

# THE IMPACT OF MINERAL DISSOLUTION ON THE CHARACTERIZATION OF PORE STRUCTURE AND MULTIPHASE FLOW PROPERTIES IN CARBONATES

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## ABSTRACT

In this study, we used core flooding techniques to mimic the uniform dissolution in carbonate rocks. Tests sequentially induced mineral dissolution and characterized the impact on multiphase flow properties. Temperature retarded acid was used to uniformly dissolve calcite in Ketton and Estailades carbonate rock cores. A single dissolution stage removed approximately 0.5% of the mass of the rocks and measurements of relative permeability and residual trapping were made after each stage along with mercury injection capillary pressure (MICP) measurements to quantify the variation of pore throat size distribution. Multiple Stages were performed on each of carbonates rocks. Images from x-ray micro-CT and medical CT were used to describe the porosity variation and observe the changes in pore structure and multiphase flow properties at scales from the  $\mu\text{m}$  to the cm.

The pore throat size distribution of the rocks was observed to both increase and become less uniform with progressive dissolution. For Ketton, the micro-pores, with size range from  $0.01\mu\text{m}$  to  $0.1\mu\text{m}$ , have less been involved in the reaction than the macro-pores ( $10\mu\text{m}$  to  $100\mu\text{m}$ ). A larger spread in capillary trapping was seen around a characteristic initial-residual curve.

## INTRODUCTION

During  $\text{CO}_2$  injection into aquifers, the injected  $\text{CO}_2$  will progressively dissolve into formation brine and leads to a decrease in pH (as a consequence of increasing  $\text{CO}_2$  partial pressure), which changes the geochemical equilibrium between the formation water and the minerals [1]. Therefore, the strong dissolution of rock matrix can be expected in the carbonate dominated reservoir. This will result in the alternation of both the intrinsic properties of rock such as porosity and pore throat size distribution, and further the change of fluid flow properties, in terms of the permeability and residual trapping. There are essentially two main types of dissolution: uniform dissolution, where a simple uniform increase in porosity along the samples is observed, and non-uniform dissolution, where the dissolution is concentrated in the upper part of the sample close to the injection sites (compact dissolution) or the certain flow path along the sample (wormholes or

channelling). Although, the above theory was developed initially for single phase flow, it is still applicable to two phase flow, when the saturation-dependent flow velocity of the brine phase is considered [2].

At the core scale (the sample size in cm), the non-uniform dissolution features were observed in depth. The formation of wormhole and channelling occurred preferentially at the core inlets regardless of the sample orientation, the temperature and the injection rates [3]. To date, little experimental data regarding the impact of dissolution on petrophysical properties as relative permeability and residual trapping exist. The former is an important descriptor in the reservoir model to predict the subsurface flow [4]. The latter is the key process for maximizing capacity and ensuring the integrity of CO<sub>2</sub> sequestration at the industrial scale [5].

The petrophysical properties measurements must be performed on the samples that can be considered as the representative elementary volume (REV) to ensure that the macroscopic petrophysical parameters are uniform at the core scale [6]. Therefore, the samples have non-uniform dissolution cannot be used for measuring relative permeability and porosity. Furthermore, although the uniform dissolution can be achieved at the pore-scale samples (sample size in mm) [7], the samples are not large enough for the direct measurement of the properties. One of the possibility of creating the uniform dissolution at core scale is to upscale the flow conditions directly from the pore-scale experiment. However, this approach usually requires high injection flow rates or long experimental time. Therefore, in most laboratory cases at core scale, the flow regime is governed by the non-uniform dissolution.

In this study, we used temperature retarded acid (RA), described below, to develop the uniform dissolution [6]. The test program sequentially induced mineral dissolution and characterized the impacts on the multiphase flow properties in Ketton and Estailades carbonate rock cores, which are characteristic of different pore structures. We examined the pore structure variation at the scales from micron to centimetre scale, by imaging rock sample with x-ray micro-CT and medical CT. A sequence of MICP measurements were conducted to characterizing the evolving pore throat size distribution.

## **EXPERIMENTAL CONDITIONS AND PROCEDURES**

Two carbonate rocks were used and their properties were summarised in table 1. These two rock samples were mainly used in the core-scale experiments for the measurement of fluid flow properties. Smaller samples (4mm diameters and 10mm length) for micro-CT observation and the MICP measurements were also drilled from the same rock blocks separately. These two types of rocks were composed of more than 99% calcite. The pore throat size distribution of both Ketton and Estailades, interpreted from the MICP tests, showed a bimodal distribution, in the figure 1. The size of inter-granular pores in Ketton was larger than the size of inter-aggregate pores of Estailades. Nitrogen (N<sub>2</sub>) and distilled water (DI) were used in our experiment (100bars and 20°C). The interfacial tension between N<sub>2</sub> and DI water was 73mN/m.

The temperature retarded acid used in this experiment was the solution composed of ester and enzyme, named Acidgen FG<sup>®</sup> (a trademark of Cleansorb Ltd.), which is an in-situ organic acid production system. The solution was usually diluted with water as a mixture of 10% w/v. It took 10.5 hours for the completion of hydrolysis of the ester at temperature 65°C. The pH of solution went up to 3.

The relationships between relative permeability/residual trapping and porosity were still uncertain in current literature. Therefore, we carefully chose small amount dissolution to catch any possible significant variation of fluid flow properties due to little change of rock porosity. In this paper, a single dissolution stage indicated that the sample was saturated with 10w/v RA and heated for the dissolution reaction. During each stage, approximate 0.5% mass of rock sample was dissolved.

The relative permeability curves were measured by using the steady state approach. The total injection rate as high as 20cc/min was used to lower the negative influence of capillary end effect, minimize the impact of minor heterogeneity of rock and measure the intrinsic relative permeability [4]. The residual trapping was measured by our novel technique, in which the use of capillary end effect resulted in a rapid construction of the initial-residual curves [5].

The samples were initially saturated with RA solution, and heated at 65°C for more than 14 hours to guarantee the completion of hydrolysis of the ester (The batch reactor experiment from the supplier indicated that 13.5 hours were sufficient.). After two dissolution stages, the large samples shown in the table 1 were used for the measurement of relative permeability and small samples were used for the MICP analysis and the micro-CT imaging. Tests continued and sequentially induced the mineral dissolution and characterized the impacts on multiphase flow properties. The rock properties as permeability, porosity and pore throat size distribution were measured after each dissolution stage. The relative permeability and residual trapping were measured after every two dissolution stages.

## **RESULTS AND DISCUSSION**

The variation of porosity in Ketton after different dissolution stages was shown in the figure 2. The homogeneously increasing porosity indicated that RA approach was an efficient way to create the uniform dissolution. The porosity increased around 0.017 for both rocks, in table 2. The permeability did not increase monotonously with the porosity in Ketton. This was possibly due to the pore blockage by the large dissociated particles released by the dissolution of grain contact parts or the cementation materials of the rock [7], and needed further investigation. In the figure 3, the residual trapping properties of Estailades almost did not change with dissolution. However, the residual trapping capacity of Ketton slightly decreased. This indicated that less gas could be trapped in Ketton with increasing porosity, which was mainly due to the fact that the macro-pores (10µm to

100 $\mu\text{m}$ ) became larger and the micro-pores (0.01 $\mu\text{m}$  to 0.1 $\mu\text{m}$ ) almost remained the same during the dissolution, as shown in the figure 4. The error source for the residual trapping measurement was mainly from the noise in the images, and detailed analysis on images could be found in our previous research [5]. The micro-CT images with resolution 4 $\mu\text{m}$  also supported the observation of pore throat size distribution, in the figure 5. The macro-pores became larger with more gran materials dissolved. The pore size distribution of Estailades remained unchanged, which needed further repeated tests. The relative permeability of Ketton were fitted by the power law, as shown in the figure 6. With little variation of porosity (from 0.219 to 0.236), the rock became more preferable to gas flow, competing with water.

## CONCLUSION

In this pioneered study, we have successfully generated uniform dissolution along the core sample and measured the change of flow properties due to the mineral dissolution. Our initial results suggested that the small amount increase on porosity could possibly result in noticeable changes on relative permeability and residua trapping in Ketton and almost no variation in Estailades, which were heavily dependent on the evolving pore throat size. In the future, more work on experiments need to be fine-tuned and error considered in more detail to quantitatively understand any changes due to acid dissolution.

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Table 1 Sample properties

Sample	Diameter [cm]	Length [cm]	Porosity [-]	Permeability [D]	Pore volume [cm <sup>3</sup> ]
Ketton	3.800	16.400	0.218	2.840	40.530
Estailades	3.800	16.400	0.279	0.196	52.180

Table 2 The change of porosity and permeability in Ketton and Estailades

	Ketton		Estailades	
	Porosity [-]	Permeability (D)	Porosity [-]	Permeability (D)
Initial	0.219	2.840	0.279	0.196
1 <sup>st</sup> dissolution	0.224	2.937		
2 <sup>nd</sup> dissolution	0.228	3.613	0.287	0.204
3 <sup>rd</sup> dissolution	0.231	3.484		
4 <sup>th</sup> dissolution	0.236	2.786	0.295	0.235

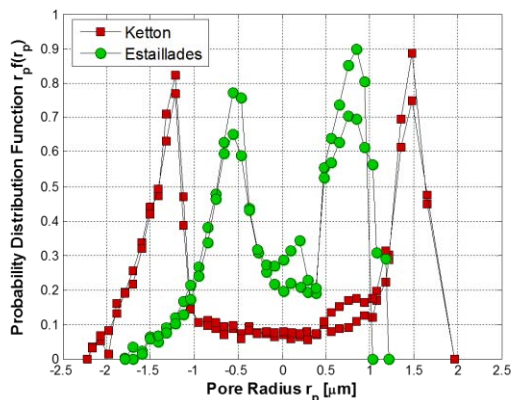


Figure 1 Pore throat size distribution of Ketton and Estailades without dissolution experiments.

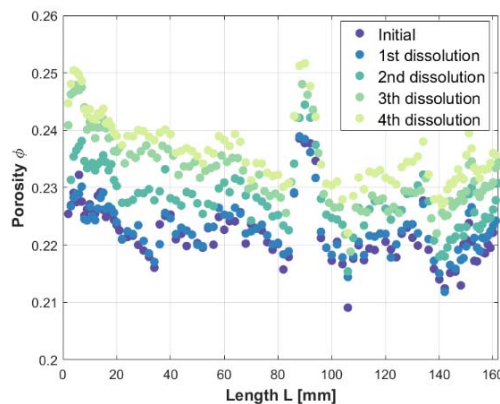


Figure 2 The variation of porosity at different dissolution stages: Ketton

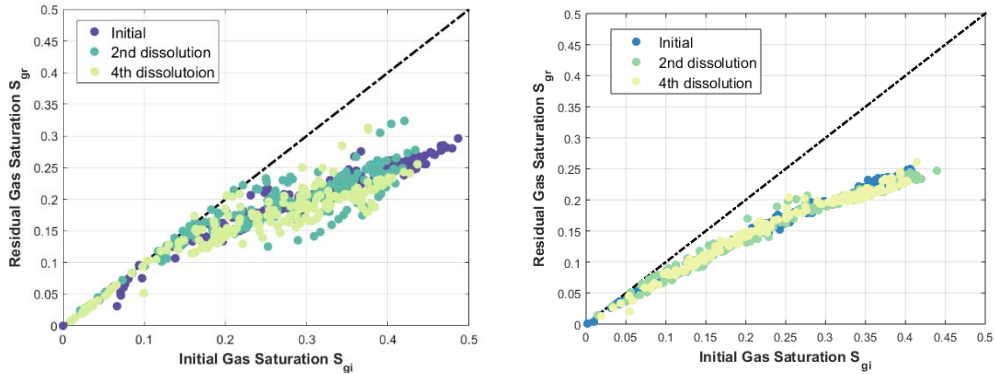


Figure 3 The Initial-residual curves at different dissolution stages: Ketton (right), Estailades (left)

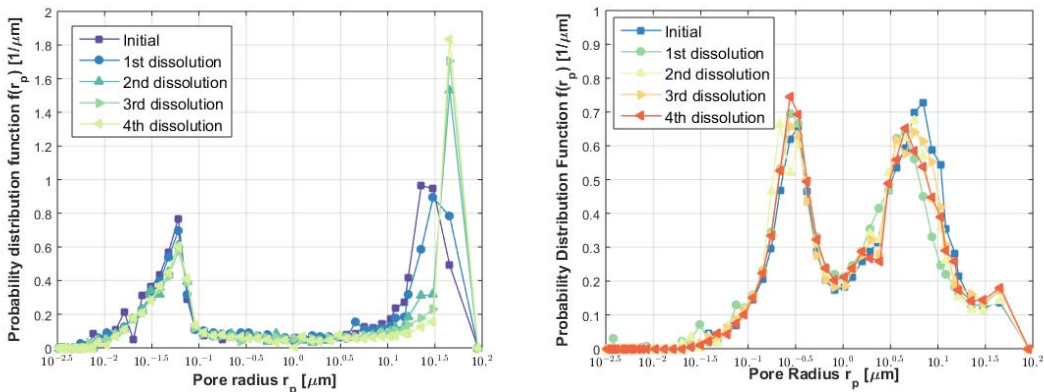


Figure 4 The pore throat size distribution interpreted from MICP tests at different dissolution stages: Ketton (right), Estailades (left)

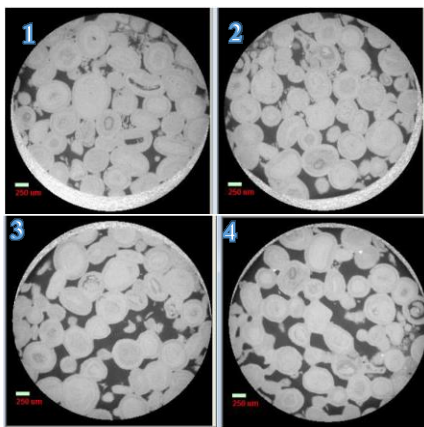


Figure 5 Micro-CT images of Ketton at different dissolution stages: 1. Initial, 2. 1<sup>st</sup> dissolution, 3. 2<sup>nd</sup> dissolution, 4. 3<sup>rd</sup> dissolution. Dark color: pore space, Grey color: grain, bright color: rubber sleeve.

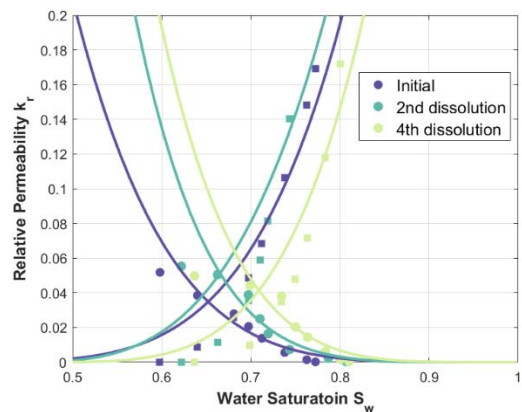


Figure 6 Relative permeability of Ketton at different dissolution stages: Round: gas, Square: water