

SUPPORTING INFORMATION FOR

Uranium and Technetium Bio-immobilization in Intermediate Scale Physical Models of a Permeable Reactive Barrier

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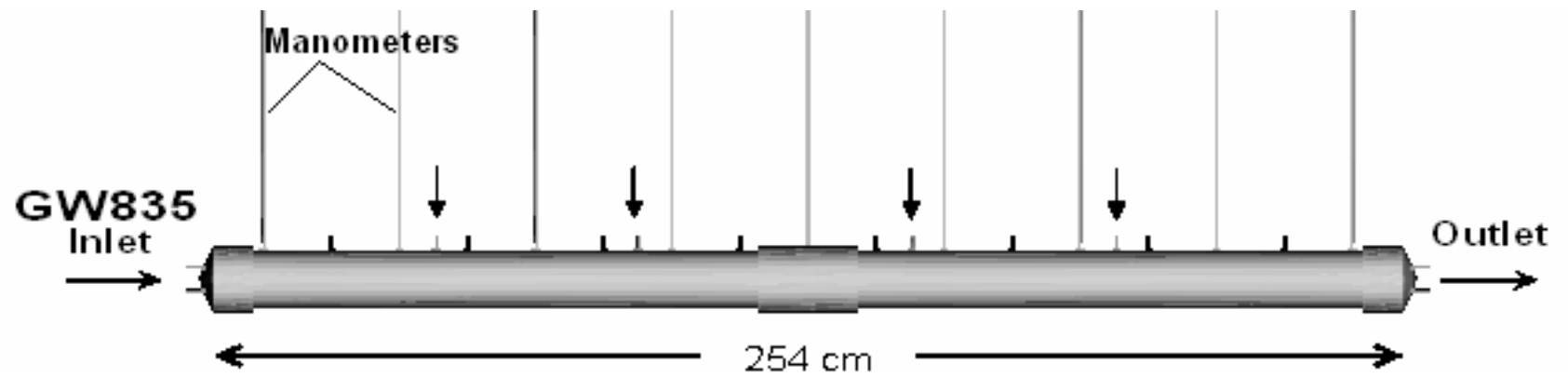


Figure 1. Diagram of the intermediate-scale physical models deployed at the FRC including 9 manometers, 8 sampling ports (no arrows) and 4 ethanol injection ports (arrows).

Characterization of Bulk Sediment: *Extraction Methods.* Soil pH was measured in a 1 part soil to 2 parts distilled (DI) water mixture using a glass electrode. P was determined by extracting 2.9 g sediment with 20 mL of 0.03 N NH_4F and 0.025 N HCl and the extract was analyzed colorimetrically. Ca, Mg, Na, Mg, and K were determined by extracting 2 g sediment with 50 mL 1 M NH_4 -acetate and the extract was analyzed by atomic absorption spectrometry. Cation exchange capacity (CEC) was determined by extracting the NH_4 -acetate treated sediment with neat EtOH, followed by hydrochloric acid (0.1 M) to replace the NH_4 . The NH_4 concentration in the extract was measured by an ALPKEM rapid flow analyzer (RF-300) and converted to CEC. Fe concentrations were determined by extracting 10 g of sediment with 20 mL of a diethylenetriaminepentaacetic acid, triethanolamine, and calcium chloride solution (0.025 M, 0.5 M, and 0.01 M, respectively) and the extract was analyzed by atomic absorption spectrometry. Nitrate and ammonium concentrations were determined by extracting 20 g of sediment with 75 mL of potassium chloride solution (2 M) and the extract was analyzed colorimetrically. Sulfate concentrations were determined by extracting 5 g of sediment with 50 mL of calcium phosphate solution (18.6 mM) and the extract was analyzed using ion chromatography. The weight of organic matter was determined as the weight difference before and after placing 10 g of dried sediment in a muffle furnace at 550 °C for 5 hours. Soluble salts were determined by extracting 30 g of sediment with DI water and the extract was analyzed with an electrical conductivity meter. The dithionite-citrate-bicarbonate extractable Fe concentration was determined by extracting ~ 0.4 g of sediment with 0.2 g of sodium dithionite, 8 mL of sodium citrate, and 1 mL of bicarbonate solution (0.3 mM and 1 M, respectively) for 3 hours. Sediment Fe(II) concentration was determined by extracting ~ 0.4 g of sediment with 10 mL of 0.5 M HCl for 1 hour. All samples were centrifuged and the total extracted Fe concentration was measured using a modified Ferrozine method (1, 2).

X-ray Diffraction. Sediment samples were ground using a mortar and pestle to a fine and visually consistent particle size, then packed into a zero background slide in a 9 mm well. The diffraction patterns were obtained using a Phillips X'Pert MPD X-ray diffractometer with $\text{Cu K}\alpha$ radiation over the

range 2 - 75 degrees 2θ . Diffraction patterns were analyzed for mineral identification using a search-match routine (Jade software, Materials Data, Inc.) with the JCPDS diffraction library (3).

X-ray fluorescence. Sediment samples (10 g) were placed in a tungsten carbide grinding vessel and ground for fifteen seconds using a Herzog HSM-100/H Semi-Automatic Pulverizer. Chemplex SpectroBlend briquetting additive (1 g) was added to the ground sediment and the mixed for six seconds. Two 38 mm Spex X-ray fluorescence (XRF) pellet caps were prepared for each sample by coating the cap bottoms with approximately four grams of boric acid. Ground sediment samples (5 g) were placed on top of the boric acid in each cap, the caps were inserted into a pellet die, and the pellet die was compressed to 35,000 psi using a Carver Press and held for three minutes. The pressure was then slowly released and the pellets were placed in a S4 Pioneer wave length dispersive XRF instrument from Bruker AXS (Madison WI). The weight percent of each metal oxide was measured using an analysis model developed for these samples and internally calibrated spectral lines. Total inorganic carbon was measured using a Leco carbon analyzer, and loss of volatiles was determined by loss on ignition after ashing in a muffle furnace.

X-ray diffraction (XRD) and XRF data were reduced to normative mineral compositions, as mole percents, using a much simplified approach based on the method for the normative reduction of bulk compositions of igneous rocks (4, 5). In each case, the XRD results were taken to represent the major mineral components of the samples. For the FRC Background sediment, these were quartz (SiO_2), muscovite [$\text{KA}_{12}\text{Si}_3\text{AlO}_{10}(\text{OH})_2$], and clinocllore [$(\text{Mg},\text{Al},\text{Fe})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$]; to account for Na and Ca in the bulk results, plagioclase feldspar [$(\text{Na},\text{Ca})(\text{Al},\text{Si})_4\text{O}_8$] was added, arbitrarily. For the Maynardsville Limestone, the minerals were orthoclase (KAlSi_3O_8), sanidine (KAlSi_3O_8), clinocllore [$(\text{Mg},\text{Al},\text{Fe})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$], dolomite [$(\text{CaMg})(\text{CO}_3)_2$], calcite (CaCO_3), and quartz (SiO_2). Only the listed, ideal mineral formulae were used. The bulk weight percent data were first converted to mole fractions, then logical step-wise mineral equivalents were calculated and subtracted from each component element, and the procedure was repeated, in turn. For the FRC Background sediment, all K

was attributed to muscovite, and its compositional equivalent was subtracted from the totals for K_2O , SiO_2 , and Al_2O_3 . This procedure was then followed, according to the mineral formulae, for Fe and Mg to chloritoid; Na and Ca to plagioclase; and Si to quartz. For the Maynardsville Limestone, the sequence was: all Mg was attributed to dolomite; all Ca to calcite; all Fe and Mg to chloritoid; all K to orthoclase; and all Si to quartz.

Sediment Sample Collection. Sediment samples were collected from the sample ports of the EtOH stimulated model and from the control model after 7 and 4 months of operation, respectively, in an Ar headspace. Hollow plastic tubes were inserted into the sample ports and finger pressure was applied to the open end of the tubes, creating a weak vacuum sufficient for sediment and pore fluid collection. The collected material was dispensed immediately into Ar filled serum bottles, which were quickly resealed, purged with Ar and refrigerated. Ports were left exposed to the atmosphere for less than 5 minutes after sample collection.

Sequential Extraction of Sediment Samples. Sediment subsamples were removed from the serum bottles in a nitrogen filled glove bag and were rinsed first with a known mass of deoxygenated DI water; next with deoxygenated, 1 M HCO_3^- ; and finally were incubated with concentrated nitric acid for ~ 24 hours. The mass of uranium extracted from the sediment by rinsing with DI water and HCO_3^- was considered to be U(VI) and the mass of uranium extracted during the acid incubation was considered to be U(IV).

X-ray Absorption Near Edge Spectra (XANES). Anoxic sediment subsamples were washed with pore fluid from the physical models, the fines were collected and the resulting wet pastes were mounted in ~ 5 mm slots within plexiglass sample holders and sealed with Kapton film covered with Kapton tape. This type of sample preparation has been previously demonstrated to preserve the anoxic integrity of the sample for more than 8 hours (data not shown).

The undulator of the insertion device was tapered to reduce variation in the incident x-ray intensity to less than 20 % over the scanned U L_{III} -edge region from 17.1 to 17.4 keV. The incident x-ray intensity

was monitored using an ionization chamber filled with a 1:1 mixture of He:N₂ gas. The fluorescent x-ray intensity was monitored by using an ionization chamber filled with Xe gas, solar slits, and an x-ray filter in the Stern-Heald geometry (6). Aluminum foil was used to minimize absorption of unwanted low energy x-rays and a platinum coated mirror was used to remove x-rays of higher harmonic energies. A uranyl phosphate U(VI) standard was measured in transmission mode using an ionization chamber filled with Ar gas and x-rays that penetrated the sample. The XANES measurements were made in quick scanning mode (~ 2 min per scan) and as many as 5 scans were collected from 6 different locations, for a total of 30 spectra per sample. The percentage of U(VI) to U(IV) in each sample was estimated by comparing the energy of the spectra at half the edge step to the U(IV) standard and the amount of uranium in each sample was estimated relative to the maximum fluorescent step height.

Mössbauer Spectroscopy. A 7 µm natural abundance Fe metal foil was used for velocity calibration of the spectrometer and isomer shifts were expressed relative to the center of the Fe metal resonance. Bulk sediment subsamples were transferred into TFE or nylon cups in an inert-gas filled glove box (Vacuum Atmospheres) to achieve ~ 5 mg Fe/cm² of cross-sectional area. The cup was then transferred to the sample positioner rod and inserted into a WEB Research/Janis Model SHI-850-5 closed-cycle refrigerated (CCR) cryostat, then purged with He gas. This cryostat is capable of reaching temperatures in the region of 4 K without adding liquid cryogenes. Spectra were acquired in 1024 channels with a drive system operating with a triangular waveform. The γ-ray source was nominally 50 mCi (1.85 GBq) ⁵⁷Co dispersed in a Rh matrix as 10% by weight (Ritverc GmbH, St. Petersburg, Russia). Sample temperature was controlled and equilibrated at 4, 77, or 298 K with a WEB model 320 auto-tuning temperature controller, and the spectrum obtained at a velocity range of ∇4 or ∇12 mm/s. A black precipitate, which was separated from the acid digestion of the stimulated sediment samples, was pooled into a single sample and its Mössbauer spectrum recorded at 4K over a ±12 mm/s velocity range.

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Table 1. Mineralogy of the physical model packing materials (left) and extraction characterization of the physical model packing materials (right). Please see the FRC website for a more detailed description of GW835 analytes <<http://public.ornl.gov/nabirfrc/sumgwarea2.cfm>>.

Mineralogy

Sediment Extraction

FRC Background sediment			Maynardsville Limestone			FRC Background sediment		
Mineral	Formula	% Weight	pH	8.9				5.2
Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	51.7	P (ppm)	<0.1				1.7
Clinochlore	$(Mg_{0.525}Fe_{0.475})_5Al(Si_3Al)O_{10}(OH)_8$	33.7	K (ppm)	37.0				92.0
Plagioclase	$(Na_{0.24}Ca_{0.76})(Si_{0.56}Al_{0.44})O_8$	4.9	Ca (ppm)	3660.0				880.0
Quartz	SiO_2	9.7	Mg (ppm)	315.9				145.8
Maynardsville Limestone			Na (ppm)	16.1				16.1
			B (ppm)	0.0				0.1
			Cu (ppm)	1.2				0.8
			Mn (ppm)	0.4				8.4
			Fe (ppm)	3.0				8.0
			Zn (ppm)	0.7				1.2
			NH4-N (ppm)	0.4				1.2
			NO3-N (ppm)	1.8				9.3
			SO4-s (ppm)	92.4				131.1
			CEC (meq/100g)	3.7				12.9
			Sol. Salts (mS/cm)	1.1				0.3
			% OM, loss on ignition	2.7				4.0
			DCB extractable Fe (ppm)	304				6820
			0.5 HCl extractable Fe (ppm)	430				19

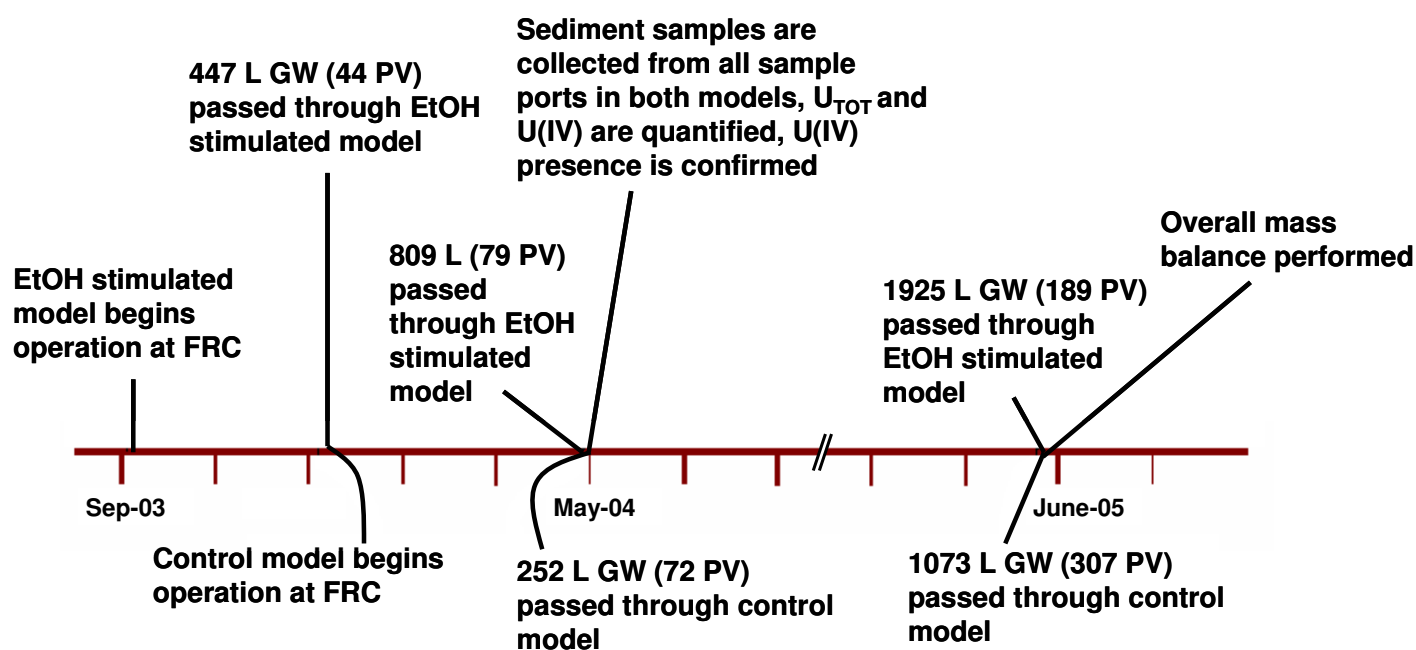


Figure 2. Experimental timeline for the stimulated (upper) and the control (lower) columns.

Table 2. Average contaminant removal rates in individual ports during 12.5 months of stimulated model operation. Upper rows contain rates calculated during the first 2.5 months (early); Lower rows contain rates calculated during 2.5 – 12.5 months of operation (late). Missing data indicate that concentrations were below the detection limit and negative rates indicate that concentrations were frequently higher at the subsequent port. Rate data terminate at month 13 due to lack of additional tracer. Measured rates were ~ 10 x greater than those measured during push-pull test with EtOH serving as electron donor (manuscript 25).

	Port 1	Port 2	Port 3	Port 4	Port 5	Port 6	Port 7	Port 8	Outlet
Tc, pM/hr	36.3	6.18E-01	3.72	-2.02	2.03	-4.28E-01	-	-	-
U, μ M/hr	3.39E-01	-1.54E-03	4.00E-02	-1.77E-02	2.70E-02	3.86E-03	2.76E-03	-6.01E-04	1.27E-03
NO ₃ , mM/hr	6.44E-02	-	-	-	-	-	-	-	-
SO ₄ , mM/hr	4.66E-02	-1.75E-03	7.60E-03	1.93E-03	4.80E-03	2.13E-04	-1.37E-03	-6.28E-05	-2.59E-03
Tc, pM/hr	42.4	1.23	-8.09E-01	3.36	2.25	2.69	2.14E-01	-	-
U, μ M/hr	3.17E-01	9.16E-03	-2.93E-02	3.48E-02	1.53E-02	2.83E-02	6.76E-03	-5.30E-04	1.88E-03
NO ₃ , mM/hr	5.45E-02	-	-	-	-	-	-	-	-
SO ₄ , mM/hr	6.43E-02	5.02E-03	-1.05E-02	3.59E-03	9.14E-03	6.06E-03	5.11E-03	1.15E-03	1.26E-03
	maximum rate of removal in EtOH stimulated model		maximum rate of removal in EtOH stimulated field push-pull tests						
Tc, pM/hr	42.4		3.50						
U, μ M/hr	3.39E-01		2.00E-02						
NO ₃ , mM/hr	6.44E-02		1.00E-02						
SO ₄ , mM/hr	6.43E-02		-						

Table 3. Results of mass balance performed on U and Tc after 20 months of stimulated column operation and 16 months of control operation. The stimulated column removed significantly more U and Tc mass per liter of groundwater.

	Stimulated Column	Control Column
U_{TOT}, mg	1786	218
Tc_{TOT}, mg	0.11	0.06
Total volume of groundwater, L	1925	3313
U removal efficiency, mg/L	0.93	0.07
Tc removal efficiency, mg/L	5.7E-05	1.8E-05

Table 4. Description of XANES measurements from sediment samples and standards.

Sample Description	Fluorescence Step Height	Relative amount of U in sample compared to stimulated model port 4	Energy (eV \pm 0.3 eV) at half the U LIII-edge step of the normalized absorption data	U(IV) (% \pm 10 %)
Stimulated Port 1	0.003	0.52	17164.25	98
Stimulated Port 2	0.0027	0.46	17164.46	92
Stimulated Port 4	0.0058	1.00	17164.67	85
Control Port 3	0.0017	0.29	17164.2	100
U(IV) Standard			17164.2	100
U(VI) Standard			17167.3	0

a. The fluorescence step height can be used to determine the relative total U concentration in samples by keeping all experimental conditions constant.

Redox Calculations for Stimulated Physical Model. Sulfate concentrations were routinely measured in the physical model pore water but sulfide was not. At pH 7.66, the average pH in all ports along the model, HS^- is the predominant species. The Nernst equation was used to estimate the redox potential in the physical model assuming decreases in sulfate concentration resulted in proportional sulfide concentrations. The sulfate concentrations were zero in port 8 but here we use 1E-04 as an approximation in the Nernst equation.

Table 5. Measured sulfate and approximated sulfide concentrations used in the Nernst Equation to calculate representative Eh values from in the stimulated column.

Stimulated Column Port	Average Measured Sulfate, mM	Approximated Sulfide, mM	E _H , mV
Inlet	1	1E-04	-240
Port 4	0.10	0.9	-277
Port 8	1.E-04	1	-299

Sulfate/Sulfide Half Reaction:



Nernst Equation:

$$E_H = E_H^o - \frac{2.303RT}{n_e F} \log K$$

$$E_H = 248mV - \left[2.303 \frac{\left(\frac{8.314J}{mol-K} \right) \left(\frac{298K}{1} \right)}{(8moleq) \left(\frac{96485J}{moleq-V} \right) \left(\frac{V}{1000mV} \right)} \right] \log \frac{[HS^-]}{[SO_4^{2-}][H^+]^9}$$