Spatiotemporal Distribution of Precipitates and Mineral Phase Transition During Biomineralization Affect Porosity–Permeability Relationships

Microfluidic investigations

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Abstract
Enzymatically induced calcium carbonate precipitation is a promising geotechnique with the potential, for example, to seal leakage pathways in the subsurface or to stabilize soils. Precipitation of calcium carbonate in a porous medium reduces the porosity and, consequently, the permeability. With pseudo-2D microfluidic experiments, including pressure monitoring and, for visualization, optical microscopy and X-ray computed tomography, pore-space alterations were reliably related to corresponding hydraulic responses. The study comprises six experiments with two different pore structures, a simple, quasi-1D structure, and a 2D structure. Using a continuous injection strategy with either constant or step-wise reduced flow rates, we identified key mechanisms that significantly influence the relationship between porosity and permeability. In the quasi-1D structure, the location of precipitates is more relevant to the hydraulic response (pressure gradients) than the overall porosity change. In the quasi-2D structure, this is different, because flow can bypass locally clogged regions, thus leading to steadier porosity–permeability relationships. Moreover, in quasi-2D systems, during continuous injection, preferential flow paths can evolve and remain open. Classical porosity–permeability power-law relationships with constant exponents cannot adequately describe this phenomenon. We furthermore observed coexistence and transformation of different polymorphs of calcium carbonate, namely amorphous calcium carbonate, vaterite, and calcite and discuss their influence on the observed development of preferential flow paths. This has so far not been accounted for in the state-of-the-art approaches for porosity–permeability relationships during calcium carbonate precipitation in porous media.

Article Highlights

• We record a detailed pore geometry evolution during EICP with synchronized pressure measurements

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• We observe that the porosity–permeability relationship is strongly influenced by the complexity of the pore structure (Quasi-1D vs. Quasi-2D)
• The evolution and preservation of flow paths during EICP treatment with constant flow can significantly affect the apparent permeability

Keywords Biomineralization · EICP · Microfluidics · Porosity–permeability relationship

1 Introduction

Biomineralization offers an environmentally more sustainable technology to replace the use of Portland cement (Terzis and Laloui 2018), which is known to be energy demanding and has significant impact on global CO₂ emissions (Andrew 2019). Microbiologically or enzymatically induced calcium carbonate precipitation (MICP/EICP) refers to a bio-geochemical process, which is already intensively investigated for its potential to substitute and complement the use of Portland cement in various applications of civil and environmental engineering (Nething et al. 2020; Phillips et al. 2013a; Rahman et al. 2020; Akyel et al. 2022). The overall process relies on the hydrolysis of urea and the precipitation of calcium carbonate:

\[
\text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \xrightarrow{\text{urease}} 2\text{NH}_4^+ + 2\text{HCO}_3^- + \text{OH}^- \quad (1)
\]

\[
\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \downarrow + \text{H}^+ \quad (2)
\]

Urea (CO(NH₂)₂) hydrolyzes irreversibly into ammonium and inorganic carbon, which is in general a very slow reaction, but can be catalyzed by the enzyme urease. This can speed up the reaction by several orders of magnitude (Benini et al. 1999; Krajewska 2009, 2018). The most common approaches to obtain urease for geotechnical application are either extracting it from jack-bean meal—then referred to as EICP—or produce it locally using microbial activity—referred to as MICP. In order to induce the precipitation of calcium carbonate, a source for calcium ions has to be present, which, in this work, is ensured through the addition of calcium chloride and can be provided in the form of ice-melt on the commercial scale (Phillips et al. 2016; Kirkland et al. 2021).

The precipitation of calcium carbonate itself is a complex combination of nucleation, crystal growth, and changes of the crystal structure (van Paassen 2009). Calcium carbonate has six different polymorphs, i.e., calcite, aragonite, vaterite, mono-hydrocalcite, ikaite, and amorphous calcium carbonate (ACC). Their thermodynamic stability decreases from calcite to ACC (El-Sheikh et al. 2013). In accordance with Ostwald’s step rule, usually the least-stable phase forms first, which then transforms into more stable polymorphs (Cöelfen and Antonietti 2008) [as cited in Wang et al. (2019b)]. Generally, calcite crystals are rhombohedral, vaterite is spherical, and ACC is irregularly shaped (Rodriguez-Blanco et al. 2011). Moreover, the density of ACC is lower (ρ = 2.18 g/cm³) than that of calcite (ρ = 2.71 g/cm³) or vaterite (ρ = 2.65 g/cm³) (Rodriguez-Navarro et al. 2015; Nebel 2008).

EICP or MICP in porous media are typically applied for stabilizing soils or for creating and improving hydraulic barriers. In soil stabilization, the precipitated calcium carbonate acts as cement-stabilizing loose material, for example, to control fugitive dust or...
to produce construction material, like bio-bricks or other more complex bio-cemented spatial structures (Arab et al. 2021; Nething et al. 2020; Hamdan and Kavazanjian 2016; Akyel et al. 2022). In this case, mechanical properties like Young’s modulus and shear modulus are of great interest and have been extensively studied (van Paassen 2009; Dejong et al. 2013; Mujah et al. 2017). In creating hydraulic barriers, to prevent or to remediate leakages in the subsurface, the key parameter to be controlled is the intrinsic permeability, which is strongly coupled to the porosity. (Phillips et al. 2013a, b; Hommel et al. 2018). A useful tool to predict and plan field applications is numerical simulation on the scale of representative elementary volumes (REV) (Cunningham et al. 2019; Minto et al. 2019; Landa-Marbán et al. 2021), which inherently relies on upscaled porosity–permeability relationships (Ebigbo et al. 2012; Hommel et al. 2016). The literature provides many different approaches of porosity–permeability relationships, which are used to model pore-space alterations on the REV scale, like Kozeny–Carman type, Thullner biofilm relation, or Verma-Pruess type, to name only a few (Pandey et al. 2015; Thullner 2010; Verma and Pruess 1988). As reviewed by Hommel et al. (2018), many of them do not lead to fundamentally different permeability alterations compared to a simple power-law relationship with a suitable exponent $\eta$:

$$\frac{k}{k_0} = (\frac{\phi}{\phi_0})^{\eta}, \quad (3)$$

with $k$ being the intrinsic permeability and $\phi$ the porosity; $k_0$ and $\phi_0$ are the initial values, respectively. Therefore, this simple approach should be the first choice unless substantial pore-scale information is available and justifies more sophisticated approaches.

Recent studies addressed how pore-scale factors determine the evolution of porosity and permeability driven by pore-space alteration, like precipitation or biofilm growth:

Effects of biofilm growth have been investigated by Jung and Meile (2021) using Stokes simulations of an idealized system. They concluded that the Péclet (Pe) and the diffusive Damköhler (Da) numbers (see SI for their definition) determine the biofilm distribution. High Pe numbers result in a homogeneous distribution of the biofilm. As a consequence, the resulting porosity–permeability relationships are closer to the classical Kozeny–Carman relationship.

In contrast, high Da numbers lead to preferential biofilm growth. This leads to a rapid decrease in the permeability even though the reduction in the porosity is small.

Experimentally, there have been several studies on the laboratory-scale where biofilm accumulation and its effect on the hydrodynamics have been studied. Cunningham et al. (1991) used reactors filled with glass beads and different types of sand. Their results indicated substantial interaction between mass transport, hydrodynamics, and biofilm accumulation at the fluid-biofilm interface. Furthermore, naturally bioluminescent biofilm experiments in meso-scale flat plate reactors were performed in the work of Sharp et al. (1999). With dye tracer studies, they were able to visualize the formation of flow channels during a continuous injection of the nutrient solution. In a recent experimental approach, the effect of biofilm growth on the permeability has been studied using microfluidic glass cells (Hassannayebi et al. 2021). Based on their experimental approach, the main mechanisms for biofilm aggregation were identified as adsorption, filtration, and bacterial growth, resulting in the formation of preferential flow paths. Supported by numerical simulations, they hypothesized that the increased velocity in the remaining flow paths may prevent further biomass aggregation and keeps them open. This contradicts the conclusions of the numerical study of Jung and Meile (2021), since they did not account for detachment and subsequent filtering processes of the biomass.
Similar to the work of Jung and Meile (2021), a numerical study was performed by Niu and Zhang (2019), addressing how mineral precipitation—instead of biofilm growth—influences the permeability of a porous medium. Ni and Ratner (2008) looked at advection-dominated systems ($Pe > 1$) and distinguished between reaction-limited cases and transport-limited cases. In the reaction-limited case, the precipitates form uniformly at the solid–fluid interface resulting in a porosity–permeability relationship with a constant exponent. In contrast, for the transport-limited cases, the precipitated minerals develop mostly near the pore throats where the fluid velocity, and thus reactant supply, is relatively high. This in turn results in a more rapid reduction in the permeability for a given reduction in the porosity and, consequently, cannot be represented reliably by a simple power-law relationship with a constant exponent.

Recently, investigations which are more specific to the pore-scale phenomena in processes of MICP and EICP were reported. In an experimental study, Mountassir et al. (2014) investigated MICP treatment in fractures using flow cells with a length of 20 cm and fractures of varying widths (1–20 mm) and apertures (0.1–0.5 mm). They observed the formation of flow channels within a fracture during MICP treatment, which becomes more distinct as precipitation progresses. They conclude that the effect of channeling enhances precipitation in regions of low flow velocities, whereas it is inhibited in the remaining high velocity channels.

Wang et al. (2019a) showed in their experimental study that the use of a microfluidic chip made out of polydimethylsiloxane (PDMS) is beneficial for studying MICP on the pore-scale. They found that calcium carbonate crystals form both at narrow pore throats and in open pore bodies during no-flow conditions. In two follow-up studies, Wang et al. (2019b, 2021) observed through high-resolution optical microscopy crystals of different shape. They hypothesized them to be different calcium carbonate polymorphs, which evolve during a staged injection strategy of the cementation solution. They observed that during the initial stage of the precipitation process, mainly irregularly shaped CaCO$_3$ precipitates (assumed to be ACC) formed, which later transform to spherical or rhombohedral crystals (assumed to be vaterite and calcite, respectively). At later time scales, rhombohedral calcium carbonate (calcite) was the dominant shape.

In the work of (Zambare et al. 2020), the mineralogy of MICP was studied using single-cell drop-based microfluidics. Using Raman microspectroscopy, they found that ACC occurred first, followed by the formation of vaterite, while the ratio of ACC to vaterite decreased during time. Due to the observation of autofluorescence of the precipitates and further analysis using energy dispersive X-ray spectroscopy (EDX), they presumed the additional presence of calcite. This is in agreement with the hypothesis of Wang et al. (2021), that ACC forms first and is later on transformed into vaterite and calcite.

Kim et al. (2020) performed an EICP experiment in a glass cell using a staged injection strategy and observed the pore-space alteration with optical microscopy. Assuming a semispherical as well as a cylindrical shape of the precipitates to estimate the volume of the evolving precipitates, they were able to conclude on the kinetics of the precipitation process by comparing the results to a simplified kinetic model. The main focus of these microfluidic investigations was on the kinetics of the biomineralization process.

In contrast to that we recently developed an experimental workflow that combines optical microscopy and high-resolution X-ray computed tomography ($\mu$XRCT) together with continuous pressure measurements in order to investigate the hydraulic effects, like the reduction in the intrinsic permeability. This enables us to directly relate changes of the pore space to changes in permeability (Weinhardt et al. 2021a). The utilized microfluidic cell was PDMS-based and the pore geometry consisted of four linearly aligned pore bodies.
connected with pore throats. Due to the simplified geometry, we were able to compare the experimental results with a mathematical model that couples reactive transport with phase changes due to precipitation (von Wolff et al. 2021).

We present in this study an analysis of both the previous experiments in the simple pore structure (Quasi-1D-structure) and additional new microfluidic experiments with a more complex pore structure (Quasi-2D-structure). A focus is put also on how different injection strategies, constant versus step-wise reduced inflow, affect precipitation and porosity–permeability relationships. In the Quasi-1D-structure, the location of individual precipitates, whether in a pore throat or in a pore body, for example, is expected to have a much larger effect on the porosity–permeability relationship than in the Quasi-2D-structure, where the porous medium offers more degrees of freedom for flow paths to develop. It is demonstrated that mechanisms like shearing off and redeposition of small precipitates, which strongly affect the development of flow paths, are dependent on these boundary conditions imposed in the experiments. And we discuss how this affects the parameterization of functions to approximate the obtained porosity–permeability relationships. Taking the perspective of a modeler, it is an important goal of this fundamental experimental study to derive porosity–permeability relationships also on a larger scale, i.e., the REV scale (Hommel et al. 2018), and we can show that preferential flow is a major process to consider. It is important to consider the occurrence of preferential flow development in the context of boundary conditions. Constant flux (Neumann-type boundary condition) might lead to the development of preferential flow paths, while constant pressure differences (Dirichlet-type boundary condition) might minimize the development of such preferential flow paths (Zhang and Klapper 2014).

Based on our results, we therefore hypothesize that the (co)existence and transformation of differently shaped polymorphs strongly influence the resulting permeability reduction which has so far not been discussed in literature.

2 Materials and Methods

In this work, two sets of experiments are considered with different designs of the porous medium and different injection strategies. The first set of experiments consists of three experiments using a PDMS-based microfluidic cell with a simple 1D structure and are referred to as Quasi-1D-experiments 1-3. The corresponding data set includes time-resolved images obtained from optical microscopy, flow rates, pressure measurements and a μXRCT dataset obtained from one of the experiments after reaching its final state. The data corresponding to this study are available at Weinhardt et al. (2021b) and Vahid Dastjerdi et al. (2021), while details on the experimental methods are given by Weinhardt et al. (2021a). In the second set of experiments, we used microfluidic glass cells with a more complex structure, referred to as Quasi-2D-experiments 1-3. Besides the structure and the material, also the injection strategy varies slightly compared to the Quasi-1D-experiments. The resulting dataset includes again time-resolved images of optical microscopy and synchronized flow and pressure data (Weinhardt et al. 2022). In the following, the microfluidic setup and the experimental procedure are described, including the fabrication and designs of the microfluidic cells, the preparation of the chemical solutions, and the injection strategies (2.1). Furthermore, the imaging techniques including optical microscopy and μXRCT scanning are described and the necessary steps of the processing are detailed (2.2).
2.1 Microfluidic Setup and Procedure

2.1.1 Preparation of Reactive Solutions

The reactive solutions were prepared according to the procedure and concentrations described in Weinhardt et al. (2021a): Solution 1 contained calcium chloride dihydrate and urea (MERCK©) at equimolar concentrations of $1/3 \text{ mol/L}$. Solution 2 contained the enzyme urease extracted from jack-bean meal (Sigma-Aldrich©). To prepare Solution 2, a jack-bean-meal suspension at a concentration of $5 \text{ g/L}$ was stirred for 17 hours at $8 ^\circ \text{C}$ and subsequently filtered twice through a cellulose membrane with a filter size of $0.45 \mu \text{m}$ before use in experiments.

2.1.2 Microfluidic Cells

We used two different types of microfluidic cells: (1) a PDMS-based microfluidic cell for the *Quasi-1D-structure*; (2) a glass cell for the *Quasi-2D-structure*. The corresponding pore structures are shown in Fig. 1.

The PDMS-based cells were produced using the general workflow of soft lithography (Xia and Whitesides 1998; Karadimitriou et al. 2013). The microfluidic cell consists of an inlet channel, an outlet channel, and two channels connected to the pressure sensors (type MPS0/MPS3 from Elveflow, Paris, France). The domain of interest in this case is the pore structure that consists of four pore bodies with a diameter of $D_{\text{pore}} = 500 \mu \text{m}$ connected with pore throats with a width of $D_{\text{throat}} = 125 \mu \text{m}$. All features are extruded in

![Dimensions of the two types of porous media structures: Top: Quasi-2D-structure made out of glass. Bottom: Quasi-1D-structure made out of PDMS. White refers to pore space and black to solid. The porous domains, for which porosities and permeabilities are defined in this work, are framed in gray.](image)
through-plane to an extent of 85 μm. The porous domain in this case has the dimensions 7 × 0.5 × 0.085 mm.

The glass cells were purchased from Micronit®, Enschede, The Netherlands, and are made out of Borosilicate glass. Similar to the previously described PDMS-based cells, the glass cells also consist of an inlet and an outlet channel, including distribution channels and two additional channels that are connected to the pressure sensors. However, the pore structure is different. The solid matrix consists of pillars of various sizes, ranging from diameters between 200 and 700 μm. The pore space (white) inbetween is initially fully connected and its extension in the through-plane is 35 μm. The porous domain in this case has the dimensions 20.5 × 11.9 × 0.035.

2.1.3 Injection Strategy

The microfluidic cells were fully saturated with deionized water prior to the microfluidic experiments. Solutions 1 and 2 were co-injected into the glass cells using syringe pumps from CETONI GmbH, Korbussen, Germany, at controlled flow rates; they mix in a T-junction right before they enter the cell through an inlet tube. The outlet tube was connected to a reservoir with a constant head, elevated 10 cm above the cell. The precipitation process was observed and visualized by optical microscopy (see 2.2), and the flow and pressure data were logged continuously. The setup was designed in a way that the pressure sensors were connected in parallel to the inlet and outlet channels to enable reliable measurements of pressure differences across the porous domain of interest, for details see (Weinhardt et al. 2021a). With that we are able to measure the pressure drop of the porous domain reliably and synchronized with the pore-space alteration observed through optical microscopy.

The detailed injection procedures varied slightly between the six experiments and are summarized in Table 1. They differ in terms of the total duration of the experiment, the type of pressure sensor that was used with different measurement ranges, the flow rates, and the residence times in the porous domain. The experiments with the simple pore structure (Quasi-1D-1 - 3) were conducted by applying constant flow rates of the two syringes with a total flow rate of 0.02 μL/s. The duration of experiment Quasi-1D-2 was shorter in time compared to the others since the pressure limit of the pressure sensor was reached after 3.1 hours of injection (also see Weinhardt et al. [2021a]).

| Experiment | Flow rate [μL/s] | Res. time [s] | Sensor [mbar] | Duration [h] | Re | Pe |
|------------|-----------------|---------------|---------------|--------------|----|----|
| Quasi-1D-1 | 0.02            | 6             | 70            | 5.0          | 0.04 | 5 |
| Quasi-1D-2 | 0.02            | 6             | 70            | 3.1          | 0.04 | 5 |
| Quasi-1D-3 | 0.02            | 6             | 70            | 5.1          | 0.04 | 5 |
| Quasi-2D-1 | 0.04, 0.02, 0.01| 90–360        | 70            | 41.4         | 8E-4 – 3E-3 | 1–4 |
| Quasi-2D-2 | 0.04, 0.02, 0.01| 90–360        | 70            | 25.9         | 8E-4 – 3E-3 | 1–4 |
| Quasi-2D-3 | 0.01, 0.04      | 360           | 1000          | 26.4         | 3E-3 | 4 |

Table 1 Injection procedure: Flow rate corresponds to the total flow of both reactant solutions, Residence time refers to how long the reactive solutions sojourn in the porous domain, Sensor defines the range of the pressure sensor, Duration corresponds to the total duration of the experiment, Re and Pe are the Reynold’s and Péclet numbers with regard to the porous domain, where the height of the cell was chosen as the characteristic length, and the diffusion coefficient of carbonate ions in water (D = 8.04E − 10 m²/s) was used for determining the Pe (von Wolff et al. 2021).
For the experiments with the complex structure, the initially applied flow rate was 0.04 μL/s. For the experiments Quasi-2D-1 and Quasi-2D-2, the flow rate was decreased to 50% once the limit of the pressure sensor was reached. This procedure was repeated twice before the cell was flushed with deionized water to stop the reaction. It has to be mentioned that experiment Quasi-2D-1 required an intermediate restart and resaturation after approximately 26 hours due to leakage and clogging issues in the inlet zone of the cell. The relatively high flow rates during the resaturation process may have led to experimental artifacts, like the initiation of a preferential flow path and will be discussed in Sect. 3. For experiment Quasi-2D-3, a MPS2 pressure sensor with an increased range of 1000 mbar was used, and the applied flow rate was initially constant at 0.01 μL/s for two hours and then constant at 0.04 μL/s until the end of the experiment. For all experiments, we have creeping-flow conditions, i.e., Reynolds numbers < 1. The corresponding Péclet numbers (Pe) range between 1 and 5, indicating a slightly advection-dominated flow regime. The Damköhler number (Da) in our experiments is not straightforward to define, since two reactions are occurring in parallel: (1) the hydrolysis of urea and (2) the precipitation of calcium carbonate (see SI for the definitions of the dimensionless numbers). Even though the precipitation rate depends inter alia on the available surface, supersaturation of the bulk, and other factors, it is rather fast compared to the urea hydrolysis (Hommel et al. 2016). Therefore, the precipitation rate is often considered to be controlled by the rate of ureolysis (Landa-Marbán et al. 2021; Qin et al. 2016). According to Feder et al. (2021) and Hommel et al. (2020), the hydrolysis can be assumed to be a first-order kinetic reaction with respect to the concentration of urea. However, due to relatively short residence times in the porous domain and high enough initial concentration of urea, the hydrolysis rate can be assumed as constant throughout the domain, meaning that the influent and effluent concentrations were approximately equal (von Wolff et al. 2021; Jackson et al. 2021; Connolly et al. 2015).

2.2 Imaging

In this study, we used both optical microscopy and μXRCT scanning, in order to observe the precipitation processes in the microfluidic cells.

2.2.1 Optical Microscopy

During the experiment, we used transmitted light microscopy, which allowed us to observe the process time-resolved. A custom-made microscope has been used as described in Karadimitriou et al. (2012) that allows to visualize samples with a resolution of 0.5–20 μm/pixel. In this study, the resolution of the first data set with the Quasi-1D-structure was between 3.17 and 3.36 μm/pixel and between 8.93 and 9.31 μm/pixel for the second data set with the Quasi-2D-structure. The frame rates ranged between 1 and 0.1 fps, but not all of the recorded images were used for further processing. Details can be found in the description of the respective datasets (Weinhardt et al. 2021b, c).

2.2.2 μXRCT Scanning

In this study, we analyze the reconstructed and segmented μXRCT data set, obtained from one of the Quasi-1D-structure experiments (Vahid Dastjerdi et al. 2021). The microfluidic cell was scanned after the precipitation experiment using an open and modular XRCT device described
in Ruf and Steeb (2020). Therefore, the scan visualizes the precipitates at their final state, and, thus, not time-resolved. The resolution was 4.25 μm/pixel. Details on the segmentation can be found in Weinhardt et al. (2021a) and operating parameters in the description of the dataset Vahid Dastjerdi et al. (2021).

2.2.3 3D Reconstruction from 2D Images

As already outlined, images obtained from optical microscopy are time-resolved in this study. However, in order to derive the volume change, we need to reconstruct from 2D projections to 3D objects. As proposed in Kim et al. (2020) and elaborated in detail by Weinhardt et al. (2021a), a convenient way in microfluidic precipitation experiments is to assume certain shapes of individual crystals, like cylinders, semispheres, spheres, or spheroids, as shown in Fig. 2. The projection area of a crystal aggregate (A) is converted into an equivalent radius (r_eq), Eq. 4. Based on the r_eq and the height of the microfluidic cell (H), the volume of individual crystal aggregates can be quantified according to Eq. 5a–5c. Using the 3D dataset obtained from μXRCT imaging, we can identify the best-matching shape assumption in terms of volume estimation, derived from the projection area of each individual crystal.

However, this approach can only be applied, if we can distinguish individual crystal aggregates, as it is the case for the Quasi-1D-structure. In the case of the Quasi-2D-structure, recorded with less resolution and increased injection time, it has been observed that precipitates grow together and at some point cannot easily be distinguished or separated by image processing anymore. In that case, the 3D volume is estimated by assuming a frustum shape of the aggregates as illustrated in Figure 2. It is defined by the Euclidean distance of the center of a pixel, segmented as solid, to the center of the closest pixel, segmented as void space, (dist(i)) and the angle (α) that determines the slope of the frustum (Eq. 5d). In contrast to the previous approaches, the angle (α) is adjustable and must be defined before processing.

\[
r_{eq} = \sqrt{\frac{A}{\pi}}
\]

(4)

\[
V_{cylindrical} = \pi r_{eq}^2 H
\]

(5a)

\[
V_{semisphere} = \begin{cases} 
\frac{2}{3} \pi r_{eq}^3 & r_{eq} < H \\
\frac{2}{3} (3Hr_{eq}^2 - H^3) & r_{eq} > H
\end{cases}
\]

(5b)

\[
V_{spheroid} = \begin{cases} 
\frac{4}{3} \pi r_{eq}^3 & 2r_{eq} < H \\
\frac{2}{3} \pi r_{eq}^2 H & 2r_{eq} > H
\end{cases}
\]

(5c)

Fig. 2 Hypothetical shape of crystal aggregates from left to right: cylinder, semisphere, spheroid, frustum
3 Results and Discussion

3.1 Validation of the Reconstruction Method

To begin with, we consider only the data gathered from $\mu$XRCT scans (Vahid Dastjerdi et al. 2021). Therefore, the projection of all planes from the $\mu$XRCT images were used as a hypothetical 2D image, since this would correspond to what could be observed by optical microscopy. Based on the projections of the precipitates, their volumes were calculated assuming four different shapes, respectively. In Fig. 3 on the right, the procedure is shown for one exemplary crystal in the porous domain. The top part of this figure gives the 2D projection of the $\mu$XRCT images. As a reference, the real 3D structure, as obtained from the $\mu$XRCT scan, is shown on the right and below that are the other shape assumptions illustrated, i.e., semisphere, spheroid and frustum, the latter one with the angle $\alpha = 71^\circ$.

\[
V_{\text{frustum}} = \sum_{i=1}^{n} \min\{\text{dist}(i) \cdot \tan(\alpha), H\}
\]  

(5d)

![Diagram showing the procedure of volume calculation for one exemplary crystal](image)

**Fig. 3** Volume derived from projection area of the XRCT-scan for different shape assumptions, including their coefficient of determination ($R^2$) with respect to the reference volume. Top: 2D projection of the domain. Right: Reconstructed shapes for one exemplary precipitate.
On the left of that figure, the volumes derived from the projected areas are plotted against the actual volume derived from the 3D data set, where the latter is the reference volume. Therefore, the bisector, shown as black solid line, corresponds to the perfect match of the volume derived from the projection with the reference volume. Each data point represents one crystal in the entire scanned domain. The assumption of a cylindrical shape clearly overestimates the volume of the crystal aggregates, which can be expected since the crystals do not fill the entire height of the micro-fluidic cell everywhere. The approach of the spheroidal shape is in quite good agreement with the reference volume over the entire range of sizes, while the semispherical approach, proposed by Kim et al. (2020) mainly underestimates the volume of the crystals. In the case of the frustum-shape assumption, we have a parameter \( \alpha \), determining the slope, as an adjustable (tunable) parameter. In this case, the best fitting value is \( \alpha = 72^\circ \). Based on the coefficient of determination \( (R^2) \), it can be concluded that the spheroidal shape as well as the frustum shape are best choices to determine the volume from a projected area. Note that this is a pragmatic and empirical way with the aim to estimate the overall volume change of precipitates from 2D projections in a more sophisticated way.

3.2 Crystal Growth and Transformation of Calcium Carbonate Polymorphs

We observe in our studies that different types of precipitates occur in the microfluidic cells. They differ in terms of gray-scale value when they are recorded through optical microscopy. In Fig. 4, a time series from 4 to 24 h is shown for the experiment Quasi-2D-2. There are precipitates with darker appearance that mainly stay at their original position and grow over time, as well as lighter ones, irregularly shaped, which are more likely to be transported with the flow. Since different polymorphs of calcium carbonate can occur, and indeed their occurrence in the context of MICP has been reported in recent microfluidic

![Fig. 4 Time series of a small section of Experiment Quasi-2D-2 from 4 to 24 h: transformation of lighter appearing precipitates (hypothesized to be ACC) to darker appearing precipitates (hypothesized to be vaterite or calcite). A corresponding video is provided in the SI (V_Transformation.mp4)
investigations (Wang et al. 2021; Zambare et al. 2020), it seems likely that these are different polymorphs. During the initial stage of the precipitation process, mainly lighter irregularly shaped CaCO₃ precipitates (hypothesized to be ACC) formed, which later on transformed into darker crystals (hypothesized to be vaterite and calcite). In Fig. 4, such a transformation can clearly be seen in the area marked with a dashed circle: from the time stamps at 04:00 h until 12:00 h two darker precipitates are surrounded by irregularly shaped lighter precipitates. At time stamp 16:00 h, two additional darker precipitates form within the aggregation of irregularly shaped lighter precipitates. These darker precipitates grow within time, while the surrounding lighter precipitates seem to disappear in favor of the darker ones.

In fact, we cannot distinguish with certainty between these different polymorphs of CaCO₃ with our setup; however, our observations indicate that formation of ACC at early stages of the precipitation process, followed later by transformation into vaterite or calcite, is very plausible. Even though we use EICP with a continuous injection of the reactive solutions, these findings are in agreement with the ones reported in (Wang et al. 2021; Zambare et al. 2020) who used MICP and a staged injection or a batch system, respectively. This occurrence of different polymorphs and their transformation have substantial effects on the porosity–permeability relation, which will be further discussed in Sects. 3.3.2 and 3.3.3.

### 3.3 Porosity–Permeability Relation

In this subsection, we present our experimental results with the focus on the porosity–permeability relationship. We identified different key mechanisms that influence the shape of the porosity–permeability relationships. At first, the initial geometry of the porous domain, in our case the Quasi-1D-structure compared to the Quasi-2D-structure, is discussed. Furthermore, time dependence and two kinds of injection strategies, namely constant flow vs. step-wise decreased flow imposed at the boundary, are evaluated. Subsequently, the role of preferential flow paths during precipitation are evaluated and discussed. In order to evaluate porosity changes from 2D projections, the segmented images of all experiments were processed further, based on the approach described in Sect. 2.2. In this case, we used the assumption of a frustum shape for the precipitates using a slope with an angle of α = 72°, since this has been shown in Sect. 3.1 to fit best in terms of volume estimation. Since the permeability can be calculated from the pressure data, we can relate the obtained average quantities, porosity and permeability, to each other. Both the segmented images and the log data, including flow rates and pressure measurements, can be found in Weinhardt et al. (2021b, 2022).

#### 3.3.1 Effect of the Pore Structure (Quasi-1D vs Quasi-2D)

In Fig. 5, the normalized permeability is plotted over the change of the porosity for all six experiments in a log-log graph. Here, it needs to be mentioned that the experiment Quasi-2D-1 had to be restarted and resaturated, and, therefore, the data shown in this figure start when precipitation has already been present in the domain (see Sect. 2.1). It can be clearly observed that the experiments using the Quasi-1D-structure have a very dominant decrease in the normalized permeability within 10% of porosity reduction. Comparing it to a simple power-law relationship (Eq. 3), the exponents, \( \eta \), are roughly in the range of 30–100. This wide range of values for the exponents can be explained by the rather simple
and one-dimensional structure of the porous domain. If one single location in the domain is clogged or close to clogging, the permeability decreases, even though the overall change of pore space is not significant. We can conclude from this that at least for this specific geometry, the location of the precipitates dominates the decrease in permeability rather than the porosity as a averaged quantity. It has to be noted that the pore morphology chosen for the microfluidic cell only consists of four pore cavities connected with pore throats, it has to be noted that this cannot considered as being representative for a porous medium.

In contrast, the experiments using the Quasi-2D-structure show a different behavior. The geometry itself can generally be considered as closer to representing a 2D porous medium. Compared to the Quasi-1D-structure, there is now another degree of freedom in the lateral direction, so fluids can flow even though some individual pore throats might be locally clogged. This leads to a smoother porosity–permeability relationship. Comparing them again to simple power-law relationships, the exponents range between 3 and 7. This is in agreement with what has been reported in the literature. To describe precipitation processes, widely used exponents are in a range between 1 and 9 (Hommel et al. 2018).

We can conclude that for quasi-1D systems, like the Quasi-1D-structure, the location of the precipitates is much more important than the overall porosity reduction. In contrast, in more realistic porous media, like the Quasi-2D-structures, this local effect is averaged out to some extent, which leads to smoother porosity–permeability relationships. However, among these three Quasi-2D-experiments, differences exist, and phenomena and mechanisms leading to this will be discussed below.

### 3.3.2 Time Dependence and Injection Strategies

We discuss how the occurrence of amorphous calcium carbonate (ACC), its further transformation to vaterite or calcite, that has been described in Sect. 3.2, as well as the applied injection strategy influence the porosity–permeability relationship. We consider the occurrence of ACC and its transformation to other polymorphs of calcium carbonate as very plausible. This hypothesis is therefore used below for interpreting particular hydraulic
responses. We note, however, that the currently available data do not allow for an unequivocal identification of those irregularly shaped precipitates as ACC. This would require other sophisticated experimental techniques, such as Raman microspectroscopy as in the work of Zambare et al. (2020). In Fig. 6, the two experiments Quasi-2D-2 and Quasi-2D-3 are directly compared to each other. In the early stages, approximately during the first five

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**Fig. 6** Temporal evolution of the porosity–permeability relationship for the Experiments Quasi-2D-2 and Quasi-2D-3. Top left: Experimental data points including fitted power law relationships with the exponents 10 (early stage), as well as 5 and 3 for the later stages, respectively. Top right: Segmented images of the whole domain at time stamp 25 h. Bottom: series of unprocessed microscopy images after 02:00, 15:00 and 25:00 h. The corresponding data points are highlighted with circles in the graph above. See Video V_TimeDependentPoroPerm.mp4 in the SI for the complete temporal evolution.
hours of both experiments, the decrease in the permeability is rather fast compared to the porosity reduction. This results in a rather high exponent ($\eta = 10$) of the fitted power-law relationship. This early decrease in permeability has also been described in previous MICP experiments (Phillips et al. 2013b), while numerical modeling led to an underestimation of the initial reduction in permeability (Hommel et al. 2013). We hypothesize that the reason for this early disproportional decrease in the permeability is the relatively high ratio of ACC present in the domain, compared to the crystalline polymorphs vaterite or calcite. The optical microscopy images in Fig. 6 at the time stamp 02:00 h hours show this amorphous aggregation of precipitates surrounding the crystalline polymorphs. Since ACC is hydrated in the early stages of a precipitation process, it has a relatively low density (Rodriguez-Navarro et al. 2015). Moreover, due to the small size of the ACC precipitates in the early stages, the surface area, where shear forces act on, is higher compared to later stages. Therefore, it can be transported with the flow and temporally clog pathways, especially when the overall pressure drop is still low, as it is the case in the early stages of the experiment. The pressure drop can be interpreted as a proxy for the average flow velocity, which again is a proxy for the shear stresses acting on the precipitates. In addition to that in the early stages, precipitates might not be as well-attached to the surface yet, and there is more space available where they can be transported to. While precipitation continues and time passes, the amount (~ volume) of ACC reduces due to its possible transformation to vaterite or calcite and the available void space reduces. As a consequence, temporally clogged pathways become passable again, and the fitted power-law relationships have smaller exponents in the later stage. While the early stage for both experiments is quite similar, the curves diverge toward the end. This can be explained by the different injection strategies of the experiments, namely a step-wise decreased flow rate in Experiment Quasi-2D-2 and a constant flow boundary in the Experiment Quasi-2D-3. The curve for Experiment Quasi-2D-2 shows a quite smooth porosity–permeability relationship with an exponent of 5. In contrast, the data set of experiment Quasi-2D-3 shows a plateau between 10 and 15 h, which corresponds to the normalized porosities between 0.65 and 0.55. Both experiments globally show a rather homogeneous distribution of the precipitates, which indicates reaction-limited conditions as described in Sect. 2.1. However, on the sub-pore scale, we can observe that flow paths develop locally through detachment, transport, and filtering of ACC. This phenomenon cannot be explained by state-of-the-art theoretical descriptions of precipitation processes in porous media, which so far only differentiate between reaction- and transport-limited regimes; the phenomenon is also mostly neglected in theoretical computational studies like (Niu and Zhang 2019; Jung and Meile 2021; von Wolff et al. 2021). While in Experiment Quasi-2D-3, with a constant flow rate, these flow paths stay open, in Experiment Quasi-2D-2 with a reduced flow rate, the growth of the existing precipitates dominates over the transport of loose precipitates with the consequence that flow paths can close. This temporal evolution is also visualized in the Video V_TimeDependent-PoroPerm.mp4 in the SI.

It seems that the exact positions of precipitate formation and flow path development are difficult—if not impossible—to reproduce. This depends inter alia on initial nucleation sites present in the domain (Weinhardt et al. 2021a) and can therefore be considered a stochastic process. Still, it is plausible to conclude that the polymorphism of calcium carbonate has a substantial impact and promotes these detachment and reattachment scenarios of loose precipitates (mostly ACC), thus leading to the evolution of preferential flow paths. Due to the presence of preferential flow paths, the porosity–permeability curve is shifted toward lower porosities at almost constant permeabilities—meaning it temporally flattens the curve and reduces the exponent of the overall fitted power-law relationship. This effect can
be reduced by step-wise decreasing the injection rate and, therefore, reducing the exposure of calcium carbonate precipitates to shear stress.

3.3.3 Dominant Preferential Flow Path

Moreover, in the case of the Experiment Quasi-2D-1, we see an even more dominant shift of the porosity–permeability relationship in Fig. 5. A clear preferential flow path can be identified in the top of the domain and the precipitation pattern throughout the domain is quite heterogeneous (see Fig. 7a). Here, it needs to be mentioned that during this experiment the

Fig. 7 Subdomain approach to account for preferential flow paths. Experimental data from the Quasi-2D-1 experiment during a 5-hour interval and a constant flow rate of 0.04 μL/s. a segmented image at the end of the interval. b Representation as one REV. c Representation as two subdomains with individual permeabilities, $k_1$ and $k_2$. The cross-sectional proportions are 1/15 for domain 1 and 14/15 for domain 2. d Porosity–permeability relationship in a log-log-plot. The values are normalized to the initial state of the interval. Comparison of the two approaches to the experimental dataset. e Section of the domain, white is void space, black is solid and gray indicates the increment in precipitates during the five hour interval
microfluidic cell had to be resaturated by applying relatively high flow rates using deionized water (see Sect. 2.1). This has probably caused a breakthrough at the top of the domain by flushing out some precipitates and has led to an artificially created dominant preferential flow path (see SI for further explanations). Note that we now discuss the results of the Quasi-2D-1 experiment during the period after its restart and before reducing the flow rate. This means that precipitates already exist inside the cell, and that during this 5-hour interval, a constant flow rate of 0.04 μL/s was applied. Thus, after continuing the experiment at a constant flow rate, this flow path stays open, while increased precipitation is noticed in its surrounding. This temporal evolution is visualized in Fig. 7e), where a small section of the domain is given. For that, time-resolved binarized images (white is void, black is solid) are summed up over a period of 5 h. The resulting gray-scale values represent the time period during which a precipitate has been at the corresponding location (the darker, the longer). The changes of the precipitates within the flow path (indicated by a gray frame around them) are relatively small compared to the gray areas in the surrounding of the flow path. In addition, the video, V_DominantPreferentialFlowPath.mp4, given in the SI, shows the transport of small precipitates into the vicinity of the flow path. From this it can be concluded that the pore-space alteration due to transport of loose precipitates into the pore throats next to the flow path might have been more important than the growth of individual crystals in the preferential flow path. During a constant flow rate, the small crystals (hypothesized to be ACC) are transported along the flow path and at bifurcations also into smaller pore throats. This consequently leads toward a separation of the preferential flow path from the rest of the domain, which again locally increases kinetic energy in the flow path concomitant with detachment and transport of smaller crystals. Therefore, at constant-flow boundaries, this channeling is a self-enhancing process, which was similarly observed during MICP treatment of fractures (Mountassir et al. 2014). In addition to that we showed that this strongly affects the developing porosity–permeability relationship.

Due to this dominant preferential flow path in the top of the domain, the precipitation pattern is quite heterogeneous. Thus, the corresponding apparent porosity–permeability relationship deviates strongly from the classical power-law relationship. This can be explained by the fact that the domain cannot be described as one single representative elementary volume (REV) anymore, which may be difficult to adapt in REV-scale modeling efforts and highlights the relevance of pore-scale modeling. In order to explain the behavior of the porosity–permeability relation, we compare two assumptions: the first one is that we assume the domain to be one single REV and define one permeability: $k_{\text{tot}}$(Fig. 7b). The other assumption would be to split the domain into two subdomains, each with an individual permeability, $k_1$ and $k_2$ (Fig. 7c). In that case, one REV represents the upper part including the preferential flow path and the second one represents the rest of the domain. Since we observed that the flow path stayed open, we assign a constant permeability to Domain 1. The permeability of Domain 2 is calculated by a power-law relationship with the exponent 7. Since the flow is parallel to the interface of the subdomains, we can use the arithmetic mean to calculate the averaged permeability of both subdomains. In Fig. 7d, the two approaches are compared to the measured experimental data. We can see that with the assumption of two subdomains, we can reproduce the shape of the apparent porosity–permeability curve of the experimental data.
4 Conclusions

In this study, enzymatically induced calcium carbonate precipitation (EICP) was investigated in microfluidic cells during a continuous injection of the reaction solutions. The design of the microfluidic cells allowed for reliable continuous pressure and flow rate monitoring during the precipitation. From these pressure and flow rate measurements, the permeability reduction of the porous domain was obtained. Since the cells are transparent, we were able to use optical microscopy to observe the growth of the crystal aggregates synchronized with the pressure measurements. Analyzing a μXRCT-scan, we found that assumptions of spheroidal or frustum shape approximate the volume of precipitates the best when estimating the change in pore volume based on the 2D-projected images from optical microscopy. Thus, we were able to accurately relate porosities and permeabilities and to identify the following key mechanisms during EICP treatment:

- In the Quasi-1D-structure, the changes in permeability are dominated by the location of the precipitates rather than by the overall porosity reduction, leading to very high exponents (30–100, Eq. 3) which are hard to determine when trying to match permeability/porosity data with a simple power-law. In contrast, for the Quasi-2D-structures, which are, of course, closer to reality, the effect of single pore-throat clogging is less important, which leads to much smoother porosity–permeability relationships with smaller exponents (3–7, Eq. 3).

- We observed that particularly in the early stages of the precipitation process mainly small, irregularly shaped precipitates (hypothesized to be ACC) formed, which, due to their small size and density, would be more likely to be transported with the flow, and may have temporarily clogged pathways. Possible additional factors are that in the early stages, these precipitates are not as well-attached to the surface yet, and that there is more space available into which they can be transported, compared to later stages when most of the void space has been occupied. This consequently results in a high permeability reduction at early times and a power-law exponent of around 10 in our case. In later stages, ACC appears to transform to vaterite or calcite and consequently reduces the slope of the porosity–permeability data with power-law exponents between 3 and 5 (Eq. 3).

- With constant-flow boundaries, flow paths evolve and remain open due to shearing off and redepositing of the small precipitates. This leads to a shift in the porosity–permeability relationship with the consequence of reduced exponents of the corresponding fitted power-law relationship. Under step-wise decreased flow boundary conditions, which can be interpreted as moving toward an approximation of constant-head conditions, these effects are not seen, since the kinetic energy of the fluid and, consequently, the shear forces, to which the precipitates are exposed, remain approximately constant.

- Preferential flow paths form and appear to persist under continuous flow conditions. As a consequence, the resulting heterogeneous precipitation pattern, identified on the pore-scale, leads to difficulties for the macro-scale definition of the correct REV with its upscaled parameter permeability. In consequence, this would justify the use of dual-porosity models for approximating permeability on the macroscale. However, this only holds for constant-flow conditions, where the flow enforces preferential flow paths as soon as the matrix is sufficiently impermeable.
This study raises further research questions. For example, how EICP treatment could be optimized for fractured porous media, where obviously preferential flow paths already exist. Fluorescence microscopy, as well as micro-scale particle image velocimetry (μPIV), would enhance our, for now qualitative, observations by measuring the velocities in the flow paths and by quantifying the portion of autofluorescent calcite in the domain. Also Raman microspectroscopy, as performed by Zambare et al. (2020), would be necessary to be certain about the occurrence and transformation of ACC to more stable calcium carbonate polymorphs. Furthermore, experiments with varying inlet concentrations would be expedient for field-scale applications where locally concentrations vary. Moreover, it needs to be understood in what way these findings can be extrapolated to more realistic, fully three-dimensional porous media. In that case, flow has an additional degree of freedom which potentially affects the evolution and persistence of preferential flow paths and their length scales, while different surface properties might also influence the precipitation process. Even though we are convinced that constant flow boundary conditions will also lead to the evolution of preferential flow paths, the question how this will affect the porosity–permeability relationship still remains. Therefore, further investigations using column experiments are needed which would require time-resolved tomographic imaging techniques, for example nuclear magnetic resonance or μXRCT measurements as used in (Bray et al. 2017; Fridjonsson et al. 2011).

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Data Availability The experimental dataset is available in the data repository of the University of Stuttgart (DaRUS). It contains images of optical microscopy together with the log data, including flow rates and pressure measurements and can be accessed via the link: https://doi.org/10.18419/darus-1799 (Weinhardt et al. 2022).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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