REPORT ON RADIONUCLIDE BINDING IN CEMENT SYSTEMS

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

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REPORT ON RADIONUCLIDE BINDING IN CEMENT SYSTEMS

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Abstract

A series of radial diffusion and advection experiments have been undertaken and examples are presented where significant results have been obtained. In the diffusion experiments the effects of high ionic strength and cellulose degradation products (CDP) on the mobility of strontium are described at both tracer and tracer plus carrier concentrations. Ca migration in the same radial configuration has been observed using autoradiography. The advection experiments required the development and manufacture of a purpose designed cell, the new cell is described and the results for ^{90}Sr and ^{45}Ca are presented. All experiments have been undertaken on intact samples of the cementitious medium.

Introduction

This paper describes examples from a series of diffusion and advection experiments. These dynamic experiments aim to understand the interaction between cementitious media and radionuclides relevant to the geological disposal of radioactive waste.
The cementitious media being studied are NRVB (Nirex Reference Vault Backfill) and a waste packaging grout containing PFA (pulverised fuel ash). The experiments on the PFA grout have not yielded any evidence of diffusion and it has been assumed that precipitation has occurred due to very low solubility. Consequently, the discussion here concentrates on the NRVB experiments. The radionuclides being studied are ^{90}Sr, ^{45}Ca, ^{241}Am, ^{152}Eu and ^{75}Se. Migration of ^{90}Sr and ^{45}Ca has been observed in the diffusion and advection experiments but there is currently no evidence of migration of ^{241}Am and ^{152}Eu. The ^{90}Sr experiments ran smoothly with manageable durations (stabilising at <200 days) and as a consequence it was also possible to undertake experiments demonstrating the effects of high ionic strength and the presence of CDP on Sr mobility.

The ^{75}Se diffusion experiments have been running for six months and migration has not been observed.

Diffusion Experiments

The radial diffusion experimental technique uses small pre-cast cylinders of the cementitious matrix under investigation, in this case, NRVB. The appropriate concentration of radionuclide tracer and carrier (if required) is introduced into a cavity in the centre of the cylinder which is then sealed and placed in a solution previously equilibrated with the solid matrix. The increase in concentration of the isotope in the external solution is then determined at defined time intervals.

^{90}Sr Diffusion

Tracer only (13.5 kBq of ^{90}Sr) and tracer with carrier (13.5 kBq of ^{90}Sr with 21.8 mg Sr as $Sr(NO_3)_2$; equivalent to ~10^{-3} mol dm^{-3} if fully equilibrated with the receiving solution) radial diffusion experiments on NRVB were undertaken using ^{90}Sr in the presence and absence of CDP. Two similar tracer only experiments were undertaken where the ionic strength of the solution was increased. In the first of these experiments sufficient Na/KCl was added to produce a 0.1 mol dm^{-3} solution. In the second experiment the same mass of Na/KCl was added to the central core with the tracer, the purpose was to create a high ionic strength gradient that would equilibrate to 0.1 mol dm^{-3} as the experiment progressed. These experiments were originally devised because the ionic strength of the CDP solutions was noted to be higher (most likely due to the 80°C production temperature) than the NRVB equilibrated water.

The ^{90}Sr diffusion experiments proceeded fast enough to be monitored via the increase of concentration in the surrounding solution. Figure 1 below show the results.

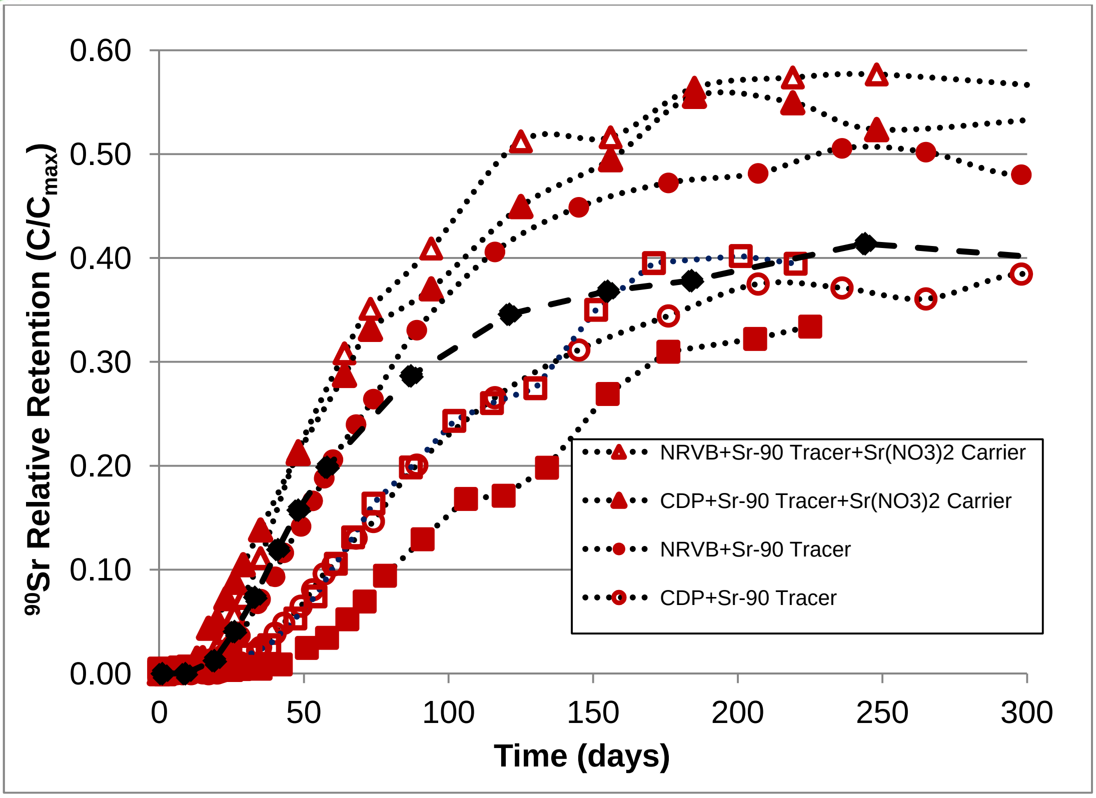

Figure.1 *Results of the ^{90}Sr diffusion experiments*

The effect on the migration of ^{90}Sr caused by the presence of CDP is seen to be significant at tracer concentrations where, contrary to expectations, migration was significantly slowed and retention on the NRVB increased. The effects were not evident in the carrier experiments where the Sr concentration was increased with non-active $Sr(NO_3)_2$. The high ionic strength tracer only experiment produced very similar results to the CDP tracer only experiment. The gradient ionic strength experiment produced the slowest initial breakthrough and subsequent diffusion. However the gradient ionic strength results are still increasing and may converge with the high ionic strength experiment.

A tracer only experiment using gluconic acid (in the lactone form, i.e. with no counter ions) as a surrogate for the CDP was also undertaken. The results, shown in black on fig. 1, initially resembled the carrier experiments but upon stabilisation the retention on the NRVB was similar to the high ionic strength and CDP tracer only experiments.

The results show that there is an effect on ^{90}Sr migration at tracer concentrations due to the presence of CDP and/or the increased ionic strength. At this stage there is insufficient evidence to confirm which effect is dominant under any given set of experimental conditions.

The slowing of Sr migration could be due to the formation of a ternary complex between a component of the CDP, the surface of the cement matrix and Sr, or enhanced ion exchange with calcium in the cement phases in the matrix. Increasing electrostatic interaction is believed to be the reason why diffusion is slowed as the ionic strength increases.

Ca-45 Diffusion

There had been an expectation to observe some mobility of calcium in the cementitious systems being investigated primarily because calcium is present in high concentration in both solid (> 25% w/w) and solution (~800 ppm or ~ $2x10^{-2}$ mol dm^{-3}). The addition of ^{45}Ca was so small in comparison that isotope exchange would be the only effect observed. However, it is not clear how migration would be driven by isotope exchange and the mechanism may simply be slow diffusion across a very small ^{45}Ca concentration gradient.
The short half-live of ^{45}Ca (163 days) could also be an issue if mobility was slow. After one year, and with no breakthrough of ^{45}Ca, one of the NRVB experiments was stopped and the cylinder sectioned for autoradiography. This was done because of the need to establish whether the decay of ^{45}Ca had rendered it difficult to detect on the autoradiography plates. The resulting images are shown below.

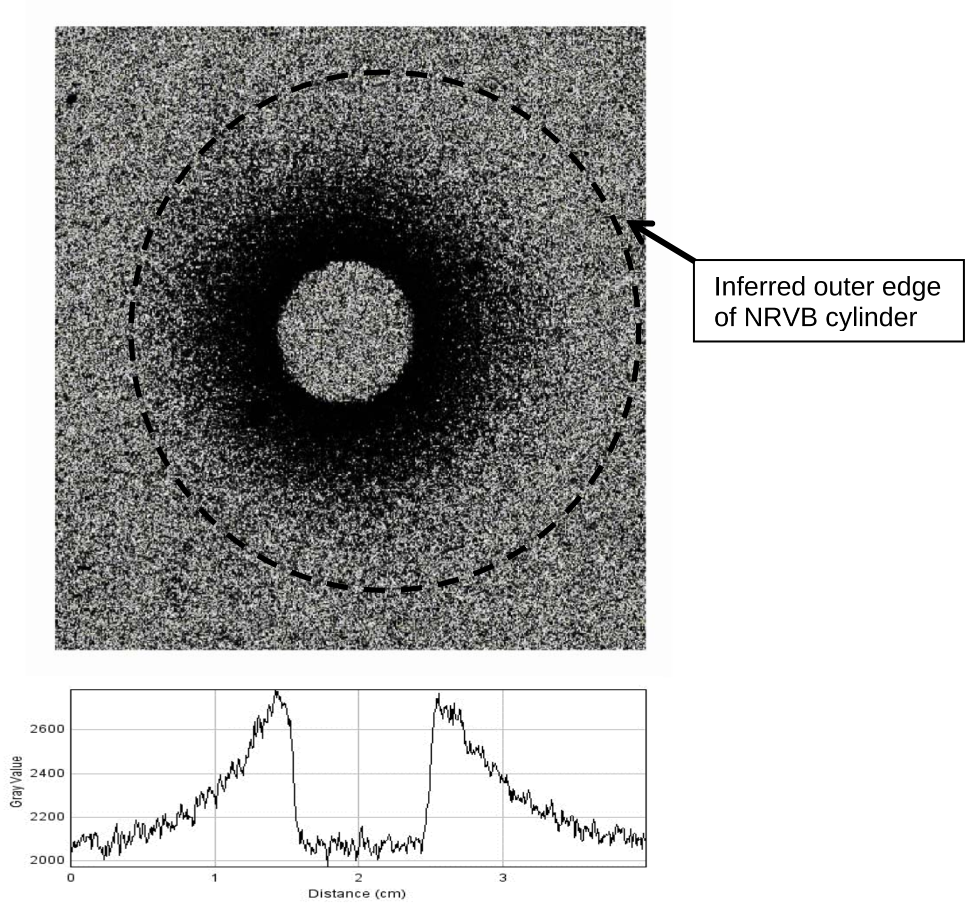

Fig. 2 *Autoradiograph and intensity plot of NRVB cylinder from the ^{45}Ca diffusion experiments (central core "plugged" to shield highest activity at inner walls).*

It is clear that ^{45}Ca has moved into the NRVB matrix from the central core, penetration appears to be several millimetres. The image of the activity in the matrix has been made clearer by screening, with a plastic plug (absorbing the beta radiation from ^{45}Ca decay), the much higher activity present on the surface of the core. The unshielded autoradiograph and intensity plot are shown below.

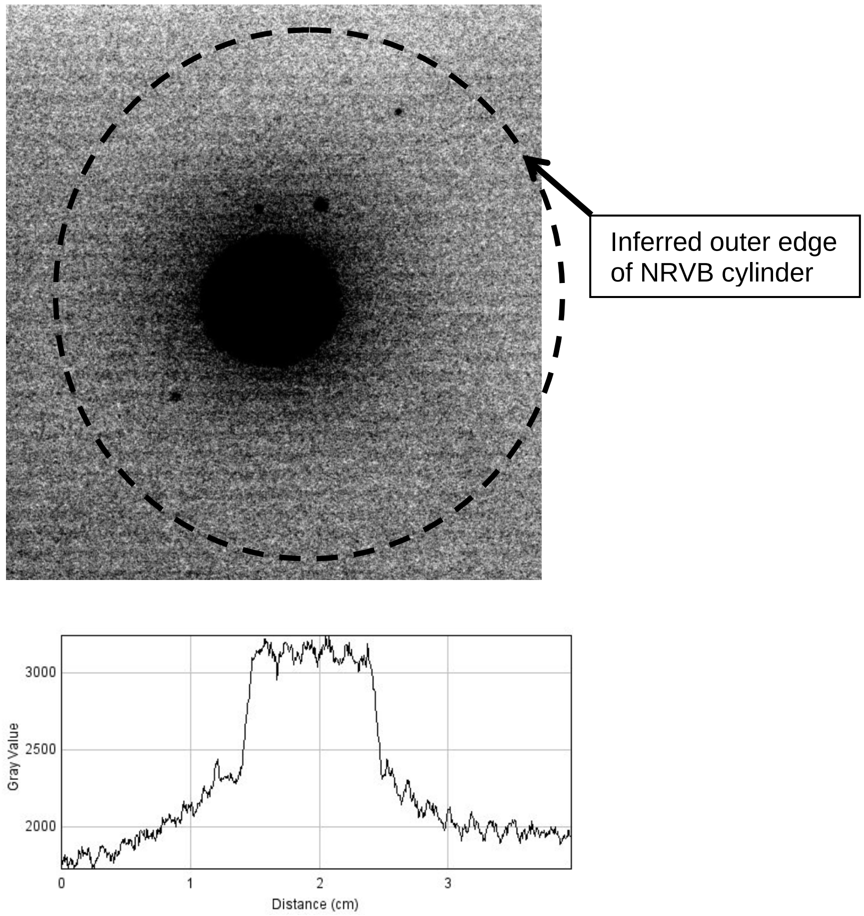

Fig. 3 *Autoradiograph and intensity plot of NRVB cylinder from the Ca-45 diffusion experiments (central core "unshielded" to show highest activity at inner walls)*

It should be noted that the intensity plots are not calibrated and it is only possible to infer relative concentrations. The unshielded figures demonstrate that a significant proportion of the ^{45}Ca has remained on the inner walls of the central core. Additionally the 2 cm^3 of solution remaining in the core when the experiment was halted, was removed and analysed by liquid scintillation counting and the ^{45}Ca activity concentration was found to be at background.

Advection Experiments

A radial advection apparatus has been designed and manufactured and is now operational. Results for ^{90}Sr and ^{45}Ca in the presence and absence of CDP have been obtained. The photographs below show the main parts dismantled and the completed set up. The apparatus has been manufactured to enable testing of cementitious cylinders with similar dimensions those used in the diffusion experiments. The “eluent” is pushed from the steel reservoir through the cylinder using N_2 pressure. The whole system is effectively closed to O_2 and CO_2 ingress up to the end of the sample collection tube where interaction with the atmosphere is limited by the small internal diameter of the teflon tubing.

Fig.4 *Photographs of the advection apparatus*

The ^{90}Sr and ^{45}Ca plots below show that the method works. Flow rate control using N_2 pressure remains an issue as outgassing is visible within the cell at the NRVB surface. The "step" changes and data gaps observed in the results were generally associated with interventions e.g. refilling the reservoir, changing the gas bottle or clearing blocked tubing.

<u>Ca-45 Advection</u>

Figures 5 and 6 below show the results of the ^{45}Ca advection experiment using NRVB equilibrated water.

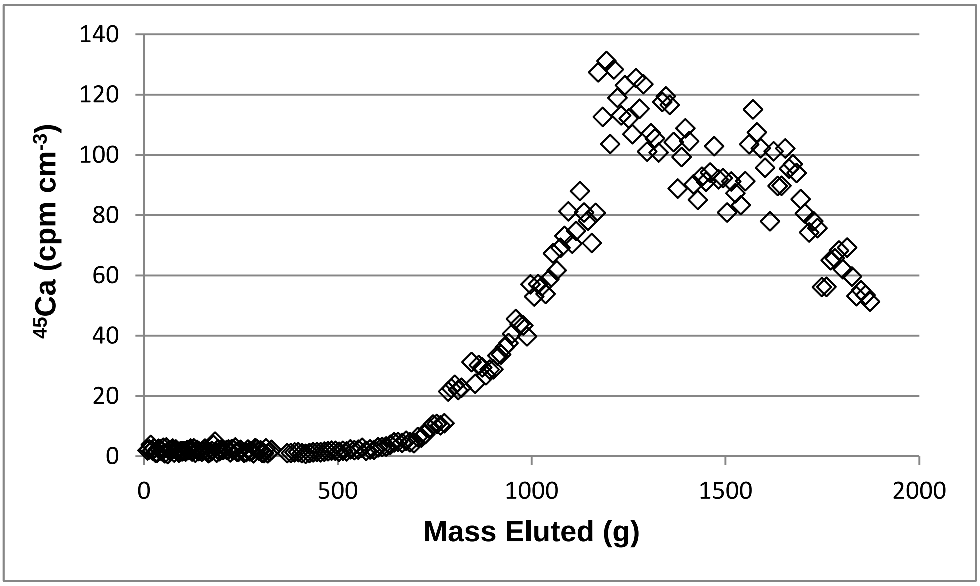

Fig.5 *Graph showing advection of ^{45}Ca through NRVB*

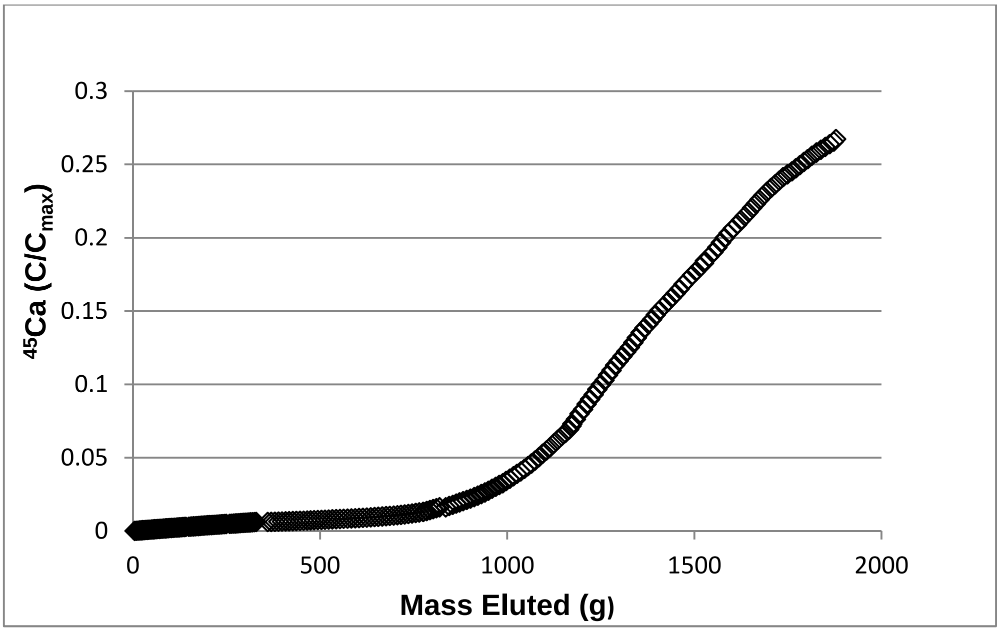

Fig.6 *Graph showing cumulative ^{45}Ca results*

The recovery of ^{45}Ca was less than 30% implying that over 70% was retained on the NRVB..A similar experiment which ran for the same total flow was undertaken using a CDP solution and no ^{45}Ca was eluted. The runs were stopped before the elution of ^{45}Ca had ceased so that autoradiographs could be produced, the resulting images are shown as figures 7 and 8.

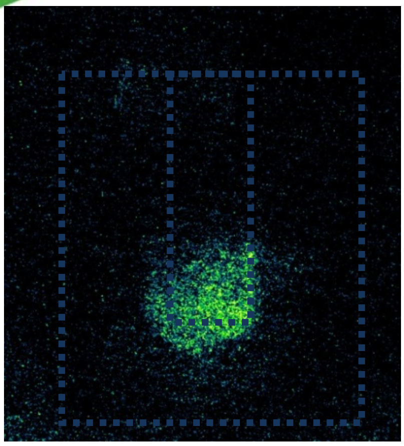

Fig.7 *Autoradiograph of NRVB cylinder showing* ^{45}*Ca distribution (no CDP present)*

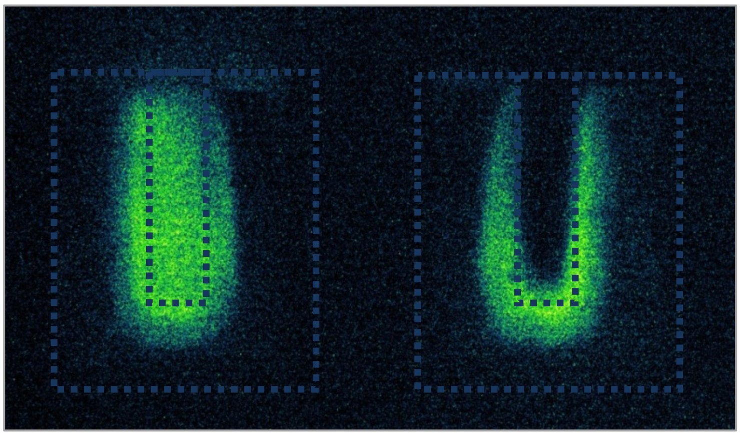

Fig.8 *Autoradiograph of NRVB cylinder showing* ^{45}*Ca distribution (CDP present)unshielded image on the left, clay shielding placed in central well on right hand image.*

The autoradiographs clearly show that ^{45}Ca is retained on the NRVB much more significantly in the presence of CDP. There was a delay after ending the experiment prior to producing the image shown as figure 7 and further decay of the ^{45}Ca will have occurred. As a consequence the ^{45}Ca intensities shown in figures 7 and 8 are not directly comparable.

Sr-90 Advection

Figures 9 and 10 below show the results of the ^{90}Sr advection experiments. Runs in the absence of CDP and in the presence of CDP solution are shown. Figure 10 is a cumulative plot of the data shown in figure 9. Both runs were stopped before the elution of ^{90}Sr had ceased so that autoradiographs could be produced.

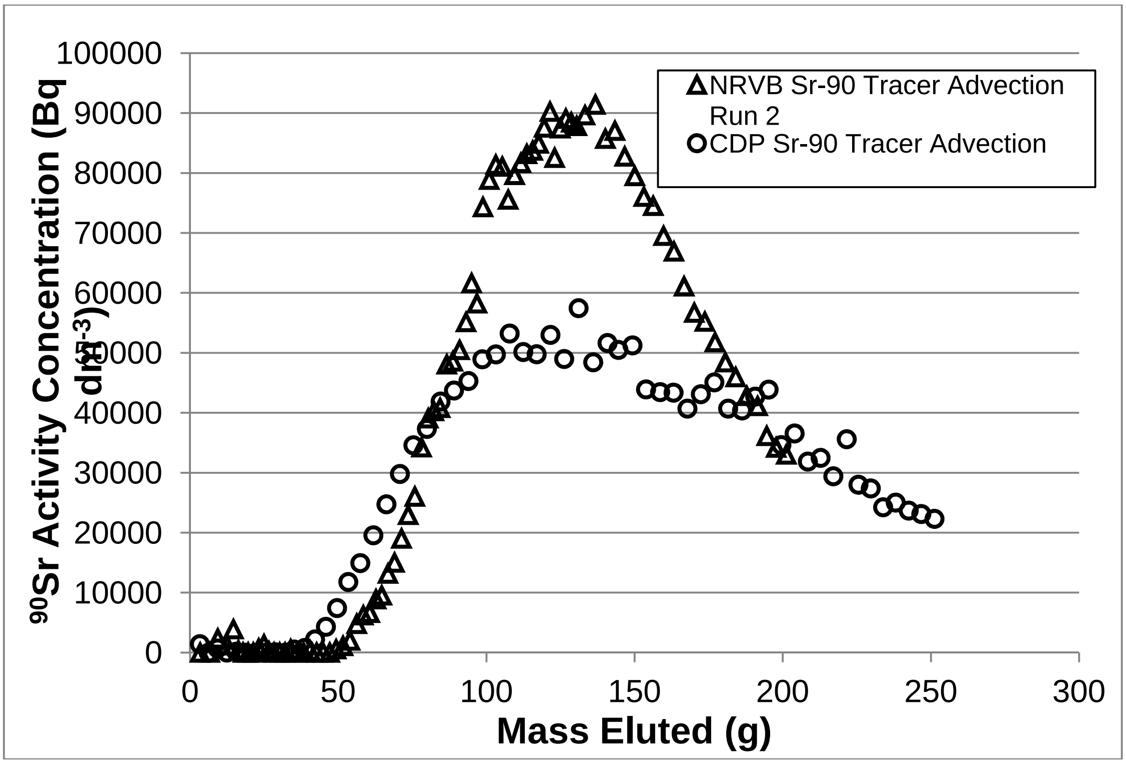

Figure 9 *Graph showing results of the advection of* ^{90}*Sr through NRVB in the presence and absence of CDP*

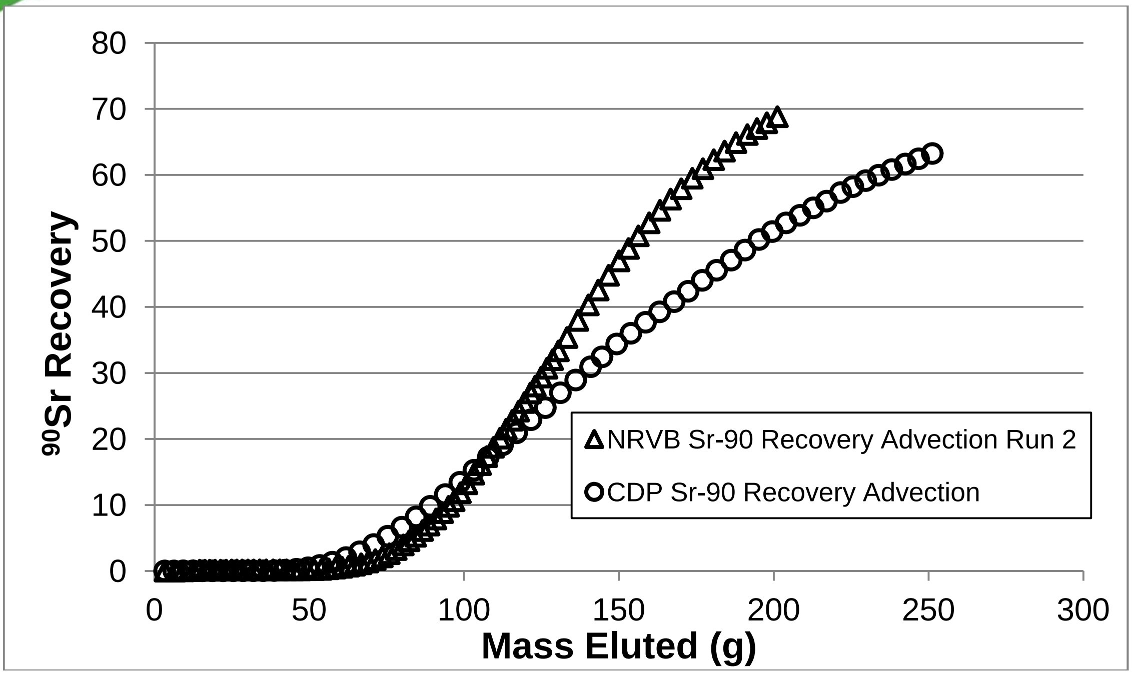

Figure 10 *Graph showing cumulative results of the advection of ^{90}Sr through NRVB in the presence and absence of CDP*

There are clear differences in the elution profiles, the most obvious being the reduced peak height of the CDP experiment. The same mass of tracer was added to each run and there is an indication that more ^{90}Sr is retained in the presence of CDP. However, it is also clear that the CDP profile has a longer tail, implying that all the ^{90}Sr will eventually elute.

The autoradiographs are shown below.

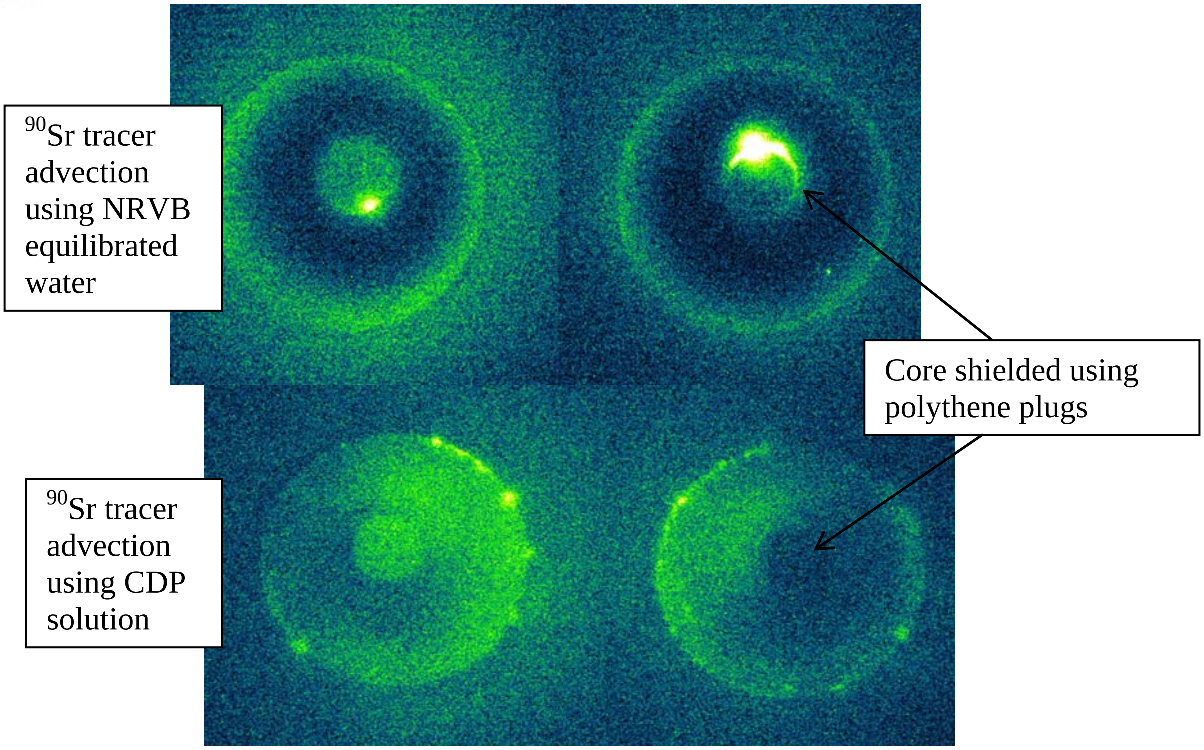

Figure 11 *Autoradiographs from the ^{90}Sr tracer advection experiments*

<u>*NRVB equilibrated water*</u>

- There is a distinct ring of ^{90}Sr tracer activity within the NRVB matrix extending to the outer edge.
- Spots of activity are absent from the outer edge.
- There is a ring of inactivity surrounding the central core.
- The central core has significant residual activity present, this is particularly evident on the upper right image where the intense activity can be clearly seen despite the shielding (Note that this cylinder has had two active runs).

- There is a possibility that the outer ring is Sr and calcite co-precipitation caused by the ingress of atmospheric carbon dioxide similar to that observed in the trial advections.
- The outer ring of activity could also be evidence of the tracer tail being eluted.

CDP solution

- More tracer is present in the NRVB matrix than seen in the NRVB equilibrated water experiment.
- The tracer is more evenly distributed than in the absence of CDP although there are distinct areas where more tracer is present, suggesting preferential flow or an artefact associated with the position of the tracer injection.
- There are spots of tracer activity on the outer edge which appear to be contiguous with the areas of possible preferential flow.
- There is residual tracer activity in the central core but none of the very intense spots seen in the central core of the NRVB equilibrated water experiment.
- The ring of activity around the outer edge is present though not as extensive as in the NRVB equilibrated water experiment.
- There is a possibility that the outer ring is Sr and calcite co-precipitation caused by the ingress of atmospheric carbon dioxide similar to that observed in the trial advections.

Advection – concluding remarks

The advection experiments show that there are clear differences in mobility between the radionuclides tested. The comparison between ^{90}Sr and ^{45}Ca is significant. The ^{45}Ca results indicate a strong interaction with the NRVB which is most likely due to a combination of isotope exchange and solubility limitation. The ^{45}Ca results in the presence of CDP may indicate that precipitation/dissolution of an organic Ca salt is the dominant effect. Additional work will be required to confirm this. The ^{90}Sr results indicate that it is more mobile than ^{45}Ca and has a less significant interaction with the solid matrix.

Acknowledgement

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