

Siderite dissolution used for lead and copper remediation

Füllenbach, L. C.^{a*}, Oelkers, E. H.^a

^aUniversity College London, London WC1E 6BT, UK (*l.fuellenbach@ucl.ac.uk, eric.oelkers@ucl.ac.uk)

Heavy metal contamination of soils and aquifers can be treated at neutral pH conditions using iron phases, which bind and therefore immobilize the contaminants. The iron hydroxides that sequester the contaminants, however, become unstable in more acidic environments and hence prone to release the heavy metals. The naturally abundant ferrous iron carbonate siderite (FeCO_3) is therefore a promising mineral for *in situ* remediation efforts: it dissolves in acidic environments but concurrently undergoes oxidation to form iron hydroxides that sequester metals, thereby generating alkalinity which facilitates metal removal and stabilizes the precipitated iron hydroxides. Siderite is readily available in peat bogs, but also occurs in many subsurface reservoirs that are of interest for CO_2 sequestration. Therefore, siderite could also allow for immediate remediation of heavy metals that may be released during CO_2 driven mineral dissolution in the subsurface CO_2 injection. In this study we investigate the efficacy of simultaneous siderite dissolution and Fe(III)-hydroxide precipitation for *in situ* Pb and Cu immobilization from acidic aqueous solutions imitating such waste waters.

Short-term (6-12 h) and long-term (336h) batch experiments conducted at ambient laboratory conditions show that the surficial dissolution of siderite leads to an increase in pH from 3.1 to 4.8, and initiates nano-particulate iron hydroxide formation on the surface of the siderite grains as well as in suspension. Key factors in the uptake of Pb and Cu from the acidic aqueous solution were revealed to be the solid to fluid ratio, siderite surface area, and time. An increased amount of heavy metal was removed from aqueous solution with higher solid to liquid ratio (up to 6 g/L), while no significant difference in rates of heavy metal removal was observed from differences in initial heavy metal concentrations (0.24 – 0.48 mmol/L Pb, 0.79 – 1.6 mmol/L Cu). A higher surface area of siderite grains of < 63 μm in size is preferential to that of grains > 63 μm , as it provides a higher overall reaction rate. Lead and copper removal from solution commenced immediately subsequent to siderite immersion and continued gradually over time. The release of ferrous iron into solution from siderite dissolution slowed over time, but iron hydroxide formation visibly increased with time, suggesting that the rate of iron hydroxide precipitation resembles the rate of siderite dissolution. Secondary Fe phase precipitation – represented by the decrease of Fe in solution – is most pronounced and occurred most rapidly in Pb bearing solutions from which Fe concentration dropped down from 8.5 to 0.2 mg/kg. In comparison, 2.2 mg/kg Fe was still present in Cu containing solutions after 336 hours. Over time, the initial concentrations of Pb and Cu in solution gradually decreased by 47.1 % and 38.6%, respectively. From a batch experiment with a solution containing both Pb and Cu, no preference was observed for one metal over the other. Although Pb was detected on the siderite grains covered with surficial nano-particulate precipitates by X-ray fluorescence mapping, the type of bonding of the metal(s) needs to be determined.

Owing to the precipitation of nano-scale Fe-hydroxide particles during siderite dissolution, which are known to be highly reactive and have great potential for adsorption of Pb, Cu and other heavy metals, we propose that very fine-grained siderite may offer a promising low-cost material for *in situ* remediation of acidic contamination plumes.