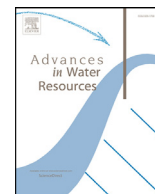




Contents lists available at ScienceDirect

Advances in Water Resources

journal homepage: www.elsevier.com/locate/advwatres

Effects of pore-scale precipitation on permeability and flow

Catherine Noiriel^{a,*}, Carl I. Steefel^b, Li Yang^b, Dominique Bernard^c^a Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, Université de Toulouse, Université Paul Sabatier, CNRS, IRD, 14 avenue Edouard Belin, F-31400 Toulouse, France^b Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720, United States^c CNRS, Université de Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux, UPR 9048, F-33608 Pessac, France

ARTICLE INFO

Article history:
Available online xxxKeywords:
Calcite precipitation
Growth velocity
Growth rate
Porosity
Permeability
X-ray microtomography

ABSTRACT

The effects of calcite precipitation on porous media permeability and flow were evaluated with a combined experimental and modeling approach. X-ray microtomography images of two columns packed with glass beads and calcite (spar crystals) or aragonite (Bahamas ooids) injected with a supersaturated solution ($\log \Omega = 1.42$) were processed in order to calculate rates of calcite precipitation with a spatial resolution of 4.46 μm . Identification and localization of the newly precipitated crystals on the 3D images was performed and results used to calculate the crystal growth rates and velocities. The effects of carbonate precipitation were also evaluated in terms of the integrated precipitation rate over the length of the column, crystal shape, surface area and pore roughness changes. While growth was epitaxial on calcite spar, calcite rhombohedra formed on glass beads and clusters of polyhedrons formed on aragonite ooids. Near the column inlet, calcite precipitation occurred preferentially on carbonate grains compared to glass beads, with almost 100% of calcite spar surface area covered by new crystals versus 92% in the case of aragonite and 11% in the case of glass beads. Although the experimental chemistry and flow boundary conditions in the two columns were similar, their porosity-permeability evolution was different because the nucleation and subsequent crystal growth on the two substrates (i.e., calcite spar and aragonite ooids) was very different. The impact of mineral precipitation on pore-scale flow and permeability was evaluated using a pore-scale Stokes solver that accounted for the changes in pore geometry. For similar magnitude reductions in porosity, the decrease in permeability was highest within the sample that experienced the greatest increase in pore roughness. Various porous media models were generated to show the impact of different crystal growth patterns and pore roughness changes on flow and permeability-porosity relationship. Under constant flow rate boundary conditions, precipitation resulted in an increase in both the average and maximum velocities. Increases in pore roughness led to a more heterogeneous flow field, principally through the effects on the fastest and slowest velocities within the domain.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Mineral precipitation plays a critical role in many geological processes, including sediment diagenesis, hydrothermal circulation and alteration, biomineralization, and CO_2 sequestration [1–6]. Precipitation of minerals like calcite can cause significant reduction in permeability and a reorganization of the flow field in reservoirs by altering the shape, size and connectivity of the pores, the roughness of their surfaces, and by partial or complete obstruction of flow in pore throats. Developing a full understanding of the feedbacks between geochemical reactions and flow and transport characteristics at the

reservoir scale requires investigations of precipitation mechanisms at the pore-scale.

Three rate-determining mechanisms have been identified to describe calcite precipitation from aqueous solution [7], (i) diffusive transport and/or adsorption of lattice ion, (ii) surface spiral growth, and (iii) surface nucleation involving polynuclear growth. These mechanisms involve different dependences of the precipitation rate, r_{ppt} ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), on the supersaturation ($1-\Omega$):

$$r_{ppt} = k \left[\exp \left(\frac{m \Delta G}{R^* T} \right) - 1 \right]^n = k (\Omega^m - 1)^n \quad (1)$$

with k the rate constant ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), ΔG the Gibbs free energy change of the overall reaction ($\text{J}\cdot\text{mol}^{-1}$), Ω the saturation index, R^* the gas constant ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T the absolute temperature (K), and n and m the semi-empirical constants that depend on the

* Corresponding author. Tel.: +33 5 61 33 30 16; fax: +33 5 61 33 25 60.
E-mail address: catherine.noiriel@get.obs-mip.fr (C. Noiriel).

kinetic behavior involved in the chemical reaction. Here r_{ppt} is the rate normalized against the reactive surface area, S_r (m^2). A value of $n = 1$ (linear rate law) has been attributed to crystallization limited by adsorption of lattice ions [7], and in some cases to a multi-source spiral growth mechanism [8]. A second order equation ($n = 2$) may be used to describe growth at single screw dislocation by the spiral mechanism [8], while higher order dependences ($n > 2$) can be applied to growth both at screw and edge dislocation [9] or growth by 2D nucleation [8].

Porosity-permeability evolution in rocks results from the interplay between reaction kinetics and mass transport. Two parameters, i.e., the Péclet (Pe) and Damköhler (Da) numbers, defined locally as: $Pe = uL^*/D_m$ and $Da = k_r L^{*2}/D_m$, where u is the fluid velocity ($m \cdot s^{-1}$), D_m is molecular diffusion ($m^2 \cdot s^{-1}$), k_r is a first order kinetic constant (s^{-1}), and L^* is a characteristic length (m), e.g., the pore size [10,11], are commonly used to describe the physical evolution of the pore space to capture the possible feedback between the flow regime and the geochemical alteration, e.g., [12–15]. Although precipitation of calcite in natural systems is often assumed to be kinetically-controlled, i.e., independent of mass transport rates [16], precipitation rates can vary along flow paths due to changes in the fluid saturation index, temperature and pressure, and the presence of bacterial communities, inhibitors or (in)organic impurities [17–31]. In addition, several studies have reported that both crystal location, morphology and growth rate are closely related to the mineral surface properties [17,32–36], which make mineralogical heterogeneities of the pore walls an important factor for understanding calcite nucleation and growth in porous media.

The distribution of new precipitates leads to a decrease of porosity with resulting changes in the pore-size distribution, and in some cases, in pore roughness. These effects in turn can modify flow and permeability. Description of permeability evolution in the presence of pore-scale heterogeneities is still challenging, as micro-heterogeneities are often ignored in flow and reactive transport codes at the macroscopic (or Darcy) scale.

Most permeability reduction models consider at least an exponential or power-law dependence of permeability to porosity, and sometimes integrate the effects of tortuosity, shape factor, specific surface area or pore shape [37–39]. Using a simple model of cylindrical pores, Ghezzehei [40] established differences in permeability of up to three orders of magnitude between uniform and non-uniform precipitation models. The uniform model corresponds to a coating of the cylindrical pore with precipitate of uniform thickness, while in the non-uniform model the pore contains several rectangular precipitate crystals of various sizes separated by equal distance. The author proposed a modified formulation of the Kozeny–Carman model [37] to correct for pore-scale distribution of the precipitates. Although this model has been extensively modified to improve the estimation of the permeability when porosity changes, it seems that modifications at micro-scale are too diverse to be captured by only a small number of macro-scale parameters such as porosity and/or tortuosity of cylindrical pores.

Advances in non-invasive and non-destructive techniques like X-ray microtomography (XMT) have allowed for characterization of flow or geometry changes over time at the pore-scale during dynamic processes or experiments, see e.g., [14, 41] for a review. In particular, characterization of pore geometry and pore-space distribution is possible [42–44]. The dynamics of the fluid-rock interface can also be followed through time [45, 46]. Even if it is difficult to define pore roughness to the extent that it depends on the resolution and scale of observation, the changes in pore or surface roughness can be examined [47]. The 3D geometry derived in this way can be used for discrete calculations of porous media properties such as permeability and transport, e.g., see [48] for a review.

The present study is focused on the effects of calcite precipitation on changes in pore geometry, permeability and flow at the

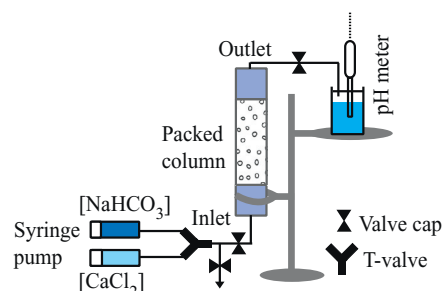


Fig. 1. Schematic of the plug-flow column experimental setup.

pore-scale. These effects are investigated both experimentally and numerically through an idealized representation of porous rock columns representing very simple analogs of a calcareous sandstone. Glass beads and calcite spar crystals or aragonite ooids were selected to test the effects of the substrate composition on precipitation under similar chemistry and flow conditions. The characterization of the pore structure, which is crucial for determination of flow in porous media, was carried out before and after precipitation experiments using X-ray microtomography (XMT) at a resolution of $4.46 \mu m$. The first part of the paper is devoted to the identification, localization and characterization of the newly precipitated crystals and to the determination of crystal growth velocity and growth rate from XMT images. The discrete 3D geometry is then used as an input for permeability calculations, and several models of precipitation were generated and examined to test the effects of precipitation-induced micro-scale changes on permeability and flow properties.

2. Experimental and modeling procedure

Experiments were designed to study the effects of precipitation and substrate composition in columns packed with glass beads and calcite crystals or aragonite ooids. X-ray microtomography (XMT) allowed for the investigation of the crystallization processes in porous media by monitoring changes in porosity, pore geometry, and surface roughness. Because of the high initial porosity and permeability of the columns, experimental determination of permeability based on the pressure difference between the inlet and outlet was not possible. Instead, permeability was computed directly from the 3D discrete geometry of the samples after image segmentation using a Stokes solver.

2.1. Precipitation experiments

Two samples (REAC-1 and REAC-3) consisting of the contents of cylindrical plug-flow column reactors of 6.5 mm diameter and approximately 12 mm length were prepared by packing a mixture of glass beads and crushed calcite spar or aragonite ooids (Table 1, see also [36] for more details about sample REAC-1). The glass beads used here were acid-washed soda-lime glass in the range $425\text{--}600 \mu m$ (Sigma G8772). Calcite that began as centimeter-size Iceland spar crystals was crushed in an agate mortar and then sieved in the range $355\text{--}500 \mu m$. Aragonite ooids, which come from oolitic sand sampled on the seabed in Bahamas, were also sieved in the range $355\text{--}500 \mu m$. All the materials were washed with deionized water, cleaned ultrasonically, and dried at $50^\circ C$ prior to column assembly.

Each reactor was injected with a 50/50 mixture of $0.002 M CaCl_2$ and $0.004 M NaHCO_3$ at a flow rate of $0.5 cm^3 \cdot h^{-1}$ ($Q = 1.38 \cdot 10^{-10} m^3 \cdot s^{-1}$) using a multi-channel syringe pump (Fig. 1), inducing a calcite saturation index ($\log \Omega$) of 1.42 (see [36] for calculation details). The reactors were saturated with deionized water under vacuum prior to experiments and injected with an acidic solution (deionized water + HCl, pH 4.0) for 5 h at a flow rate of $20 ml \cdot h^{-1}$ ($Q = 5.56$

Download English Version:

<https://daneshyari.com/en/article/6380637>

Download Persian Version:

<https://daneshyari.com/article/6380637>

[Daneshyari.com](https://daneshyari.com)