

Remediation scenarios at UK nuclear legacy sites

C.L. Thorpe, G.W.T. Law, J.R. Lloyd and K. Morris
Research Centre for Radwaste Disposal, University of Manchester
(correspondence: katherine.morris@manchester.ac.uk)

ABSTRACT

This project concerns the ongoing remediation of UK nuclear legacy sites with particular focus on in situ remediation strategies. Microcosm based studies have been used to investigate the effectiveness of bioremediation approaches such as bio-stimulation whereby an electron donor is added to the subsurface to stimulate bioreduction. Here microbial action changes the geochemistry of sediments leading to a favorable change in radionuclide speciation. Redox active radionuclides can be reduced down to their less soluble form however the system is complicated by the presence of non-redox active radioactive contaminants such as Sr-90 and the presence of key non-radioactive contaminants such as nitrate.

This report presents the findings of two investigations, the first into the effect of nitrate on bioreduction scenarios. Here the presence of nitrate during bioreduction scenarios is investigated and shown not to inhibit progression to radionuclide reducing conditions. Some beneficial effects are observed. In the second investigation the behavior of key non redox active radionuclide Sr-90 during bioreduction. It was observed that the presence of moderate nitrate concentrations 10-100 mM in the sediment can also benefit the removal of Sr-90 from solution. These effects are attributed to a rise in pH observed during nitrate reduction that increased the sorption and precipitation of Sr-90 as carbonate mineral phases. The microbiology, mineralogy and geochemistry of sediment microcosms are investigated in this multidisciplinary project.

INVESTIGATION 1

INTRODUCTION

Radioactively contaminated land is characterised by high nitrate (10-100 mM) and at a key UK site, Sellafield, the sediment pH ranges from mildly acidic (pH 5.5) to alkaline (pH>9). These present challenging conditions for bioremediation approaches whereby an electron donor is added to the sub-surface to stimulate bioreduction. Here, sediment microcosms were used to study the influence of high nitrate on the in-situ microbial community and progression of terminal electron accepting processes (TEAPs) in sediments representative of the Sellafield site.

RESULTS

Rates of bioreduction at low pH (5.5) were found to be inhibited initially compared to bicarbonate-amended microcosms (pH 6.8). However, the presence of nitrate apparently enhanced bioreduction in the mildly acidic sediments by the production of OH⁻ and HCO₃⁻ ions during microbially mediated denitrification. For sediment microcosms with initial pH 5.5 and with nitrate amendments between 0.3 and 10 mM the pH rose

to pH 6.8 and 7.5 respectively. In both systems, after pH modification a subsequent increase in the rate TEAPs was observed. In the very high nitrate microcosms initially buffered to pH 6.8-7.0 by bicarbonate addition to the groundwater prior to sediment incubation, the pH rose to 9.5 and Fe(III)-reduction then proceeded.

To further characterise the biogeochemistry of key microcosms, 16SrRNA analysis was performed. Low nitrate (0.3mM) sediments showed a diverse range of microorganisms whilst after incubation with 10mM nitrate there was a community shift to Bacilli and in the high pH system with 100mM nitrate Bacilli and Alphaproteobacteria made up >95% of the clone library. This shift is likely due to the dominance of denitrification in this treatment. Further sub-culturing work isolated novel microorganisms responsible for Fe(III)-reduction at pH 9.5 and 16SrRNA analysis showed *Serratia liquifaciens* and *alkaliphilus* made up 98% of the subculture clone library.

XRD indicated that the Fe-carbonate phase siderite was the dominant product of microbial Fe(III) reduction at pH 7 and pH 9.5. Sequential extractions on sediment microcosms and

PHREEQC modelling of these systems determined that Fe-carbonate phases were the likely products of Fe(III) reduction at pH in sediment microcosms.

CONCLUSIONS

This study indicates that whilst high nitrate can initially inhibit TEAPs, denitrification can benefit bioreduction treatments via the production of OH⁻ and bicarbonate. In mildly acidic sediment this can increase microbial activity and promote mineral precipitation. This study shows that metal reduction in these sediments is not inhibited by the alkaline pH (<9) resulting from high nitrate scenarios.

INVESTIGATION 2

INTRODUCTION

Sr-90 and Tc-99 are problematic radionuclides that can be found together as groundwater contaminants at nuclear legacy sites. Tc-99 is a redox active radionuclide which can be removed from solution via biotransformation to poorly soluble Tc(IV)₁, whereas Sr-90 occurs as the Sr²⁺ ion and its mobility is controlled by sorption and precipitation reactions_{2,3}. Thus, the differing geochemistry of these two key contaminants provides a challenge for the remediation of nuclear sites.

At Sellafield, Cumbria, UK, Sr-90 and Tc-99 are both contaminants in groundwaters₄. One scenario considered for remediation of Tc-99 at nuclear facilities is bioreduction₅. Here, the in-situ microbial community is stimulated with an electron donor and a cascade of terminal electron accepting processes is established, a process known as "bioreduction". Previous work shows Tc-99 is removed from solution concurrent with Fe(III)-reduction usually via reductive precipitation to Tc(IV).

Sr-90 can be removed from solution by precipitation as strontium carbonate or inclusion in Fe or Ca carbonate minerals as the pH increases in the presence of carbonate species₃. The optimum pH both for Sr sorption to mineral surfaces and for precipitation has been shown to be pH > 8_{2,3} whilst background groundwaters at the Sellafield site are mildly acidic with pH of ~ 6₆. Research from our group into bio-reduction in high nitrate sediments has revealed a rise in pH concurrent with de-nitrification and attributed to the production of OH⁻ and HCO₃⁻. Bicarbonate production and increased pH has been shown to lead to the precipitation of carbonate minerals and may provide a mechanism for the removal of Sr-90 from solution₃. Furthermore the microbial community has been shown to be capable of Fe(III)-reduction above pH 9 potentially providing an additional mechanism for Tc reduction and removal from solution. Results from a series of

bioreduction experiments exploring these processes in representative Sellafield sediments will be presented.

RESULTS

Preliminary results show removal of Sr from pore waters as bioreduction takes place. This has been observed to coincide with an increase in pH. Figure 1 shows a typical bioreduction scenario where a cascade of terminal electron accepting processes is observed over a period of 60 days. Cations Sr and Ca are shown to be removed from solution compared to a sterile control in which no change in geochemistry was observed. Also observed was an increase in carbonate in solution during and after nitrate reduction. CO₃²⁻ and HCO₃⁻ are produced during nitrate and Fe reduction.

At the point of submission experiments with pure mineral systems are underway to further understand the role of Fe(III)-Fe(II) mineral transformations in Sr removal from solution. Further work is planned to investigate how the Sr is bound in the solid phase and the effect of sediment reoxidation on the removed strontium.

Further experiments will determine whether the observed retention of Sr in the solid phase is due to increased sorption to sediment minerals with increasing pH or precipitation as carbonate mineral phases. It is likely that both play a part. Of particular interest is the role that microbial action and reduction of Fe minerals play in strontium geochemistry.

REFERENCES

- 1 Morris K., Livens F.R., Charnock J.M., Burke I.T., McBeth J.M., Begg J.D., Boothman C., Lloyd J.R.
- 2 An X-ray absorption study of the fate of technetium in reduced and reoxidised sediments and mineral phases. *Applied Geochemistry*, **2008**, 23, 603- 617.
- 3 Langley S, Gault A. G., Ibrahim A., Takahashi Y., Renaud R., Fortin D., Clark I. D. and Ferris F. G., Sorption of Strontium onto Bacteriogenic Iron Oxides. *Environmental Science and Technology*, **2009**, 43: 1008-1014.
- 4 Roden E. E., Leonardo M. R. and Ferris F. G., Immobilization of strontium during iron biomineralization coupled to dissimilatory hydrous ferric oxide reduction. *Geochimica et Cosmochimica Acta*, **2002**, 66, 16, 2823–2839.
- 5 BNFL, SCLS Phase 1- conceptual model of contamination below ground at sellafield. Nuclear sciences and technology services, **2003**, 47.
- 6 NABIR, US department of Energy/Office of science, Environmental remediation science division.

Available: <http://www.lbl.gov/NABIRarchive/index.html>, Accessed 05 March 2010.

7 Wilson P.D. The nuclear fuel cycle from ore to waste. Oxford Science Publications. OUP, 1996.

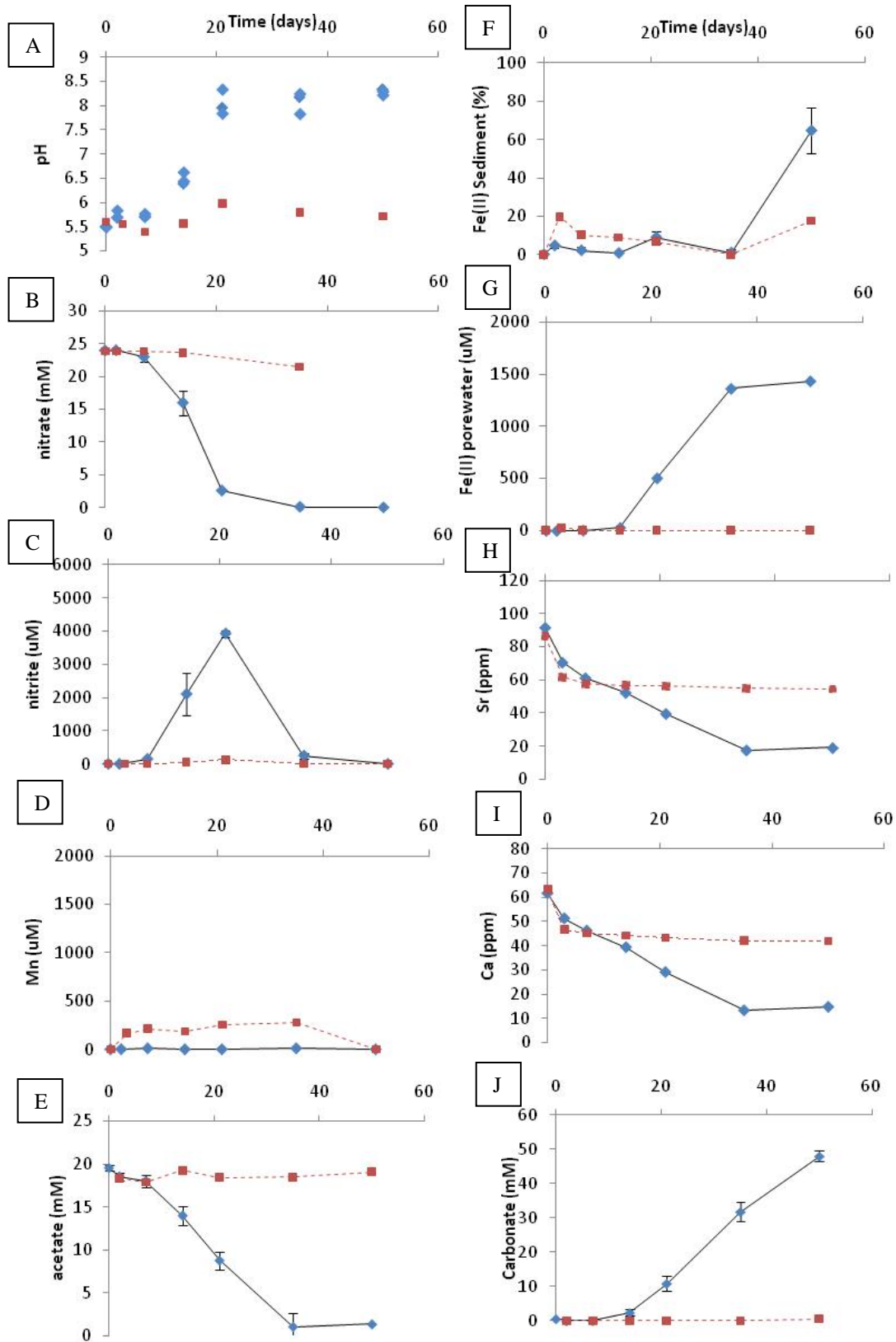


Figure 1 A typical bioreduction scenario showing the concentration of key chemical species in solution over time. A) pH, B) Nitrate, C) Nitrite, D) Mn, E) acetate, F) % Fe(II) ingrowth into sediments, G) Fe(II), H) Strontium, I) Calcium and J) Carbonate (HCO_3^-). As 10mM nitrate is reduced the pH increases, nitrite appears transiently, followed by Fe in sediment and porewaters. Concentrations of Sr and Ca in solution decrease during bioreduction.