MEASUREMENTS OF THE KINETICS AND THERMODYNAMICS OF THE UPTAKE OF RADIONUCLIDES

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

SKIN

DELIVERABLE D2.1

COLLABORATIVE PROJECT (CP)

Reporting period: 01/01/2011-31/12/2013

Grant agreement N°269688

Submitting organizations: LU
Due date of deliverable: Month 24
Actual submission: Month 27

Start date of the project: 01 January 2011
Duration: 36 months

Project co-funded by the European Commission under the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities (2007 to 2011)		
Dissemination Level		
PU	Public	×
RE	Restricted to a group specified by the partners of the project	
CO	Confidential, only fro partners of the project	

Introduction

This paper describes a few 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 results for the PFA grout will not be available until mid-2013 so the discussion here concentrates on the NRVB experiments. The radionuclides being studied are Sr-90, Ca-45, Am-241, Eu-152 and Se-75. In addition a small amount of work has been undertaken investigating the effect of CDP (cellulose degradation products) and the mobility of Sr-90.

Diffusion Experiments

The experimental set up was described in the review of the first year of WP2.

The Sr-90 and Ca-45 experiments produce results relatively quickly and details are provided below. The Eu-152 and Am-241 experiments are being left to run for the maximum amount of time and will be concluded mid to late 2013. The Se-75 experiments will commence early 2013.

Sr-90Diffusion

The radial diffusion experimental technique uses small pre-cast cylinders of the cementitious matrix under investigation, in this case, NRVB. An appropriate concentration of Sr-90 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. Radial diffusion experiments on NRVB have been undertaken using Sr-90 in the presence and absence of CDP or gluconate (a surrogate for the CDP mixture).

The Sr-90 diffusion experiments proceeded fast enough to be monitored via the build of concentration in the surrounding solution. Figures 1-3 below show the results of the experiments. The effect on the migration of Sr-90 caused by addition of CDP is seen to be significant at tracer concentrations where, contrary to expectations, migration was significantly slowed. The effect was not evident in the carrier experiments when a higher concentration of non-active Sr was used. The use of gluconate as a potential surrogate for the CDP had no discernible effect on Sr migration.

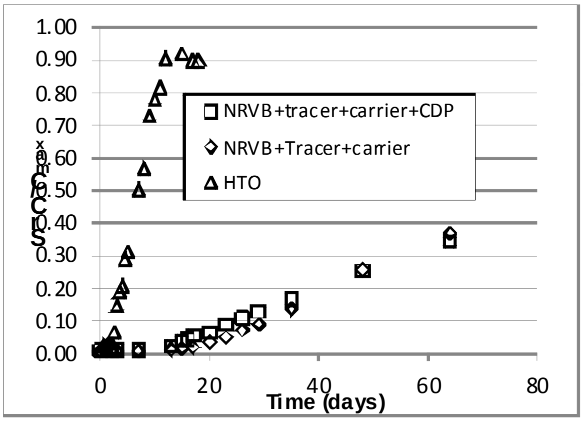

Fig.1 *Results using Sr carrier and Sr-90 tracer*

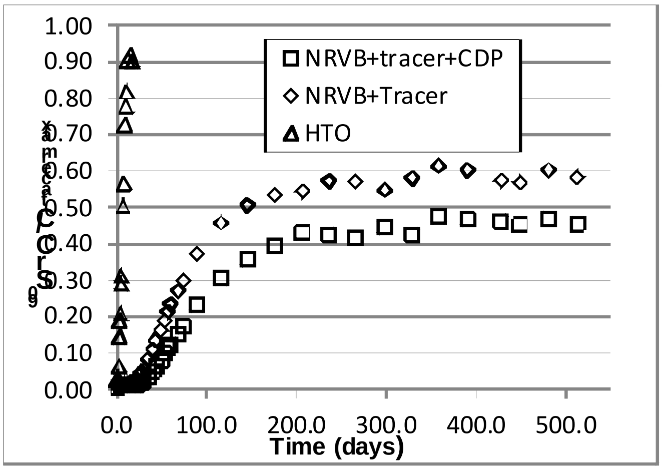

Fig.2 *Results using Sr-90 tracer only*

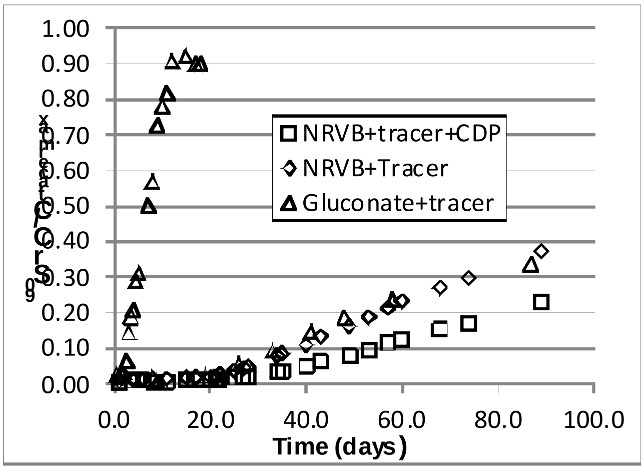

Fig. 3 *Results using gluconate instead of CDP*

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. The results demonstrate that gluconate is not a suitable surrogate for CDP in this type of experiment.

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}). However the addition of Ca-45 was so small in comparison that isotope exchange would be the only migration mechanism observed.

The short half-live of Ca-45 (163 days) could also represent a problem if mobility was slow. After one year, and with no breakthrough of Ca-45, 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 Ca-45 had rendered it difficult to detect on the autoradiography plates. The resulting images are shown below.

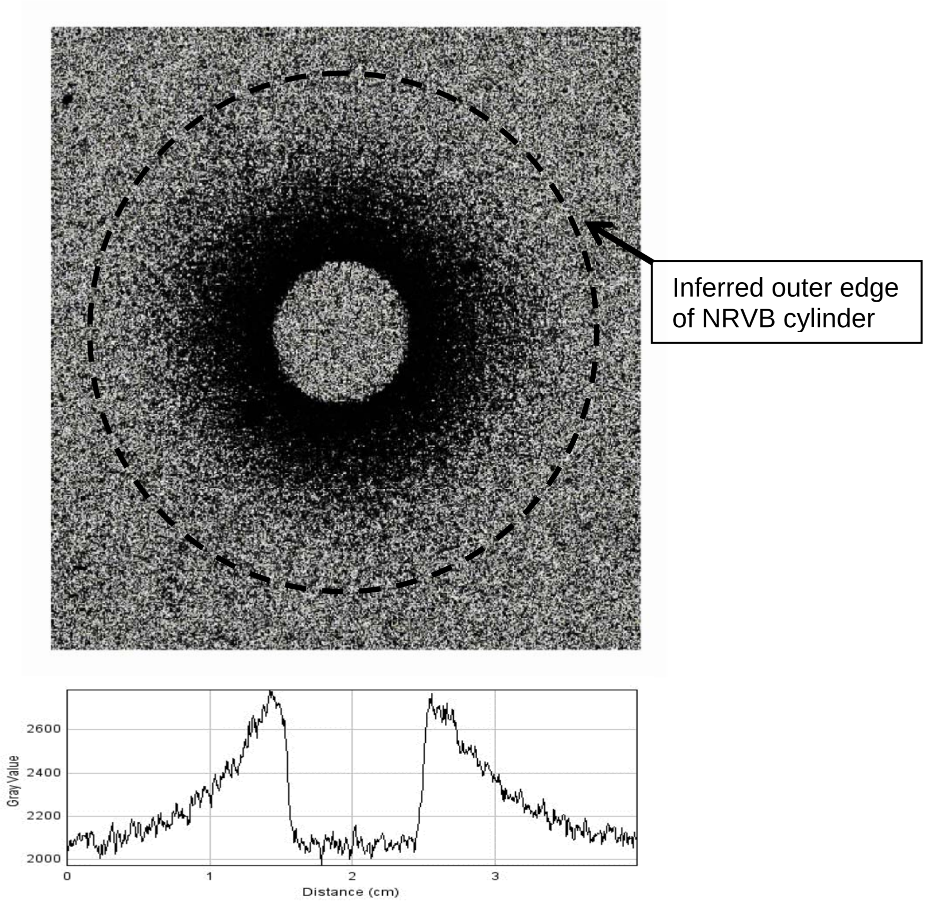

Fig. 4 *Autoradiograph and intensity plot of NRVB cylinder from the Ca-45 diffusion experiments (central core "plugged" to shield highest activity at inner walls).*

It is clear that Ca-45 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 Ca-45 decay), the much higher activity present on the surface of the core. The unshielded autoradiograph and intensity plot are shown below.

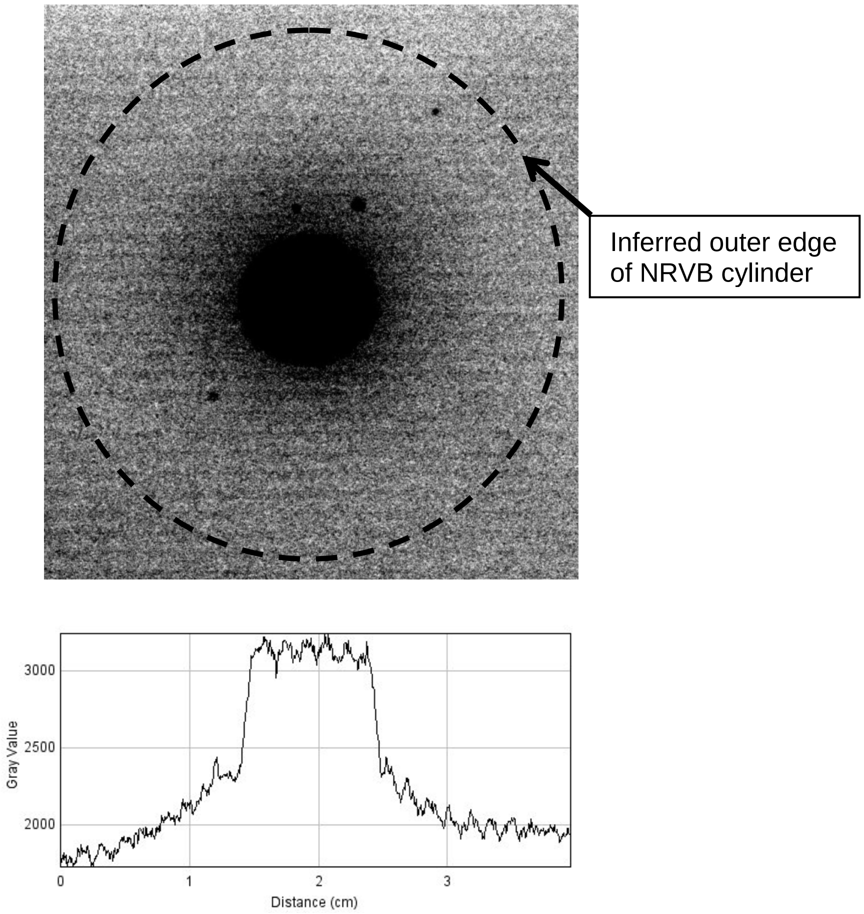

Fig. 5 *Autoradiograph and intensity plot of NRVB cylinder from the Ca-45 diffusion experiments (central core "unshielded" to show highest activity at inner walls)*

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 Ca-45 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 Ca-45 activity concentration was found to be at background.

Advection Experiments

A radial advection apparatus has been designed and manufactured and is now operational. Initial results for H-3 Sr-90 and Ca-45 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.6 *Photographs of the advection apparatus*

The HTO and Sr-90 and Ca-45 plots below show that good progress is being made and the results are in line with expectations. Flow rate control using N_2 pressure remains an issue. 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.

H-3 Advection

Figs.7 and 8 below show the results of the H-3 advection experiment. H-3 provides the conservative case where sorption to the solid phase should be at a minimum and mobility in the liquid phase maximised. It can be seen that the experiment proceeds quickly and that over 85% of the H-3 injected is recovered.

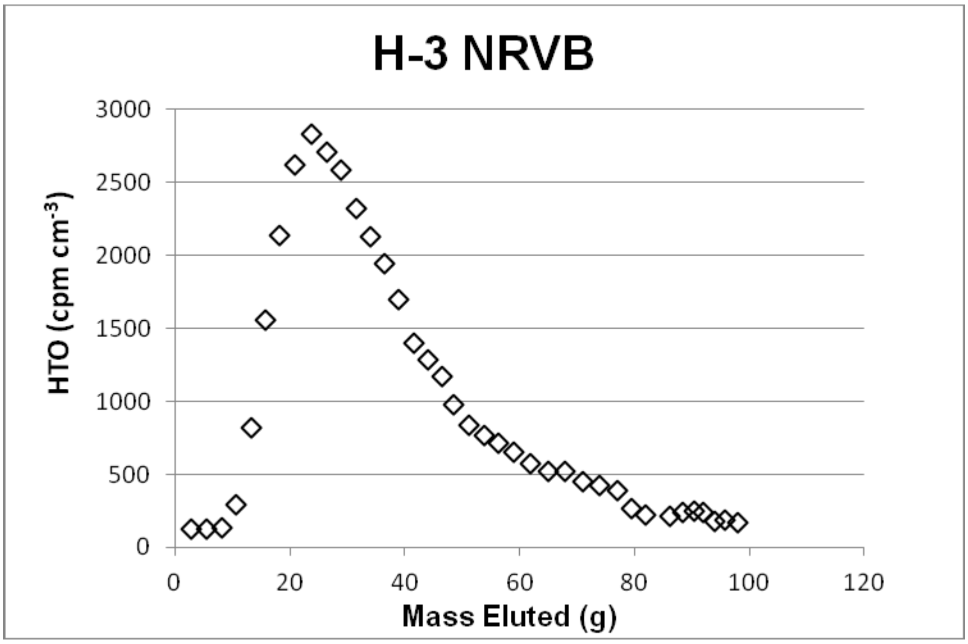

Fig.7 *Graph showing advection of H-3 through NRVB*

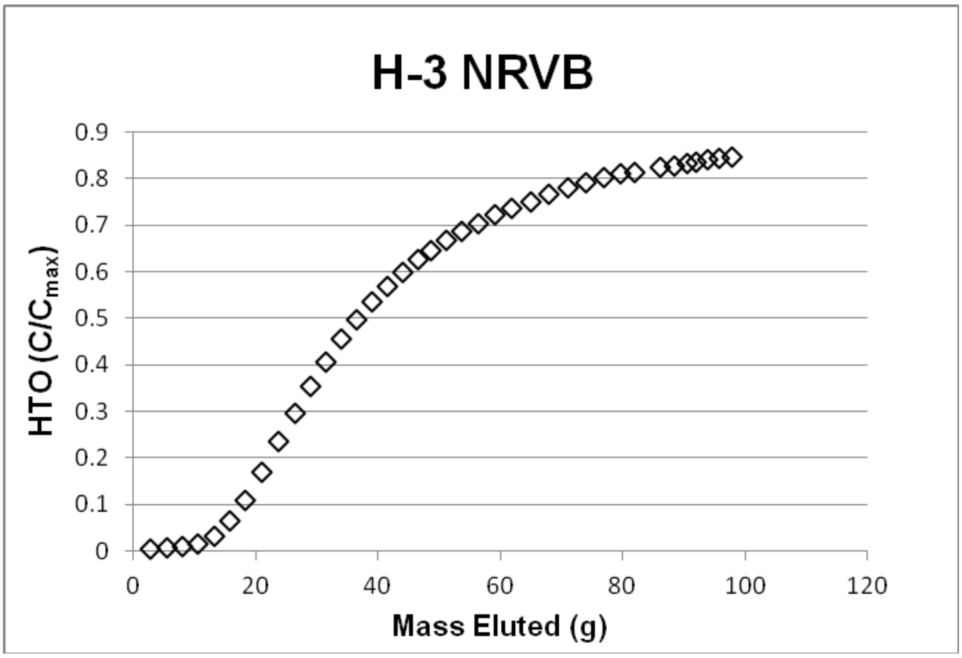

Fig.8 *Graph showing cumulative H-3 results*

Ca-45 Advection

Figs.9 and 10 below show the results of the Ca-45 advection experiment. The contrast to the H-3 results is marked with 50-60 times more eluent being required prior to breakthrough being observed. The recovery of Ca-45 is much reduced when compared to H-3 and although the experiment is not yet completed it can be seen that a recovery of ~35% could be reasonably anticipated.

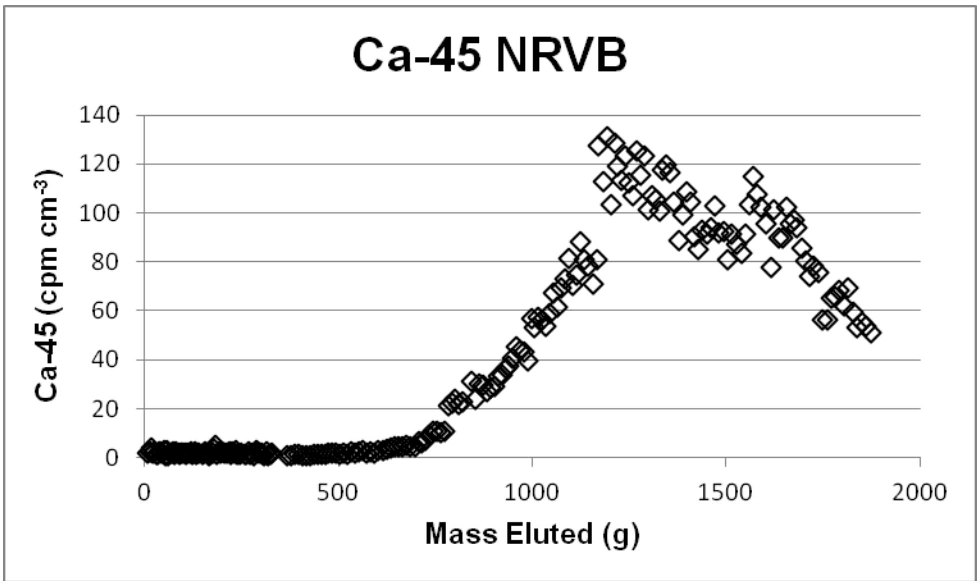

Fig.9 *Graph showing advection of Ca-45 through NRVB*

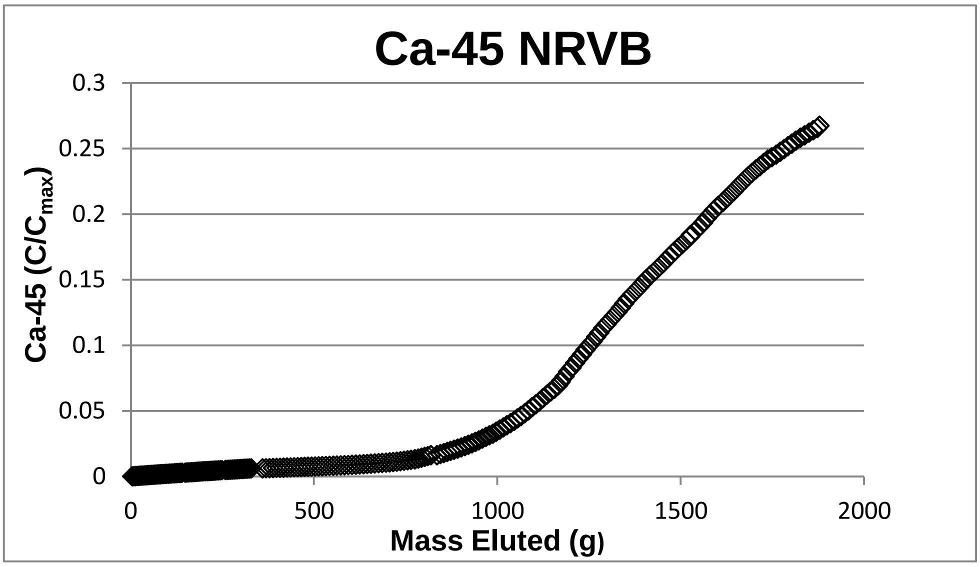

Fig.10 *Graph showing cumulative Ca-45 results*

<u>*Sr-90 Advection*</u>

Figs.11 and 12 below show the results of the Sr-90 advection experiment. The results are different to both the H-3 and Ca-45 results. The recovery of Sr-90 is ~85% similar to H-3 and very different to Ca-45.

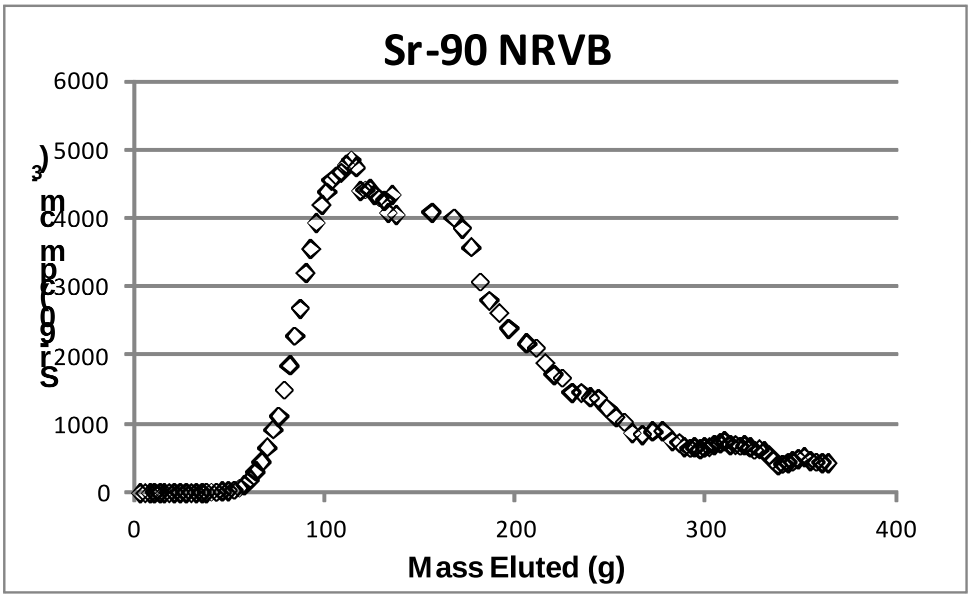

Fig.11 *Graph showing advection of Sr-90 through NRVB*

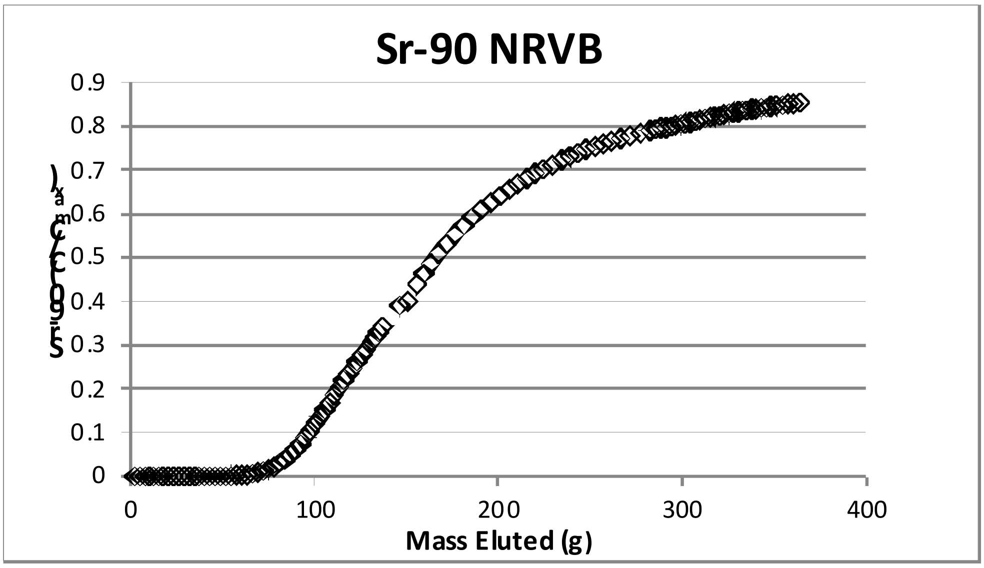

Fig.10 *Graph showing cumulative Sr-90 results*

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Advection – concluding remarks

The advection experiments show that there are clear differences in mobility between the radionuclides tested. As expected, H-3 behaved conservatively being subject primarily to dispersion it moved very quickly through the cylinder (although the long "tail" suggests some interaction with the NRVB matrix). The comparison between Sr-90 and Ca-45 is significant and both radionuclides are retained to a much greater extent than H-3. The Ca-45 results indicate a strong interaction with the NRVB which is most likely due to a combination of isotope exchange and solubility limitation. The Sr-90 results indicate higher mobility than Ca-45 and a less significant interaction with the solid matrix. Isotope exchange with Ca in the solid matrix will be less efficient for Sr-90 than Ca-45 and the solubility of Sr is not limited in the system.

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