CO$_2$-induced dissolution of low permeability carbonates. Part II: Numerical modeling of experiments

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A B S T R A C T

We used the 3D continuum-scale reactive transport models to simulate eight core flood experiments for two different carbonate rocks. In these experiments the core samples were reacted with brines equilibrated with pCO_2 = 3, 2, 1, 0.5 MPa (Smith et al., 2013 [27]). The carbonate rocks were from specific Marly dolostone and Vuggy limestone flow units at the IEAGHG Weyburn-Midale CO$_2$ Monitoring and Storage Project in south-eastern Saskatchewan, Canada. Initial model porosity, permeability, mineral, and surface area distributions were constructed from micro tomography and microscopy characterization data. We constrained model reaction kinetics and porosity–permeability equations with the experimental data. The experimental data included time-dependent solution chemistry and differential pressure measured across the core, and the initial and final pore space and mineral distribution. Calibration of the model with the experimental data allowed investigation of effects of carbonate reactivity, flow velocity, effective permeability, and time on the development and consequences of stable and unstable dissolution fronts.

The continuum scale model captured the evolution of distinct dissolution fronts that developed as a consequence of carbonate mineral dissolution and pore scale transport properties. The results show that initial heterogeneity and porosity contrast control the development of the dissolution fronts in these highly reactive systems. This finding is consistent with linear stability analysis and the known positive feedback between mineral dissolution and fluid flow in carbonate formations. Differences in the carbonate kinetic drivers resulting from the range of pCO_2 used in the experiments and the different proportions of more reactive calcite and less reactive dolomite contributed to the development of new pore space, but not to the type of dissolution fronts observed for the two different rock types. The development of the dissolution front was much more dependent on the physical heterogeneity of the carbonate rock. The observed stable dissolution fronts with small but visible dissolution fingers were a consequence of the clustering of a small percentage of larger pores in an otherwise homogeneous Marly dolostone. The observed wormholes in the heterogeneous Vuggy limestone initiated and developed in areas of greater porosity and permeability contrast, following pre-existing preferential flow paths.

Model calibration of core flood experiments is one way to specifically constrain parameter input used for specific sites for larger scale simulations. Calibration of the governing rate equations and constants for Vuggy limestones showed that dissolution rate constants reasonably agree with published values. However the calcite dissolution rate constants fitted to the Marly dolostone experiments are much lower than those suggested by literature. The differences in fitted calcite rate constants between the two rock types reflect uncertainty associated with measured reactive surface area and appropriately scaling heterogeneous distribution of less abundant reactive minerals. Calibration of the power-law based porosity–permeability equations was sensitive to the overall heterogeneity of the cores. Stable dissolution fronts of the more homogeneous Marly dolostone could be fit with the exponent n = 3 consistent with the traditional Kozeny–Carman equation developed for porous sandstones. More impermeable and heterogeneous cores required larger n values (n = 6–8).

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1. Introduction

Chemical interactions are known to have a major effect on rock porosity and permeability evolution and may alter the behavior or performance of natural and engineered reservoir systems. Such reaction-induced permeability evolution is of particular importance for the optimization of acid stimulation and CO$_2$-enhanced oil recovery in carbonate reservoirs and has drawn considerable attention over the past decades (e.g., [1–27]). Predicting reaction-induced permeability evolution is also very important for geologic CO$_2$ sequestration technologies designed to mitigate greenhouse

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gas emissions, because changes in rock porosity and permeability fundamentally affect the amount of CO_2 that can be ultimately stored in the reservoir. This is particularly true for the transition of CO_2-EOR fields to permanent CO_2 storage, because the use of alternating water and gas floods to extract hydrocarbons will change the reservoir storage capacity. CO_2 dissolution into reservoir fluids during EOR flooding mildly acidifies the resident brines and causes carbonate minerals to dissolve sometimes resulting in the formation of highly porous and conductive channels (often referred to in the petroleum acidizing literature as "wormholes," e.g., [6]). Despite the large number of experimental and numerical studies devoted to understanding permeability evolution in carbonate rocks, only a few of them have made direct, comprehensive comparisons between predictive models and experimental data (e.g., [18–19]). The result is a lack of proper quantitative calibration, which limits the application of essential features of chemical fluid-rock interactions at laboratory or reservoir scales.

Many research efforts (e.g., [7–11,13]) have employed the continuum modeling approach to explore key factors that affect mineral dissolution and related reactive transport processes, particularly focusing on investigation of the formation and development of unstable dissolution fronts or wormholes. Golfier et al. [7–9] presented a detailed study of dissolution channel development during acid dissolution of a porous medium. These authors outlined a three-dimensional Darcy-scale dissolution model that was derived from the pore-scale Stokes equation and volume-averaging theory, and summarized the governing equations and upscaling techniques used to determine macroscopic properties such as mass transfer coefficients, and dispersion properties. They further used the derived continuum model to examine the effects of advection, diffusion and reaction on wormhole formation, and developed parameter diagrams to describe different dissolution regimes and the transitions between them. More importantly, their results confirmed that the Darcy-scale continuum model was able to capture the general trends and patterns of wormhole formation. Panga et al. [10] have developed a more rigorous two-scale continuum model for simulations of wormholes in carbonate rocks by averaging pore scale physical and chemical behaviors into a continuum formation, so as to maintain the scale dependence of carbonate dissolution and transport processes. This model has also been used to analyze the influences of physical factors such as dispersion, heterogeneity magnitude, acid level, and pore-scale mass transfer on wormhole creation and pore volume required for breakthrough [10–11].

The continuum models that were used for simulation and analysis of carbonate dissolution processes are capable of predicting dynamic evolution of rather complex dissolution structures and wormhole geometry. However in most of these models mineral dissolution is often simplified as a one-component, first-order kinetics reaction that cannot provide a viable account of geochemical evolution due to mineral alteration. Furthermore, one of the largest challenges or uncertainties facing continuum-scale reactive-transport models is whether or not the so-called macroscopic properties (e.g., chemical rate kinetics, porosity–permeability relationships, reactive surface area expressions) can effectively describe the physical and chemical behaviors exhibited at the pore scale (e.g., [28–29]). For example the direct use of chemical rate kinetics measured from laboratory-based batch experiments to describe mineral alteration and associated reactive transport processes in continuum models, although quite common in the literature, has been questioned by recent researchers. Szecsody et al. [30] have found that directly implementing batch experiment-based chemical kinetics failed to reproduce reactive transport processes observed in column experiments. The fact that dissolution rates are several of orders of magnitude lower when measured in the field than the laboratory reflects a potential scale

dependence of reaction kinetics [31]. A number of numerical studies (e.g., [32–40]) have also recognized the scaling effects of macroscopic transport and geochemical reaction properties by comparison of continuum and pore-scale models, and attributed such scale dependence to pore-scale heterogeneities. Specifically, Li et al. [32] have developed a pore-scale network model to study the scale dependence of geochemical reaction kinetics controlling mineral dissolution and precipitation. Comparison of reaction rates averaged from pore-scale modeling results with those obtained by the continuum model using laboratory-measured chemical kinetics showed that scaling effects became important as pore-scale heterogeneity increased or acid levels were elevated within porous formations. They also used the same approach to examine the dependence of reaction rates on heterogeneous distribution of reactive minerals at a pore scale, finding larger scaling effects of reaction rates for a porous medium either with small mineral abundances or with large clusters of reactive minerals [33]. All of these findings emphasize the importance of calibrating macroscopic parameters used in the continuum models by either pore-scale simulations or experimental data in order to effectively account for scaling effects.

In this study we applied a three-dimensional continuum reactive transport model to simulate CO_2 core flood experiments performed by Smith et al. [27]. The numerical results were integrated with experimental data to analyze and interpret CO_2 injection-induced carbonate dissolution phenomena from the pore to core scale. Specifically, we developed a comprehensive reactive transport modeling framework to interpret experimental results, and study the interplay between carbonate reactivity, flow velocity, effective permeability, and heterogeneity on the development of stable and unstable dissolution fronts. An empirical approach was developed and combined with advanced imaging techniques to capture the major pore structures and connectivity with a continuum representation, thereby leading to an improved understanding of effects of multi-scale heterogeneity on mineral alteration processes. This work adds to a growing body of experimental and numerical studies directed at understanding alteration processes for CO_2 injection and storage in carbonate reservoirs (e.g., [18–21,24–26]). Our work differs from other studies in that the numerical model was constrained against detailed characterization data, and time-dependent solution chemistry and differential pressure data for two types of relatively low permeability rocks containing varying amounts of dolomite, calcite, and pore space. The rock formations studied here are specific to the reservoir flow units at the IEAGHG Weyburn-Midale CO_2 Monitoring and Storage Project in south-eastern Saskatchewan, Canada (http://ptrc.ca/projects/weyburn-midale; [26]).

2. Methods

2.1. Overview of laboratory core-flood experiments

The experiments that form the basis of the three-dimensional numerical reactive-transport modeling study are discussed briefly here. All references to experimental data and procedures are from Smith et al. [27]. Eight individual carbonate core samples collected from the Weyburn-Midale (Canada) CO_2-enhanced oil recovery and storage site were tested to study the relationship between fluid flow, heterogeneity, and reaction by combining characterization, pressure/permeability, and solution chemistry data. These cores are from the Vuggy limestone V-6 unit (higher calcite abundance; lower initial porosity and permeability) or Marly dolostone M-3 unit (higher dolomite abundance; higher porosity and permeability). All experiments were conducted at 60 °C under constant 0.05 mL/min flow and 12.4 MPa fluid outlet pressure to prevent