



	Experiment title: Incorporation of strontium(II) in alkaline leachate affected sediments	Experiment number: EC 740
Beamline: BM26a	Date of experiment: from: 28Jan 2011 to: 31 Jan 2011	Date of report: 30 Aug 2012
Shifts: 12	Local contact(s): Sergey NIKITENKO	<i>Received at ESRF:</i>
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Report:

Objectives of the original proposal

1. Use EXAFS analysis to determine the speciation of sorbed Sr²⁺ in Sellafield sediments under geochemical conditions representative alkaline leachate affected groundwaters.
2. Characterise Sr²⁺ speciation during the aging of alkaline contaminated sediments in the presence and absence of CO₂.
3. Determine changes in local bonding environment of Sr²⁺ in natural systems using XAS combined with chemical leaching procedures and electron microscopy investigations.

Publications reporting results from the beamtime.

1. Wallace SH; Shaw S; Morris K; Small JS; Fuller AJ; Burke IT (2012) **Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: Implications for ⁹⁰Sr mobility at contaminated nuclear sites**, *Applied Geochemistry*, **27**, pp.1482-1491.

Abstract: Strontium-90 is a beta emitting radionuclide produced during nuclear fission, and is a problem contaminant at many nuclear facilities. Transport of ⁹⁰Sr in groundwaters is primarily controlled by sorption reactions with aquifer sediments. The extent of sorption is controlled by the geochemistry of the groundwater and sediment mineralogy. Here, batch sorption experiments were used to examine the sorption behaviour of ⁹⁰Sr in sediment–water systems representative of the UK Sellafield nuclear site based on groundwater and contaminant fluid compositions. In experiments with low ionic strength groundwaters (<0.01 mol L⁻¹), pH variation is the main control on sorption. The sorption edge for ⁹⁰Sr was observed between pH 4 and 6 with maximum sorption occurring (K_d ~ 103 L kg⁻¹) at pH 6–8. At ionic strengths above 10 mmol L⁻¹, and at pH values between 6 and 8, cation exchange processes reduced ⁹⁰Sr uptake to the sediment. This exchange process explains the lower ⁹⁰Sr sorption (K_d ~ 40 L kg⁻¹) in the presence of artificial Magnox tank liquor (IS = 29 mmol L⁻¹). Strontium K-edge EXAFS spectra collected from sediments incubated with Sr²⁺ in either HCO₃⁻ buffered groundwater or artificial Magnox tank liquor, revealed a coordination environment of ~9 O atoms at 2.58–2.61 Å after 10 days. This is equivalent to the Sr²⁺ hydration sphere for the aqueous ion and indicates that Sr occurs primarily in outer sphere sorption complexes. No change was observed in the Sr sorption environment with EXAFS analysis after 365 days

incubation. Sequential extractions performed on sediments after 365 days also found that ~80% of solid associated ^{90}Sr was exchangeable with 1 M MgCl_2 in all experiments. These results suggest that over long periods, ^{90}Sr in contaminated sediments will remain primarily in weakly bound surface complexes. Therefore, if groundwater ionic strength increases (e.g. by saline intrusion related to sea level rise or by design during site remediation) then substantial remobilisation of ^{90}Sr is to be expected.

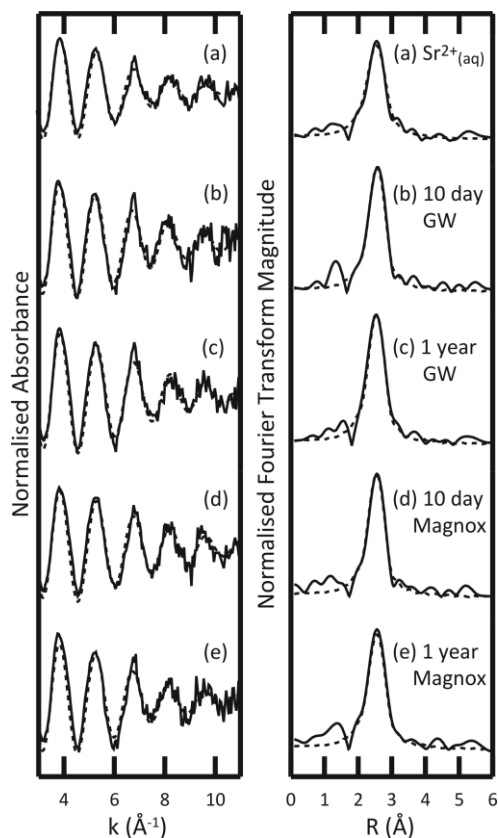


Figure 1: Background subtracted Sr K-edge EXAFS spectra (left hand side) and related Fourier transformations (right hand side) collected from a $3000 \text{ mg L}^{-1} \text{ Sr}^{2+}$ solution and sediment samples aged with Sr^{2+} for 10 or 365 days in buffered groundwater (“GW”) or artificial Magnox tank liquor (“Magnox”). Dashed lines represent model fits produced in DLExcurv V1.0 using the parameters listed in Table 1 below.

Table 1. Sr K-edge EXAFS model fitting parameters where n is the occupancy ($\pm 25\%$), r is the interatomic distance ($\pm 0.02 \text{ \AA}$ for the first shell, $\pm 0.05 \text{ \AA}$ for outer shells), $2\sigma^2$ is the Debye-Waller factor ($\pm 25\%$), and R is the least squares residual.

Sample	Shell	n	$R \text{ (\AA)}$	$2\sigma^2 \text{ (\AA}^2\text{)}$	R
Buffered GW 10 days	O	9	2.61	0.022	30.7
Buffered GW 365 days	O	9.3	2.58	0.022	27.6
Magnox 10 days	O	8.5	2.59	0.021	27.9
Magnox 365 days	O	8.9	2.60	0.024	35.0
Sr^{2+} solution	O	9.1	2.58	0.031	26.3

2. Thorpe C. L., Lloyd J. R., Law G. T. W., Burke I. T., Shaw S., Bryan N. D. and Morris K. **Strontium sorption and incorporation behaviour during bioreduction in nitrate impacted sediments**, *Chemical Geology*. (2012) 306-307, 114-122.

Abstract. The behaviour of strontium (Sr^{2+}) during microbial reduction in nitrate impacted sediments was investigated in sediment microcosm experiments relevant to nuclear sites. Although Sr^{2+} is not expected to be influenced directly by redox state, bioreduction of nitrate caused reduced Sr^{2+} solubility due to an increase in pH during bioreduction and denitrification. Sr^{2+} removal was greatest in systems with the highest initial nitrate loading and consequently more alkaline conditions at the end of denitrification. After denitrification, re-release of Sr^{2+} back into solution occurred coincident with the onset of metal (Mn(IV) and Fe(III)) reduction which caused minor pH changes in all microcosms with the exception of the bicarbonate buffered system with initial nitrate of 100 mM and final pH of ~ 9. In this system ~ 95 % of Sr^{2+} remained associated with the sediment throughout the progression of bioreduction at high pH. Analysis of this pH 9 system using X-ray absorption spectroscopy (XAS) and electron microscopy coupled to thermodynamic modelling suggested that Sr^{2+} became partially incorporated within carbonate phases which were formed at higher pH. This is in contrast to all other systems where final pH was < 9, here XAS analysis showed that outer sphere Sr^{2+} sorption predominated. These results provide insight into the likely environmental fate of the significant radioactive contaminant, ^{90}Sr , during changes in sediment biogeochemistry induced by bioreduction in nitrate impacted nuclear contaminated environments.

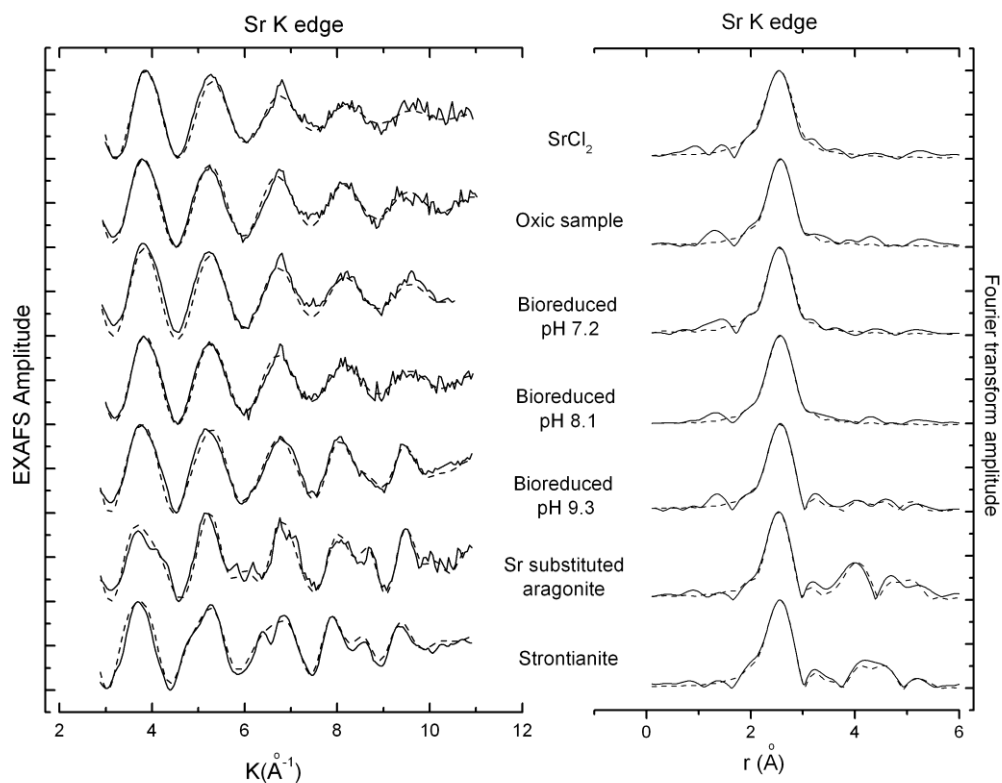


Figure 2. Experimental (solid) and theoretical best fit (dashed) EXAFS spectra and corresponding Fourier transforms obtained for (from top to bottom): SrCl_2 aqueous standard, oxic sediment sample, bioreduced pH 7.2 sample, bioreduced pH 8.1 sample, bioreduced pH 9.3 sample, Sr substituted aragonite standard and strontianite standard. Solid lines are the data and dashed lines are the fits to the data produced in DLExcurv V1.0. .

Table 2 Parameters obtained from EXAFS data fitting of Sr K-edge spectra from Sr^{2+} associated with sediment at various sediment conditions

Sample	Shell No	Bond	C.N.	R(Å)	$2\sigma^2$ (Å ²)	R-factor
SrCl_2	1	Sr-O	8.75	2.60	0.029	23.0
Oxic sample pH 7	1	Sr-O	8.83	2.61	0.019	22.1
Bioreduced pH 7.2	1	Sr-O	8.68	2.60	0.020	18.0
Bioreduced pH 8.1	1	Sr-O	8.89	2.61	0.021	19.6
Bioreduced pH 9.3 (1)	1	Sr-O	8.03	2.60	0.024	27.9
Bioreduced pH 9.3 (2)	1	Sr-O	8.19	2.61	0.021	20.2
	2	Sr-C	2.68	3.03	0.015	
	3	Sr-Sr	2.78	4.18	0.029	
	4	Sr-Sr	2.47	4.88	0.024	
Strontianite	1	Sr-O	9*	2.64	0.027	20.3
	2	Sr-C	6*	3.04	0.032	
	3	Sr-Sr	6*	4.22	0.029	
	4	Sr-Sr	4*	4.97	0.033	
Sr substituted aragonite	1	Sr-O	9*	2.59	0.015	29.1
	2	Sr-C	6*	2.98	0.031	
	3	Sr-Ca	6*	4.02	0.020	
	4	Sr-Ca	4*	4.87	0.013	

*= fixed . N is the occupancy (+/- ~ 25 %), $R(\text{Å})$ (is the interatomic distance (+/- ~ 0.02Å), $2\sigma^2$ is the Debye-Waller factor (Å²) and R (least squares residual) is a measure of the overall goodness of fit.

3. Wallace SH; Shaw S; Morris K; Small JS; Fuller AJ; Burke IT (2012- in preparation) **Alteration of sediments by hyperalkaline cement leachate: Implications for strontium adsorption and incorporation**, for submission Fall 2012, currently available as a final draft.

Abstract: The use of cementitious materials is ubiquitous at nuclear facilities and in radioactive waste packaging. Water in contact with fresh cement produces a highly alkaline solution dominated by K and Na hydroxides causing localised areas of high pH groundwater at the concrete/soil interface. Silicate minerals within sediments and clay barrier materials are known to alter to zeolite and feldspathoid phases under these conditions. The effect of alkaline pore fluid induced weathering reactions on the mobility of radionuclides is not well understood, especially with respect to potentially highly soluble fission products such as ^{90}Sr (as Sr^{2+}). Here we used 20 g.L^{-1} batch experiments containing sediments representative of the UK Sellafield nuclear site in a pH 13.5 high ionic strength cement-based leachate to investigate Sr^{2+} sorption as a function of time. Experiments initially contained 20 ppm Sr^{2+} (spiked with $30 \text{ Bq.mL}^{-1} \text{ }^{90}\text{Sr}$ tracer) and were sampled from 2 days up to one year (one experiment was aged for one year at 70°C). Change in Sr speciation within sediments was determined using X-ray absorption spectroscopy and sequential extraction techniques. At 2 days $72.6 \pm 8.6\%$ ^{90}Sr was removed from solution, which rose to $93.8 \pm 3.3\%$ at 10 days but then decreased to 81.8% after a year. In the 70°C aged sample sorption increased to $98.0 \pm 2.5\%$. This suggests that initial alteration enhances Sr sorption but further recrystallisation releases some sorbed Sr. Sequential extractions show that the majority (65-75%) of ^{90}Sr remains in the MgCl_2 exchangeable fraction even after one year. In the 70°C aged sample, $25.2 \pm 5.8\%$ ^{90}Sr was found to be residual. EXAFS analysis revealed two Sr-OSi(Al) bond distances at 3.69 and 3.84 Å in a 10 day sample and at 3.57 and 3.83 Å in a one year sample, consistent with weak Sr sorption to aluminosilicate phases. EXAFS spectra from a 70°C aged sample contain evidence for a single Sr-O-Si(Al) bond distance at 3.45 Å consistent with Sr incorporation in the neoformed zeolite phase chabazite. These results indicate that alkaline altered sediments could be a sink for ^{90}Sr in the environment.

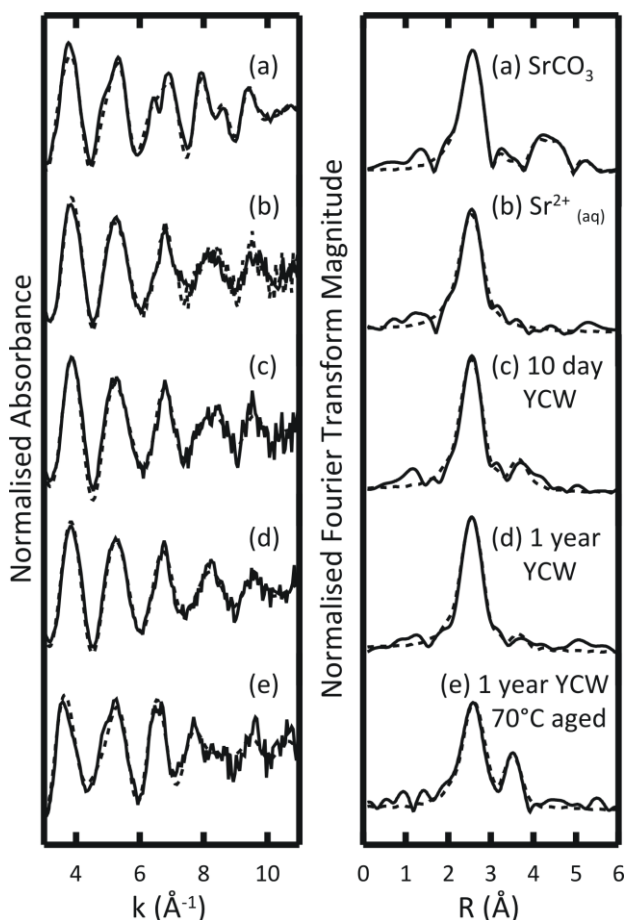


Figure 3 Background subtracted Sr K-edge EXAFS spectra (left hand side) and related Fourier transformations (right hand side) collected from a $3000 \text{ mg L}^{-1} \text{ Sr}^{2+}$ solution and sediment samples aged with Sr^{2+} for 10 or 365 days, and additional a sample aged for 365 days at 70°C . Dashed line represent model fits produced in DLExcurv V1.0 using the parameters listed below

Table 3 Sr K-edge EXAFS model fitting parameters where n is the occupancy ($\pm 25\%$), r is the interatomic distance ($\pm 0.02 \text{ Å}$ for the first shell, $\pm 0.05 \text{ Å}$ for outer shells), $2\sigma^2$ is the Debye-Waller factor ($\pm 25\%$), and R is the least squares residual. *Fixed

Sample	Shell	n	R (Å)	$2\sigma^2$ (Å ²)
Sr^{2+} solution	O	9.1	2.58	0.031
SrCO_3	O	9*	2.64	0.027
	C	6*	3.04	0.032
	Sr	6*	4.22	0.029
YCW 10 days	Sr	4*	4.97	0.033
	O	8.5	2.59	0.025
YCW 365 days	Si(Al)	2.7	3.79	0.020
	O	7.8	2.60	0.024
YCW 365 days + 70°C	Si(Al)	1.2	3.84	0.018
	O	8.2	2.67	0.027
	Si(Al)	5.5	3.45	0.028