DIAMOND'10 Conference
Decommissioning, Immobilisation and Management of Nuclear Waste for Disposal
15-16 December 2010
Manchester, UK

An investigation of the environmental mobility and transport of technetium-99 in porous media

C.L. Corkhill, S.A. Banwart and M. Romero-González
Cell-Mineral Research Centre, Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield
(correspondence: c.corkhill@sheffield.ac.uk)

ABSTRACT
In this paper, we outline the objectives for a two year study into the environmental mobility and transport of technetium-99. Technetium-99 is a problematic nuclear waste form with a long half life (2.1 x 10^5 years) and high environmental mobility in its oxidised pertechnetate ($Tc(VII)O_4$) form. The focus of the planned investigation is on the mobility of ^{99}Tc in a variety of porous media under varying geochemical conditions. It will include experimental batch studies of ^{99}Tc and parallel flow-cell studies using ^{99m}Tc, an isomer state of ^{99}Tc commonly used in medical imaging applications, imaged by a γ camera to provide non-invasive quantitative modelling of technetium-99 transport. This will enable direct measurement of techentium-99 transport and will contribute to the understanding of ^{99}Tc behaviour in the environment.

INTRODUCTION
Technetium-99 is a β-emitting radioactive fission product of ^{235}U, formed in nuclear reactors. It is a problematic component of waste from the nuclear fuel cycle due to its long half-life (2.1 x10^5 years) and high environmental mobility. In its oxidised form, the pertechnetate ($Tc(VII)O_4$) anion is highly mobile and its biological and geochemical behaviour presents a major challenge to nuclear waste disposal strategies. The redox chemistry of ^{99}Tc is crucial in governing its mobility. It has been shown that ^{99}Tc can be removed from aqueous solution via the reduction of pertechnetate to the insoluble form Tc(IV) (as TcO_2-like phases) through abiotic mechanisms using Fe(II)-containing minerals under anoxic conditions and via indirect and direct (i.e. enzymatic) microbial mechanisms (e.g. Lloyd et al. 2000).

Colloid transport can enhance or reduce the mobility of metal contaminants and significantly influence their long-term fate and effect in the environment. For example, it has been shown that phosphate inhibits the mobility of uranium by forming uranyl-phosphate complexes (e.g. Macaskie et al. 1995), while carbonate can significantly increase the mobilisation of uranium (e.g. Ulrich et al. 2008). ^{99}Tc reduction mechanisms will be markedly influenced by complex, interdependent factors such as the presence of organic and inorganic complexing agents and the properties of aqueous and solid phases.

The primary objective of this investigation is to characterise the mobility and transport of ^{99}Tc in a variety of porous media under varying geochemical conditions and in the presence of different complexing ligands. We will investigate the potential for enhancement or remediation of ^{99}Tc by varying chemical parameters and improve the understanding of the processes controlling technetium-99 mobilisation and transport under transient flows, which is critical to improving transport models, and in bioremediation engineering.

EXPERIMENTAL APPROACH
A combined batch and flow cell experimental approach will be used to explore ^{99}Tc quantification and transport in a variety of porous media such as sand, sediment and heterogeneous compositions under varying geochemical parameters e.g. pH, Eh, solute composition and concentration.

Batch experiments
Batch experiments, a precursor to flow cell experiments, will aid identification of geochemical parameters to recreate in flow cell studies. Technetium-99 concentration analysis will be conducted using liquid scintillation counting. Geochemical and mineralogical analyses of batch experiments will give an insight into the effect of varying geochemical properties on technetium geochemistry and transport through porous media.

Flow cell experiments

Flow cell experiments will be designed to follow the transport and mobility of technetium-99 under constant flow through the various types of porous medium. We will extend the methodology of Bridge et al. (2006 & 2009) who investigated the importance of colloids as vectors for sorbing contaminants. In these studies, and as shown in Figure 1, time lapse fluorescence imaging was used to visualise and quantify the mobilisation of colloid particles and solutes in sand under transient flow.

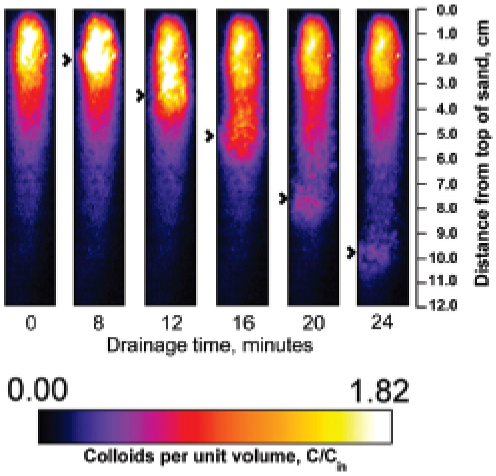

Figure 1 Time lapse fluorescence images at six time intervals during drainage of quartz sand containing 1.9µm carboxylate-modified latex microspheres (Bridge et al. 2009)

In these studies, measurements of standard concentrations were used to determine calibration relations for the fluorescent tracer used. The relationship between the emitted fluorescence (per pixel intensity, F_p) and the concentration (per pixel, C_p) of a dilute fluorescent tracer is directly proportional, allowing for the quantitative imaging of fluorescent particles (Huang et al. 2002).

Using the imaging methodology applied in these studies, we aim to develop the approach of Lear et al. (2010) and Law et al. (2010) who used a gamma camera to image the location of ^{99m}Tc, an isomer state of ^{99}Tc commonly used in medical imaging applications, in bioreduced sediments.

Therefore, the objective of the flow cell studies is to develop a methodology for non-invasive quantitative imaging of ^{99}Tc distribution and transport. Once established, this methodology will enable the continuous visualisation of ^{99}Tc transport at cm-resolution in real time and will provide a novel, quantitative insight into technetium-99 mobility and transport.

XAS investigation

The nature of Tc species produced from the reduction of Tc(VII) is diverse. In this study, we aim to investigate the redox state and coordination environment of Tc using spatially resolved X-ray absorption spectroscopy techniques in order to improve current speciation models of ^{99}Tc in the environment.

KEY OUTCOMES

The expected outcomes of the proposed investigation are:

1. To develop and test a methodology for the non-invasive quantitative imaging of ^{99m}Tc through various porous media

2. To determine the effect of differing geochemical parameters on the mobility and transport of ^{99}Tc

3. To improve current speciation models of ^{99}Tc in stimulated environmental conditions.

REFERENCES

Bridge J. W., Banwart S. A., and Heathwaite A. L. 2006. Non-invasive quantitative measurement of colloid transport in mesoscale porous media using time lapse fluorescence imaging. *Environmental Science and Technology* **40**, 5930-5936.

Bridge J. W., Heathwaite A. L., and Banwart S. A. 2009. Measurement of colloid mobilisation and re-deposition during drainage in quartz sand. *Environmental Science and Technology* **43**, 5769-5775.

Huang W. E., Smith C. C., Lerner D. N., Thornton S. F. and Oram A. 2002. Physical modelling of solute transport in porous media: evaluation of an imaging technique using UV excited fluorescent dye. *Water Research*, **36**, 1843-1853.

Law G. T. W., Geissler A., Boothman C., Burke I. T., Livens F. R., Lloyd J. R. and Morris K. 2010. Role of nitrate in conditioning aquifer sediments for technetium bioreduction. *Environmental Science and Technology* **44**, 150-155.

Lear G., McBeth J. M., Boothman C., Gunning D. J., Ellis B. L., Lawson R. S., Morris K., Burke I. T., Bryan N. D., Brown A. P., Livens F. R. and Lloyd J. R. 2010. Probing the biogeochemical behaviour of technetium using a novel nuclear imaging approach. *Environmental Science and Technology* **44**, 156-162.

Lloyd J. R., Sole V. A., Van Praagh C. V. G. and Lovely D. R. 2000. Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. *Applied and Environmental Microbiology* **66**, 3743-3749.

Macaskie L. E., Empson R. M., Lin F. and Tolley M. R. 1995. Enzymatically-mediated uranium accumulation and uranium recovery using s *Citrobacter* sp. immobilised as a biofilm within a plug-flow reactor. *Journal of Chemical Technology and Biotechnology* **63**, 1-16.

Ulrich K., Ilton E. S., Veeramani H., Sharp J. O., Bernier-Latmani R., Schofield E. J., Bargar J. R. and Giammer D. E. 2009. Comparative dissolution kinetics of biogenic and chemogenic uraninite under oxidising conditions in the presence of carbonate. *Geochimica et Cosmochimca Acta* **73**, 6065-6083.