

Experimental and numerical investigation of focused flow through porous media due to mineralization

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The chemical input to the world's oceans from subsurface microbial biofilms in mid-ocean ridge hydrothermal systems has been difficult to quantify due to their inaccessibility. Results from experiments in a novel flow-through experimental apparatus using non-invasive monitoring of mixing via infrared imaging coupled to a 2D solute transport model allows the evaluation of changes in permeability, hydraulic conductivity and flow velocity during mixing of two end-member fluids within porous media. Initial Tests were conducted using instantaneous precipitation of amorphous Fe(III) oxyhydroxide upon mixing NaOH (1.2M) with FeCl₃ (0.4M) at the range of temperatures tested (25 to 40°C), according to the reaction:



Results indicate clear alteration of fluid flow vectors after 4.3 minutes of mixing, corresponding to the precipitation of 0.059 g FeOOH and a reduction in bulk porosity of 11.6% over only 35% of the flow cell. The NaOH solution was subsequently focused through a high permeability zone at double the starting velocity as Fe(III) precipitation increasingly blocked flow until complete blockage of all fluid outflow due to mineral precipitation occurred at 8 minutes. The corresponding bulk chemistry of the outflow changed from complete titration of the NaOH solution initially, to an excess of 9.56 mM/s in the outflow at the time of clogging as the availability of FeCl₃ becomes limiting. This technique successfully quantifies mm-scale changes in permeability due to amorphous FeOOH, a biofilm analogue, allowing non-invasive monitoring in real-time on spatial scales relevant to microbial biofilms.

F,Cl-rich mineral assemblages from burned spoil-heaps in the Rosice-Oslavany coalfield, Czech Republic

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Unusual Si-Al deficient and F,Cl-rich oxide-sulphosilicate-sulphate mineralization was found on burned spoil-heaps at Oslavany and Zastávka in the Rosice-Oslavany coalfield, Czech Republic. The assemblage typically forms irregular, zoned nodules ~5–15 cm in size enclosed in the common pyrometamorphic material of the piles, i.e. hematite-rich clasts, paralavas and clinkers. Their cores are usually formed by fine-grained mixture of gypsum and brucite with relics of anhydrite and periclase, respectively; locally, portlandite was found. The cores are rimmed by (or intersected by veinlets of) dark gray aggregates of medium- to fine-grained mixture of gypsum, anhydrite, Mn-rich srebrodolskite ($X_{\text{Mn}} \sim 0.4$), magnesioferrite, unnamed Ca₄(Mn,Fe)₂O₇, and F,Cl-rich silicates that commonly replace anhydrite and gypsum. Prevailing F,Cl-rich minerals are fluorellestadite and Cl-rich hydroxyllellstadite ($X_{\text{Cl}} \leq 0.25$). Rarely, inclusions of subhedral crystals of Fe,Si,Cl-rich mayenite (≤ 3.2 apfu Fe³⁺, ≤ 2.2 apfu Si, ≤ 4.6 apfu F+Cl) were found in ellestadite at both localities; in Oslavany, it is associated with cuspidine. In Zastávka, assemblage with fluorite and F,Cl-rich Ca-silicates (rondorfite and kumtyubeite replaced by ellestadite and bultfontainite / cuspidine-like mineral) was rarely encountered. Surface and cavities of the nodules are sometimes covered by Mg-sulfates (epsomite-kieserite) and needles of gypsum. The observed oxide-sulfosilicate-sulfate assemblage is a high-grade pyrometamorphic product of the original dolomite-anhydrite-gypsum protolith, at $T_{\text{min}} > 800^\circ\text{C}$. The most probable source of F is a thermal decomposition of fluorite and micas while chlorine was most probably released from the organic matter.

Burning spoil-heaps in the Rosice-Oslavany coalfield are characterized by high-grade pyrometamorphism followed by multi-stage mineral assemblages formed at lower temperature [1]. Similar oxide-sulfosilicate-sulphate assemblages were rarely found in nature e.g. in marble xenoliths in ignimbrites [2] or tephrites [3], and also on burning coal spoil-heaps [4].

[1] Dokoupilová *et al.* (2007) *Min Mag* **71**, 443-460.

[2] Galuskina *et al.* (2009) *Am Mineralogist* **94**, 1361-1370.

[3] Baumgärtl and Cruse (2007) *Aufschluss* **58**, 257-400. [4]

Sharygin (2010) *Proc. ICCFR (Berlin)* 162-170.