Examination of Cr(VI) treatment by zero-valent iron using in situ, real-time X-ray absorption spectroscopy and Cr isotope measurements

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Abstract

A series of replicate flow-through cell experiments was conducted to characterize Cr isotope fractionation during Cr(VI) treatment by granular zero-valent iron (ZVI). Synthetic groundwater containing 50 mg L⁻¹ Cr(VI) was pumped upward through a custom-made cell packed with ZVI under anaerobic conditions. The geochemical evolution of the system was monitored using pH and redox measurements, while aqueous effluent samples were retained for analysis of cations and Cr isotopes. Real-time, in situ X-ray absorption near edge structure (XANES) spectroscopy collected via a Kapton® window in the cell provided additional information on the speciation of the reaction products. Increases in $\delta^{53}\text{Cr}$ values corresponding to decreases in Cr(VI) concentration suggested the occurrence of redox processes. Spectroscopic results correlated well with the isotope data, indicating reduction of Cr(VI) to Cr(III). The isotope data did not appear to follow a single trend. A two-stage system was proposed to explain the complex isotope trend, where the rapid Cr removal was associated with very little fractionation ($\epsilon = -0.2\text{‰}$), whereas slower removal was associated with a greater degree of fractionation ($\epsilon = -1.2$ to -1.5‰). Reactive transport modeling was used to quantify distinct isotope fractionation values (ϵ), differentiated by a significant change in the Cr removal rate.

28

29 **1 Introduction**

30 Chromium has four stable isotopes, ^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr , with natural abundances of
31 4.35%, 83.8%, 9.5%, and 2.37%. Redox reactions have been shown to induce isotope
32 fractionation, with the greatest shifts predicted to occur during reduction of tetrahedrally-
33 coordinated Cr(VI) to Cr(III), which is octahedrally-coordinated (Schauble et al., 2004). The
34 lighter isotopes are preferentially reduced, resulting in an enrichment in the heavy isotopes in the
35 remaining unreacted Cr(VI) pool. This enrichment is measured as the change in $^{53}\text{Cr}/^{52}\text{Cr}$, where
36 elevated $\delta^{53}\text{Cr}$ values in the remaining Cr(VI) are indicative of reduction.

37 Remediation of Cr(VI)-contaminated groundwater focuses on the reduction of this mobile
38 and highly toxic form to the less toxic Cr(III). Reduction is generally followed by rapid
39 precipitation of the sparingly soluble Cr(III), often as $\text{Cr}(\text{OH})_3$ or a mixed Cr-Fe hydroxide solid
40 phase in the presence of Fe (Blowes et al., 1997). Laboratory experiments have demonstrated
41 that the degree of fractionation is dependent on the mechanism of removal and the electron
42 donor, as summarized in Table 1. Materials used to induce reduction in these experiments
43 include ferrous iron, both as $\text{Fe}(\text{II})_{\text{aq}}$ and in the form of Fe(II)-bearing minerals (Ellis et al., 2002;
44 Berna et al., 2010; Døssing et al., 2011; Kitchen et al., 2012; Basu and Johnson, 2012), organic
45 carbon (Kitchen et al., 2012; Jamieson-Hanes, Gibson et al., 2012), Cr-reducing bacteria (Sikora
46 et al., 2008; Han et al., 2012), and hydrogen peroxide (Zink et al., 2010). A large range of values
47 has been reported for Cr isotope fractionation during reduction of Cr(VI) (Table 1). In several
48 cases, a general trend has been observed showing an increase in reduction rate is correlated with
49 a decreasing degree of fractionation (Sikora et al., 2008; Basu and Johnson, 2012), which has
50 been simulated by reactive transport modeling (Wanner and Sonnenthal, 2013). Additionally,

Ellis et al. (2004) demonstrated that little to no fractionation occurs during sorption of Cr(VI) to goethite and γ -alumina.

Enriched $\delta^{53}\text{Cr}$ values have also been observed in field samples collected at both anthropogenically and naturally contaminated sites, but system heterogeneities and complex flow regimes have posed considerable challenges for data interpretation (Ellis et al., 2002; Izbicki et al., 2008; Berna et al., 2010; Raddatz et al., 2011; Villalobos-Aragón et al., 2012; Wanner, Zink, et al., 2012; Wanner, Eggenberger, Kurz, et al., 2012; Izbicki et al., 2012). Jamieson-Hanes, Gibson, et al. (2012) explored the potential influence of transport by comparing Cr(VI) reduction by organic carbon in a batch and a column experiment. A significant difference was observed in the isotope behaviour under static and saturated flow conditions, and was attributed to the presence of multiple Cr removal mechanisms. Reactive transport modeling of these experiments identified a two-part isotope curve along the column (Jamieson-Hanes, Amos, et al., 2012), in which the slower rate of Cr removal was associated with a greater degree of isotope fractionation.

Granular zero-valent iron (ZVI) is frequently used for the treatment of Cr(VI) in groundwater, particularly in the construction of permeable reactive barriers (PRBs) (Blowes et al., 1997; Blowes et al., 2000; Jeon et al., 2008). Remediation is achieved via the reduction of Cr(VI) to Cr(III) by Fe^0 :

(1)

or the reduction of Cr(VI) by aqueous ferrous iron:

73 which is produced through equation (1) or following the reduction of water by Fe^0 :

75 Reduction is then followed by precipitation as $Cr(OH)_3$:

77 or by precipitation of mixed Fe(III)-Cr(III) hydroxide:

79 or by precipitation of mixed Fe(III)-Cr(III) (oxy)hydroxide (Blowes et al., 1997):

81 The rate of Cr(VI) removal has been reported to be dependent on Cr(VI) concentration, pH, and
82 surface area of the iron (Gould, 1982):

83 $\frac{d[Cr(VI)]}{dt} = -k \cdot S[Cr(VI)]^{0.5}[H^+]^{0.5}$ (7)

84 where $\frac{d[Cr(VI)]}{dt}$ is in units of mol L⁻¹ bulk s⁻¹, k is the rate constant normalized to the surface area
85 of the ZVI (L H₂O m⁻² Fe s⁻¹), S is the reactive surface area of ZVI (m² Fe L⁻¹ bulk), and
86 $[Cr(VI)]$ and $[H^+]$ are in units of mol L⁻¹ H₂O. However, the rate of reduction has been often
87 reported as first order with respect to Cr(VI) with no dependence on pH (Gheju, 2011, and
88 references therein).

The objective of this study was to determine whether the complex Cr isotope behaviour observed in Jamieson-Hanes, Gibson, et al. (2012) using organic carbon is observed during reduction of Cr(VI) using other reactive materials. In this study, granular ZVI was used to treat Cr(VI) under saturated flow conditions. A flow-through cell approach was implemented to facilitate real-time, in situ measurements of the Cr reaction product by X-ray absorption near-edge structure (XANES) spectroscopy. Analyses of water chemistry and stable Cr isotope ratios were performed to further characterize the treatment system. Reactive transport modeling was used to provide a quantitative analysis of the system. Controlled laboratory experiments such as these provide additional insight into the behaviour of Cr isotope fractionation during reduction of Cr(VI) under saturated flow conditions, such as those found in real-world groundwater plumes.

2 Materials and Methods

2.1 Flow-through cell design

Three replicate flow-through cells (FTCs) were designed and fabricated for this experiment using high-density polyethylene (HDPE). The overall cell dimensions were $7 \times 5.5 \times 2.5$ cm, with an open-faced indentation measuring $1.5 \times 3 \times 0.5$ cm (2.25 mL volume, 4.5 cm^2 face area) on one side to contain the experimental material (Figure 1). This exposed face was covered by an 80 μm -thick Kapton® film to allow transmission of X-rays. A HDPE frame was bolted onto the face of the cell to hold the Kapton® film in place, creating a gas-tight seal with an O-ring. Ports measuring 2 mm in diameter were installed at the bottom and top of the cell for inflow and outflow, respectively.

2.2 *Experimental setup*

Fresh ZVI (Connelly GPM Inc., Chicago, IL) was acid-washed with 1 M HCl and conditioned with Ar-purged deionized (DI) water under anaerobic conditions to remove oxide coatings. This process was intended to simulate the aging of a permeable reactive barrier in contact with CaCO₃-saturated, low-oxygen groundwater, which is representative of the major characteristics of typical groundwater composition (Gui et al., 2009). Three FTCs, designated as A, B, and C, were packed with ZVI within an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI) under a 3.5% H₂/balance N₂ atmosphere with approximately 6-8 g of conditioned ZVI, resulting in a porosity of approximately 50%. Nitex® mesh screen with 210 µm openings (Sefar, Depew, NY) and glass wool was placed in both end ports to distribute flow and prevent the ZVI from clogging the cell. After packing, the cells were sealed under anaerobic conditions.

Each cell was saturated with Ar-purged DI water just prior to the beginning of the experiment. A conservative tracer test was conducted on cell A to evaluate transport characteristics. The tracer solution was prepared by dissolving NaCl in Ar-purged DI water to achieve a final Cl⁻ concentration of 350 mg L⁻¹. The flow rate was set to be the same as that used in subsequent Cr(VI) treatment experiments. Samples were collected every 12 seconds over a 40 minute period during which the tracer solution was applied. The cell was completely flushed with Ar-purged DI water at the conclusion of the tracer test. Tracer samples were weighed and diluted 50x with 5 mL of high-purity water, then filtered with 0.45 µm filters for analysis by ion chromatography (Dionex DX 600).

An input solution of 50 mg L⁻¹ Cr(VI) was prepared by dissolving K₂Cr₂O₇ (99+% Baker Analyzed ACS Reagent) in synthetic groundwater, composed of Ar-purged DI water saturated

with respect to CaCO_3 . The target pH of the input solution was 8.00 – 8.50. Anaerobic conditions were maintained during the experiment by protecting the solution with an Ar-filled Mylar™ balloon. The solution was pumped in an upward direction through the cell using a peristaltic pump (Ismatec™, Cole-Palmer, Montreal, QC) with 0.89 mm ID Pharmed® pump tubing (Cole-Parmer, Vernon Hills, IL). A pump speed of 0.5 mL min^{-1} (approx. 25 pore volumes per hour) was implemented so that complete Cr(VI) breakthrough would occur after 24 hours due to loss of ZVI reactivity.

At the effluent end of the cell, flow-through microelectrodes (Microelectrodes, Inc., Bedford, NH) were installed in series to measure pH and redox conditions. The electrodes were conditioned with 10% HCl for 5 minutes under flow-through conditions prior to calibration with pH 7 and 10 buffers, which bracketed the expected pH range of the experiment. The redox microelectrode performance was verified with ZoBell's solution (Nordstrom, 1977) and Light's solution (Light, 1972). Data was logged on two Orion Star A321 portable meters (Thermo Scientific); the reference microelectrode was connected to both meters using a patch cord.

2.3 *X-ray absorption spectroscopy*

Synchrotron-based XANES spectroscopy was performed at beamline 13-BM-D at the Advanced Photon Source, Argonne National Laboratory (Argonne, IL). Spectra were collected at the Cr K-edge (5989 eV) in bulk mode with an unfocused incident beam ($\sim 0.5 \times 10 \text{ mm}$). Finely ground reference materials were spread onto polyethylene terephthalate (PET) tape (Scotch Magic Tape, 3M, St. Paul, MN) and layered to achieve a thickness of 300-500 μm . Spectra for solid-phase reference materials, including Cr(0), Cr(OH)_3 , and $\text{K}_2\text{Cr}_2\text{O}_7$, were collected in transmission mode. An aqueous Cr(VI) reference standard was created by saturating silica sand with the 50 mg L^{-1} Cr(VI) input solution in a plastic cylinder with a Mylar window, then

collecting XANES spectra in fluorescence mode. Spectra were collected throughout the FTC experiment in fluorescence mode, capturing both the signal from the solid-phase Cr and any aqueous Cr. The Kapton® window of the cell was positioned at a 45° angle to the incident beam; the fluorescence detector (12-element Canberra High-Purity Germanium) was positioned at a 45° angle to the window of the cell. The dimensions of the beam corresponded to approximately 0.05 cm², or 1.1% of the cell face area. The beam was positioned in the top third of the window of the cell, near the effluent end. Scans were relatively rapid (~7 minutes), and were collected continuously throughout the entire experiment at the same position. At the conclusion of the experiment, after complete Cr(VI) breakthrough had been achieved, the beam was positioned at the bottom, middle, and top areas of the cell window. Several scans were taken at each of these locations to evaluate the spatial variability of the Cr.

Post-processing of the XANES data was carried out using the program ATHENA, which is a component of the IFEFFIT software package (Ravel and Newville, 2005). The spectrum for Cr(0) was shifted to the theoretical K-edge energy of 5989 eV; all other spectra were shifted accordingly. Unknown spectra during the FTC runs were merged in groups of three chronologically (i.e. 1+2+3, 4+5+6, etc.), and the mid-point of the total elapsed time for the three scans was assigned as the time for the merged scan. Linear combination fitting (LCF) was performed on normalized spectra in the range between -20 eV and 30 eV relative to the edge to estimate the relative amounts of Cr(0), Cr(III), and Cr(VI) at various times during the experiment. Statistics indicating the goodness of fit are provided along with the LCF results in Table 2.

2.4 *Aqueous sampling*

Effluent samples were collected continuously with a fraction collector (Retriever® 500, Teledyne ISCO, Lincoln, NE). Sampling rates varied between 4 and 6 samples an hour; full sample vials were removed from the fraction collector at least every 4 hours to minimize evaporation. The mass of the sample was measured by subtracting the mass of the empty vial from the mass of the full vial. At each sample collection time, external pH measurements were performed on the most recent sample to compare to the in situ measurements. External pH measurements were performed using a gel-filled combination pH electrode (Thermo Scientific) calibrated with pH 7 and 10 buffers.

The remaining aqueous samples were filtered at 0.2 µm and stored at 4°C. Every fifth sample was used for Cr(VI) analysis. Concentrations of Cr(VI) were measured immediately on a Hach DR 2800TM spectrophotometer using the 1,5-diphenylcarbohydrazide method at 540 nm (Greenberg et al., 1992). Approximately every sixth sample was acidified to pH < 2 with trace-metal grade HNO₃; total Cr concentrations and concentrations of other cations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES; Thermo Scientific iCAP 6500) on these samples upon return to the University of Waterloo.

2.5 *Measurement of Cr isotope ratios*

Sample preparation and Cr isotope analysis was conducted following the techniques described in Jamieson-Hanes, Gibson et al. (2012). Acidified samples were spiked with a ⁵⁰Cr-⁵⁴Cr double-spike solution of known isotopic composition prior to oxidation with ammonium persulfate. The oxidized spike-sample mixtures were loaded onto Bio Rad AG1-X8 anion exchange resin that had been conditioned with trace metal grade HNO₃. Impurities such as Fe, V,

and Ti were removed by flushing with high-resistivity (18.2 MΩ·cm) water. Reduction to Cr(III) was achieved by saturating the resin with 2 N HNO₃ for 2 h, after which the purified samples were eluted and prepared for analysis.

Cr isotope measurements were performed on a multi-collector ICP-MS (Thermo Scientific Neptune), allowing the simultaneous measurement of all four Cr isotopes, ⁵⁰Cr, ⁵²Cr, ⁵³Cr, and ⁵⁴Cr, along with ⁴⁹Ti, ⁵⁰V, and ⁵⁶Fe to correct for isobaric interferences. Polyatomic interferences of ⁴⁰Ar¹⁴N on ⁵⁴Cr and ⁴⁰Ar¹⁶O on ⁵⁶Fe were avoided by off-centre peak analysis in medium resolution mode. Instrumental mass bias was corrected using a double-nested iterative routine, and the true isotopic composition of the samples was expressed as δ⁵³Cr in per mil (‰) relative to the NIST SRM 979 Cr isotope standard, where:

$$\delta^{53}\text{Cr} = \left[\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{standard}}} - 1 \right] \times 1000\text{‰} \quad (8)$$

Samples were normalized to daily measurements of SRM 979. (see Electronic Annex for long-term stability of SRM 979 measurements, Figure EA-1). Uncertainty of the isotope measurements was calculated to be ±0.04‰ based on two times the root-mean-square difference of eight unknown samples prepared in duplicate (one duplicate pair per batch of prepared samples), following the approach of Basu and Johnson (2012).

2.6 Reactive transport modeling

The reactive transport code MIN3P (Mayer et al., 2002) was used to simulate Cr isotope fractionation and related geochemical changes in the flow through cells. The model employs the formulation of Gibson et al. (2011) describing isotope fractionation, which was subsequently used by Jamieson-Hanes, Amos, et al. (2012) to simulate Cr isotope fractionation in an organic

220 carbon system. Chromium reduction reactions (Equations 1 and 2) were each treated as two
 221 separate reactions to describe the reduction of each isotope. For example, Equation 1 was
 222 simulated as:

224 and

226 where the effective rate parameters k_{52} and k_{53} are a function of the overall effective reaction rate
 227 constant (k_{eff}):

$$228 \quad k_{eff} = k_{52} + k_{53} \quad (11)$$

229 and the isotope fractionation factor (α_{53}):

$$230 \quad \frac{k_{53}}{k_{52}} = \alpha_{53} R_{53} \quad (12)$$

231 where R is the isotope ratio.

232 The simulated reaction network included Cr(VI) reduction by Fe^0 (Equation 1) and Fe^{2+}
 233 (Equation 2), the reduction of water by Fe^0 (Equation 3), and the precipitation of Cr hydroxide
 234 (Equation 4). In addition, the model allowed for the precipitation or dissolution of aragonite,
 235 ferrihydrite, ferrous hydroxide and ferrous hydroxy carbonate. Modeled reactions, reaction rate
 236 expressions, and model parameters are summarized in Tables 3 and 4. Cr reduction rates were
 237 modeled to be independent of pH to facilitate model calibration in this highly coupled system.

Reactions with ZVI (Equations 1 and 3) were modeled using the formulation of Jeon et al. (2007) to simulate the decline in ZVI reactivity induced by the precipitation of secondary minerals:

$$S(x, t) = S_0 \exp \left(- \sum_i \alpha_i \varphi_i(x, t) \right) \quad (13)$$

where $S(x, t)$ is the reactive surface area of iron at a specific location along the flow path and time ($\text{m}^2 \text{ iron L}^{-1} \text{ bulk}$), S_0 is the initial reactive surface area of the iron ($\text{m}^2 \text{ iron L}^{-1} \text{ bulk}$), α_i is the proportionality constant for mineral phase i , and φ_i is the volume fraction of mineral phase i at a specific location and time ($\text{m}^3 \text{ mineral m}^{-3} \text{ bulk}$).

The rate expression for the reduction of water by Fe^0 ($R_{\text{Fe}^0-\text{H}_2\text{O}}$) was not considered to be dependent on the volume fraction of ZVI:

$$R_{\text{Fe}^0-\text{H}_2\text{O}} = k S_0 \exp(\alpha_i \varphi_i(x, t)) \quad (14)$$

whereas this variable ($\varphi_{\text{Fe}^0-\text{Cr(VI)}}(x, t)$) was included in the rate expression for the reduction of Cr(VI) by Fe^0 to simulate the dependence of the reaction on the availability of surface sites (Table 4):

$$R_{\text{Fe}^0-\text{Cr(VI)}} = k S_0 \exp(\alpha_i \varphi_i(x, t)) \{^{52}\text{CrO}_4^{2-}\} \{\varphi_{\text{Fe}^0-\text{Cr(VI)}}(x, t)\} \quad (15)$$

3 Results and Discussion

3.1 Cell flow characteristics

Results from the conservative tracer test were modeled using the Stanmod CXTFIT 2.1 software package (Toride et al., 1999). A 1σ band-pass filter was applied to the experimental data to eliminate outliers prior to fitting. Measured Cl^- concentrations and the modeled breakthrough curve are included in the Appendix (Figure EA-2). Approximately 5 min elapsed between the first appearance of Cl^- in the effluent and complete breakthrough. Fitting in CXTFIT generated a dispersion coefficient estimate of $7.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. Assuming a typical diffusion coefficient of $1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Freeze and Cherry, 1979), the calculated longitudinal dispersivity is then $1.2 \times 10^{-3} \text{ m}$. Linear velocity was calculated as approximately 2.1 m d^{-1} . The results of the tracer test demonstrate that the flow regime in the flow-through cells was representative of conditions observed in similar laboratory column experiments using 100% Connelly ZVI to treat Cr(VI) (Jeen et al., 2008; Gui et al., 2009).

During the treatment experiments, effluent volume was monitored by weighing sample vials before and after sample collection. In all three replicate experiments a decreasing trend in sample mass was observed over time relative to the first sample (Figure EA-3). This change in effluent discharge likely indicates a decrease in the pore volume and hydraulic conductivity due to secondary mineral precipitation and/or gas bubble formation and elution of bubbles. The peristaltic pump was set at a fixed number of revolutions per minute, so a decrease in hydraulic conductivity within the cell would result in an increase in system pressure, and thus a slight decrease in flow rate.

3.2 Aqueous geochemistry

The pH and Eh data for replicate experiments A, B, and C are plotted in Figure 2. Periodic external pH measurements made over the course of each experiment were found to differ significantly from the internal pH values measured by the microelectrode. This discrepancy may be due to a combination of the high flow rate and the high aqueous K^+ concentration ($\sim 35 \text{ mg L}^{-1}$), causing a streaming potential in the microelectrodes. External values were found to be in better agreement with previous experiments using the same geochemical system (Jamieson-Hanes, 2012); thus, pH data from the microelectrode was discarded and interpretations are based on external measurements.

Initially, all three replicate experiments exhibited a significant increase in pH, from input values of 8.38 (A), 8.15 (B), and 8.23 (C), up to a maximum value of 10.42 (A), 9.57 (B), and 10.40 (C). Corrosion of ZVI under anaerobic conditions coupled with the reduction of water results in a characteristic increase in pH (Equation 3; Blowes et al., 2000). Reduction of Cr(VI) by ZVI also results in an increase in pH, while the subsequent precipitation of Cr(III)-Fe(III) (oxy)hydroxides produces H^+ . However, it has been shown that overall an increase in pH is observed in this type of system with these combined reactions (Powell et al., 1995; Blowes et al., 1997; Blowes et al., 2000):

After reaching a maximum pH value at early time, the pH in all replicate experiments followed a general decreasing trend to a final value of 8.4 – 8.8, approaching input pH values.

Measured values of Eh followed a general trend toward reducing conditions in all three replicate experiments throughout the first 7 – 8 hours, reaching a minimum of -180 mV (B).

After this time, the Eh values began to increase. This trend corresponds well with the inflection point observed in the Cr(VI) breakthrough curve (see Section 3.3), where reducing conditions prevailed during the period of most rapid Cr removal.

3.3 Cr(VI) removal

Effluent Cr(VI) concentrations for experiments A, B, and C are plotted in Figure 2. Every fifth sample was analyzed for Cr(VI) at the time of sample collection; adjacent samples were acidified and analyzed for total Cr. Later analysis of the Cr(VI) samples for total Cr by ICP-OES showed good agreement between the measurements (linear regression, slope = 0.99, $R^2 = 0.96$), suggesting that any reduced Cr(III) was rapidly removed from solution. Consequently, all total Cr data is reported interchangeably as Cr(VI) or Cr in the following results and discussion.

Generally, the Cr(VI) breakthrough curves were well matched between the replicate experiments. Complete Cr(VI) removal was initially observed in the cell effluent. After 1 hour, the reactivity of the ZVI began to decline and the effluent Cr concentration began to increase. At first a rapid increase in Cr concentration was observed; after 6-7 hours the Cr breakthrough curve became shallower, reaching a plateau that slowly approached the input concentration by the end of the experiment. For comparison, breakthrough of the Cl⁻ tracer occurred within approximately 5 minutes. Chromium removal rates were calculated for all three experiments as the change in [Cr(VI)] over time, using Equation 7. The rates were found to differ between the two regions of the breakthrough curves by an order of magnitude. From the beginning of the experiment until ~7.5 hours, the calculated Cr removal rates were $3 - 4 \times 10^{-8} \text{ mol L}^{-1} \text{ bulk s}^{-1}$; after ~7.5 hours the calculated rates slowed to $4 \times 10^{-9} - 1 \times 10^{-8} \text{ mol L}^{-1} \text{ bulk s}^{-1}$. Rate constants (k) were calculated using Equation 7, and were also found to change significantly in magnitude after approximately 7.5 hours of elapsed time in each experiment. Values at early time ranged from 1.2×10^{-2} to $4.1 \times$

$10^{-2} \text{ L H}_2\text{O m}^{-2} \text{ Fe s}^{-1}$, while values at later time ranged from 2.4×10^{-4} to $2.8 \times 10^{-4} \text{ L H}_2\text{O m}^{-2} \text{ Fe s}^{-1}$. Figure EA-4 shows the predicted Cr(VI) concentrations vs. time as calculated with a single rate constant using the measured pH values and a constant surface area, in comparison with the measured Cr(VI) data from FTC A, B, and C. This figure demonstrates that a single k value using the rate law specified in Equation 7 is not sufficient to accurately describe the trend in Cr(VI) concentration observed in the FTC experiments.

3.4 *In situ Cr speciation*

Experiment A was conducted at the University of Waterloo. Experiments B and C were carried out at the Advanced Photon Source to collect real-time, in situ XANES measurements. At early time, XANES spectra most closely resembled the Cr(0) standard (Figure 3). Connelly ZVI contains up to 0.2 wt % Cr as determined by aqua regia digestion (Connelly GPM, written communication). It is not unexpected that Cr(0) would be the strongest signal detected prior to accumulation of Cr from the input solution. However, it is expected that the Cr(0) contained in the ZVI would be stable, particularly under reducing conditions, therefore would not contribute to the aqueous Cr concentration or isotope composition. As the experiment progressed, the shape of the spectra became more similar to Cr(OH)₃ (Figure 3), suggesting that Cr(VI) removal proceeded *via* reduction to Cr(III) and precipitation of a Cr hydroxide phase.

During the first few hours of the experiment, the pre-edge 3d-4p peak indicative of the presence of Cr(VI) was absent. Over time, a very small Cr(VI) pre-edge feature became apparent (see shaded area in Figure 3). Each cell was packed with ZVI and saturated with input solution, which continued to flow throughout the experiment. Under the X-ray beam, Cr would be detected in both the solid phase and the aqueous phase. As the reactivity of the ZVI was depleted, effluent Cr(VI) concentrations increased and breakthrough occurred. It is likely that the

minor contribution of Cr(VI) to the XANES spectra at later time was due to the presence of aqueous Cr(VI) within the cell, not solid-phase Cr(VI). X-ray absorption spectroscopy does not allow sorbed Cr(VI) on the surface of the ZVI to be distinguished from aqueous Cr(VI). However, the increase in the small Cr(VI) pre-edge feature coincides temporally with the increase in aqueous Cr(VI) concentration as detected in the effluent. This trend is consistent with the interpretation that the Cr(VI) signal was derived from aqueous Cr rather than Cr(VI) at the ZVI surface.

Linear combination fitting (LCF) was performed on the spectra depicted in Figure 3, using Cr(0), Cr(OH)₃, and Cr(VI)_{aq} (silica sand saturated with the input solution containing dissolved K₂Cr₂O₇) as reference materials. Table 2 shows the results of the fitting; the reported χ^2 value provided by the Athena software describes the goodness of fit. In general, the fit was very good, with χ^2 values less than 0.1 for almost all spectra. As well, the fit improved over time as the signal strength increased due to the increase in Cr abundance. Both experiments B and C showed a general increasing trend in the proportion of Cr(OH)₃ with time, which corresponds with the visual observations of the spectra. The LCF results also showed a slight increase in the proportion of Cr(VI) with time, although it never exceeded ~ 6% of the total signal. A decrease in the proportion of Cr(0) was also observed. The pre-existing Cr(0) derived from the ZVI is expected to be stable, particularly under reducing conditions. Thus it is likely that the background signal of Cr(0) from the ZVI was constant, but the mass of Cr(III) and Cr(VI) increased with time, resulting in a decrease in the relative proportion of Cr(0) as compared to the total mass of Cr.

The same XANES spectra from Figure 3 are plotted as energy vs. X-ray absorption in Figure 4. Without normalization, this plot shows a general increase in signal intensity which is

attributed to accumulation of solid-phase Cr on the surface of the iron over the course of the experiment. This increasing trend in signal intensity is particularly clear in the spectra for experiment C because the background Cr(0) signal was much less than in B. Figure 4 also shows a rapid increase in the Cr(III) signal intensity during the initial 8 hours of the experiment and slower increase in intensity thereafter, consistent with the Cr(VI) removal rates.

At the conclusion of each experiment, the pump was turned off and the cell ports were sealed to halt the flow of water. XANES spectra were then collected at three positions along the length of the cell window, designated as bottom (closest to input), middle, and top (closest to effluent). A plot of energy vs. X-ray absorption (i.e. not normalized) shows an increase in intensity, consistent with a greater accumulation of Cr at the base of the flow-through cell, and a general decrease in the intensity of the Cr signal towards the top of the cell (Figure 5). This trend is consistent with a higher aqueous Cr(VI) concentration near the inlet, resulting in an accumulation of Cr(III) at the bottom compared to the rest of the cell. After the reactivity of the ZVI closest to the inlet declined, the Cr(VI) front progressed upward through the cell, eventually breaking through at the effluent end. Although wide (~ 10 mm), the limited vertical height of the beam (~ 0.5 mm) provided only spot measurements covering 1.1% of the total area of the cell. As a result, the positions selected for post-experimental analysis in experiment C exhibited a clear gradient, whereas B did not, likely due to the very small areas covered by the beam. Beamtime was limited, as with every experiment; it would have been preferable to extend the study of spatial variation, however this was not possible with the available beamtime.

3.5 Cr isotope fractionation

Chromium isotope analyses were performed only on samples from experiments B and C, because these were the experiments conducted in tandem with the in situ XANES measurements.

The Cr isotope signature of the input solution had values of $\delta^{53}\text{Cr} = 0.00 \pm 0.04 \text{ ‰}$ (B) and $\delta^{53}\text{Cr} = -0.03 \pm 0.04 \text{ ‰}$ (C) relative to SRM 979. Effluent samples at early times had low Cr concentrations and positive $\delta^{53}\text{Cr}$ values; increases in Cr concentrations during the arrival of the Cr front were associated with decreases in $\delta^{53}\text{Cr}$ values (Figure 6). The overall degree of fractionation was relatively low, attaining a maximum $\delta^{53}\text{Cr}$ of $0.47 \pm 0.04 \text{ ‰}$ relative to the input for FTC B, and $0.48 \pm 0.04 \text{ ‰}$ relative to the input for FTC C.

Although the Cr breakthrough curves were similar for B and C, small deviations can be observed in the isotope data when plotted vs. time (Figure 6). Plotted as $\delta^{53}\text{Cr}$ vs. fraction of Cr remaining, these deviations become more apparent (Figure 7). Previous studies have frequently used the Rayleigh model to describe Cr isotope fractionation during reduction of Cr(VI) (Ellis et al., 2002; Schoenberg et al., 2008; Sikora et al., 2008; Berna et al., 2010; Zink et al., 2010; Døssing et al., 2011; Raddatz et al., 2011; Villalobos-Aragón et al., 2012; Wanner, Zink, et al., 2012; Kitchen et al., 2012; Wanner, Eggenberger, Kurz, et al., 2012; Han et al., 2012; Basu and Johnson, 2012; Wanner and Sonnenthal, 2013; Wanner et al., 2013). The Rayleigh model is described as (Clark and Fritz, 1997):

$$\frac{R}{R_0} = f^{(\alpha-1)} \quad (17)$$

where R is the isotope ratio, R_0 is the initial isotope ratio, α is the fractionation factor, and f is the fraction of Cr(VI) remaining in solution. In the case of both experiments B and C, visual inspection of the isotope data suggested the presence of two different Rayleigh trends, differentiated by an inflection point at $f = 0.7 - 0.8$ that defines two stages in the experiment (Stage 1 at early time, and Stage two at later time).

Stage 1 was characterized by rapid Cr removal, and can be seen at the beginning of the Cr breakthrough curve where a steep slope was observed up to ~ 7 hours elapsed time ($f = 0$ to $f = 0.7 - 0.8$). Very little isotope fractionation was associated with these samples.

Stage 2 was characterized by slower Cr removal. After ~ 7 hours, the breakthrough curve had a shallower slope as the effluent approached the input Cr concentration ($f = 0.7 - 0.8$ to $f = 1$). Isotope values for these samples showed a greater degree of fractionation.

3.6 Reactive transport simulations

Both heterogeneous (direct; Equation 1) and homogeneous (indirect; Equation 2) pathways for Cr(VI) reduction have been reported for ZVI systems (Gheju and Balcu, 2011). The reactive transport simulations carried out with MIN3P (Mayer et al., 2002) in this study assumed Cr(VI) reduction followed both pathways, where the direct pathway was considered to be the faster reaction with little isotope fractionation and the indirect pathway was considered to be the slower reaction with a greater degree of fractionation. Although these pathways are consistent with the literature (Mayer et al., 2001), the exact mechanisms in the current study cannot be confirmed. However, these mechanisms provide a realistic scenario for modeling purposes and provided a reasonable fit to the measured data (Figures 6 and 7).

For convenience, the extent of fractionation is expressed in terms of isotope fractionation using the epsilon notation (ϵ) according to the following equation:

$$\epsilon = (\alpha - 1) \times 1000\text{‰} \quad (18)$$

Simulation results shown in Figures 6 and 7 indicate for the fast removal mechanism (Stage 1) the value $\epsilon_{B1} = \epsilon_{C1} = -0.2 \text{‰}$. The degree of fractionation observed here is similar to that reported

for sorption of Cr(VI) onto iron oxides (Ellis et al., 2004, see Table 1); however, it is not possible to determine the exact mechanisms leading to Cr removal in this system. For the slower mechanism (Stage 2) the simulations indicate $\varepsilon_{B2} = -1.2$, and $\varepsilon_{C2} = -1.5$ ‰ for FTC B and C, respectively.

Based on the simulation results, the apparent fractionation observed in the $\delta^{53}\text{Cr}$ vs. f plots cannot readily be translated to intrinsic fractionation values during Stages 1 and 2. The observed fractionation at any given time in the effluent water is a function of the relative proportions of the fast and slow mechanisms, and also a function of the rates of the two mechanisms over the length of the columns. For example, the ratio of the rate for the fast mechanism to the rate for the slow mechanism for FTC C reached a maximum of 342 at 1 hour and decreased logarithmically throughout the experiment to minimum values near 0.001 at the end of the experiment (Figure 8).

The rapid decline in the reaction rate for the Stage 1 mechanism in the simulations, shown by the sharp increase in Cr breakthrough up to about 5 hours (Figure 6), is probably due primarily to the depletion of the reactive iron, modeled as a dependence on the mineral volume fraction ($\varphi_{0_FeO-Cr(VI)}$, Table 4). This observation suggests that only a small amount of the iron (0.12 % and 0.10%) reacted via the fast Stage 1 mechanism. Conceptually, this change could reflect a depletion of reactive surface sites, or possibly the saturation of sorption sites; however, the modeling does not distinguish the nature of potential reaction mechanisms. The decline in the reaction rate for the Stage 2 mechanism, shown by the gradual increase in Cr concentrations from about 5 hours to the end of the experiment, is primarily a function of the decreasing rate of Fe^{2+} released from the reduction of water by ZVI (Equation 3). The simulated decrease in this reaction rate is attributed to the passivation of the iron surface by secondary mineral precipitation

(Equation 13), as has been shown previously for ZVI systems (Jeen et al., 2007; Gui et al., 2009; Jeen et al., 2012; Jeen et al., 2013).

Very similar isotope fractionation values were determined for each stage in experiments B and C. A clear difference between the experiments is the f value at which the change in stage occurred. For experiment B, faster Cr removal was observed until f was ~ 0.7 , whereas faster removal continued until f was ~ 0.8 for experiment C. Most likely this difference in inflection point was due to heterogeneities in the reactive material, such as grain size distribution. Surface area measurements were performed using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938), providing a value of $3.73 \pm 0.25 \text{ m}^2 \text{ g}^{-1}$. Despite similar masses of ZVI packed in cells B and C (6.12 g), even small heterogeneities in grain size distribution could result in differences in reactive surface area between the experiments. These differences most likely determined the point in the experiment at which the stage changed. Additionally, the discrepancy between the ϵ values for Stage 2 may also stem from heterogeneities in ZVI surface area.

3.7 Correlating Cr isotope behaviour with reaction rate

The real-time, in situ nature of these experiments does not provide a definitive distinction between reaction mechanisms of Cr(VI) removal by ZVI. The inability to distinguish between aqueous and solid-phase Cr in the XANES spectra hampers attempts to positively identify the presence of Cr(VI) sorbed on the ZVI surface. However, the combination of reactive transport modeling and the specification of distinct rate constants and isotope fractionation values indicates the influence of two different reduction mechanisms. The data exhibits a very clear correlation between reaction rate and the degree of Cr isotope fractionation. Basu & Johnson (2012) observed a similar correlation during batch experiments conducted to reduce Cr(VI) with minerals found in PRBs composed of Fe^0 , including Fe(II)-doped goethite, FeS, green rust, and

FeCO₃. Isotope fractionation in their study was found to be significantly greater than values determined here, ranging from $\epsilon = -2.11 \text{ ‰}$ to $\epsilon = -3.91 \text{ ‰}$ (Table 1). They surmised that the larger isotope fractionation observed for Fe(II)-doped goethite may be due to a small amount of Fe(II) released into solution (i.e. closer to the value attributed to Fe(II)_{aq}, $\epsilon = -4.2 \text{ ‰}$; Kitchen et al. (2012)). In contrast, the smaller isotope fractionation of $\epsilon = -2.67 \text{ ‰}$ for FeCO₃ was attributed to reduction on the mineral surface, which may have been further affected by an accumulation of reaction products and the build-up of a diffusive barrier between the mineral and the bulk solution. It is reasonable to assume that similar mineral phases may have formed within the ZVI-containing system described in the current study, therefore some similarities in the Cr removal mechanism(s) may exist. However, the degree of fractionation in the current study is significantly less than that observed in Basu & Johnson (2012), further demonstrating the complexity of isotope fractionation, even in a seemingly simple geochemical system. The presence of multiple reductants in the subsurface, each with its own ϵ value, generates significant uncertainty during any attempt to evaluate the extent of reduction in a real-world groundwater plume.

A similar two-stage isotope curve was described for the reduction of Cr(VI) by organic carbon under saturated flow conditions in Jamieson-Hanes, Amos, et al. (2012). Although preliminary observations identified a linear isotope trend (Jamieson-Hanes, Gibson, et al., 2012), reactive transport modeling suggested a two-mechanism system. A detailed characterization of the reactive material (leaf mulch) was not performed; therefore identification of the exact mechanisms was not possible. However, a similar relationship was observed between the degree of isotope fractionation and the rate of Cr removal; fast removal resulted in minimal fractionation, while slow removal resulted in greater fractionation. Although the ϵ values

determined for reduction of Cr(VI) by ZVI are significantly different than those for reduction by organic carbon, similarly complex isotope behaviours exist in both experimental systems.

3.8 Influence of experimental design

Whereas the vast majority of laboratory-generated Cr isotope fractionation values are derived from static batch experiments (Table 1), the experiments in this study were characterized by saturated flow conditions. The influence of experimental design, i.e. batch vs. continuous flow, should be taken under consideration during the investigation of Cr isotope fractionation behaviour. Typically, one reactant is found to be limiting throughout the course of a batch experiment, whereas a flow-through experiment exhibits changing conditions. A batch experiment design cannot be expected to capture the transition from one limiting reactant to another, such as that seen under saturated flow conditions. Jamieson-Hanes, Gibson, et al. (2012) speculated that the influence of transport was a potential cause for the change in isotope behaviour observed between analogous batch and column experiments using organic carbon mixed with silica sand. The complex isotope behaviours observed in the current study illustrate the combined effects of water flow, solute transport and geochemical reactions on Cr isotope fractionation. Although static batch experiments provide significant insight into Cr(VI) removal mechanisms and associated isotope fractionation, the results presented here indicate that laboratory studies under saturated flow conditions may better demonstrate the inherent complexity of isotope behaviour, and provide an important step in the interpretation of isotope measurements made in field settings.

4 Conclusions

Results from this study show that Cr(VI) treatment by ZVI under saturated flow conditions can generate complex isotope fractionation behaviour, which probably reflects changes in the predominant reaction mechanism and corresponding changes in reaction rate. Flow-through cell experiments exhibited characteristics typical of remediation systems applied for Cr(VI) treatment by ZVI, including increased pH and a trend toward reducing conditions. Breakthrough occurred as the reactivity of the ZVI was depleted, increasing the Cr(VI) concentration in the effluent nearly to the input value. Real-time, in situ X-ray absorption spectroscopy measurements were collected through a Kapton® window in the flow-through cell, which indicated that Cr(VI) was reduced to Cr(III), likely as Cr(OH)₃. Measurements of Cr isotope ratios on effluent samples also indicated the presence of redox processes with positive $\delta^{53}\text{Cr}$ values; however, the data did not follow a typical Rayleigh curve with a single effective isotope fractionation value. Reactive transport modeling was used to quantify the changes in isotope fractionation during the experiments. A two mechanism conceptual model adequately described the observed inflection point in the isotope fractionation factor around $f = 0.7 - 0.8$. The simulation results are consistent with a rapid removal mechanism with an isotope fractionation of $\varepsilon = -0.2$, and a slower removal mechanism, resulting in a greater degree of fractionation; $\varepsilon = -1.2 \text{ ‰}$ (B) and $\varepsilon = -1.5 \text{ ‰}$ (C).

The presence of a complex isotope trend during the reduction of Cr(VI) by ZVI under saturated flow conditions indicates that the application of a single isotope fractionation value may not be sufficient to describe some systems. Previous studies using organic carbon to treat Cr(VI) under static and dynamic flow conditions suggest that a multi-mechanism interpretation may be more appropriate (Jamieson-Hanes, Amos, et al., 2012). A flow-through cell setup such as the one described in this study is valuable because multiple parameters can be monitored

concurrently during Cr(VI) treatment to improve characterization of the processes and interpret the isotope data. However, characteristics of the spectroscopic technique did not allow for definitive identification of Cr removal mechanisms, limiting the extent of the interpretation.

Chromium isotope measurements have become a complementary analytical technique to be used alongside traditional geochemical methods for characterizing groundwater systems. Nevertheless, the interpretation of Cr isotope data may be challenging, as it can be convoluted by the nature of reductant and system heterogeneities, and may be influenced by transport processes (Jamieson-Hanes, Gibson, et al., 2012). Overall, it appears that although Cr isotope measurements are a strong indicator of mass-transfer processes, the successful application of this tool to characterize groundwater plumes will require an extensive understanding of the subsurface, including aquifer materials and flow systems.

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687

689 **Table 1.** Summary of published Cr isotope fractionation results from laboratory experiments
 690 examining reduction and sorption of Cr(VI).

Reaction type	Material	Experiment type	Isotope fractionation (ε)	Reference
Reduction	magnetite	batch	-3.5 ‰	Ellis et al. (2002)
	estuarine sediment (Fe(II)-bearing minerals)	batch	-3.3 ‰	
	pond sediment (Fe(II)-bearing minerals)	batch	-3.5 ‰	
	<i>Shewanella oneidensis</i> (≤ 100 μM lactate)	batch	-4.11 ‰	Sikora et al. (2008)
	<i>Shewanella oneidensis</i> (10 mM lactate)	batch	-1.75 ‰	
	natural sediment (Fe(II)-bearing minerals)	batch	-3.07 ± 0.11 ‰ and -2.38 ± 0.10 ‰	Berna et al. (2010)
	H ₂ O ₂ (pH < 1)	batch	-3.54 ± 0.35 ‰	(Zink et al., 2010)
	H ₂ O ₂ (pH ~ 7)	batch	-5 ‰	
	Fe(II) _{aq} (fixed)	batch	-3.6 ‰	Døssing et al. (2011)
	Fe(II) _{aq} (constant addition)	batch	-1.5 ‰	
	Fe(II)-doped goethite	batch	-3.91 ± 0.16 ‰	Basu and Johnson (2012)
	FeS	batch	-2.11 ± 0.04 ‰	
	green rust	batch	-2.65 ± 0.11 ‰	
	siderite	batch	-2.67 ± 0.25 ‰	
	ISRM sediments	batch	-3.18 ± 0.09 ‰	
	<i>Pseudomonas stutzeri</i> (aerobic conditions)	batch	-2 ± 0.4 ‰	Han et al. (2012)
	<i>Pseudomonas stutzeri</i> (denitrifying conditions)	batch	-0.4 ± 0.2 ‰	
	organic carbon	batch	-3.5 ‰	Jamieson-Hanes, Amos, et al. (2012)
	organic carbon	column	-3.5 ‰ and 0.8 ‰	
	Fe(II) _{aq}	batch	-4.20 ± 0.11 ‰	Kitchen et al. (2012)
	organic reductants	batch	-3.11 ± 0.11 ‰	

(humic acid, fulvic acid,
mandelic acid +
goethite/alumina)

Sorption	γ -alumina	batch	0.00 %	Ellis et al. (2004)
	goethite	batch	-0.35 to -0.70 %	

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Table 2. Results of linear combination fitting on XANES spectra from FTC experiments B and C using reference materials including solid Cr(0) and Cr(OH)₃, and aqueous Cr(VI). Unknown spectra were merged in groups of three samples collected chronologically and the mid-point of the total elapsed time for the three scans was assigned as the time for the merged scan. Weights of the three standards used for fitting were not forced to sum to 1; percentages were calculated relative to the sum of the fitted weights.

	Elapsed time (hours)	Percentage of given standard			χ^2
		Cr(0)	Cr(OH) ₃	Cr(VI) _{aq}	
FTC B	0.2	49.2	50.8	0.0	0.0737
	2.0	19.3	80.7	0.0	0.0143
	3.4	14.8	85.2	0.0	0.0147
	5.1	14.4	85.2	0.4	0.0130
	6.4	12.5	86.0	1.6	0.0096
	7.6	12.5	85.7	1.7	0.0103
	16.4	10.8	86.2	3.0	0.0106
	23.8	9.0	86.9	4.1	0.0078
FTC C	0.2	63.3	36.7	0.0	0.2962
	1.6	27.4	72.6	0.0	0.0724
	3.9	6.2	90.5	3.3	0.0251
	5.1	7.4	88.6	4.0	0.0117
	6.4	6.9	89.0	4.1	0.0130
	7.6	4.9	91.5	3.6	0.0155
	16.4	3.0	91.9	5.1	0.0100
	22.0	3.0	91.3	5.7	0.0095

699 **Table 3.** Reactive transport model parameters.

Physical Parameters – FTC B and C			
Flow rate (ml min ⁻¹)	0.5		
porosity	0.51		
Dispersivity (m s ⁻¹)	1.2 x 10 ⁻³		
1-D model length (cm)	3		
Discretization interval (cm)	0.03		
Component Concentrations	Initial Condition	Inflow Boundary	
		FTC B	FTC C
pH	8.23	8.23	8.23
⁵² CrO ₄ ⁻² (mol L ⁻¹)	8.98158 x 10 ⁻¹¹	7.66039 x 10 ⁻⁴	7. 8111049 x 10 ⁻⁴
⁵³ CrO ₄ ⁻² (mol L ⁻¹)	1.01842 x 10 ⁻¹¹	8.6861 x10 ⁻⁵	8. 8570119 x10 ⁻⁵
⁵² Cr(OH) ₂ ⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
⁵³ Cr(OH) ₂ ⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
Fe ²⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
Fe ³⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
K ⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	3.90 x 10 ⁻⁴	3.90 x 10 ⁻⁴
H _{2(aq)} (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
CO ₃ ²⁻ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	2.50 x 10 ⁻³	2.50 x 10 ⁻³
Ca ²⁺ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.18 x 10 ⁻³	1.18 x 10 ⁻³
Cl ⁻ (mol L ⁻¹)	1.0 x 10 ⁻¹⁰	1.00 x 10 ⁻³	1.00 x 10 ⁻³

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701 **Table 4.** Reactive transport model reaction equations, rates and parameters.

Primary Reactions:			
	Parameter	FTC B	FTC C
$Fe^0(s) + 2H^+ \rightarrow Fe^{2+} + H_2(aq)$	$\log k$	-9.5	-9.5
$R_{Fe^0-H_2O} = kS_0 \exp(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t))$	S_0	10144	10144
	α_{ferri}	900	900
	φ_{0_ferri}	1.0×10^{-10}	1.0×10^{-10}
	α_{arag}	25	25
	φ_{0_arag}	1.0×10^{-10}	1.0×10^{-10}
$0.667 {}^{52}CrO_4^{2-} + Fe^0 + 4H^+ \rightarrow Fe^{2+} + 0.667 {}^{52}Cr(OH)_2^+ + H_2O$	$\log k$	-2.4	-2.29
$R_{Fe^0-{}^{52}Cr(VI)}$	S_0	10144	10144
	α_{ferri}	900	900
$= k_{52}S_0 \exp(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t))$	φ_{0_ferri}	2.0×10^{-10}	1.0×10^{-10}
$\{ {}^{52}CrO_4^{2-} \} \{ \varphi_{Fe^0-Cr(VI)}(x,t) \}$	α_{arag}	25	25
	φ_{0_arag}	1.0×10^{-10}	1.0×10^{-10}
	$\varphi_{0_Fe^0-Cr(VI)}$	6.0×10^{-4}	5.0×10^{-4}
$0.667 {}^{53}CrO_4^{2-} + Fe^0 + 4H^+ \rightarrow Fe^{2+} + 0.667 {}^{53}Cr(OH)_2^+ + H_2O$	α_{53}	0.9998	0.9998
$R_{Fe^0-{}^{53}Cr(VI)}$	ε	-0.2	-0.2
$= k_{53}S_0 \exp(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t))$			
$\{ {}^{52}CrO_4^{2-} \} \{ \varphi_{Fe^0-Cr(VI)}(x,t) \}$			
${}^{52}CrO_4^{2-} + 3Fe^{2+} + 6H^+ \rightarrow {}^{52}Cr(OH)_2^+ + 3Fe^{3+} + 2H_2O$	$\log k$	2.18	2.18
$R_{Fe^{2+}-{}^{52}Cr(VI)} = k_{52} \{ {}^{52}CrO_4^{2-} \} \{ Fe^{2+} \}$	α_{53}	0.9988	0.9985
	ε	-1.2	-1.5
${}^{53}CrO_4^{2-} + 3Fe^{2+} + 6H^+ \rightarrow {}^{53}Cr(OH)_2^+ + 3Fe^{3+} + 2H_2O$			
$R_{Fe^{2+}-{}^{53}Cr(VI)} = k_{52} \{ {}^{53}CrO_4^{2-} \} \{ Fe^{2+} \}$			
Secondary Reactions: $R = k \left(1 - \frac{IAP}{K}\right)$			
${}^{52}Cr(OH)_{3(am)} + H^+ \rightarrow {}^{52}Cr(OH)_2^+ + H_2O$	$\log k$	-5.7	-5.7
${}^{53}Cr(OH)_{3(am)} + H^+ \rightarrow {}^{53}Cr(OH)_2^+ + H_2O$	$\log K$	-0.75	-0.75
$Fe(OH)_{2(s)} + 2H^+ \rightarrow Fe^{2+} + 2H_2O$	$\log k$	-8.7	-8.7
	$\log K$	13.9045	13.9045
$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$	$\log k$	-5.7	-5.7
	$\log K$	-4.36	-4.36
$Fe_2(OH)_2CO_{3(s)} + 2H^+ \rightarrow 2Fe^{2+} + CO_3^{2-} + 2H_2O$	$\log k$	-8.0	-8.0
	$\log K$	-0.0753	-0.0753
$Fe(OH)_{3(am)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O$	$\log k$	-6.7	-6.7
	$\log K$	4.891	4.891

702 k – effective rate constant

703 S_0 – initial reactive surface area of the iron (m^2 iron L^{-1} bulk)

704 α_i – proportionality constant for mineral phase i

705 φ_i – volume fraction of mineral phase i (m^3 mineral m^{-3} bulk)

706 α_{53} – fractionation factor

707 ε – isotope fractionation value

708 K – equilibrium constant (mol L^{-1} H_2O)

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711 **Figures**

Figure 1. Schematic of the flow-through cell setup. Input solution was pumped upward through the cell; effluent passed through the flow-through pH and redox microelectrodes before being collected in the fraction collector. A Kapton® window allowed the passage of the X-rays at an incident angle of 45°. The detector was positioned at 90° to the beam to collect the X-ray fluorescence emitted from the material in the flow-through cell.

Figure 2. Changes in chemical composition of water phase over time for experiments A, B, and C. Measured parameters include Cr(VI) concentrations on approximately every fifth sample (reported relative to the input concentration), pH data from external measurements, and Eh data using a flow-through microelectrode set to log approximately every one minute.

Figure 3. Normalized Cr XANES spectra collected in situ during the progression of experiments B and C, identified by elapsed time in hours. Spectra were collected approximately every 7 minutes; sequential spectra were merged in groups of three for improved statistics. Reference materials include Cr(0), Cr(OH)₃, and Cr(VI)_{aq} (silica sand saturated with the experimental input solution). The grey bar indicates the position of the 3d-4p pre-edge feature characteristic of Cr(VI). Experiment B is plotted on the left; experiment C is plotted on the right.

Figure 4. XANES spectra collected in situ throughout experiments B and C, plotted as X-ray absorption vs. energy (i.e. not normalized). Timestamps illustrate the increase in absorption as reacted Cr accumulated on the surface of the reactive material. Overall absorption is less for experiment C due to the lower background signal from Cr(0) in the ZVI. Experiment B is plotted on the left; experiment C is plotted on the right.

Figure 5. XANES spectra collected at the conclusion of the experiment after the flow had been halted, plotted as energy vs. X-ray absorption (i.e. not normalized). Spectra were collected at three positions along the length of the Kapton® window, including bottom (near input), middle, and top (near effluent). Experiment B is plotted on the left; experiment C is plotted on the right.

Figure 6. Effluent Cr(VI) concentrations and $\delta^{53}\text{Cr}$ values for experiments B and C. Simulation results are shown for Cr(VI) (dashed line) and $\delta^{53}\text{Cr}$ (solid line). The $\delta^{53}\text{Cr}$ value of the input solution was 0.00 ‰. Error bars represent the analytical uncertainty calculated from unknown samples prepared in duplicate, with a value of ± 0.04 ‰. Isotope data is absent for samples in which the Cr concentration was too low for analysis.

Figure 7. Isotope results for experiments B and C plotted as $\delta^{53}\text{Cr}$ vs. the fraction of Cr remaining in solution (f). Reactive transport simulations (solid line) generated isotope fractionation values: $\epsilon_{B1} = -0.2 \text{ ‰}$, $\epsilon_{B2} = -1.2 \text{ ‰}$, $\epsilon_{C1} = -0.2 \text{ ‰}$, and $\epsilon_{C2} = -1.5 \text{ ‰}$, where the numbers 1 and 2 refer to Stages 1 and 2. Elapsed time in hours is indicated for data points correlating to XANES spectra plotted in Figures 3 & 4. Error bars represent the analytical uncertainty calculated from unknown samples prepared in duplicate, with a value of $\pm 0.04 \text{ ‰}$.

Figure 8. Simulated ratio of Stage 1 and Stage 2 reaction rates for FTC C along the length of the cell at 1, 5, 10 and 25 hours. Ratios are shown on a logarithmic scale to demonstrate the continued change in the ratios at later times.