performed based on the invasion of mercury and simulated porosimetry. These simulations demonstrated that the sample of Indiana Limestone studied could have a lower capillary barrier (P_c ; Eq. 1) to filling than the Pink Dolomite sample, although both had similar final saturations as a fraction of their total pore sizes. Further analysis is required to determine which of these rock types is more suitable for CO₂ injectivity. Instead, the model rock samples considered in this study are intended to provide a basis for developing a framework for imaging and pore network extraction relevant to carbon storage in deep carbonate saline aquifers.

Through this study, the groundwork has been established for the evaluation of these two types of carbonates. Statistical distributions of these properties could be used to generate larger stochastic networks for core scale simulations, and were determined for each property based on a mean and standard deviation.

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