AN INTEGRATED APPROACH TO ASSESS THE PETROPHYSICAL PROPERTIES OF ROCKS ALTERED BY ROCK/FLUID INTERACTIONS (CO2 INJECTION)

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ABSTRACT

The geological storage of CO2 is considered increasingly as a solution to reduce significantly the emissions in the atmosphere in a near future. Deep aquifers or depleted hydrocarbon reservoirs are considered as the best potential candidates. Previous experimental and numerical work has evidenced that CO2 injection can lead to severe rock/fluid interactions depending on the thermodynamic conditions, the nature of the fluids in place, the rock composition and also the hydrodynamic regime. In the near wellbore region, wormhole dissolution patterns are observed due to the non equilibrium of the geochemical reactions. In the far field region, a homogeneous modification of the pore structure is expected because the dissolution regime is uniform.

This paper is related to the phenomena occurring in the far field region. The experimental results demonstrate that the permeability evolution as a function of the dissolution degree is highly dependent on the pore structure and can be as high as 70% increase for roughly 2 porosity units improvement. The second part of the paper is related to the interpretation of the results using the pore network approach. The pore network approach gives a first analysis of the evolution of the rock in terms of porosity and permeability at different dissolution regime. The reaction-limited regime is simulated by uniform dissolution while the reverse case is simulated by pore-body dissolution in diffusion predominant regime and by the pore-throat dissolution in the convection predominant regime. The quantitative comparison with the experimental results indicates the scenario that enables to reproduce satisfactorily the permeability evolution.

INTRODUCTION

Rock/fluid interactions during CO2 injection

One very specific feature of the CO2 injection is the possibility for rock/fluid interactions. When injecting in the reservoir, which can be an aquifer or a waterflooded oil reservoir, one fraction of the CO2 dissolves into the brine and forms H₂CO₃, which dissociates to give a weak acid that has the potential to react with the host rock formation (calcite, dolomite, anhydrite, etc …).
Rock/fluid interaction phenomena in presence of CO2 have been observed both in laboratory and field studies on samples submitted to CO2 injections. Reactive-transport experiments in presence of CO2 have been performed both in sandstones (Ross et al., 1982) and carbonates (Svec and Grigg, 2001; Grigg and Svec, 2003). The results demonstrated that a modification of the rock structure can either improve or impair the permeability value depending on the driving geochemical processes (precipitation/dissolution reactions), which are functions of the rock fabric, the brine composition and also the thermodynamic conditions. Recent experimental investigations have evidenced that the flow regime also has a significant impact on the modification of the permeability since it controls the residence time of the reacting fluids within the porous medium (Egermann et al., 2005). In the near wellbore region, wormhole dissolution patterns are observed due to the non equilibrium of the geochemical reactions. In the far field region, a homogeneous modification of the pore structure is expected because the dissolution regime is uniform.

These evolutions of the rock structure have also been observed from field tests. The thin section analysis of samples cored in the far-field region of a CO2-flooded area showed dissolution of anhydrite (Mathis et al., 1984). Kane (1979) reported nearly 50% injectivity improvement attributed to the rock dissolution on the SACROC field. In other reservoir studies, Kamath et al. (1998), Christman and Gorell (1990) and Prieditis et al. (1992) did not record any rock/fluid interaction impact on the petrophysical properties demonstrating that this process is very case dependant.

**Evolution of the petrophysical properties**

Taking account of the evolution of the petrophysical properties as a function of rock structure modification is very important to properly model the injectivity variations but also the pressure field in the reservoir, which can induce severe stress variations that can be detrimental to the well or the reservoir integrity (fracture activation, completion failure, …). To be relevant, the porosity and permeability measurements must be performed on samples that can be considered as representative elementary volume to insure that the macroscopic petrophysical parameters are uniform at the core scale. This assumption is no longer valid for samples that are affected by wormhole dissolution patterns, which is the most common case in the laboratory studies due to the operating conditions (Svec and Grigg, 2001; Grigg and Svec, 2003; Egermann et al., 2005; Izgec et al.). It is then very important to develop an adapted procedure to prepare altered samples in a controlled manner and with a homogeneous modification of the pore structure so that the macroscopic porosity and permeability measurements provide a sound basis for modeling purposes.
Several authors have looked at the modeling of the petrophysical properties' evolution following the flow of a reactive or particle containing fluid through a rock. In a pioneering work Schechter and Gidley (1969) developed a model representing the effect of surface reactions in a porous medium on its properties. The solid consists of a bundle of short cylindrical pores with a given size distribution randomly dispersed. It is demonstrated that the larger pores determine the response of the system to acid and that diffusion limited surface reactions lead to the formation of wormholes. Much later Christman and Edgar (1983) using the same type of model demonstrate the effect of the pore size distribution on the dissolution kinetic behavior, while they recognize the limitations of the model due to the lack of pore intersections. A more macroscopic approach (a geochemical simulator assuming chemical equilibrium between the flowing aqueous solution and the one-dimensional porous medium) is proposed by Walsh et al. (1984) to model precipitation and dissolution of solids during flow through porous media. Békri et al. (1995) use the reconstructed porous medium approach to study the dissolution of porous media. They provide numerical proof that the dissolution patterns depend on the dominant phenomenon. Reaction-limited process gives uniform dissolution while transport limited process can give compact dissolution (diffusion predominant) or wormhole-type dissolution (convection predominant).

More recently pore network models have been proposed to study structure evolution and petrophysical properties change due to particle capture (Ochi and Vernoux, 1999) or asphalt precipitation (Sahimi et al. 2000). Baht and Kovscek (1998) use a pore network model to describe deposition and dissolution in diatomite. Pore network models are flexible, can account for different phenomena occurring at the pore scale such as capillarity or pore size and structure evolution. Finally they permit calculation for different petrophysical parameters relevant for single phase or multiphase flows.

The present paper describes an integrated study covering both the experimental and the modeling aspects of the evolution of the petrophysical properties of samples submitted to a rock structure modification. The first part is dedicated to the experimental work, where the apparatus and the associated procedures to obtain a homogeneous alteration of the rock structure are described. Then, the results collected on two carbonate rock-types are presented. The second part is focused on the interpretation of these results using of a Pore Network approach. The initial parameterization (prior rock structure alteration) is first presented and then several scenaria of dissolution are tested and compared against the experimental observations. In the last section the results are discussed and the comparison between simulation and experimental data is commented.

**EXPERIMENTAL ALTERATION OF ROCKS**

**Principle of the homogeneous alteration process**

The understanding and the modeling of the wormholing process have been studied a lot to control and optimize the acidizing stimulation treatment of production wells (Daccord et al., 1989, Bazin et al., 2001). One of the major result of these studies is that the
dissolution regime can be mapped as a function of two dimensionless numbers, the Peclet and Damköhler, in a $P_e / P_e D_a$ plot (Schechter and Gidley, 1968; Daccord et al. 1993; Bekri et al. 1995 and 1997):

$$P_e = \frac{v_0 l}{D}, \quad D_a = \frac{\kappa}{v_0} \quad \text{and} \quad P_e D_a = \frac{\kappa l}{D}$$

where $v_0$ is the fluid velocity, $l$ a characteristic length of the pore, $D$ the molecular diffusion coefficient and $\kappa$ the chemical reaction rate (Figure 1). In most laboratory cases, the regime is governed by wormholes or compact dissolution (sharp front of dissolution at the inlet face).

![Figure 1: Dissolution regime as a function of the Peclet and the Damköhler numbers](image)

The upper part of the graph is very interesting since it corresponds to a uniform dissolution regime of the pore space. The experimental procedures and the set-up described hereafter aim at working in this region by placing a static reactive solution quasi-instantaneously in the pore space, which corresponds to $P_e$ roughly equal to zero (gray area in Figure 1).

**Data acquisition**

**Experimental set-up**

It is mainly composed of a core holder cell, where one “slice” of the rock sample is mounted. The typical size of the sample is 50 mm in diameter and 30 mm in length to enhance the lateral surface over the pore volume ratio. This is particularly important to insure that the acid placement in the pore space will happen uniformly at the sample scale. The end-pieces of the core holder are connected to four different types of devices:

- A nitrogen injection system that enables to displace the brine down to low saturation value,
• A brine injection system in order to remove the products of the reaction before measuring the new permeability value,
• A vacuum pump connected to both sides of the core holder in order to prevent gas trapping during the acidizing process,
• A buffer cell filled half with acid and pressurized nitrogen in order to place quasi-immediately and homogeneously the acid in the pore volume.

The principle of the apparatus is described in Figure 2. The differential transducer used to measure the evolution of the permeability as a function of the rock alteration degree is chosen according to the permeability value in order to work in the optimal range of the device. In the case of extremely high permeability, the differential pressure measurements were double-checked using one U-tube system based on gravity head differences. A Back Pressure Valve (BPV) was also mounted in all the experiments and was used during the cleaning periods, when fresh brine is inject to remove the products of the reaction. Because the acid reaction produces some CO2 in the gas phase, the BPV enables to expel it very quickly from the sample by dissolution into the fresh brine. Therefore, only 5 pore volumes were needed to reestablish a fully saturated state with the initial brine for permeability measurement.

**Figure 2: experimental apparatus used for homogeneous alteration**

Specific procedures were developed to obtain both a good characterization of the sample prior and after the rock alteration and also a recording of the evolution of the permeability during the intermediate states of the rock alteration:

- Mercury porosimetry on companion plug,
Dry weight,
- Saturated weight and evaluation of the initial porosity $\phi^0$,
- NMR measurement for porosity check,
- Initial permeability measurement: $k_w^0$,
- Nitrogen flooding to decrease the brine saturation down to $S_{w\text{i}}$,
- Core holder put under vacuum for 2 hours,
- Injection of the acid solution (pH=1) from the two sides of the core holder at high pressure gradient to insure quasi-instantaneous placement in the pore structure. Waiting time around 20 minutes to let the acid fully react with the rock.
- Cleaning of the inlet end-piece to prevent injecting “fresh acid” in the porous medium,
- Miscible displacement of the products of the reaction by fresh brine using the BPV to fasten the dissolution of the produced CO$_2$ in the injecting fluid,
- Measurement of $k_w^i$ corresponding to the $i^{th}$ acid treatment
- The procedure is then repeated from the nitrogen injection step to restart a new treatment,
- Dismantle the sample when the expected permeability variation is reached,
- Saturated weight
- NMR measurement for porosity check,
- Oven at 80°C for two days and dry weight
- Mercury porosimetry of the altered sample.

One advantage of this protocol is that the permeability variation, which is of the main interest, can be followed continuously. Because the sample is never dismounted during the subsequent treatments to avoid breaking and failures (especially with fragile rock-types), only the overall porosity variation can be measured using this protocol. In the results presented hereafter, we have assumed that the intermediate variations of the porosity were directly proportional to the treatment number since the same volume of acid is placed during each treatment.

**Experimental results**

**Petrophysical properties**

The tests were conducted on two carbonate rock-types, whose petrophysical properties are gathered in Table 1. The first rock-type is a low-permeability rather homogeneous limestone, whereas the second one is much more permeable and exhibits two distinct classes of pores (bimodal distribution: Figure 4).

Figure 3a demonstrates that the permeability evolution as a function of the porosity increase is clearly dependent on the initial rock structure. The overall permeability improvement reaches respectively 30% and 70% for the limestone (Rock 1) and the bimodal carbonate (Rock 2). Figure 3b confirms that the proposed procedure enables to alter the rock structure homogeneously without creating wormhole patterns as in conventional acid injection.
Table 1: Petrophysical properties of the altered samples

<table>
<thead>
<tr>
<th>Name</th>
<th>Length</th>
<th>Diameter</th>
<th>$\phi^0$</th>
<th>$\phi^f$</th>
<th>$d\phi$</th>
<th>$k^0$</th>
<th>$k^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock 1</td>
<td>1.9 cm</td>
<td>5 cm</td>
<td>22.9 %</td>
<td>24.5 %</td>
<td>1.6 PU</td>
<td>1.76 md</td>
<td>2.35 md</td>
</tr>
<tr>
<td>Rock 2 (bimodal)</td>
<td>2.07 cm</td>
<td>5 cm</td>
<td>27.7 %</td>
<td>29.5 %</td>
<td>1.8 PU</td>
<td>468 md</td>
<td>762 md</td>
</tr>
</tbody>
</table>

Figure 3: (a) Evolution of the petrophysical properties ($k / \phi$) for two different rock-types of carbonate samples – (b) picture of three samples of Rock 2: initial, altered homogeneously and heterogeneously (by continuous acid injection to favor wormhole pattern)

Rock structure modifications

The mercury porosimetry measurements done prior and after the alteration are shown in Figure 4. The mean hydrodynamic radius that can be calculated from the Swanson approach (1981) has been also added to the graphs in order to locate the pore size that rules most the permeability value. Whatever the rock-type, the distribution for small pore radii is rather unaffected (some deviations could be attributed to the fact that the measurements could not be done on the same plugs but on sister plugs). This is certainly due to the presence of irreducible water saturation before the acidizing process, which prevent the smaller pore from rock/fluid interactions. Major modifications of the distribution occur for the larger pore radii, where the acid solution was placed, but in a different manner according to the rock-type. For Rock 1, the distribution is increased for the intermediate pore radii, whereas it decreases slightly for the largest ones. Exactly the opposite process was observed for Rock 2. This behavior is certainly related to the pore structure, which differs significantly from Rock 1 to Rock 2. It simply means that the volume of acid in contact with intermediate pores is certainly more important for Rock 1...
leading to a more pronounced alteration of this pore class. These results are also very consistent with the macroscopic permeability measurements since the largest permeability increase is obtained with the rock-type where the alteration on the largest pores was more pronounced (Rock 2).

![Rock 1 pore size distribution](image1)

![Rock 2 pore size distribution](image2)

*Figure 4: mercury porosimetry curves prior and after the acid treatments – the dotted line is located at the mean hydraulic radius size \( r_h \) calculated with the Swanson technique (1981)*

The above results also confirm that the acid is placed in the “flowing” pore space fraction, which is more prone to alteration through the circulation of reactive mobile brine. Therefore, it is expected that the proposed approach leads to very similar rock structure alterations comparing to a “true” CO2 flooding process.

**INTERPRETATION USING A PORE NETWORK MODEL**

The objective of this section is to use the pore network approach in order to provide a first analysis of the evolution of the rock porosity and permeability due to CO2 induced dissolution. A comparison with the experimental results can indicate the most probable dissolution scenario through which the properties' alteration occurs. Then other rock properties, such as the relative permeability curves, can be calculated with the same model.

A brief description of the network model approach is given in Appendix. Additional details on the model characteristics and construction can be found elsewhere (Laroche and Vizika, 2005). The network consists of three-dimensional cubic lattice formed by pore-bodies (nodes) interconnected by pore-throats (bonds) respecting the converging-diverging nature of pores. The initial parametrization is anchored on experimental measurements characterizing the rock structure (mercury porosimetry) and also the
macroscopic petrophysical properties (porosity, permeability). This approach was applied to Rock 1 and the best match of the experimental capillary pressure was obtained with the pore size distribution and the numerical parameter presented in Figure 5 and Table 2, respectively. Figure 6 shows also a very good agreement between the gas/water relative permeability curves calculated by simulating gas invasion in a network fully saturated with water and the ones obtained experimentally, using a standard Unsteady State technique interpreted with full account of capillary end effects.

**Dissolution scenarios**

As presented earlier, the dissolution regimes can be mapped as a function of $P_e$ and $D_a$ as described in Figure 1:

- **the uniform dissolution** corresponds to a reaction-limited regime, where the dissolution occurs uniformly over all the solid walls. This regime can be simulated by uniform increase of pore-body and pore-throat diameters,
- **the compact dissolution** corresponds to a diffusion predominant regime, where the dissolution occurs around the wider parts of the pore space. This regime can be simulated by the enlargement of pore-body,
- **the wormholing dissolution** corresponds to a convection predominant regime, where the dissolution is mostly located along the main flow paths. This later regime can be simulated by the enlargement of the pore-throat.

![Graph a](image1.png)

![Graph b](image2.png)

**Figure 5:** (a) mercury saturation vs. throat radius curve from mercury invasion $P_c$ curve and the subsequent cumulative pore-throat radius distributions calculated with the best scenario - (b) comparison between the experimental and the numerical mercury capillary pressure

**Table 2:** Geometrical parameters and calculations of porosity and permeability
The dissolution of the rock is simulated using the PNM by changing the model parameterization according to the three different regimes of the dissolution identified in the literature. Five dissolution scenarios combining these different processes have been tested and are described hereafter. The dissolved thickness is denoted by $\tau$. Based on this thickness, the dimensions of a pore/throat after dissolution can be related to its original dimensions for each scenario investigated. In the work presented in this paper, we only vary the value of $\tau$ to evaluate the corresponding evolution of the permeability as a function of the porosity. Therefore, there is no direct calculation of $\tau$ for a given state of rock alteration:

- **S1**: dissolution in the rock is assumed to be reaction-limited regime. The radii of both pore-bodies and pore-throats are uniformly increased ($R = R_0 + \tau$ and $r = r_0 + \tau$).
- **S2**: dissolution in the rock is assumed to be diffusion predominant regime. Only the radii of pore-bodies are uniformly increased ($R = R_0 + \tau$ and $r = r_0$).
- **S3**: dissolution in the rock is assumed to be convection predominant regime. Only the radii of pore-throats are uniformly increased ($R = R_0$ and $r = r_0 + \tau$).
- **S4**: dissolution in the rock is assumed to be reaction-limited regime and the pore-bodies grow two times faster than the pore-throats ($R = R_0 + 2\tau$ and $r = r_0 + \tau$).
- **S5**: dissolution in the rock is assumed to be reaction-limited regime with pore-bodies and pore-throats grow proportionally to their radii ($R = \tau.R_0$ and $r = \tau.r_0$).

Schechter and Gidley (1969) have pointed out the instability of the dissolution, large pores grow faster than the small ones in some cases of the dissolution process. Scenario
S4 and S5 can represent this instability. If we assume that on the conducted experiment, the local dissolution rate is proportional to the offered pore volume over its surface, the pore bodies grow $AR/3$ times faster than the pore-throats. The average aspect ratio that is used to match the existing experimental data was found equal to 5.24. This implies that the experimental data will follow the scenario S4.

Based on this approach, the alteration of Rock 1 at $S_{wi}$ was investigated. Different stages of dissolution of the rock are denoted by different values of dimensionless thickness $\tau$. Then, the pore size distribution corresponding to the 60% $(1-S_{wi})$ of the volume occupied by the acid are updated according to the considered scenario and effective network are constructed. Finally, the permeability and porosity change associated with a particular $\tau$ is found. Figure 7 represents the permeability versus the porosity relationship for the five scenaria investigated. The power-law form exhibited in Figure 7 suggests that the network results can be expressed according to

$$\frac{K}{K_0} = \left(\frac{\Phi}{\Phi_0}\right)^\gamma$$

where the power-law form exponent $\gamma$ is related to the selected scenaria. It is worth pointing out that the experimental data also follow this trend (Figure 7).

As expected, the results indicate that S2 (pore-body enlargement only) leads to limited permeability improvement, whereas S3 (pore-throat enlargement only) leads to a sharp increase of the permeability for a limited porosity variation. The dissolution scenario that corresponds most to the experimental data is S4 and is based on a reaction-limited regime that takes into account the available quantity of acid in the different classes of pores. Since the acid is placed quasi-instantaneously and reacts without circulating, this scenario is in good agreement with the experimental protocol that was followed to obtain the rock alteration.
Figure 7: Evolution of the permeability vs the normalized porosity using the different dissolution scenarios (the experimental dissolution results are represented by crosses).

Figure 8: Comparison between the calculated and the experimental pore size distribution of the altered rock by dissolution.

Figure 8 shows the pore size distribution that can be calculate from the most probable scenario of dissolution (S4) using the Pore Network Model. The results are very consistent with the evolution of the pore size distribution that was observed experimentally, with an increase for the intermediate pore radii and a slight decrease for the largest ones.

CONCLUSIONS

An original experimental procedure has been proposed to obtain homogeneous rock structure alteration. The Pore Network Model approach was tested to simulate the evolution of permeability of one rock submitted to this homogeneous rock structure
alteration. Several scenaria of rock alteration combining the three different dissolution regimes (reaction-limited, diffusion-limited and convection-limited) that can occur according to the operating conditions have been tested. It appears that the most probable dissolution scenario (evolution of the dissolution thickness according to the available acid volume contained in the pore) gives the best results by comparison with the reported experimental data. This approach seems to be suitable to identify the dissolution mechanisms of one rock submitted to rock alteration and to provide quantitative information on the evolution of the petrophysical properties. An interesting perspective of this approach is to use it as an analysis for other petrophysical data like the relative permeability curves. The proposed methodology can have many applications for assessment of future CO2 storage sites, where severe rock/fluid interactions are expected. This type of experimental data and modeling are necessary to improve reliability of the large scale simulations concerning the pressure profiles within the reservoir and reservoir integrity issues related to stress variations.

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