The effect of oxidizing agents and surfactants on chalk recrystallization

A. JOHNSSON[1]*, D. BELOVA[1,3], L.Z. LAKSHTANOV[2] AND S.L.S. STIPP[1]

[1]Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (aj@nano.ku.dk)
[2]Institute of Experimental Mineralogy RAS, Chernogolovka, Russia (leonid@iem.ac.ru)
[3]Institute of Geology, KRC of RAS, Petrozavodsk, Russia.

Coccoliths are preserved in chalk, presumably because some component in biogenic calcite inhibits recrystallisation. We treated chalk with oxidizing agents and surfactants to test if changing surface composition would alter recrystallisation rates. Maastrichtian chalk samples of nearly pure calcite were treated with 0.1% solutions of the surfactants SDBS, Triton and CTAB, in 0.1 M Tris buffer and 1:1 basic, oxidising solutions of 12% NaOCl:1 M NaOH, 3% H_2O_2:1 M NaOH. After treatment, we monitored reaction in calcite-equilibrated solutions with pH=8.3, I=0.1 M NaCl. Recrystallization rates were derived from uptake of $^{14}CO_3^{2-}$ tracer where solid/liquid was 50 g/L and experiments lasted ~ 3 months.

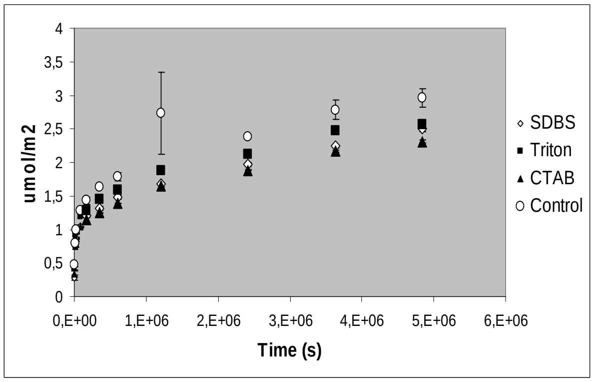

Figure 1. Formation of calcite in surfactant-treated chalk.

The mass of newly formed calcite was derived from a formula modified from Curti *et al.* [1]. Fig. 1 shows recrystallized calcite normalised by surface area as a function of time for surfactant-treated samples. Rates of recrystallization were $3x10^{-13}$ and $4x10^{-13}$ moles m^{-2} s^{-1} in the surfactant and oxidizing experiments. Neither surfactants nor oxidizing agents increased the rate of chalk recrystallization, indicating that the compound(s) that define the difference between biogenic and inorganically produced calcite, are not solubilised by a surfactant nor removed by oxidation.

[1] Curti *et al.* (2005) *Geochim. Cosmochim. A.* **69**, 1721-37

In situ removal of arsenic: Column studies

RICHARD B JOHNSTON[1]* AND PHILIP C. SINGER[2]

[1]EAWAG,8600- Dübendorf, Switzerland
(*correspondence: Rick.Johnston@eawag.ch)
[2]University of North Carolina at Chapel Hill
(psinger@email.unc.edu)

In situ treatment

By injecting aerated water into an aquifer which contains elevated levels of dissolved Fe(II), localized oxidizing conditions can be created. Fe(II) is then oxidized *in situ*, creating fresh ferric surfaces which can subsequently adsorb Fe(II), allowing low-Fe water to be abstracted for some time. A series of column experiments using goethite-coated sand were conducted to simulate this process, and to determine if *in situ* treatment could simultaneously remove Fe(II) and As(III). Retardation factors for O_2, Fe(II), and As(III) were estimated by measuring the number of pore volumes at which 50% breakthrough occurred. Experiments were conducted at pH 7.0, 7.5, and 8.0, and simulated using a geochemical model.

Results and Discussion

The observed retardation of oxygen, iron and arsenic was in good agreement with theory.

Iron retardation during abstraction phases increased with increasing pH, and matched stoichiometric mass balance calculations from oxygen retardation during injection phases. Duplicate columns showed good agreement. Geochemical modeling predicts that retardation factors should increase with increasing treatment cycle numbers, as sediments become increasingly coated with fresh ferric surfaces. This 'ripening effect' was observed at pH 8.0 only.

Arsenic retardation showed less pH dependence, and a ripening effect was seen at pH 8.0 only. However, substantial retardation was consistently noted the first time Fe(II) and As(III) were co-injected on the column; this is interpreted as a electrochemical effect, as adsorbed Fe(II) increases the surface potential. This effect did not persist in subsequent cycles, indicating that the product of Fe(II) oxidation is different from the goethite originally present.

Mass balance calculations, as well as independent batch experiments, indicate that goethite has a substantially higher capacity for Fe(II) than for As(III).

These experiments suggest that *in situ* treatment is a promising approach for obtaining safe drinking water from aquifers containing elevated levels of dissolved arsenic and iron.