Effects of solution supersaturation on barite precipitation in porous media and consequences on permeability: experiments and modelling

Jenna Poonoosamy¹, Martina Klinkenberg¹, Guido Deissmann¹, Felix Brandt¹, Dirk Bosbach¹, Urs Mäder², Georg Kosakowski³

¹ Institute of Energy and Climate Research (IEK-6): Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

² Rock Water Interaction, Institute of Geological Sciences, University of Bern, CH-3012 Bern, Switzerland

³ Laboratory for Waste Management, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Abstract

The understanding of porosity evolution in porous media due to mineral reactions and its impact on the transport of fluids and solutes is important, as this is a key factor in the long-term behaviour of underground engineered systems. The implementation of such coupled processes into numerical codes requires a mechanistic understanding of the relevant precipitation/dissolution processes in porous media and model validation with quantitative experiments. In this context, we conducted a series of flow-through column experiments to investigate the effect of supersaturation on barite precipitation mechanisms (e.g. nucleation) and consequential permeability changes. These experiments were modelled using the reactive transport code OpenGeoSys-GEM. Although the Kozeny-Carman equation is widely applied in numerical models describing porosity and permeability changes due to mineral dissolution and precipitation, it distinctively underestimated the permeability changes observed in the experiments. Instead, a porosity-permeability relationship involving a critical porosity at which the permeability decreases significantly had to be considered in the model. Post-mortem characterization (Scanning Electron Microscopy) highlighted the importance of including pore-scale information on passivation processes in order to get a better match between experimental and simulated results.

Keywords: porosity clogging, celestine, solid solutions, reactive transport, nucleation

1. INTRODUCTION

Precipitation or dissolution of minerals in porous media alters the rock porosity. As pore space geometry, connectivity, radii and shapes define the transport of fluids and solutes, the alteration of porosity also modifies the transport properties of the rocks (e.g. permeability). In natural systems, porosity changes are a result of the complex interactions between physical and (bio) chemical processes. Mineral reactivity and the feedback loop to transport properties of porous media is of interest in various fields, such as engineered barrier systems in nuclear waste repositories, CO₂ sequestration and permeable reactive barriers (Xie et al., 2015 and references therein).

The evolution of these natural and artificial systems, in which the coupling of chemical reactions and transport is important, is often addressed with the help of reactive transport simulations. So far, reactive transport models are usually based on a continuum approach in which a heterogeneous porous medium is approximated by a representative elementary volume (REV), i.e. by a volume that provides a meaningful statistical average of its microstructural properties (Bear, 1972). Reactive transport codes can tackle the complex coupling of porosity changes and alteration of transport properties (Hayek et al., 2011, 2012; Marty et al., 2009; Perko et al., 2015, Poonoosamy et al., 2018). These couplings are usually accounted for by the use of empirical laws, for example the Kozeny-Carman equation (porosity - permeability relation) or Archie's law (porosity - diffusivity relation) or variants thereof.

Recent experimental studies to test the implementation of process couplings (e.g. between porosity and permeability changes) in reactive transport codes (Poonoosamy et al., 2015, 2016; Chagneau et al., 2015; Rayjaguru et al., 2019) have shown the limitations of continuum scale models when it comes to predicting changes in the transport properties in porous media due to mineral precipitation and consequent porosity changes. The change of transport properties depends not only on porosity changes but on more complicated pore space changes (pore geometry and connectivity) that are not accounted for in continuum-scale reactive transport approaches. In addition, the heterogeneity in porous media likely controls the mass fluxes and residence time in the reactive media and are known to control the effective rates of mineral dissolution (Wen and Li, 2017; Jung and Navarre-Sitchler, 2018a, 2018b, Poonoosamy et al. 2019, Berkowitz et al. 2015). As a result, kinetic rates and effective surface areas must be provided by other data sources (e.g. Bouissonnié et al., 2018). Moreover, the mineral growth mechanism and consequently morphology (shape and roughness) of precipitates can have a significant impact on the transport properties of the porous media (Vankeuren et al., 2017, Stack et al., 2015, Noiriél et al., 2016, Godinho et al., 2015, 2016).

The present investigation focuses on the effects of processes occurring at the pore scale, i.e. mineral growth mechanisms and their influences on the macroscopic transport properties of porous media using flow through column experiments. Following the approaches of Poonoosamy et al. (2015), column experiments, comprising the reaction of celestine (SrSO₄) with dissolved barium to precipitate barite (BaSO₄), were employed as model systems and operated under controlled conditions. The choice of barite is justified as its formation is of concern in oil and gas extraction (Fu et al., 2012; Oddo and Tomson, 1994), in geothermal reservoirs and hydraulic fracturing

(Vengosh et al., 2014; Mundhenk et al., 2013) and as an important mineral for the retention of radium for nuclear waste disposal (Vinograd et al., 2018; Klinkenberg et al., 2018; Brandt et al., 2018). Here, we evaluate the influence of solution supersaturation on barite precipitation, including the potential for the formation of (Ba,Sr)SO₄ solid solutions, with particular focus on nucleation mechanisms in porous media. The microstructural study of the reacted porous media is supported by theoretical calculations to explain the impact of solution supersaturation on barite precipitation mechanisms and permeability. We model the experiments and evaluate the discrepancies between existing models and experimental work to identify their limitations.

2. EXPERIMENTAL METHODS

2.1 Setup of reactive transport experiments

The experimental design consisted of acrylic columns with an inner diameter of 0.01 m and a length of 0.22 m, as depicted in Fig. 1. The experimental design was modified from the quasi-2D system of Poonoosamy et al. (2015) to a 1D system for a better assessment of permeability changes. The columns were filled with a granular celestine layer (Q1) as reactive medium, sandwiched between two layers of quartz sand (Q0 and Q2). The inlet and outlet were positioned at the bottom and upper end of the column, respectively. Barium chloride (BaCl₂) solutions (at 100, 10, and 1 mM) were injected into the three columns at a constant flow rate of 15 $\mu\text{L min}^{-1}$ ($2.5 \times 10^{-10} \text{ m}^3 \text{ s}^{-1}$) to react with the celestine in the Q1 layer.

Fig. 1: Schematic representation of the setup of the column experiments.

The Q0 and Q2 regions consisted of sand (grain size 0.1 to 0.3 mm) compacted to a porosity, Φ , of 0.46 ± 0.02 . The celestine layer consisted of 20 and 63 μm grains with a Brunauer-Emmett-Teller (BET) surface area of $0.077 \text{ m}^2 \text{ g}^{-1}$. The celestine layer was compacted to a porosity of 0.46 ± 0.02 . The pore volume of the column was estimated at 7.9 mL, based on the porosity of the porous media.

The inlet and outlet were connected to a pressure sensor (PX26-005DV or PX26-015DV from Omega Engineering Inc.) coupled to a data logger for a live monitoring of differential pressure. Differential pressure measurements allow for the determination of the permeability of the porous media (cf. eq. S1.2 in Supplement S1). The initial permeability of the sand and celestine layers (Q1 region) were $8.1 (\pm 0.1) \times 10^{-12}$ and $1.34 (\pm 0.6) \times 10^{-14} \text{ m}^2$ respectively. Details on the porous media, porosity and permeability calculations are provided in Supplement S1. The initial transport properties of the columns are summarized in Table 1.

2.1.1 Reactive transport experiment

Three experiments at different BaCl₂ concentrations as well as one control experiment were carried out (Table 1). The control experiment, which consisted of the injection of a BaCl₂-free saturated SrSO₄ solution, did not induce any chemical reaction and served as reference material.

The packed columns were flushed with carbon dioxide (CO₂) to remove trapped air in the pores prior to the injection of solution into the column. This step ensured a fully water-saturated porous medium given the high solubility of CO₂ in water. A degassed solution saturated with respect to SrSO₄ (Sr

concentration $6.7 \times 10^{-4} \text{ mol L}^{-1}$) was then pumped into the column at a constant flow rate of $120 \mu\text{L min}^{-1}$ ($2 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$ or 2.73 pore volume per day) for 5 hours. Afterwards, the flow rate was reduced to $15 \mu\text{L min}^{-1}$ for 24 hours. A solution saturated with SrSO_4 was used during these steps to prevent the dissolution of the celestine. To prevent BaSO_4 precipitation in the Q0 region, 1 mL of pure water was injected into the column followed by the BaCl_2 solution at a constant flow rate.

As the BaCl_2 solutions reached the celestine layer, the precipitation of BaSO_4 was expected, due to the lower solubility of barite compared to celestine ($K_{\text{sp}}^0(\text{BaSO}_4) = 10^{-9.97}$ and $K_{\text{sp}}^0(\text{SrSO}_4) = 10^{-6.63}$; Hummel et al., 2002) at 298.15 K and 1 atm:

Given the difference in molar volume between SrSO_4 ($46.25 \text{ cm}^3 \text{ mol}^{-1} = 4.625 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) and BaSO_4 ($52.1 \text{ cm}^3 \text{ mol}^{-1} = 5.21 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) (Helgeson et al., 1978), the dissolution of SrSO_4 followed by isomolar BaSO_4 precipitation is likely to cause a porosity decrease of about 12%, which would modify the permeability of the Q1 region.

The experiments were carried out in duplicate at room temperature for 500 hours (~57 pore volumes exchange). In one set of experiments, the pressure difference across the column was constantly monitored and the effluent was sampled every 60 hours (during syringe exchange). In the other set of experiments, the effluent composition was controlled twice in 24 hours. The sampled effluents were filtered using MF-Millipore™ Membrane Filter, $0.45 \mu\text{m}$ pore size and analysed by ion exchange chromatography (IC) for anions (Cl with a detection limit of $5.6 \times 10^{-4} \text{ M}$ and analytical errors of 1% and SO_4 with a detection limit of $4.2 \times 10^{-4} \text{ mM}$ and analytical errors between 1 to 5% for SO_4) and by inductively coupled plasma - optical emission spectrometry (ICP-OES) for cations (with a detection limit of $1.14 \times 10^{-5} \text{ M}$ and $2.18 \times 10^{-5} \text{ mM}$ for Sr and Ba, respectively, and an analytical error of < 1%). The ion concentrations in the effluents from the duplicated experiments were consistent (cf. Supplement S2), giving an estimated reproducibility of >95% on the total bulk mineral temporal evolution in the system.

Table 1:

Composition of injected solutions and properties of the porous media in the column experiments.

	Experiment 1	Experiment 2	Experiment 3	control
Flow rate [$\text{m}^3 \text{s}^{-1}$]	2.5×10^{-10}	2.5×10^{-10}	2.5×10^{-10}	2.5×10^{-10}
BaCl ₂ concentration [mmol L^{-1}]	100	10	1	0
Saturated solution of SrSO ₄	NA	NA	NA	yes
Initial pH [-]	5.6	5.6	5.6	5.6
Temperature [$^{\circ}\text{C}$]	25	25	25	25
Permeability, k_s , Q0 and Q2 (sand region) [m^2]	8.1×10^{-12}	8.1×10^{-12}	8.1×10^{-12}	8.1×10^{-12}
Permeability, k_{Q1} , Q1 (celestine region) [m^2]	1.64×10^{-14}	1.67×10^{-14}	3.00×10^{-14}	1.34×10^{-14}
Porosity, Φ , Q0 and Q2 (sand region) [-]	0.46	0.46	0.46	0.46
Porosity, Φ , Q1 (celestine region) [-]	0.46	0.46	0.46	0.46

NA: Not Applicable

2.1.2 Post-experimental analysis

Prior to the solid analyses, the pore solution was removed by flushing air through the columns. One column of each duplicate experiment was embedded with resin.. Araldite XW396/XW397 resin was injected into the columns under vacuum, to impregnate the porous media. A 0.02 m long segment, including the reacted celestine layer and both interfaces, was cut from each of the columns. The samples were then longitudinally sliced into two sections and polished for SEM measurements. The solid from the other column, was removed and collected for grain morphology characterisation and powder X-ray diffraction (XRD) analysis

A FEI Quanta 200F electron microscope, equipped with EDS (Apollo X silicon drift Detector, EDAX) was used to investigate the chemical and microstructural changes in the porous media. Measurements were undertaken using a back scattered electron (BSE) detector in low vacuum mode (60 Pa) at an accelerating voltage of 20 kV and a working distance of 10 mm. To determine the chemical composition of selected grains, EDS spot analyses were performed (detection limit ~0.1 wt.%). Additional elemental mappings (C, Si, Sr, S, Ba) of the interfaces were carried out to visualize the elemental distribution at the precipitation and dissolution fronts across the Q1 region. The maps were recorded at a magnification of 200 and a resolution of 512 x 400 pixels, with a pixel size of 2.78 μm .

Given that BaSO₄ and SrSO₄ can form solid solutions (Prieto et al., 2009), XRD analyses of the material retrieved across the Q1 region were carried on a Bruker D4 diffractometer (Bragg-Brentano geometry) with Cu K α radiation (λ Cu K α = 1.5418 Å) at ambient temperature within a 2 θ -range from 5 to 120° with a step size of 0.02° and a dwell time of 2 s, to confirm the nature of the newly formed precipitates.

2.2 Numerical model

Reactive transport modelling of the experiments was performed using OpenGeoSys-GEM (Shao et al., 2009; Kosakowski and Watanabe, 2014); the numerical setup followed Poonoosamy et al. (2018). The detailed model setup including the thermodynamic data of aqueous, gaseous and solid species considered in the chemical system, and the molar volumes, are given in Supplement S5. The formation of a (Ba,Sr)SO₄ solid solution in the system was considered only in the case of experimental evidence.

The Kozeny-Carman equation is commonly used to describe the permeability of porous media and can be written as follows:

$$k = \frac{\Phi^3}{\tau(1-\Phi)^2 s^2} \quad (2)$$

where k is the permeability, Φ is the porosity, τ is the tortuosity, and s the specific surface area of the grains (see Hommel et al., 2018 and references therein). For situations in which the pore space is not changing during the course of the simulation, the parameters and their relations can be in principle estimated for each modeled material.

For the case of mineral dissolution/precipitation processes, not only bulk properties like porosity change, but also the underlying structure of the pore space. As a result, the relations between change in porosity, tortuosity and specific surface area need to be re-parameterized. This is not possible with information from common chemical solvers used in reactive transport codes. Consequently, empirical formulations, parameterizing the complex evolution of the pore space geometry to porosity changes as the only parameter, are used. Examples of such simplified relations are given in equations 3 and 4 (e.g. Xie et al., 2015; Poonoosamy et al., 2018).

$$k = k_0 \left(\frac{1-\Phi_0}{1-\Phi} \right)^2 \left(\frac{\Phi}{\Phi_0} \right)^3 \quad (3)$$

$$k = k_0 \left(\frac{\Phi}{\Phi_0} \right)^3 \quad (4)$$

where k and k_0 [m²] are the current and initial permeabilities, Φ and Φ_0 are the current and initial porosities, respectively. In absence of an *a priori* specifically parameterized relation, we base our numerical setup in OpenGeoSys-GEM on the generic relation given in equation 4.

The reaction rates, dm/dt [mol s⁻¹], of dissolution and precipitation processes were calculated following Palandri and Kharaka (2004). In our continuum scale simulations, barite was assumed to precipitate instantaneously (i.e. as soon as an oversaturation is reached) and only the dissolution kinetics of celestine were taken into account. The dissolution rate of celestine at pH = 5.6 (i.e. pH of the experiment) was calculated based on the equation given in Palandri and Kharaka (2004) with reaction rate constant from Dove and Czank (1995).

$$\frac{dm}{dt} = -S_A k_r (1 - \Omega) \quad (5)$$

where S_A [m^2] is the reactive surface area of celestine, k_r ($10^{-5.66} \text{ mol m}^{-2} \text{ s}^{-1}$) is the dissolution rate constant at 298.15 K, and Ω is the saturation state of the solution, i.e. the ratio of the ion activity product of $\text{Sr}(\text{aq})$ and $\text{SO}_4(\text{aq})$ in solution to the solubility product constant of celestine. In our simulations, reactive surface areas are calculated as follows

$$S_A = V \times a \quad (6)$$

where V [m^3] is the volume of the mineral, a [$\text{m}^2 \text{ m}_{\text{mineral}}^{-3}$] is a mineral's specific surface area (i.e., surface area per volume of the mineral phase). The reactive surface area for the dissolving celestine was updated following 2 different models. In model 1, the reactive surface area is scaled linearly to the volume of the mineral:

$$S_{A(t)} = S_{A(0)} \frac{V_{\text{cel}(t)}}{V_{\text{cel}(0)}} \quad (7)$$

where $S_{A(0)}$ and $V_{\text{cel}(0)}$ are the initial surface area and mineral volume of celestine, and $S_{A(t)}$ and V_t the surface area and volume at time t . Model 2 accounts for a reduced mineral reactivity due to surface passivation by the precipitation of secondary minerals:

$$S_{A(t)} = a[V_{\text{cel}(0)} - K_p(V_{\text{precipitate}(t)})^p] \quad (8)$$

where a is the specific surface area of celestine, and K_p is the proportionality factor that can be obtained assuming that when $t \rightarrow \infty$, $S_A(\infty) = 0$. $V_{\text{precipitate}}$ is the volume of barite or solid solution that precipitated. This model is based on [Daval et al. \(2009\)](#) to reproduce passivation processes on crystal surfaces. The exponent p is related to the particle size distribution ($>2/3$ for particles of non-spherical shape). We choose $p = 1$, as is implemented in the CHESS software ([van der Lee and De Windt, 2002](#)) and in accordance with [Daval et al. \(2009\)](#). In our simulations, K_p was fitted to a value of 1.988 such that the volume ratio of initial celestine to final barite matched the experimental findings.

Geometrical surface area and BET surface area tend to overestimate the reactive surface area as they do not take into account the hydrological accessibility of the reactive phases ([Helgeson et al., 1984](#); [Maher et al., 2006](#); [Peters, 2009](#); [Molins et al., 2012](#)). Here, a reactive surface area of $20,000 \text{ m}^2 \text{ m}^{-3} = 0.925 \text{ m}^2 \text{ mol}^{-1} = 0.005 \text{ m}^2 \text{ g}^{-1}$ (i.e. much less than $0.077 \text{ m}^2 \text{ g}^{-1}$ BET surface area) was chosen for celestine, a fitted value from [Poonoosamy et al. \(2015\)](#) for a similar system.

3. RESULTS

3.1 Experimental results

3.1.1 Mineral transformation in the column

The cation and anion concentrations in the column effluents (breakthrough curves) for experiments 1 to 3 are reported in Fig. 2a, 3a and 4a and tabulated in tables S1a, S1b and S1c in Supplement S2. Based on the chemical composition of the effluents and the amount of BaCl_2 that was injected into the columns, the amounts of dissolved celestine and precipitated BaSO_4 (in pure barite or in

(Ba,Sr)SO₄ solid solution) were calculated and are depicted in Fig. 2b, 3b and 4b as functions of time. In all experiments, aqueous chloride, Cl(aq), is detected in the effluent after roughly 8.8 hours (Fig. 2(a), 3(b), 4(a)), consistent with the theoretical residence time (8.78 hours) calculated from the pore volume of the column and the pumping rate.

In experiment 1, the concentration of aqueous barium, Ba(aq), in the effluent is non-zero, approaching the inlet concentration (100 mmol L⁻¹) with time, thus indicating that an excess of Ba(aq) is injected into the column per unit time and that the dissolution rate of celestine controls the net reaction rate. Between 9 and 80 hours, the effluent concentrations of Ba(aq) and aqueous strontium, Sr(aq), remain constant. The amount of BaSO₄ that precipitated per unit time ($6.6 (\pm 0.3) \times 10^{-9}$ mol s⁻¹) and celestine that dissolved per unit time ($7.0 (\pm 0.4) \times 10^{-9}$ mol s⁻¹) were constant for this period (Supplement S2). Between 80 and 300 hours, the Sr(aq) concentration at the outlet decreased significantly, indicating that the dissolution of celestine is significantly reduced, thus cutting down the supply of aqueous SO₄(aq) for further BaSO₄ precipitation. Consequently, after 300 hours, the precipitation of BaSO₄ is inhibited, and the concentration of Ba(aq) at the outlet is equal to the concentration at the inlet and the total amount of precipitated BaSO₄ in the system remains constant (Fig. 2b). The inhibition of celestine dissolution suggests a passivation mechanism. The concentration of SO₄(aq), in the effluent could not be quantified in experiments 1 and 2, as effluent samples had to be diluted several times prior to analysis. The SO₄(aq) concentration is expected to be controlled by equilibrium with respect to barite at 1×10^{-5} mol L⁻¹.

Fig. 2. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 1 (100mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

Fig. 3. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 2 (10mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

Fig. 4. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 3 (1mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

In experiment 2, the Ba(aq) concentration in the effluent remained rather low throughout the experiment, (varying between 0.01 to 0.1mM), while the Sr(aq) concentration was constant at about 10 mmol L⁻¹, showing that all Ba(aq) injected into the column had reacted. The calculated dissolved celestine and precipitated barite per unit time were thus constant throughout the experiment at $2.43 (\pm 0.04) \times 10^{-9}$ (barite precipitation) and $2.46 (\pm 0.08) \times 10^{-9}$ mol s⁻¹ (celestine dissolution) (cf. Supplement S2). In this experiment, the precipitation of barite is transport limited i.e. limited by the supply of barium in the injected solution, with the amount of barite precipitating per unit time equal to the number of moles of injected Ba(aq) per unit time. After 500 hours, similar amounts of BaSO₄,

i.e. 4.5 and 4.36 mmol, had precipitated in experiments 1 and 2, respectively (Fig. 2(b) and Fig. 3(b)), resulting in a net porosity decrease from 0.46 ± 0.01 to 0.43 ± 0.01 in both cases.

In experiment 3, essentially no Ba(aq) was detected in the effluent (Ba(aq) < 0.007 mM i.e. below detection limit). The $\text{SO}_4(\text{aq})$ concentration of initially about 0.76 mmol L^{-1} , originating from the saturated SrSO_4 solution injected in the preparatory steps of the experiment, decreased with time. The concentration of $\text{Sr}(\text{aq})$ (approx. 1.2 mmol L^{-1}) coming out of the column is higher than the injected Ba(aq) concentration (1 mmol L^{-1}) indicating that, in this experiment, the dissolution of celestine is faster than the precipitation of BaSO_4 . The dissolution and precipitation rates were evaluated at $3.1 (\pm 0.01) \times 10^{-10} \text{ mol s}^{-1}$ and $2.38 (\pm 0.01) \times 10^{-10} \text{ mol s}^{-1}$ respectively, remaining constant throughout the duration of the experiment (see Supplement S2). Similar to experiment 2, the precipitation of barite is transport limited i.e. limited by the barium supply. At the end of the experiment, 0.583 mmol of celestine had dissolved and 0.45 mmol of BaSO_4 had precipitated resulting in a net porosity decrease of 0.9%, which is within the uncertainty of the initial porosity. The amounts of minerals in the system and the porosity changes occurring in experiments 1 to 3 are included in Table 2 (section 3.1.3).

3.1.2 Microstructural changes and characterization

The characterization of the reacted porous media using SEM (Fig. 5, 6, 7 and 8) combined with EDS showed the formation of a Ba-rich phase (pure barite or $(\text{Ba},\text{Sr})\text{SO}_4$ solid solution) in the Q1 layer. For comparison, the control experiment without Ba is depicted in Fig. 5h. Our SEM investigation revealed that Ba-rich precipitates were limited to the Q1 region in all experiments.

Fig. 5 depicts EDS maps of the upstream and downstream interfaces of the reactive zones in the various experiments. In experiment 1, the Ba-rich phase precipitated uniformly across the Q1 layer as a rim (thickness $2.9 \pm 0.8 \text{ }\mu\text{m}$) on the surface of celestine grains (Fig. 5a, b), forming a porous crust (cf. Fig. 6). In experiment 2, a distinct zonation across the Q1 region was observed: close to the upstream interface, the Ba-rich phase forms thin rims of $2.4 \pm 1.5 \text{ }\mu\text{m}$ thickness on the celestine (Fig. 5c); in a transition zone of 6 mm width in the middle of Q1, an increase in the thickness of the rims ($4.8 \pm 1.5 \text{ }\mu\text{m}$) was observed (Fig. 5d); in the third zone, of about $1.5 \pm 0.1 \text{ mm}$ width close to the downstream interface, mostly uncoated celestine grains occur with small amounts of a Ba-rich phase that precipitated along the cleavages in the celestine grains (Fig. 5e), and at “step” - like features of the crystals (Fig. 7c). In experiment 3, a sharp dissolution and precipitation front of $0.5 \pm 0.1 \text{ mm}$ width developed at the upstream interface (Fig. 5f); no further Ba-rich phase precipitation in the Q1 layer was observed. At the dissolution/precipitation front, the celestine grains had completely dissolved. The growth of the Ba-rich phase seemingly started at the surface of the celestine grains but later spread orthogonally to the surface, changing significantly the pore architecture. The average thickness of the overgrowth by the barium-containing phase was estimated at $7.40 \pm 3.5 \text{ }\mu\text{m}$. Fig. 8 (a) shows the morphology of the newly crystalized barite where almost all of the celestine grains at the upstream interface have reacted. Our observations also suggested that the Ba-precipitates coated the dissolving celestine grains which, upon complete dissolution, created a hole in the shape of the original celestine grain (incrustation pseudomorphs). Additional SEM images illustrating this feature

more clearly are provided in Supplement S6. In all cases, the Ba-rich phase grows anisotropically on the surface of the celestine grains, creating a bicontinuous morphology of alternating channels and oriented overgrowths (Fig. 6, 7 and 8). The newly formed phases are porous and exhibit rough surfaces.

EDS spot measurements on the Ba-rich phases that precipitated in experiments 1 and 2 generally showed the presence of Sr. However, the collected spectra represent the average composition of the interaction volume of the electron beam with the sample, which is large compared to the rim thickness, thus including contributions from remaining celestine. At the resolution of our powder XRD measurements, only a pure barite phase could be detected in experiment 1 and 2, besides the initial celestine. EDS spot measurements of the larger Ba-rich phase precipitated in experiment 3 revealed a cationic composition of 84 at. % Ba and 16 at.% Sr, indicating the formation of a Ba-rich solid solution. XRD measurements of the material from the reaction zone of experiment 3 indicated the presence of a pure barite phase, and a minor fraction of a Sr-enriched solid solution (cf. Supplement S3, Fig. S3.1). This was inferred from a shift of the celestine diffraction peaks to lower 2theta angles, which is typical for a solid solution when SrSO_4 incorporates larger atoms, i.e. barium, in its crystal lattice (Ceccarello et al., 2004).

Fig. 5: EDS maps of the upstream (a, c, f, and h) and downstream interfaces (b, e, and g) of the reactive zone for experiments 1, 2, 3 and the control. Dark blue: Si indicating the quartz sand, light blue: Ba indicating Ba-rich phases, yellow: Sr indicating celestine. For experiment 2, most of the barium rich phases are precipitated in the middle of the reactive zone at 0.1755 m (d).

Fig. 6. SEM-BSE image of reacted celestine grains from experiment 1. (a), (b), (c) shows the surface roughness of the newly formed precipitate. In (b), the arrow points to the unreacted celestine under the (brighter) barite crust.

Fig. 7. SEM-BSE image of the reacted celestite grains from experiment 2. (a) shows celestine particles (arrows) covered with a barite crust in the upstream region, (b) and (c) are samples collected at the interface of the unreacted celestine where barite precipitated on the cleaved surfaces. The brightness correlates to the Ba concentration in the solid.

Fig. 8. SEM-BSE image of the reacted grains from experiment 3. (a) in the upstream Q1 interface, (b) is the newly Ba-rich phase and (c) crystals at the interface of the dissolution/precipitation front.

3.1.3 Permeability changes during the reaction

Fig. 9 depicts the evolution of the permeability of the whole system (k_{tot}) and of the Q1 region (k_{Q1}) during the individual experiments. The temporal changes in permeability of the celestine layer (Q1) were calculated considering precipitation only in the Q1 region, assuming that the change in the permeability in the sand regions (Q0 and Q2) was negligible.

Fig. 9: Evolution of permeability with time for the complete column (k_{tot}) (a) and for the Q1 region (k_{Q1}) (b). The permeability of the control experiment was monitored for 325 hours. For the

simulation of the permeability change of the Q1 region in experiment 1, the reactive surface area model 2 and the Verma and Pruess (1988) porosity-permeability relationship were used.

In experiment 1, the permeabilities k_{tot} and k_{Q1} dropped by one order of magnitude in the first 200 hours and remained almost constant afterwards at about $5 \times 10^{-14} \text{ m}^2$ and $2 \times 10^{-15} \text{ m}^2$, respectively. The changes in permeability correlate with the temporal evolution of barite precipitation (cf. Fig. 2b). In experiment 2, the decrease in k_{tot} was distinctively more pronounced, reaching a final value of about $1 \times 10^{-14} \text{ m}^2$ at the end of the experiment. Although slightly less barite precipitated in the Q1 region in experiment 2 than in experiment 1, the consequences on the permeability were strikingly different, with k_{Q1} in experiment 2 (about $4 \times 10^{-16} \text{ m}^2$) about one order of magnitude lower than in experiment 1. This can be correlated to the non-uniform distribution of newly formed precipitates in the system in experiment 2. In experiment 3, where a sharp reaction front developed, a more continuous decrease in the permeability was observed, leading to a final permeability of $k_{\text{tot}} = 2 \times 10^{-14} \text{ m}^2$ and of $1 \times 10^{-15} \text{ m}^2$ for the Q1 region (Fig. 9). Assuming that the permeability of unreacted celestine in the Q1 region did not change during the experiment, the permeability of the reaction front was evaluated at $9.12 \times 10^{-17} \text{ m}^2$.

Table 2 summarises the average porosities and permeabilities in the whole Q1 region at the end of the experiments, as well as values for the reaction zones (i.e. where precipitation occurred), calculated using a harmonic mean and assuming that no porosity change occurred in the Q1 section without precipitation of Ba phases. In Fig. 10, the experimentally-derived permeabilities are plotted as function of porosity versus commonly used porosity-permeability relationships implemented in reactive transport codes (equations 3 and 4). For comparison, the fitted porosity-permeability relationship proposed by Verma and Pruess (1988), using the experimental data in Table 2, is also shown. Verma and Pruess (1988) proposed a porosity-permeability relationship as follows:

$$k = k_0 \left(\frac{\Phi - \Phi_{\text{critical}}}{\Phi_0 - \Phi_{\text{critical}}} \right)^n \quad (9)$$

where k_0 and Φ_0 are the initial permeability and porosity respectively. Φ_{critical} and n are the critical porosity and the exponent with the general relation; $1 \leq n \leq 6$, for $0.8\Phi_0 \leq \Phi_{\text{critical}} \leq 0.9\Phi_0$. The critical porosity of a porous medium refers to the porosity at which the medium becomes practically impermeable. In our case, Φ_{critical} and n were fitted to 0.37 ($0.86 \Phi_0$) and 5, respectively, to match the experimental data points.

It is evident from Fig. 10 that no simple relation between permeability (k) and porosity (Φ) exists in this case. The decrease in permeability of the Q1 region is linked to the morphology (roughness and porosity) of the newly formed phase, which depends on the local supersaturation. In addition, the oriented growth of the barite phases, orthogonal to the surface of the dissolving grain, significantly modifies the pore architecture, decreasing the permeability. Understanding the mechanisms involved as well as the parameters that influence crystal growth in porous media would help to interpret the microstructural changes and their impact on permeability.

Table 2

Amounts of solids, permeability (k) and porosity, (Φ), in the Q1 region and the reaction zones after 500 hours.

	unit	Experiment 1	Experiment 2	Experiment 3
BaSO ₄ precipitated (in Q1)	[mmol]	4.50 ± 0.25	4.36 ± 0.07	0.45 ± 0.07
SrSO ₄ total (in Q1)	[mmol]	5.58 ± 0.25	5.71 ± 0.07	9.50 ± 0.07
average porosity Q1 region	[-]	0.43 ± 0.01	0.43 ± 0.01	0.46 ± 0.01
average permeability Q1 (k_{Q1})	[m ²]	1.98×10^{-15}	3.71×10^{-16}	1.8×10^{-15}
width of reaction zone ^a	[m]	11×10^{-3}	9.55×10^{-3}	0.5×10^{-3}
porosity in reaction zone	[-]	0.430	0.426 ^b	0.405 ^c
permeability in reaction zone	[m ²]	1.98×10^{-15}	2.8×10^{-16}	9.12×10^{-17}

^a: length where Ba precipitates were observed

^b assuming 4.36 mmol BaSO₄ precipitated and 4.39 mmol celestine remain in the reaction zone (9.55 mm).

^c assuming a complete replacement of 0.45 mmol celestine by 0.45 mmol BaSO₄ in the reaction zone (0.5 mm).

Fig. 10: Permeability versus porosity changes according to variants of the Kozeny-Carman equation (equations 3 and 4, as used in numerical models) compared to experimental data points and a fitted law following Verma and Pruess (1988). The experimental datasets are the porosity and respective permeability of the reaction zones (Table 2).

3.2. Reactive transport simulation

Reactive transport modelling of the experiments was performed to evaluate the impact of supersaturation on mineral precipitation and the consequences on permeability evolution, using two different reactive surface area models. Based on the experimental observations and thermodynamic considerations (cf Supplement S3), we considered the formation of a pure barite phase in experiments 1 and 2 (supported by XRD measurements) and a (Ba,Sr)SO₄ solid solution in experiment 3 (XRD and EDS spot measurements).

3.2.1 Reactive surface area model 1

In experiment 1, this model predicts the absence of a precipitation or dissolution front after 500 hours, but a continuous precipitation of barite across Q1. Fig. 2 quantitatively compares the experimental and simulated chemical evolution of the system, indicating discrepancies between the two. The modelled amount of celestine that reacted and the amount of barite that precipitated are higher than those calculated from the experimental data, although the predicted effluent concentrations at the end of the experiment agree reasonably well with the observations. Thus, in contrast to the experimental findings, the model predicts the consumption of practically all celestine in Q1 (Fig. 11a).

The dissolution of celestine and consequential barite precipitation (as well as the effluent composition) in experiment 2 are reproduced well by the model (Fig. 3a, b), but the simulated distribution profile of the newly formed precipitate is different from what is observed experimentally. According to the model, barite precipitates mostly in the upstream half of Q1 (Fig. 11b), whereas, in experiment 2, barite precipitated mainly in the middle of Q1 (Fig. 5c and 5d).

Furthermore, the model predicts a complete dissolution of celestine at the upstream interface, in contrast to the experimental observations.

Our model predicts the presence of a precipitation front of the solid solution for experiment 3 (Fig. 11c). This is qualitatively in good agreement with experimental observations (elemental mapping shown in Fig. 5). The modelled effluent ion concentrations and total amounts of minerals dissolving (celestine) and precipitating (i.e. BaSO_4 in the solid solution) match the experimental data (Fig. 4a, b). From our experimental data and solution chemistry, it is not possible to distinguish between the amount of undissolved celestine and SrSO_4 present in the $(\text{Ba,Sr})\text{SO}_4$ solid solution. Only the total amount of SrSO_4 present in the system can be calculated, which is matched by the model predictions for experiment 3. The simulated total amounts of undissolved celestine and SrSO_4 in the solid solution constituting the total amount of SrSO_4 in the system with time are shown in Supplement S7.

3.2.2 Reactive surface area model 2

Model 2 accounts for a passivation mechanism, i.e. the newly formed barium-phase precipitates on the surface of the celestine, thus reducing its reactive surface area and therefore its dissolution rate. In experiment 1, the simulation predicts a uniform precipitation of barite throughout Q1 without a precipitation front (Fig. 11a right) and with a significant amount of undissolved celestine in the system. Although the model shows some discrepancies with the experimentally measured effluent concentrations at the early stages of the experiment (Fig. 2a), the total temporal changes in the amounts of solids are rather well reproduced by the model (Fig. 2b). In the case of experiment 2, the model predicts a virtually uniform distribution of barite along the Q1 region with a slight decrease close to the upstream boundary (Fig. 11b, right), which contrasts to the experimental observations (Fig. 5) that depict a preferential precipitation of barite in the central part of Q1. The model predicts that, after about 400 hours, the dissolution of celestine strongly decreases, reducing the concentration of $\text{Sr}(\text{aq})$ and consequently increasing the concentration of $\text{Ba}(\text{aq})$ at the outlet (Fig. 3a). The modelled and experimental temporal changes in the system are in good agreement for the first 400 hours, after which the dissolution of celestine is predicted to slow down, in contrast to the experimental observations. In experiment 3, although the model predicts correct effluent compositions (Fig. 4a) and corresponding amounts of minerals (Fig. 4b) in the system, the sharp precipitation and dissolution front is not well reproduced by the model (Fig. 11c, right). A significant amount of celestine is predicted to remain undissolved at the upstream interface, in contrast to the experimental observations (cf. Fig. 5f).

Fig. 11. Simulated fractions of precipitated phases (pure barite in experiment 1 and 2, and solid solution in experiment 3) and remaining celestine solids in the Q1 region after 500 hours ((a), (b), (c) refer to experiments 1, 2, and 3, respectively according to reactive surface area model 1 on the left and model 2 on the right). The experimental molar fractions of Sr and Ba in the system, estimated from the respective areas of the EDS maps reported in Fig. 5, are presented here for qualitative comparison.

Based on the agreement between the observed and simulated spatial distributions of the newly formed precipitates, it can be inferred that the mineral transformation with time is better described by reactive surface area model 2 for experiments 1 and 2 and model 1 for experiment 3. Therefore, only these models are used for the further evaluation of the respective experiments.

3.2.3 Solid-solution composition

In experiment 3, the models predict the formation of a (Ba,Sr)SO₄ solid solution as the thermodynamically most stable phase, whose composition can vary spatially and temporally (cf. Fig. 12). At the upstream interface, the model predicts the formation of a Ba-rich solid solution. Across the 'reacted' Q1 region, the predicted X_{BaSO_4} in the solid solution decreases as the pore solution gets depleted in Ba (aq). At $z = 0.171$, the model predicts a composition (Ba_{0.85}Sr_{0.15})SO₄, in good agreement with the EDS spot measurements close to the interface (section. 3.1.2). The modelled, relatively small amount of Sr-enriched solid solution was detected by powder XRD measurements.

Fig. 12. Simulated composition of the solid solution that precipitated across the Q1 region in experiment 3 according to reactive surface area model 1 at (a) 100 and (b) 500 hours.

3.2.4 Porosity and permeability changes

The reactive transport model accounts for the coupling of chemical processes leading to changes in porosity, due to dissolution and precipitation, and its impact on the transport properties (i.e. permeability) of the porous media via a variant of the Kozeny-Carman equation (cf. eq. 4). In Fig. 13, the simulated porosities at the end of the experiments ($t = 500$ h) and the permeabilities in the Q1 region calculated using equation 4, are depicted. The simulated porosity for experiment 1 (reactive surface area model 2) is 0.43 across the Q1 region, in perfect agreement to the experimental observations (cf. section 3.1.2). In the simulation of experiment 2 (reactive surface area model 2), a porosity decrease from 0.46 to 0.43 at the upstream interface was predicted after 500 hours. Further into Q1, the modelled porosity decrease was slightly less pronounced, resulting in a porosity of 0.44 at the downstream interface. The most pronounced change in porosity is calculated for experiment 3 (reactive surface area model 1), with a sharp porosity decrease to 0.41 directly at the upstream interface, due to the precipitation front. Nevertheless, the simulated porosity change during experiment 3 is quite surprising, suggesting an overall slight porosity increase (0.465) in the Q1 layer, with a maximum porosity of 0.55 about 2 mm from the upstream interface. Based on the experimental observations, this local increase in porosity can be explained by a faster celestine dissolution than barite precipitation (cf. section 3.1.1). Overall, these effects lead to a local porosity decrease at the reaction front but practically a constant overall porosity in Q1. The simulated porosity at the upstream Q1 after 500 hours is slightly above the measured porosity (0.405), suggesting that the mesh discretization of 200 μm is too coarse for modelling this experiment. Previous experimental benchmarks (e.g. [Katz et al., 2011](#); [Tartakowsky et al., 2008](#)) have shown that the modelling of such thin precipitation fronts requires very fine mesh discretization (mesh size below the REV) or a modification of the advection-dispersion equation.

The simulations using OpenGeoSys-GEM with the modified Kozeny-Carman equation (eq. 4) suggest only rather small changes in the permeability of the Q1 region and thus the total system, as a consequence of the precipitation of the Ba-containing phases. For experiments 1 and 2, a permeability decrease of the Q1 region from $1.34 \times 10^{-14} \text{ m}^2$ to $1.1 \times 10^{-14} \text{ m}^2$ at the end of the experiments was predicted; for experiment 3 practically no deviation from the initial permeability value was predicted. Thus, these predictions are in sharp contrast to the permeabilities derived from the differential pressure measurements (cf. section 3.1.3), which revealed a decrease in the permeability of the Q1 region of about 1 to 2 orders of magnitude, depending on the experiment.

Fig. 13. Simulated (a) porosity and (b) permeability across the Q1 region after 500 hours for experiments 1 (reactive surface area model 2), 2 (reactive surface area model 2) and 3 (reactive surface area model 1) according to a variant of the Kozeny-Carman equation (eq. 4).

4. DISCUSSION

The experimental observations show that the porosity and permeability changes due to mineral precipitation cannot correctly be accounted for by the Kozeny-Carman equation, as implemented in numerical reactive transport codes. The permeability of the reactive layer is closely linked to the morphology (shape, surface roughness) and cementation of the newly formed precipitates which is dependent on the supersaturation that prevails across the Q1 region. In addition, the supersaturation affects the composition of the newly formed precipitates (pure phase or solid solution). Therefore, in section 4.1 and 4.2, we evaluate the supersaturation across the Q1 region and its effect on crystal growth mechanisms and potential consequences on permeability.

4.1. Evaluation of supersaturation across the Q1 layer

Supersaturation of the solution with respect to barite (or $(\text{Ba},\text{Sr})\text{SO}_4$) across the Q1 layer is a key parameter that controls the dissolution and precipitation processes in our experiments. The supersaturation is not constant across the Q1 layer. For each experiment, the upper and lower limits of supersaturation with respect to barite are imposed by the concentration of the injected BaCl_2 solution as it reaches the reactive region (upstream) and by the barium depleted solution as it leaves the reactive region (downstream) respectively. To get an estimate of the maximum supersaturation upstream and downstream at the early stages of the experiment, the modelled $\text{SO}_4(\text{aq})$ concentration in the Q1 region was used. The simulated pore concentration in $\text{SO}_4(\text{aq})$, considering kinetically controlled celestine dissolution, is equal to 0.646 mM. For the other components, the concentrations in the injected solutions and the outlet solutions (at $t < 100 \text{ h}$), respectively, were used as input for the calculations (Table 3).

The presence/absence of a precipitation front can be explained by the supersaturation, which prevails across the Q1 region. In experiment 1, the injected solution is highly concentrated in $\text{Ba}(\text{aq})$ (100 mM); thus the pore fluid was highly supersaturated with respect to barite at any location across Q1 ($\text{SI} = \log(\Omega) > 3$). This means that barite can precipitate readily all over the Q1 region. In experiments 2 and 3, the saturation index (SI) of the pore solution across Q1 varies from 3.82 and

3.35 to 0.34 and 0.27, respectively. Consequently, barite precipitation is expected at the upstream interface and unlikely at the downstream interface, consistent with the experimental observations. In all experiments, the downstream solutions were undersaturated with respect to celestine ($\log(\Omega) < 0$) and therefore its dissolution is expected.

For each experiment, the saturation state of the pore solutions with respect to the entire compositional range of (Ba,Sr)SO₄ solid solutions at the beginning and the end of the Q1 was computed following the method of Prieto (1993). These thermodynamic considerations for solid solutions, of which an exhaustive description is given in Supplement S3, suggest the formation of a pure barite phase in experiment 1 and the precipitation of solid solutions in experiment 3. For experiment 2, our thermodynamic consideration also suggests the precipitation of a pure barite phase at the Q0/Q1 interface. The formation of a solid solution cannot be excluded but would most likely be limited to the downstream part of the reaction zone. However, no solid solutions were detected by XRD in this experiment. A confirmation of the nature of the precipitates using techniques with higher spatial resolution, e.g. synchrotron based μ -XRD or TEM of single grains, could provide support to our assessments but is beyond the scope of the present study.

Table 3

Estimation of $\log(\Omega)$ across the Q1 region for each experiment as the Ba solution reaches the Q1 interfaces. The sulphate concentration is the modelled pore concentration that prevails in the Q1 region before the BaCl₂ solution reaches the Q1 region.

Exp.	Pore solution upstream [M]	Pore solution downstream [M]	$\log(\Omega)$ barite upstream	$\log(\Omega)$ barite downstream	Ionic strength [M]
1	Ba(aq) = 1.00×10^{-1} Sr(aq) = $6.46 \times 10^{-4*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-1}	Ba(aq) = 7.00×10^{-2} Sr(aq) = $3.03 \times 10^{-2*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-1}	3.94	3.93	0.3
2	Ba(aq) = 1.00×10^{-2} Sr(aq) = $6.46 \times 10^{-4*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-2}	Ba(aq) = 1.00×10^{-5} Sr(aq) = $1.03 \times 10^{-2*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-2}	3.82	0.34	0.03
3	Ba(aq) = 1.00×10^{-3} Sr(aq) = $6.46 \times 10^{-4*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-3}	Ba(aq) = 1.00×10^{-6} Sr(aq) = $1.17 \times 10^{-3*}$ SO ₄ (aq) = $6.46 \times 10^{-4*}$ Cl ⁻ (aq) = 2.00×10^{-3}	3.35	0.27	0.005

*The sulphate concentration is the modelled pore concentration that prevails in the Q1 region before the BaCl₂ solution reaches the Q1 region. Note that the maximum SI that can prevail at the Q1/Q2 interface (before reaction) is different from the SI of the effluent.

4.2 Deciphering growth mechanisms and consequences on mineral reactivity

Molecular scale growth mechanisms are known to depend on the deviation from equilibrium which is proportional to the supersaturation. The two main mechanisms of crystal growth that need to be considered are spiral growth and nucleation-mediated growth (Sunagawa et al. 1999, Yoreo and Vekilov 2003, Dove et al. 2005). At low supersaturations, spiral growth is typically the dominant mechanism. Above a given supersaturation, nucleation-mediated growth on the crystal faces becomes the dominant growth mechanism. Nucleation can occur either in the volume of an ideally pure solution (homogeneous nucleation), or on the surface of existing solids (heterogeneous nucleation). It is generally admitted that homogeneous and heterogeneous nucleation will prevail at high and low supersaturation levels, respectively (Kashchiev and van Rosmalen, 2003, Kgler et al., 2016). In our experiments, nucleation-mediated growth is probably the favoured growth mechanism of the neo-formed precipitates due to the high supersaturation ($SI > 3$) that prevails in each experiment (cf. Fig. S3.1 in Supplement S3). At the upstream part of all experiments, according to the calculated $\log(\Omega)$, heterogeneous as well as homogeneous nucleation are possible. Given the likely nucleation of barite-rich phases, only the nucleation rate of pure barite is discussed here.

Using classical nucleation theory (Prieto, 2014; Kashchiev and van Rosmalen, 2003) (equations summarized in Supplement S4), the nucleation rates, J [$\text{m}^3 \text{s}^{-1}$] of pure barite were calculated for homogenous and heterogeneous nucleation on celestine as a function of supersaturation (Fig. 14). For experiment 1 (at $\log(\Omega)$ 3.94), both homogeneous and heterogeneous nucleation could, in principle, occur at fast rates, 10^{13} and $10^{19} \text{ m}^{-3} \text{ s}^{-1}$, respectively. The dissolving celestine grains are consequently rapidly covered by a layer of barite decreasing its reactivity after 200 hours. The observed, constant nucleation rate can explain the uniform rim thickness all over the Q1 region. There is no experimental evidence of homogeneous nucleation in the system given the absence of agglomerations of barite crystallites in the Q2 region and in the effluent.

In experiment 3 ($\log \Omega$ between 3.3 and 0.3), heterogeneous nucleation is probably the dominant mechanism, but the total number of initial nuclei is lower than in experiment 1. It is likely that there is a significant fraction of the surface of the individual celestine grains where no nucleation has occurred. Thus, the growth of nuclei will lead to dissolution of more celestine from the uncovered surfaces to form more barite as a consequence of the supply of Ba(aq) . The nucleation-mediated growth of the barite islands occurs in layers, mainly orthogonal rather than lateral to the surface of the celestine grains, which disappear due to the "mining" of celestine, leading finally to the incrustation of the pseudomorphs described above (section 3.1.2). The supply of Ba(aq) is two orders of magnitude lower than in experiment 1; thus it can be expected that the supersaturation will drop rather abruptly leading to a sharp precipitation front close to the Q0/Q1 interface.

Fig. 14: Effect of $\log(\Omega)$ with respect to nucleation rate (number of BaSO_4 nuclei per unit volume and time) and amount of barite overgrowth on celestine grains. At high supersaturations ($SI > 3$), barite overgrowth covers completely the individual celestine grains, decreasing their reactivity,

whereas at lower supersaturations ($SI \leq 3$) only parts of the celestine grains are covered, enabling further dissolution of the grains.

Experiment 2 is an intermediate between experiments 1 and 3. At the interface of the Q1 region, a thin rim of barite, comparable to experiment 1, was observed. This likely resulted from heterogeneous nucleation, which rapidly covered the complete surface of celestine grains, decreasing their reactivity and therefore hindering further dissolution. As the solution moves across the Q1 region, the Ba(aq) concentration decreases, thus the rates of heterogeneous nucleation on the surface of celestine decrease, leaving significant parts of the grain surfaces uncovered. Therefore, as the pore solution is renewed and Ba(aq) becomes available, dissolution and precipitation will continue, similar to the situation observed in experiment 3, leading to an increase in the thickness of the barite overgrowths across the Q1 region, but not to the complete dissolution of the celestine substrate over the experimental timescale. At lower supersaturations ($SI < 3$), it is more likely that the further growth of barite will occur on previously formed barite crystallites – therefore growing orthogonally to the surface – rather than nucleating new clusters on the surface of celestine, where a greater energy barrier needs to be overcome (Kashchiev, 2000).

Garcia-Ruiz and Otalora (2015), reported that, at high supersaturations (e.g. SI in experiment 1), 2-D nucleation is likely to become unstable due to higher supply of growth units at edges and vertices of the crystals. These features would grow faster, producing concave crystals, typically hopper-like but almost flat features, similar to the bicontinuous morphology observed in Fig. 6a. In Fig. 7c, nucleation of barite occurred preferentially on step-like features, suggesting a reduction of enthalpic contribution due to the interfacial energies along these crystal planes. This is common when the atomic structure of the substrate surface closely matches a particular plane of the nucleating phase. If the substrate presents a set of chemical functionalities that promote strong bonding to the nucleus, nucleation occurs preferentially on that crystal plane (Yoreo and Vekilov, 2003) such that lattice strain is minimized.

In addition to supersaturation, ionic strength can also play a role in the morphology of the newly formed barite. He et al. (1995) showed that increasing ionic strength (from 0.003 to 1) lowers the interfacial energy (by 15%) which is an important factor that can control growth morphologies (Becker et al., 2002). At high ionic strengths (e.g. in experiment 1 and 2), it can be that barite may spread more easily over the celestine grains. The ionic strength is known to increase the surface roughness of newly formed precipitates (Zhen-Wu et al., 2016). This will decrease local flow velocities thus resulting in reduced permeability.

4.3 Evaluation of modelling results

The investigated chemical processes, mineral dissolution and precipitation, change the pore scale geometry on a sub-grid scale. The reactive transport model calculates chemical and transport processes on a continuum scale and can only account for those sub-grid changes via (pre-) parameterized relationships between averaged parameters. In the following evaluation, we discuss how information from the sub-grid scale can be included in the continuum scale model.

4.3.1 Reactive surface area model

The modelling results following reactive surface area model 1 could reproduce some features of the experiments, e.g. total mineral changes and the precipitation/dissolution front observed in experiment 3. The main discrepancies observed between results of reactive surface area model 1 and experimental data of experiment 1 arise because the model does not account for the passivation of the celestine surface, i.e. a process that reduces mineral reactivity. Therefore, in these simulations, dissolution of celestine and consequent precipitation of barite will occur as long as there is celestine in the system. To reproduce the results of experiment 1, a more sophisticated reactive surface area model (model 2), which takes into account the passivation of surfaces (Daval et al. 2009), was used. The inclusion of this microstructural information in our model description enabled us to reproduce the observed decrease in celestine dissolution with time for the case of experiment 1. Nevertheless, model 2 has some limitations, it failed to reproduce the aqueous Ba and Sr concentrations in the effluent for the first 100 hours. A similar observation was found by Daval et al (2009) in describing the passivation of Ca-bearing silicates due to the formation of wollastonite. The authors reported that this difference could be due to the fluid in contact with the dissolving crystals (in this case celestine) becoming isolated from the bulk fluid, preventing the dissolved species (sulphates) from reaching the fluid/precipitate (barite) interface, i.e. pore scale processes not captured by the model.

Model 2 is not suitable for experiment 3, where complete celestine dissolution followed by (Ba,Sr)SO₄ precipitation occurred, leading to a sharp precipitation front. Although model 2 satisfactorily mimics experiment 2, this model fails to reproduce other features of this experiment, such as the non-uniform barite precipitation across the Q1 region (Fig. 5). Since none of the models can describe the surface area evolution and the reactivity of the solids over the entire range of supersaturations, our work suggests that various (alternative) reactive surface area models should be implemented in continuum-scale reactive transport codes, using solution supersaturation as a selection criterion.

4.3.2 Porosity/permeability relationship

In all cases, the experimentally observed one to two orders of magnitude changes in permeability were significantly underestimated by the reactive transport code and the implemented model for porosity-permeability relationship based on the Kozeny-Carman equation. In the experiments, a slight and partially local change in the porosity causes significant changes in permeability, since a porosity decrease from 0.46 to 0.40 caused permeability to drop by 3 orders of magnitude. To capture this effect, we introduced the critical porosity concept (porosity at which the porous medium is practically impermeable) by implementation of the porosity-permeability relationship of Verma and Pruess (equation 9) in our numerical model. The simulated permeability changes were tested for experiment 1 and were in good agreement with the experimental data (Fig. 9).

Although the original Kozeny-Carman equation contains additional terms such as tortuosity and specific surface area (see equation 2), as was pointed out by the recent review of Hommel et al (2018), the equation may significantly overestimate the permeability for complex, tortuous, heterogeneous or poorly connected porous media. In fact, the Kozeny-Carman equation was not

originally developed to describe the permeability of porous media undergoing alteration in its pore architecture. In fact, [Hommel et al \(2018\)](#) suggested that the use of exponential or Kozeny-Carman relationships do not lead to fundamentally different predictions of permeability and are not generally applicable, unless a relationship that considers a critical porosity is used, like in the approach of [Verma and Pruess \(1988\)](#). Whereas the [Verma and Pruess \(1988\)](#) relationship is also an empirical formulation, it provides a way of capturing the changes in the pore architecture that influence tortuosity and constrictivity.

5. CONCLUSIONS

We conducted a series of complementary experiments and reactive transport simulations to investigate the effect of solution supersaturation on porosity and permeability changes in porous media as a consequence of barite precipitation following celestine dissolution. The supersaturation strongly affects the nucleation rates and consequently the morphology of the newly formed phase. This, in turn, can lead to diverging changes of the pore architecture of the porous medium, which, in combination with the varying surface roughness of the precipitates, has a distinct impact on permeability, a phenomenon not covered by simple porosity-permeability relationships. It could thus be shown that the use of the (simplified) Kozeny-Carman equation, as commonly implemented in reactive transport codes (cf. [Xie et al., 2015](#), [Cochepin et al., 2008](#), [Poonoosamy et al., 2018](#)), is not suitable to correctly describe the permeability changes occurring in porous media as consequence of porosity changes induced by precipitation processes. In contrast, the [Verma and Pruess \(1988\)](#) relationship, introducing the concept of a critical porosity, gave more satisfactory results. The introduction of a critical porosity term in porosity-permeability relationships could thus be an elegant way forward to introduce pore-scale corrections into macroscopic transport models (upscaling). Nevertheless, the parameterization of such empirical relationships still remains a challenge and needs to be tested and validated for different systems (using, e.g., experimental data from [Singurindy and Berkowitz \(2003\)](#)), and the physical meaning of critical porosity needs to be explored further. For this purpose, pore-scale modelling taking into account precipitation scenarios in different pore geometries could be used to determine up-scaled parameters and parameterize power law equations of porosity-permeability relationships for use at the continuum scale (cf. [Prasianakis et al. 2017](#)). Moreover, the treatment of the evolving reactive surface areas in reactive transport models has been highlighted, in particular regarding the demand for an improved description of passivation processes on mineral surfaces that include the diffusive properties of secondary phases in further model developments. The data presented in this study are not sufficient to immediately derive constitutive equations for a more realistic description of porosity-permeability relationships and reactive surface area models (as functions of solution supersaturation) to be implemented in continuum-scale reactive transport models. Nevertheless, it could be used as a starting point for further experimental and theoretical investigations to overcome the shortcomings of the currently used approaches.

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REFERENCES

- Bear J. (1972) Dynamics of fluids in porous media. Dover Publications Inc., New York.
- Berkowitz B., Dror I., Hansen S. K. and Scher H. (2015) Measurements and models of reactive transport in geological media. *Rev. Geophys.* **54**, 930-986.
- Berner U., Kulik D. A. and Kosakowski G. (2013) Geochemical impact of a low-pH cement liner on the near field of a repository for spent fuel and high-Level radioactive waste. *Phys. Chem. Earth* **64**, 46-56.
- Bildstein O., Kervévan C., Lagneau V., Delaplace P., Crédoz A., Audigane P., Perfetti E., Jacquemet N. and Jullien M. (2010) Integrative modeling of caprock integrity in the context of CO₂ storage: Evolution of transport and geochemical properties and impact on performance and safety assessment. *Oil Gas Sci. Technol. IFP* **65**(3), 485-502.
- Brandt F., Curti E., Klinkenberg M., Rozov K. and Bosbach D. (2015) Replacement of barite by a (Ba,Ra)SO₄ solid solution at close-to-equilibrium conditions: A combined experimental and theoretical study. *Geochim. Cosmochim. Acta* **155**, 1-15.
- Becker U., Risthaus P., Bosbach D. and Putnis A. (2002) Selective attachment of monovalent background electrolyte ions and growth inhibitors to polar steps on sulfates as studied by molecular simulations and AFM observations. *Mol. Simul.* **28**(6-7), 607-632.
- Bouissonnié A., Daval D., Marinoni M., Ackerer P. (2018) From mixed flow reactor to column experiments and modeling: Upscaling of calcite dissolution rate. *Chem. Geo.* **487**, 63-75.
- Carman P. C. (1937) Fluid through granular beds. *Trans. Inst. Chem. Eng.* **15**, 150-166.
- Chagneau A., Claret F., Enzmann F., Kersten M., Heck S., Madé B. and Schäfer T. (2015) Mineral precipitation-induced porosity reduction and its effect on transport parameters in diffusion-controlled porous media. *Geochem. Trans.* **16**, 13.
- Ceccarello S., Black S., Read D., Hodson M.E. (2004) Industrial radioactive barite scale: suppression of radium uptake by introduction of competing ions. *Min. Eng.*, **17**(2), 323-330.
- Cochapin B., Trotignon L., Bildstein O., Steefel C. I., Lagneau V. and van der Lee J. (2008) Approaches to modelling coupled flow and reaction in a 2D cementation experiment. *Adv. Water Resour.* **31**(12), 1540-1551.
- Class H., Ebigbo A., Helmig R., Dahle, H. K., Nordbotten J. M., Celia M. A., Aubigane P., Darcis M., Ennis-King J., Fan Y., Flemisch B., Gasda S. E., Jin M., Krug S., Labregere D., Beni A.N., Pawar R.J., Sbai A., Thomas S. G., Trenty, L. and Wei L. (2009) A benchmark study problems related to CO₂ storage in geologic formations. *Computat. Geosci.*, **13**(4), 409-434.

626 Daval D., Martinez I., Corvisier J., Findling N., Goffé B. and Guyotac F. (2009) Carbonation of Ca-
627 bearing silicates, the case of wollastonite: Experimental investigations and kinetic modelling. *Chem.*
628 *Geol.* **265**(1–2), 63-78.

629 Dove P. M. and Czank C. A. (1995) Crystal chemical controls on the dissolution kinetics of the
630 isostructural sulfates: Celestite, anglesite, and barite. *Geochim. Cosmochim. Acta* **56**(10), 4147-4156.

631 Dove P. M., Han N., De Yoreo J.S. (2005) Mechanisms of classical crystal growth theory explain
632 quartz and silicate dissolution behaviour. *PNAS* **102** (43) <https://doi.org/10.1073/pnas.0507777102>

633 Fu Y., van Berk W. and Schulz H. M. (2012) Hydrogeochemical modelling of fluid-rock interactions
634 triggered by seawater injection into oil reservoirs: Case study Miller field (UK North Sea). *Appl.*
635 *Geochem.* **27**, 1266-1277.

636 Garcia-Ruiz J.M., Otalora F. (2015) Crystal Growth in Geology: Patterns on the Rocks. Handbook
637 of Crystal Growth, Vol. II Editors: Nishinaga T., Rudolph P. Elsevier.

638 Gaucher E.C. and Blanc P. (2006) Cement/clay interaction -a review: Experiments, natural
639 analogues, and modelling. *Waste Manage.*, **26**(7), 776-788.

640 Gaus I., Azaroual M. and Czernichowski-Lauriol I. (2005) Reactive transport modelling of the
641 impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea). *Chem. Geol.*, **217**(3-4), 319–
642 337.142

643 Godinho J. R. A., Gerke K. M., Stack A. G. and Lee P. D. (2016) The dynamic nature of crystal
644 growth in pores *Sci. Rep.* **6**, 33086

645 Godinho J. R. A. and Stack A. G. (2015) Growth kinetics and morphology of barite crystals derived
646 from face-specific growth rates *Crystal Growth & Design* **15** (5), 2064-2071.

647 Hayek M., Kosakowski G. and Churakov S. (2011) Exact analytical solutions for a diffusion
648 problem coupled with a precipitation-dissolution reaction and feedback of porosity change. *Water*
649 *Resour. Res.* **47**, W07545.

650 Hayek M., Kosakowski G., Jakob A. and Churakov S. V. (2012) A class of analytical solutions for
651 multidimensional multispecies diffusive transport coupled with precipitation-dissolution reactions
652 and porosity changes. *Water Resour. Res.* **48**, W03525.

653 He S., Oddo J. E. and Tomson M. B. (1995) The nucleation kinetics of barium sulfate in NaCl
654 solutions up to 6 M and 90°C. *J. Colloid Interface Sci.* **174**, 319-326.

655 Helgeson H. C., Delany J. M, Nesbitt H. W. and Bird D. K. (1978) Summary and critique of the
656 thermodynamic properties of Rock-Forming Minerals. *Amer. J. Sci.* **278A**, 229.

657 Helgeson H. C., Murphy W. M. and Aagaard, P. (1984) Thermodynamic and kinetic constraints on
 658 reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and
 659 the hydrolysis of feldspar. *Geochim. Cosmochim. Acta* **48**(12), 2405-2432.

660 Hommel J., Coltman, E. and Class H. (2018) Porosity-permeability relations for evolving pore
 661 space: a review with a focus on (Bio-) geochemically altered porous media. *Transp. Prous Med*
 662 <https://doi.org/10.1007/s11242-018-1086-2>

663 Hummel W., Berner U., Curti E., Pearson F. J. and Thoenen T. (2002) Nagra/PSI chemical
 664 thermodynamic data base 01/01. Universal Publishers, Parkland, Florida.

665 Jung H. and Navarre-Sitchler A. (2018) Scale effect on the time dependence of mineral dissolution
 666 rates in physically heterogeneous porous media. *Geochim. Cosmochim. Acta* **234**, 70-83.

667 Jung H. and Navarre-Sitchler A. (2018) Physical heterogeneity control on effective mineral
 668 dissolution rates. *Geochim. Cosmochim. Acta* **227**, 246-263.

669 Kashchiev D. (2000) Nucleation: Basic theory with applications. Butterworth-Heinemann, Oxford.

670 Kashchiev D. and van Rosmalen G. M. (2003) Review: Nucleation in solutions revisited. *Cryst. Res.*
 671 *Technol.* **38**, 555-574.

672 Katz G.E., Berkowitz B., Guadagni A., Marteen W.S. (2011). Experimental and modeling
 673 investigation of multicomponent reactive transport in porous media. *J. Contam. Hydrol.* 27–44.

674 Klinkenberg M., Weber J., Barthel J., Vinograd V., Poonoosamy J., Kruth M., Bosbach D. and
 675 Brandt F. (2018) The solid solution–aqueous solution system (Sr,Ba,Ra)SO₄ + H₂O: A combined
 676 experimental and theoretical study of phase equilibria at Sr-rich compositions. *Chem. Geol.*,
 677 Doi:10.1016/J.CHEMGEO.2018.08.009.

678 Kosakowski G. and Watanabe N. (2014) OpenGeoSys-Gem: A numerical tool for calculating
 679 geochemical and porosity changes in saturated and partially saturated media. *Phys. Chem. Earth,*
 680 *A/B/C* **70-71**, 138-149.

681 Kosakowski G. and Berner U. (2013) The evolution of clay rock/cement interfaces in a cementitious
 682 repository for low and intermediate level radioactive waste. *Phys. Chem. Earth, X*

683 Kügler, R.T., Beißert, K., Kind, M., (2016) Heterogeneous nucleation during the precipitation of
 684 barium sulfate, *Chem. Eng. Res. and Design*, 114, 30-38

685 Kulik D. A., Wagner T., Dmytrieva S. V., Kosakowski G., Hingerl F. F., Chudnenko K. V. and
 686 Berner U. (2013) GEM-Selektor geochemical modeling package: Revised algorithm and GEMS3K
 687 numerical kernel for coupled simulation codes. *Comput. Geosci.* **17**, 1-24.

688 Mackenzie P. D., Horney D. P. and Sivavec T. M. (1999) Mineral precipitation and porosity losses
689 in granular iron columns. *J. Hazard. Mater.*, **68**(1-2), 1-17.

690 Maher K., Steefel C. I., DePaolo D. J. and Viani B. E. (2006) The mineral dissolution rate
691 conundrum: insights from reactive transport modelling of U isotopes and pore fluid chemistry in
692 marine sediments. *Geochim. Cosmochim. Acta* **70**(2), 337-363.

693 Marty N. C. M, Tournassat C., Burnol A., Giffaut E. and Gaucher E. C. (2009) Influence of reaction
694 kinetics and mesh refinement on the numerical modelling of concrete/clay interactions. *J. Hyd.* **364**,
695 58-72.

696 Molins S., Trebotich D., Steefel C. I. and Shen C. (2012) An investigation of the effect of pore scale
697 flow on average geochemical reaction rates using direct numerical simulation. *Water Resour. Res.*
698 **48**, W03527.

699 Mundhenk N., Huttenloch P., Sanjuan B., Kohl T., Steger H. and Zorn R. (2013) Corrosion and
700 scaling as interrelated phenomena in an operating geothermal power plant. *Corros. Sci.* **70**, 17-28.

701 Noiriél C., Steefel C. I., Yang L. and Bernard D. (2016) Effects of pore-scale precipitation on
702 permeability and flow. *Adv. Water Res.* **95**, 125-137

703 Noiriél C., Luquot L., Madé N., Raimbault L., Gouze P. and van der Lee J. (2009) Changes in
704 reactive surface area during limestone dissolution: An experimental and modelling study. *Chem.*
705 *Geol.* **265**(1-2), 160-170.

706 Oddo J. E. and Tomson M. B. (1994) Why scale forms and how to predict it. *SPE Prod. Facil.* **9**, 47-
707 54.

708 Peters C. A. (2009) Accessibilities of reactive minerals in consolidated sedimentary rock: An
709 imaging study of three sandstones. *Chem. Geol.* **265**(1-2), 198-208.

710 Palandri J. L. and Kharaka Y. K. (2004) A compilation of rate parameters of water mineral
711 interaction kinetics for application to geochemical modelling. U.S. Geological Survey, Menlo Park,
712 California.

713 Perko J., Mayer K. U., Kosakowski G., De Windt L., Govaerts J., Jacques D., Danyang S. and
714 Meeussen J. C. L. (2015) Decalcification of cracked cement structures. *Comput. Geosci.* **19**(3), 673-
715 693.

716 Pina C. M., Enders M. and Putnis A. (2000) The composition of solid solutions crystallising from
717 aqueous solutions: the influence of supersaturation and growth mechanisms. *Chem. Geol.* **168**, 195-
718 210.

719 Poonoosamy J., Kosakowski G., Van Loon L. R. and Mäder U. (2015) Dissolution-precipitation
720 processes in tank experiments for testing numerical models for reactive transport calculations:
721 Experiments and modelling. *J. Contam. Hydrol.* **177-178**, 1-17.

722 Poonoosamy J., Curti E., Kosakowski G., Van Loon L. R., Grolimund D. and Mäder U. (2016)
723 Barite precipitation following celestite dissolution in a porous medium: a SEM/BSE and micro
724 XRF/XRD study. *Geochim. Cosmochim. Acta.* **182**, 131-144.

725 Poonoosamy J., Wanner C., Alt Epping P., Águila J. F., Samper J., Montenegro L., Xie M., Su D.,
726 Mayer K. U., Mäder U. , Van Loon L. R. and Kosakowski G. (2018) Benchmarking of reactive
727 transport codes for 2D simulations with mineral dissolution/precipitation reactions and feedback on
728 transport parameters. *Comput. Geosci.* <https://doi.org/10.1007/s10596-018-9793-x>

729 Poonoosamy J., Westerwalbesloh C., Mohamed G., Mahrous M., Curti E., Churakov S.V.,
730 Klinkenberg M., Kohlheyer D., von Lieres E., Bosbach D., Prasianakis N.I. (2019) A microfluidic
731 experiment and pore scale modelling diagnostics for assessing mineral precipitation and dissolution
732 in confined spaces. *Chem. Geo.* **528**, <https://doi.org/10.1016/j.chemgeo.2019.07.039>

733 Prasianakis N. I, Curti E., Kosakowski G., Poonoosamy J. and Churakov S. J. (2017) Deciphering
734 pore-level precipitation mechanisms. *Scientific Reports* **7**, 13765, doi: 10.1038/s41598-017-14142-0.

735 Prieto M., Putnis A. and Fernández-Díaz L. (1993) Crystallization of solid solutions from aqueous
736 solutions in a porous medium: zoning in (Ba,Sr)SO₄. *Geol. Mag.* **130**, 289-299.

737 Prieto M. (2014) Nucleation and supersaturation in porous media (revisited). *Mineral. Mag.* **78**,
738 1437-1447.

739 Rajyaguru A., L'Hôpital E., Savoye S., Wittebroodt C., Bildstein O., Arnoux P., Detilleux V.
740 Fatnassi P., Gouze P. and Lagneau V. (2019) Experimental characterization of coupled diffusion
741 reaction mechanisms in low permeability chalk. *Chem. Geol.* **503**, 29-39.

742 Saripalli K. P., Meyer P. D., Bacon D. H. and Freedman V. L. (2001) Changes in hydrologic
743 properties of aquifer media due chemical reaction: review. *Crit. Rev. Env. Sci. Technol.* **31**(4), 311-
744 349.

745 Scislewski A. and Zuddas P. (2010) Estimation of reactive mineral surface area during water-rock
746 interaction using fluid chemical data. *Geochim. Cosmochim. Acta* **74**, 6996-7007.

747 Shao H., Dmytrieva S. V., Kolditz O., Kulik D. A., Pfingsten W. and Kosakowski G. (2009)
748 Modeling reactive transport in non-ideal aqueous-solid solution system. *Appl. Geochem.* **24**, 1287-
749 1300.

750 Singurindy O. and Berkowitz B. (2003) Evolution of hydraulic conductivity by precipitation and
751 dissolution in carbonate rocks. *Water Resour. Res.* **39**, WE001055.

- 752 Stack A. G. (2015) Precipitation in pores: A geochemical frontier. *Rev. Mineral. Geochem.* **80**, 165-
753 190.
- 754 Sunagawa I. (1999) Growth and morphology of crystals. *Forma* **14**, 147-166.
- 755 Tartakowsky A.M., Redden G., Lichtner P.C., Scheibe T.D., Meakin P., (2008) Mixing-induced
756 precipitation: experimental study and multiscale numerical analysis. *Water Resour. Res.* **44**, 1–19.
- 757 van der Lee, J. and De Windt, L., (2002) CHESS Tutorial and Cookbook. Updated for version 3.0.,
758 Manual Nr. LHM/RD/02/13, ParisFontainebleau, France: Ecole des Mines-116 pp.
- 759 Vankeuren A. N. P., Hakala J. A., Jarvis K. and Moore J. E. (2017) Mineral reactions in scale gas
760 reservoirs: barite scale formation from reusing produced water as hydraulic fracturing fluid. *Environ.*
761 *Sci. Technol.* **51**, 9391-9402.
- 762 Vengosh A., Jackson R. B., Warner N., Darrah T. H., Kondash A. (2014) A critical review of the
763 risks to water resources from unconventional shale gas development and hydraulic fracturing in the
764 United States. *Environ. Sci. Technol.* **48**(15), 8334-8348.
- 765 Verma A. and Pruess K. (1988) Thermohydrological conditions and silica redistribution near high
766 level nuclear waste emplaced in saturated geological formation. *J. Geophys. Res.* **93**, 1159-1173.
- 767 Vinograd V. L., Kulik D. A., Brandt F., Klinkenberg M., Weber J., Winkler B. and Bosbach D.
768 (2018). Thermodynamics of the solid solution - Aqueous solution system (Ba,Sr,Ra)SO₄ + H₂O: I.
769 The effect of strontium content on radium uptake by barite. *Appl. Geochem.* **89**, 59-74.
770 <https://doi.org/10.1016/j.apgeochem.2017.11.009>
- 771 Wagner T., Kulik D. A., Hingerl F. F. and Dmytrieva S. V. (2012) GEM-Selektor geochemical
772 modeling package: TSolMod C++ class library and data interface for multicomponent phase models.
773 *Can. Mineral.* **50**, 1173-1195.
- 774 Wen H., Li L.,(2017) An upscaled rate law for magnesite dissolution in heterogeneous porous
775 media. *Geochim. Cosmochim. Acta* **210**, 289-305.
- 776 De Yoreo JJ, Vekilov PJ. (2003) Principles of crystal nucleation and growth. *Reviews in mineralogy*
777 *and geochemistry*, **54** (1), 57-93
- 778 Xie M., Mayer K. U., Claret F., Alt-Epping P., Jacques D., Steefel C., Chiaberge C. and Šimůnek J.
779 (2015) Implementation and evaluation of permeability-porosity and tortuosity-porosity relationships
780 linked to mineral dissolution-precipitation. *Comput. Geosci.* **19**(3), 655-671.
- 781 Zhen-Wu B.Y, Dideriksen K., Dideriksen K., Olsson J., Raahauge P.J, Stipp S.L.S, Oelkers E.H.,
782 (2016) Experimental determination of barite dissolution and precipitation rates as function of
783 temperature and aqueous fluid composition. *Geochim. Cosmochim. Acta* **194**, 193-210.

784 Zhu C. (2004) Coprecipitation in the barite isostructural family: 1. Binary mixing properties.
785 *Geochim. Cosmochim. Acta* **68**, 3327-3337.
786

Fig. 1: Schematic representation of the setup of the column experiments.

Fig. 2. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 1 (100mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

Fig. 3. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 2 (10mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

Fig. 4. (a) Experimental and modelled breakthrough curves, and (b) temporal evolution of the total bulk mineral amount for experiment 3 (1mM BaCl₂). Solid and dashed lines in (a) and (b) are simulated aqueous concentrations and amounts of mineral phases in the system according to reactive surface area model 1 and 2, respectively.

Fig. 5: EDS maps of the upstream (a, c, f, and h) and downstream interfaces (b, e, and g) of the reactive zone for experiments 1, 2, 3 and the control. Dark blue: Si indicating the quartz sand,

light blue: Ba indicating Ba-rich phases, yellow: Sr indicating celestine. For experiment 2, the main precipitation of Ba-rich phase occurs in the middle of the reactive zone at 0.1755 m (d).

Fig. 6. SEM-BSE image of reacted celestine grains from experiment 1. (a), (b), (c) shows the surface roughness of the newly formed precipitate. In (b), the arrow points towards the unreacted celestine under the (brighter) barite crust.

Fig. 7. SEM-BSE image of the reacted celestite grains from experiment 2. (a) shows celestine particles (arrows) covered with a barite crust at the upstream region, (b) and (c) are samples collected at the interface of the unreacted celestine where barite precipitated on the cleaved surfaces. The brightness correlates to the Ba concentration in the solid.

Fig. 8. SEM-BSE image of the reacted grains from experiment 3. (a) in the upstream Q1 interface, (b) is the newly Ba-rich phase and (c) crystals at the interface of the dissolution/precipitation front.

Fig. 9: Evolution of permeability with time for the complete column (k_{tot}) (a) and for the Q1 region (k_{Q1}) (b). The permeability of the control experiment was monitored for 325 hours. For the simulation of the permeability change of the Q1 region in experiment 1, the reactive surface area model 2 and the [Verma and Pruess \(1988\)](#) porosity-permeability relationship were used.

Fig. 10: Permeability versus porosity changes according to variants of the Kozeny Carman equation (equations 3 and 4 as used in numerical models) compared to experimental data points and a fitted law following [Verma and Pruess \(1988\)](#). The experimental datasets are the porosity and respective permeability of the reaction zones (Table 2).

Fig. 11. Simulated fractions of precipitated phases (pure barite in experiment 1 and 2, and solid

solution in experiment 3) and remaining celestine solids in the Q1 region after 500 hours ((a), (b), (c) refer to experiments 1, 2, and 3, respectively according to reactive surface area model 1 on the left and model 2 on the right). The experimental molar fractions of Sr and Ba in the system, estimated from the respective areas of the EDS maps reported in Fig. 5, are presented here for qualitative comparison.

Fig. 12. Simulated composition of the solid solution that precipitated across the Q1 region in experiment 3 according to reactive surface area model 1 at (a) 100 and (b) 500 hours.

Fig. 13. Simulated (a) porosity and (b) permeability across the Q1 region after 500 hours for experiments 1 (reactive surface area model 2), 2 (reactive surface area model 2) and 3 (reactive surface area model 1) following a variant of the Kozeny-Carman equation (eq. 4).

Fig. 14: Effect of $\log(\Omega)$ with respect to nucleation rate (number of BaSO_4 nuclei per unit volume and time) and amount of barite overgrowth on celestine grains. At high supersaturation, barite overgrowth covers completely the individual celestine grains, decreasing their reactivity, whereas at low supersaturation only parts of the celestine grains are covered, enabling further dissolution of the grains.