Biogeochemical redox cycling in hyper alkaline sediment-water systems.

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There is currently a lot of scientific interest in understanding bacterial processes at highly elevated pH. Research has been driven by fundamental curiosity about the how life can thrive in extreme environments, and also by a need to understand how contaminants are affected by biogeochemical cycling in alkaline cementitious wastes (e.g. at nuclear waste repositories). The Hoffman lime kiln contrusted at Harper Hill in Derbyshire by the Buxton Lime Company was biggest of its type and was in operation continuously, 24/7, from 1872 until it was closed in 1944. (The kiln was demolished in 1980 to make way for an industrial estate.)



Limestone-roasting for the alkali-carbonate industry on this site produced huge volumes of alkaligenerating waste. This was deposited into a valley to the north west of the kiln, and groundwater in contact with this waste has become saturated in Ca-, Na-, and K- hydroxides and is high alkaline (pH 12-13.5 - very similar in fact to a young cement porewater composition).



A groundwater spring flows northwards out of the waste filling the entire valley with pH 12-13.5 leachate. This leachate has reacted rapidly with atmospheric  $CO_2$  producing a large thickness of a custard-like carbonate precipitate that today is actively infilling the entire valley. Although unsightly and a considerate physical hazard, the leachate has greatest biogeochemical impact by completely altering the soil environment beneath the carbonate precipitate.



In summer 2009, we collected a short core through the carbonate precipitate into the highly altered peat soils below. Porewater and solid phase analysis of this core found that, despite finding pH above 12, a vertical redox profile consistent with a normal succession of terminal electron accepting processes, such as nitrate and iron(III) reduction, was found. Bacterial consortia collected from the site were also found to be able to respire and grow *in vitro* using Fe(III) as the only electron acceptor in pH 9 media, providing further evidence of the presence of a community of alkaliphile bacteria on site.



9 10 11 12 13 14 0 pH	0 50 100 150 200 0 Nitrate (aq) μΜ	0 100 200 300 0 Nitrite (aq) (μM)	0 20 40 60 80 100 • % Fe(II) Solids	
5 -		5	5	
15 - 20 -	15 - 20 -	20 -	20 -	
25 - 30 -	30	25 - 30 -	25 - 30 - Soil L	ayer
35 - 40	40	35 <b>4</b> 0	35 - 40	

The MSc project plan is to return to this site and deploy gel probes into the carbonate precipitate and soil profile in order to better determine the pore water geochemistry with higher resolution sampling and to quantify the *in situ* rates of terminal electron accepting processes by measuring the rates of accumulation of redox active species in gels. This data will be linked to culture based analysis of the vertical distribution of different groups of alkaliphile bacteria in core samples. The results produced will show if active biogeochemical redox cycling is occurring on site and how elevated pH impacts on the rates of terminal electron accepting processes within these soils.