Hydrogeology
&
Geochemistry

Effect of Stoichiometry on the Formation of Iron Sulphide (FeS) and Reduction of Permeability in a Porous Medium

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Introduction

- Precipitation of iron(II) sulphide (FeS) is related to various geoengineered processes like geothermal systems (1). It can form scale in the pipelines resulting in clogging and reduced efficiency (2).
- In nature, the concentrations of these ions can diverge strongly, which might influence the nucleation and growth of FeS. This can be amplified in a porous medium, where the concentration of anions and cations can strongly differ between pores.

Objective

- This study uses microfluidic models (PDMS-based), pressure measurements and RAMAN spectrometry to answer the following question:
- What is the interplay between FeS formation, stoichiometry, oxidation effects and flow through porous media? And can we visualize the development over time?

Methodology

- Two different solutions, Fe^{2+}-solution (dissolved $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$) and S^{2-}-solution (dissolved $Na_2S \cdot 9H_2O$) with three stoichiometric ratios: R = 1, R = 6.25 (Fe^{2+}-excess) and R = 0.16 (S^{2-}-excess) were used.

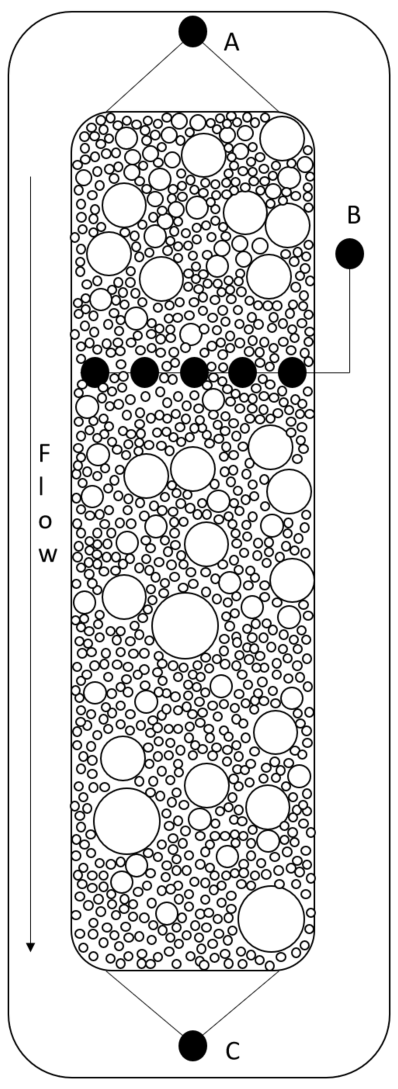

Figure 1: Simplified design of the used microfluidic models

- The Fe^{2+}-solution was injected through inlet A and the S^{2-}-solution into B (both at a flowrate of 0,01 µL/s)(Figure 1).
- An overview picture with Keyence 5000 Digital Microscope, to identify the clogging spots, and ΔP measurements with Elveflow Microfluidic Flow Controller (OB1 MK4) before the injection started (t_0), after 1.5 h (t_1), 3 h (t_2) and 4.5 h (t_3)
- The ΔP was used to calculate the relative permeability using Darcy's law.

Table 1: Moles Mohr's salt and Sodium sulphide in the solutions with different stoichiometries

Ratio	Added moles of $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$	Added moles of $Na_2S \cdot 9H_2O$	Added acid/base for pH correction
1	8 mM	8 mM	-
6.25	50 mM	8 mM	30 mM NaOH
0.16	8 mM	50 mM	50 mM HCl

Results & Discussion

- The precipitation in Figure 2 A was dominant in Fe < S experiments.
- The precipitation in Figure 2 B, C and D was dominant in Fe = S and Fe > S experiments.
- The relationship between time and permeability decrease is visualized in Figure 3A - C for the different stochiometric ratios.
- Over time, the material turned more yellow-brown. This happened to a lesser degree in experiments with R = 0.16, suggesting that the brown material is an iron oxide, which agreed with RAMAN analysis.
- The permeability values from R = 0.16 experiment differed from the rest. This difference can be explained by two effects, both related to the particle surface charge (ζ).
  - Firstly, the particles become more negatively charged when there is excess of S^{2-} (3). This makes the particles more stable, preferring nucleation over crystal growth (3 & 5).
  - Secondly, the particle surface charge of PDMS is also negative (4). The particles with a more negative surface energy, experience stronger repulsive forces making sticking less likely, resulting in less clogging.

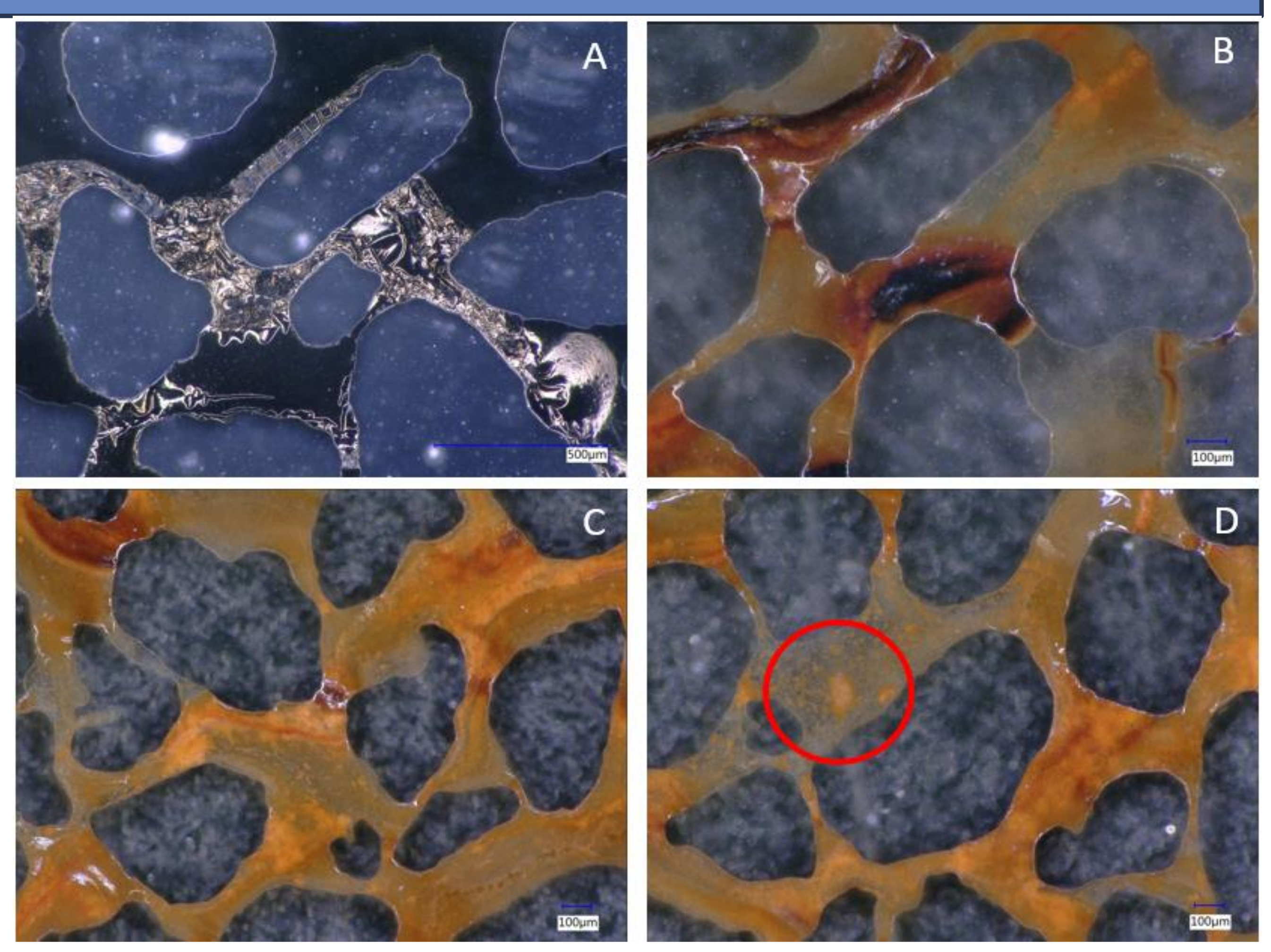

Figure 2A-D: The observed precipitation phases within the microfluidic models at different locations. All pictures were taken after 4.5 hours of injection had passed (A) precipitation photographed in a microfluidic model after 4.5 hour with an excess of sulphide. (B & C) Precipitation photographed from a microfluidic model after 4.5-hour experiment with R = 1. (D) In the red circle precipitation that was observed during an Fe > S experiment.

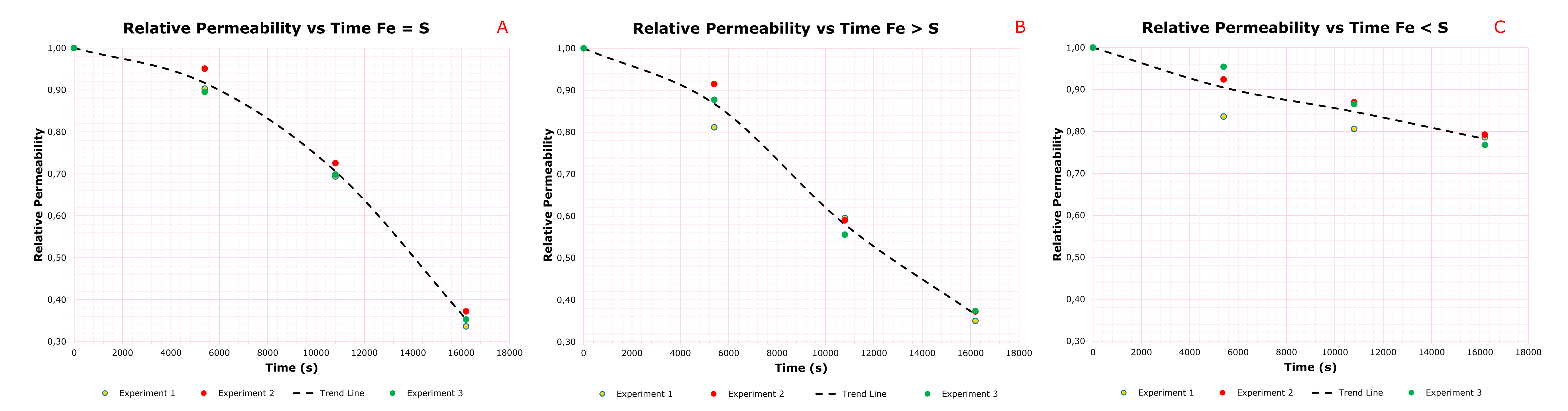

Figure 3: The relative permeability drop over a period of 4.5 hours of injection in a microfluidic model. An Fe-containing solution and S-containing solution flowed through the model resulting in precipitated material that clogged pore throats. (A), a stochiometric ratio of 1 resulting in a progressive decline from t_0 to t_3. (B), a stochiometric ratio of 6.25 resulting in linear decline over time. (C), a stoichiometric ratio of 0.16 ensuing a relative permeability decrease of roughly 20% over a period of 4.5 hour.

Take-Home Message

With increasing anions (S^{2-}) concentration relative to cations (Fe^{2+}) concentration, the particle size decreases (3). Less precipitated material stays within model due to the preference of nucleation over growth and increasing repulsive forces, resulting in a considerable amount of material being flushed out. This ensues a less significant permeability decrease over time.

References:

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