

In Situ Redox Manipulation Bench-Scale Tests: Remedial Design Support for ISRM Barrier Deployment

**Frontier Hard Chrome Superfund Site
Vancouver, WA**

October, 2002

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Executive Summary

Laboratory tests documented in this letter report were conducted to determine physical and geochemical properties needed to develop a design for implementation of the in situ redox manipulation (ISRM) technology for chromate remediation at the Frontier Hard Chrome (FHC) site. During installation of injection and monitoring wells at the FHC pilot test site, 16 sediment core samples were collected for Laboratory analysis. Laboratory experiments showed that chemical reduction yielded a redox capacity (0.26% Fe^{II}) that falls within the range of values observed in sediments analyzed from sites where field-scale deployment of the ISRM technology is currently in progress or being considered (0.1% Hanford 100D area, 0.24% Ft Lewis, 0.4% Moffett Federal Airfield, 0.3% in preliminary FHC samples). This mass of reducible iron represents a sufficient quantity for a treatment zone emplaced at FHC to remain anoxic for 100s of pore volumes, which would be expected to last tens of years, depending on aquifer flow rates and the concentration of oxidizing species in the groundwater. The geochemical analysis also indicated relatively low spatial variability in reducible iron content although some depth dependent variability was indicated.

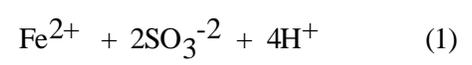
. Sieve and hydrometer analysis were conducted on selected sediment samples to provide an estimate of the spatial variability in sediment physical properties, both with depth and across the site. These analyses were targeted to verify the occurrence of and provide physical property data for three discrete hydrostratigraphic units observed during geologic characterization activities at the pilot test site. These three units within the A zone aquifer, in descending order, have been assigned the hydrostratigraphic designation of A1, A2, and A3. A generalized hydrogeologic description of the ISRM pilot test site consist of a silty clay upper confining layer to a depth of ~ 22 ft, the A1 unit from ~ 22 to 27 ft, the A2 unit from ~ 27 to 35 ft, and the A3 unit from ~ 35 to 40 ft below ground surface. The A/B aquitard was encountered at a depth of ~ 40 ft.

The A1, A2, and A3 hydrostratigraphic units are all sandy gravels, but with considerable difference in fines content and subsequently, hydraulic conductivity. Hydraulic tests conducted in pilot test site monitoring wells indicate that the A1 unit has significantly lower hydraulic conductivity than the A2 unit, while the A3 unit hydraulic conductivity is significantly higher than that observed in the A2 unit (i.e., a trend of increasing permeability with depth). Calculated hydraulic conductivities, based on sieve analysis, show this same spatial trend. Although conductivity estimates based on laboratory analysis of sediment cores are suspect due to the potential for affecting sample permeability during collection, they are useful for providing higher resolution, depth discrete hydraulic conductivity information than can usually be obtained from available wells at the site. Results from a tracer injection test and electromagnetic borehole flow meter tests conducted at the site indicate a relatively high degree of formation heterogeneity.

Results from the laboratory analyses of sediment core samples collected from the FHC site will be used in conjunction with 1) site specific geologic information obtained during installation of ISRM pilot test site monitoring wells, 2) vertical contaminant distribution data obtained by EPA using a geoprobe rig, 3) results from hydraulic tests conducted at the site, 4) electromagnetic borehole flow meter testing results, and 5) results from a conservative tracer injection test, to develop a dithionite injection scheme, based on a suite of reactive transport design analysis simulations, for deployment of the ISRM technology at FHC.

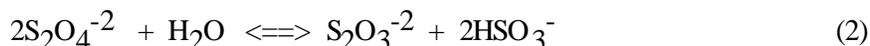
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shows that the forward rate is a function of the dithionite concentration and the square of the reducible iron concentration (rate is overall a third-order function of concentration). The aqueous Fe(II) produced has a high affinity for surfaces, so is quickly adsorbed. Therefore, Fe(II) mobility in mid- to high pH, low ionic strength groundwater is extremely limited, and iron is not expected to leach from sediments during the dithionite treatment. Aqueous iron measurements in previous studies have shown < 1% iron leaching even after 600 pore volumes of groundwater through a sediment column. Corresponding solid iron measurements of sediments used in these columns showed 4-10% loss of iron. Iron mobility is somewhat higher during the actual dithionite injection, as a high ionic strength solution of other cations (~0.3 mol/L in this case) compete for the same adsorption sites as Fe²⁺, so cause some Fe²⁺ desorption. Previous experimental transport studies with dithionite injection into sediments have shown 0 to 12% iron loss after 40 pore volumes of dithionite treatment.

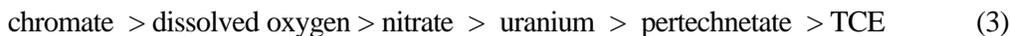
Experimental evidence from previous studies with Hanford sediments have shown that two parallel reduction reactions are needed to describe iron reduction data (i.e., a fraction of sites are quickly reduced and a fraction more slowly reduced). This may be the result of the reduction of two or more major Fe(III) phases. If the number of slowly reducing sites is small and the mass of iron is far in excess of the dithionite, reaction 1 can be reduced to a first-order reaction in which Fe³⁺ remains constant. Another reaction occurs in the system, which describes the disproportionation of dithionite in contact with sediment:



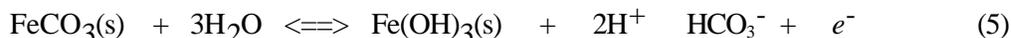
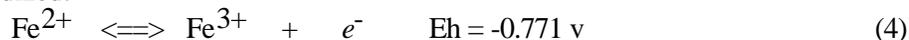
accounts for the mass loss of dithionite that cannot be used for iron reduction. Previous studies have shown that this reaction has a half-life of ~27 h (basaltic sediments). The consequence of this reaction is to limit how slowly dithionite can be reacted with (i.e., injected into) sediment in the field. If dithionite is injected too slowly, a significant amount of the mass is lost to disproportionation. Although iron(III) phases are the most significant phase that reacts with dithionite, other mineral phases present in natural sediments may also be reduced, and utilize some of the dithionite. Previous studies have shown that some Mn reduction occurs as a result of the dithionite treatment of Hanford sediment, although reduced Mn^{II} phases were only 3 to 4% relative to reduced iron phases.

2.2 Sediment Oxidation and Chromate Immobilization

The oxidation of the adsorbed and structural Fe(II) in the sediments of the permeable redox barrier occurs naturally by the inflow of dissolved oxygen through the barrier, but can additionally be oxidized by contaminants that may be present such as chromate, TCE, nitrate, uranium, or other electron acceptors. If redox equilibrium completely defined the mechanism (i.e., no effects from activation energies or surface catalysis) and contaminants are present in equal molar concentrations, they would be reduced in the following order:



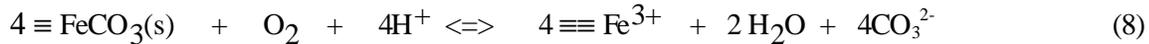
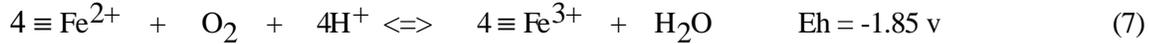
In most aquifers, dissolved oxygen in water is the dominant oxidant of reduced iron species, as contaminants are generally present in lower molar concentrations relative to dissolved oxygen. The oxidation of reduced iron in pure mineral phases is described by the following reactions first by dissolved oxygen, then with other contaminants. Fe(II) species that are known to exist in the dithionite-reduced sediments include adsorbed Fe(II) and siderite [Fe(II)CO₃]. A single mole of electrons is consumed as a mole of these species are oxidized:



The use of dissolved oxygen as an oxidant is generally divided into two electron sequences, which combined:

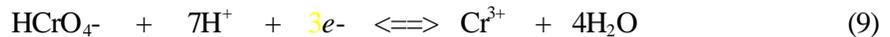


show that 4 moles of electrons are needed per mole of O₂ consumed. The rate of this reaction (6) has generally been observed to be first-order at fixed pH and the rate increases 100 fold for a unit increase in pH. Experimental evidence during iron oxidation experiments indicates that two differing reduced iron species is present (adsorbed ferrous iron and siderite). Combining the two iron oxidation half reactions with oxygen reduction:



yield 4 moles of Fe(II) are oxidized and 4 moles of electrons transferred per mole of O₂ consumed. At oxygen-saturated conditions (8.4 mg L⁻¹ O₂, 1 atm, 25 °C), 1.05 mmol L⁻¹ Fe(II) is consumed.

Experimental evidence indicates that the oxygenation of Fe(II) in solutions (pH >5) is generally found to be first order with respect to Fe(II) and O₂ concentration and second-order with respect to OH⁻. The rate of oxidation of aqueous Fe²⁺ by oxygen at pH 8 is a few minutes (Eary and Rai, 1988, Buerge and Hug, 1997). In contrast, the oxidation rate (as a half-life) observed in natural sediments [surface Fe(II) phases mainly adsorbed Fe(II) and Fe(II)CO₃] was found to be 0.3 to 1.1 h. Chromate present as a contaminant in groundwater will also oxidize Fe(II)



with 1 mole of electrons consumed per mole of chromate reduced. Cr³⁺ readily precipitates and is extremely difficult to oxidize under natural conditions, so remains permanently immobilized in the aquifer. The reduction of one mole of chromate oxidizes one mole of Fe(II) [reactions 10 and 13], or 41 mg L⁻¹ chromate is needed to oxidize the equivalent mass of Fe(II) as water saturated with dissolved oxygen [1.02 mmol L⁻¹ Fe(II)]. Chromate is considered a much stronger oxidizer than dissolved oxygen, so even at concentrations less than 41 mg L⁻¹ it may influence the iron oxidation rate.

While the precipitation of Cr(OH)₃ species as the result of the remediation process might reduce the availability of Fe²⁺ for further reactions, this process is insignificant. Over the barrier lifetime, chromate is reduced and precipitated as the Fe²⁺ species are slowly oxidized by mainly dissolved oxygen and some by chromate. As demonstrated in a long term column experiment (Szecsody et al., 1999), the Cr(OH)₃ remains immobile even in fully oxic systems for >1500 pore volumes, so there is a potential for coatings of precipitated minerals forming and remaining in the barrier zone. However, at the anticipated maximum chromate concentration of 5 mg/L (based on the treatment goal for the selected source term remediation alternative), this effect will not be large enough to significantly effect the physical or geochemical properties or significantly alter the function of the barrier. For example, based on a previous analysis of this effect for Hanford sediments, if chromate were present at 200 mg/L and the barrier had sufficient redox capacity to last 170 pore volumes, only 1% of the pore space would be occupied with Cr(OH)₃ precipitated over the life of the barrier.

3. EXPERIMENTAL METHODS

3.1 Sediment Physical Properties

The FHC sediment dry bulk density and porosity were measured on the intact cores (i.e., whole sediment properties) as well as the < 4 mm sieved fraction used in reduction/ oxidation experiments, as described below. As cores were unpacked, the wet weight, dry weight, and core volume were used to calculate the dry bulk density and porosity. Both porosities were needed to relate the geochemical results of laboratory experiment to the field scale sediment. The entire sediment size fraction was not used in laboratory experiments because large cobbles exhibit essentially no geochemical control (i.e., the surface area of gravels are extremely small relative to clays), and experiments of this scale would not be practical. Sediment oxidation experiments (described below) for 1200 pore volumes would take considerable time with a column containing the full sediment size fraction, so the < 4 mm size fraction was used.

The sediment size fractions were determined by ASTM sieve analysis (12 sediments) and additionally by hydrometer analysis to accurately determine the clay fraction (6 samples). It should be noted that some core samples contained large cobbles (nearly the same size as the sampler used), so to obtain an accurate sediment bulk density and porosity, larger cores are needed (i.e., a smaller core may occupy mainly a cobble or mainly the pore space, so is not representative). As such, bulk density, porosity, and iron content as reported for the bulk sediments are likely more affected by the sampling procedure when the analysis is conducted on 2-in cores than when it is conducted on 4-in cores. However, since the geochemical data reported for the < 4 mm fraction is independent of the large size fraction, it will not be affected by sample size.

3.2 Sediment Reduction by Dithionite in Column Systems

Sediment reduction studies conducted in 1-D columns consisted of injecting the dithionite solution at a steady rate into a sediment column and measuring the concentration of dithionite over time in the effluent for 120 to 160 h. The flux rate was chosen to achieve specific residence times of the dithionite solution in the column (2 h to 4 h) relative to the reduction rate (~5 to 7 h). The dry bulk density and porosity of the column was calculated from the dry and saturated column weight and column volume. The volumetric flow rate was calculated from the effluent volume and elapsed time. The electrical conductivity of the column effluent provided a second (dynamic) measure of the porosity, and was measured using a flow-through electrode and automatic data logging. While these experiments can provide data of the mass of reduced iron in the sediments, the method is more complex and less accurate than oxidizing sediments with dissolved oxygen (described below). Therefore, of the 7 sediments reduced, dithionite data was collected for only 3 of these experiments. This left the data logging systems free for sediment oxidation experiments. As many as five automated systems were operating simultaneously.

The dithionite concentration in the effluent was measured once per hour using an automated fluid measurement and control system (U.S. Patent 6,438,501; J. Szecsody, M. Williams, V. Vermeul). These measurements were taken with an HPLC injection valve with 15 to 52 μL loop that isolated a specified volume of the effluent. The contents of the loop were mixed with 5 to 10 mL of oxygen-free water, then injected into a UV-detector and absorbance measured at 315 nm. The sample injection took 2 minutes to flow the complete sample through the detector, and the absorbance over a 1-minute interval was averaged for a single dithionite concentration measurement. A triple-wash between injections prevented sample overlap. These fluid operations were controlled from one computer and the dithionite concentration logged on a second computer. The concentration of the dithionite influent was measured with the same automated system by manually bypassing the column at approximately 24 h intervals over the multi-day experiments. The fraction of reduced iron was calculated from dithionite breakthrough curves by determining the total mass loss (i.e., dithionite mass injected minus dithionite in the effluent) and the mass of dithionite lost to disproportionation. The remaining dithionite mass loss was used for iron reduction. This dithionite breakthrough analysis assumes that dithionite has reached a steady state mass loss due to disproportionation and that all of the iron has been reduced. The rate of iron reduction is also calculated from the steady state dithionite concentration during initial breakthrough (i.e., before the iron is all reduced).

3.3 Sediment Oxidation in Columns

Sediment oxidation studies were also conducted in 1-D columns to determine the rate at which the dithionite-reduced sediments are oxidized and to measure of the mass of reduced iron (i.e., redox capacity). These experiments consisted of injecting oxygen-saturated (8.4 mg L^{-1}) water at a steady rate (typically 2 pore volumes per hour) into a reduced sediment column and measuring the concentration of dissolved oxygen over time in the effluent for 300 to 800 h. A series of in-line micro-electrodes were used to monitor geochemical changes during oxidation and included dissolved oxygen (1 or 2 electrodes), pH, and electrical conductivity. Electrode measurements were continuously monitored, averaged, and data logged at 2 to 5 minute intervals using an automated fluid measurement and control system (U.S. Patent 6,438,501; J. Szecsody, M. Williams, V. Vermeul).. Two point calibration was conducted on the in-line oxygen electrodes at 4 - 8 h intervals (oxygen-free and oxygen-saturated solution for oxygen) using the automated system. Electrode data from calibrations were also data logged. The mass of reduced iron that was oxidized was calculated from the mass of oxygen consumed.

4. RESULTS

During installation of injection and monitoring wells at the FHC pilot test site, 16 sediment core samples were collected for Laboratory analysis. Of the 16 samples collected, seven were analyzed to determine the weight percent of available iron (dithionite reducible), 12 were subjected to sieve and hydrometer analyses to develop a particle size distribution, and all 16 were measured to determine the bulk density and porosity. These analyses were targeted to verify the occurrence of and provide physical property data for three discrete hydrostratigraphic units observed during geologic characterization activities at the pilot test site. These three units within the A zone aquifer, in descending order, have been assigned the hydrostratigraphic designation of A1, A2, and A3. A generalized hydrogeologic description of the ISRM pilot test site consist of a silty clay upper confining layer to a depth of ~ 22 ft, the A1 unit from ~ 22 to 27 ft, the A2 unit from ~ 27 to 35 ft, and the A3 unit from ~ 35 to 40 ft below ground surface. The A/B aquitard was encountered at a depth of ~ 40 ft.

4.1 Sediment Physical Property Analysis

Physical property analyses were conducted on the ten 4-inch diameter cores and six 2-inch diameter cores from the FHC site. Sediment particle size analysis of 12 samples (Figure 1, remaining in Appendix A) indicates that the three hydrostratigraphic units within the A zone are

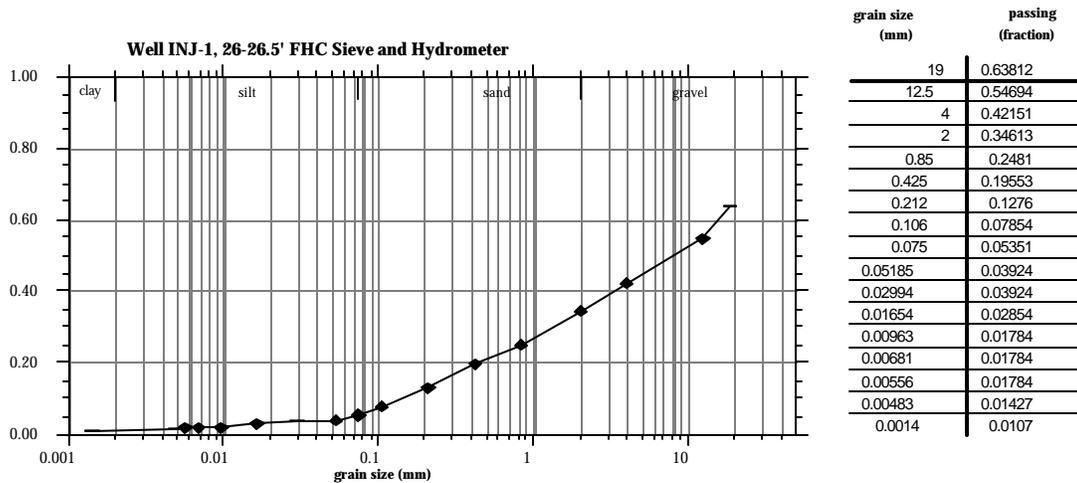


Figure 1. Sieve analysis of sediment from the 26' depth of the injection well.

Table 1. Physical, Chemical, and Hydraulic Properties of FHC Sediments.

| borehole | depth (ft) | interval ID | core dia. (in) | <4mm | laboratory sediment, < 4 mm | | | field sediment (whole) | | | | gravel % | sand % | silt/clay % | Hazen approximation | |
|-------------------------------------|---------------|----------------|-------------------|-------|---------------------------------|---|--------------------------------------|---------------------------------|---|-----------------------------|------------|-------------|-----------|----------------|---------------------|----------|
| | | | | | density (g/cm ³) | porosity (cm ³ /cm ³) | dithionite reduceable (mmol/g) | density (g/cm ³) | porosity (cm ³ /cm ³) | dithionite reduceable Fe | | | | | d ₁₀ | K (ft/d) |
| | | | | | | | | | | (mmol/g) | (wt. %) | | | | | |
| INJ-1 | 23-23.5' | A1 | 4 | 0.282 | | | | 2.27 | 0.169 | | | 71.8 | 25.1 | 3.1 | 0.65 | 1198 |
| | 26-26.5' | A1 | 4 | 0.422 | 1.74 | 0.388 | 153.2 | 2.07 | 0.143 | 64.7 | 0.36 | 57.9 | 36.8 | 5.4 | 0.13 | 48 |
| | 30-30.5' | A2 | 4 | 0.341 | 1.60 | 0.379 | 117.2 | 2.27 | 0.141 | 40.0 | 0.22 | 65.9 | 32.5 | 1.6 | 0.56 | 889 |
| | 35.5-36' | A3 | 4 | 0.307 | 1.89 | 0.304 | 104.1 | 2.12 | 0.137 | 32.0 | 0.18 | 69.4 | 28.8 | 1.8 | 0.72 | 1469 |
| | 41.5-42' | A/B aquitard | 4 | 0.503 | | | | 2.28 | 0.212 | | | | | | 0.14 | 56 |
| MW-4 | 23.5-24' | A1 | 2 | 0.425 | | | | 1.87 | 0.216 | | | 57.5 | 35.5 | 7.0 | 0.11 | 34 |
| | 29-29.5' | A2 | 2 | 0.465 | 1.68 | 0.367 | 109.7 | 1.89 | 0.199 | 51.0 | 0.28 | 53.5 | 41.6 | 4.9 | 0.21 | 125 |
| | 33-33.5' | A2 | 2 | | | | | 1.54 | | | | | | | | |
| MW-7 | 26.5-27' | A1 | 4 | 0.381 | 1.74 | 0.287 | 74.9 | 2.29 | 0.173 | 28.5 | 0.16 | 61.9 | 34.9 | 3.2 | 0.15 | 64 |
| | 29-29.5' | A2 | 4 | 0.310 | 1.74 | 0.357 | 96.6 | 2.40 | 0.134 | 29.9 | 0.17 | 69.0 | 29.2 | 1.8 | 0.68 | 1311 |
| | 37-37.5' | A3 | 4 | 0.265 | | | | 2.18 | 0.124 | | | 73.5 | 25.3 | 1.2 | 0.90 | 2296 |
| | 44-44.5' | B | 4 | | | | | 1.80 | | | | | | | | |
| | 45-45.5' | B | 4 | | | | | 2.07 | | | | | | | | |
| MW-21 | 23-23.5' | A1 | 2 | 0.493 | | | | 1.95 | 0.259 | | | 50.7 | 43.0 | 6.3 | 0.11 | 34 |
| | 30-30.5' | A2 | 2 | 0.493 | 1.73 | 0.313 | 155.8 | 1.79 | 0.196 | 76.8 | | 50.7 | 46.1 | 3.2 | 0.30 | 255 |
| | 33-33.5' | A2 | 2 | | | | | 1.33 | | | | | | | | |
| average, all wells | | | | | 1.72 | 0.342 | 116 ± 30 | 1.95 | 0.175 | 46.1 ± 18.8 | 0.26 ± 0.1 | | | | | |
| average, A1 hydrostratigraphic unit | | | | | | | | 2.09 | 0.19 | 46.6 | 0.26 | 60.0 | 35.1 | 5.0 | 0.23 | 45 |
| average, A2 hydrostratigraphic unit | | | | | | | | 1.87 | 0.17 | 49.4 | 0.28 | 59.8 | 37.4 | 2.9 | 0.44 | 645 |
| average, A3 hydrostratigraphic unit | | | | | | | | 2.15 | 0.13 | 32.0 | 0.18 | 71.5 | 27.1 | 1.5 | 0.81 | 1883 |

sandy gravels containing some silt and very little clay. More specifically, all samples contained less than 7% silt and clay, and all samples contained less than 2% clay. A representative sample of the injection well sediment (Figure 1) contains 1.7% clay. Because some of the cobbles in the cores were equal to or larger than the 2- or 4-inch diameter sample containers, there are some larger cobbles in the aquifer not sampled. As discussed previously, some core samples contained large cobbles, so to obtain an accurate sediment bulk density and porosity, larger cores are needed (i.e., a smaller core may occupy mainly a cobble or mainly the pore space, so is not representative). As such, bulk density and porosity are likely more affected by the sampling procedure when the analysis is conducted on 2-in cores than when it is conducted on 4-in cores; this effect is indicated in the physical property data contained in Table 1. The porosity for all sediments averaged 17.5%, and the dry bulk density averaged 1.95 g/cm³.

The sieve analysis was used to calculate the saturated hydraulic conductivity of the sediment using Hazen's formula, based on the 10% size fraction. These calculated values were compared with calculated conductivities obtained from hydraulic tests conducted in pilot test site monitoring wells which showed the same general trends. Although conductivity estimates based on laboratory analysis of sediment cores are suspect due to the potential for affecting sample permeability during collection, they are useful for providing higher resolution, depth discrete hydraulic conductivity information than can usually be obtained from available wells at the site.

4.2 Sediment Reduction

A series of seven column reductions followed by column oxidation experiments conducted with Frontier sediment showed that there was sufficient ferric iron that could be reduced by a sodium dithionite injection. Reduction experiments consisted of the injection of 0.08 mol/L sodium dithionite with 0.32 mol/L potassium carbonate. In three of the seven experiments the influent dithionite concentration was recorded daily and the effluent concentration was automatically analyzed once per hour over the 5 to 8-day experiments (Appendix B). In one experiment (Figure 2), the dithionite concentration is low for the first 25 hours, as it is completely consumed by iron reduction. Over the next 100 hours, the dithionite concentration slowly increases, approaching the injection concentration (large squares) by 120 hours. Considerable research of this type has been conducted with other sediments, where it has been observed that the rate of reduction of iron in the sediments is 5 to 7 hours. Therefore, roughly 5 half lives (24 to 30 h) of dithionite-sediment contact time is needed to reduce most of the accessible iron oxides. In laboratory experiments, sediments were reduced from 5-8 days to achieve as much reduction as could occur.

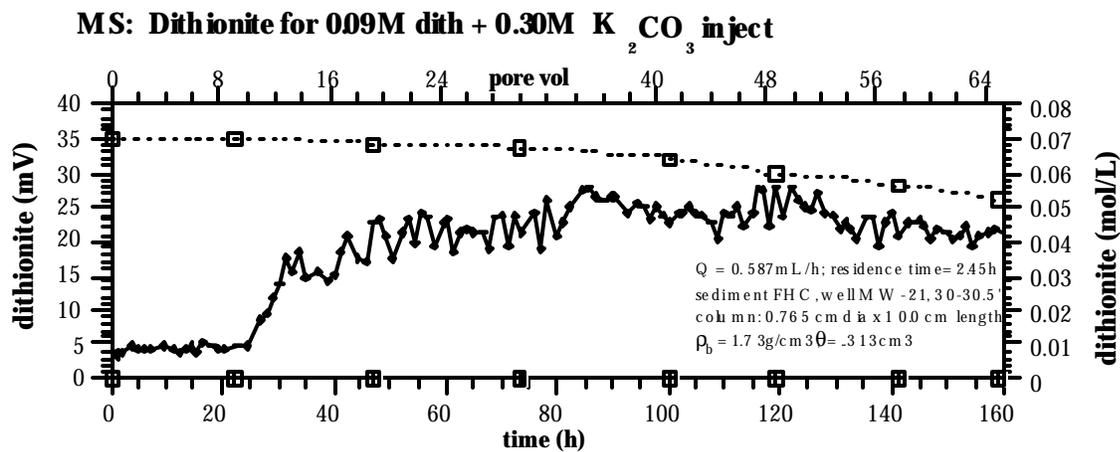


Figure 2. Reduction of Frontier sediment in a column.

4.2 Sediment Oxidation

The sediment oxidation experiments showed that the average mass of reducible iron in the Frontier Hard Chrome sediments is $46.1 \pm 18.8 \mu\text{mol/g}$ (0.26% reducible iron, Table 1). Locations that contained a higher proportion of finer grained sediments had a greater mass of reducible iron, but in general the spatial variability was low. These column oxidation experiments simulate what will naturally occur in the field (i.e., oxidizing species in groundwater flow through the reduced sediment under natural gradient conditions). The experiments are conducted until most of the reduced iron has been oxidized, as evidenced by the oxygen levels in the effluent being 80% or more of saturation (oxygen saturated water is injected in these experiments). The automated laboratory experiments contain one or two oxygen electrodes, which are continuously monitoring the oxygen concentration of the effluent and recalibrated automatically every 8 hours. This calibration data (not shown for most data sets) is used to calculate the oxygen-free and oxygen-saturated lines (Figure 3, Appendix C). The water was injected at a rate to achieve roughly 30 minutes of sediment-dissolved oxygen contact time (i.e., 30-minute residence time), so over the course of 300 hours, approximately 600 pore volumes of oxygen-saturated water was injected.

MM: Dissolved Oxygen Column, Probe 1

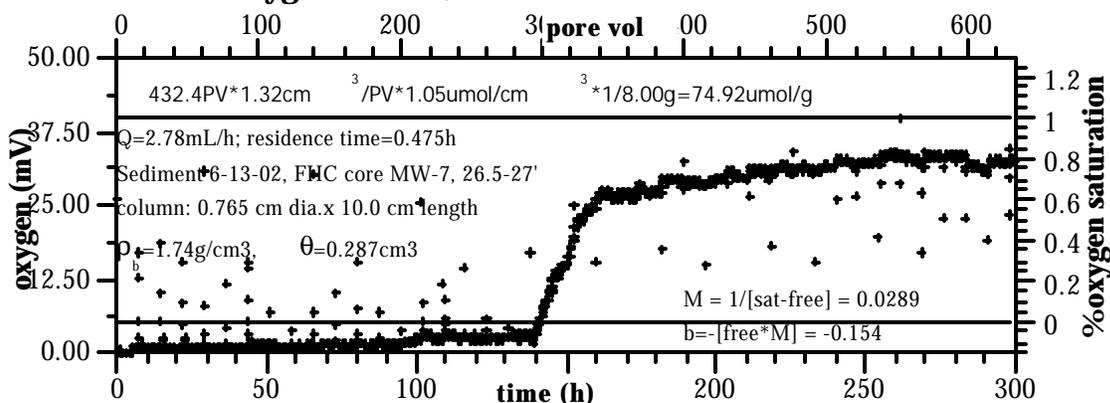


Figure 3. Oxidation of reduced Frontier sediment in a column with oxygen-saturated water.

The shape of the oxygen breakthrough curve (Figure 3) shows complete oxygen consumption for 300 pore volumes (150 h), followed by rapid oxygen breakthrough to 75% of saturation. Even by 600 pore volumes, the oxygen levels had only reached 83% of saturation. The interpretation of this breakthrough curve shape is there are at least two different ferrous iron species on the surface. Adsorbed ferrous iron or FeOH (as determined by iron extraction analysis in other studies) is quickly oxidized, and may represent the majority of the reduced iron in the sediment. A second species, siderite (FeCO_3) may be present in minor (< 20%) levels, and is slowly oxidized. Relative to the total mass of iron in the sediment, the sodium dithionite reduced a small fraction of the iron oxides. Previous studies have shown that ~20% of amorphous and crystalline iron oxides are reduced by dithionite.

5. CONCLUSIONS

Laboratory tests documented in this letter report were conducted to determine physical and geochemical properties needed to develop a design for implementation of the in situ redox manipulation (ISRM) technology for chromate remediation at the Frontier Hard Chrome (FHC) site. During installation of injection and monitoring wells at the FHC pilot test site, 16 sediment core samples were collected for Laboratory analysis. Laboratory experiments showed that chemical reduction yielded a redox capacity (0.26% Fe^{II}) that falls within the range of values observed in sediments analyzed from sites where field-scale deployment of the ISRM technology is currently in progress or being considered (0.1% Hanford 100D area, 0.24% Ft Lewis, 0.4% Moffett Federal Airfield, 0.3% in preliminary FHC samples). This mass of reducible iron represents a sufficient quantity for a treatment zone emplaced at FHC to remain anoxic for 100s of pore volumes, which would be expected to last tens of years, depending on aquifer flow rates and the concentration of oxidizing species in the groundwater. The geochemical analysis also indicated

relatively low spatial variability in reducible iron content although some depth dependent variability was indicated

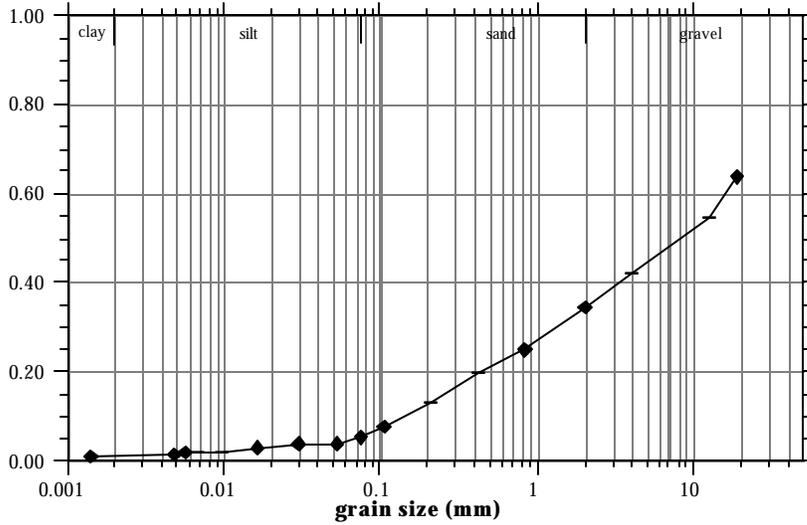
Sieve and hydrometer analysis were conducted on selected sediment samples to provide an estimate of the spatial variability in sediment physical properties, both with depth and across the site. These analyses were targeted to verify the occurrence of and provide physical property data for three discrete hydrostratigraphic units observed during geologic characterization activities at the pilot test site. These three units within the A zone aquifer, in descending order, have been assigned the hydrostratigraphic designation of A1, A2, and A3. The A1, A2, and A3 hydrostratigraphic units are all sandy gravels, but with considerable difference in fines content and subsequently, hydraulic conductivity. Hydraulic tests conducted in pilot test site monitoring wells indicate that the A1 unit has significantly lower hydraulic conductivity than the A2 unit, while the A3 unit hydraulic conductivity is significantly higher than that observed in the A2 unit (i.e., a trend of increasing permeability with depth). Calculated hydraulic conductivities, based on sieve analysis, show this same spatial trend. Results from a tracer injection test and electromagnetic borehole flow meter tests conducted at the site indicate a relatively high degree of formation heterogeneity.

6. REFERENCES

- Amonette, J., 2000, Iron Redox Chemistry of Clays and Oxides: Environmental Applications, book chapter, chapter in A. Fitch (ed.) *Electrochemistry of Clays*, CMS Workshop Lectures, Clay Minerals Society, Aurora, Co, in review.
- Balko, B., and Tratnyek, P., 1998, Photoeffects on the Reduction of Carbon Tetrachloride by Zero-Valent Iron, *J. Physical Chemistry*, 102(8): 1459-1465.
- Blowes, D., Ptacek, C., and Jambor, J., 1997, In Situ Remediation of Cr(VI) Contaminated Groundwater Using Permeable Reactive Walls: Laboratory Studies, *Env. Sci. Technol.*, 31(12): 3348-3357.
- Buerge, I. J. and S. J. Hug, 1997. Kinetics and pH Dependence of Chromium(VI) Reduction by Iron(II), *Environ. Sci. Technol.*, 31(5):1426-1432.
- Chilakapati, A., M. Williams, S. Yabusaki, C. Cole, and J. Szecsody. 2000. Optimal design of an in situ Fe(II) barrier: transport limited reoxidation, *Environmental Science and Technology*, in press.
- Eary, L., and Rai, D., 1988, Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion, *Environmental Science and Technology*, 22: 972-977.
- Fruchter, J., C. Cole, Williams, M., V. Vermeul, J. Amonette, J. Szecsody, J. Istok and M. Humphrey, Creation of a Subsurface Permeable Treatment Barrier Using In Situ Redox Manipulation, 2000, *Ground Water Monitoring Review*, 66-77.
- Johnson, T., Fish, W., Gorby, Y., and Tratnyek, P., 1998, Degradation of Carbon Tetrachloride: Complexation Effects on the Oxide Surface, *J. Cont. Hyd.*, 29, 379-398.
- Mayer, K., D. Blowes, and E. Frind. 2000. Reactive Transport Modeling of an in-situ reactive barrier for the treatment of hexavalent chromium and TCE in groundwater, *Water Resources Research*, in press.
- Szecsody, Jim E., Jonathan S. Fruchter, Vince R. Vermeul, Mark D. Williams, 1999, Results of Bench-Scale Studies for In Situ Redox Manipulation of Subsurface Sediments at the Frontier Hard Chrome Site, Vancouver, Washington, PNNL letter report, November 1999.
- Szecsody, J., A. Chilakapati, J. Zachara, P. Jardine, A. Ferreny, 1998, Importance of Flow and Particle-Scale Heterogeneity on CoII/III/EDTA Reactive Transport, *J. Hydrology*, 209(1-4):112-136.
- Szecsody, J., M. Williams, J. Fruchter, V. Vermeul, and J. Evans. 2000. Influence of sediment reduction on TCE degradation, remediation of chlorinated and recalcitrant compounds, book chapter, ed. G. Wickramanayake, *Chemical Oxidation and Reactive Barriers*, p. 369-376.
- Szecsody, J., M. Williams, J. Fruchter, V. Vermeul, 2001, In Situ Reduction of Aquifer Sediments for Remediation: 1. Iron Reduction Mechanism, submitted to *Environmental Science and Technology*
- Vermeul, V., M. Williams, J. Evans, J. Szecsody, B. Bjornstad, and T. Liikala. 2000. In situ redox manipulation proof-of-principle test at the Fort Lewis Logistics Center: final report, Pacific Northwest National Laboratory PNNL-13357, Richland, Washington.

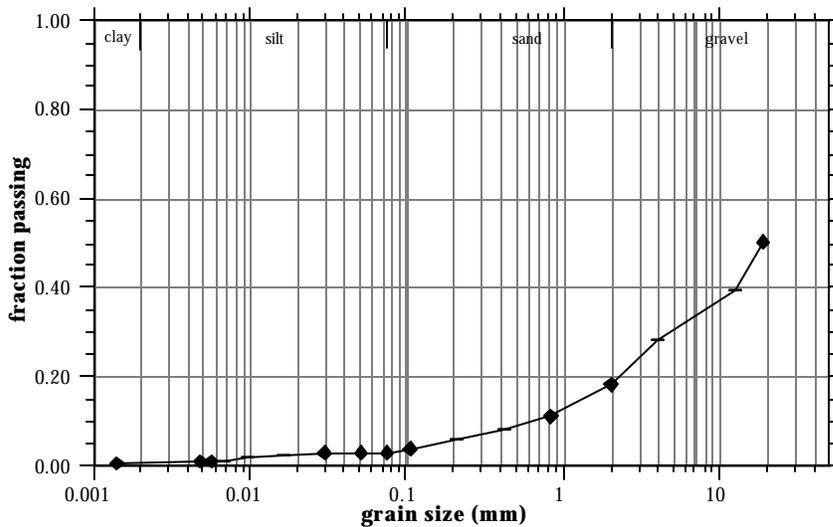
Appendix A – Grain Size Distributions of Frontier Subsurface Sediments

Well INJ-1, 26-26.5' FHC Sieve and Hydrometer



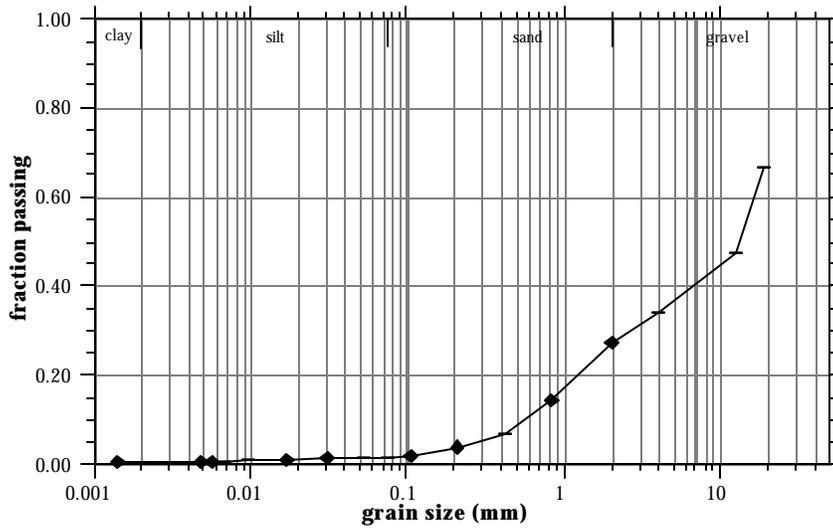
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.63812 |
| 12.5 | 0.54694 |
| 4 | 0.42151 |
| 2 | 0.34613 |
| 0.85 | 0.2481 |
| 0.425 | 0.19553 |
| 0.212 | 0.1276 |
| 0.106 | 0.07854 |
| 0.075 | 0.05351 |
| 0.05185 | 0.03924 |
| 0.02994 | 0.03924 |
| 0.01654 | 0.02854 |
| 0.00963 | 0.01784 |
| 0.00681 | 0.01784 |
| 0.00556 | 0.01784 |
| 0.00483 | 0.01427 |
| 0.0014 | 0.0107 |

Well INJ-1, 23-23.5' FHC Sieve and Hydrometer



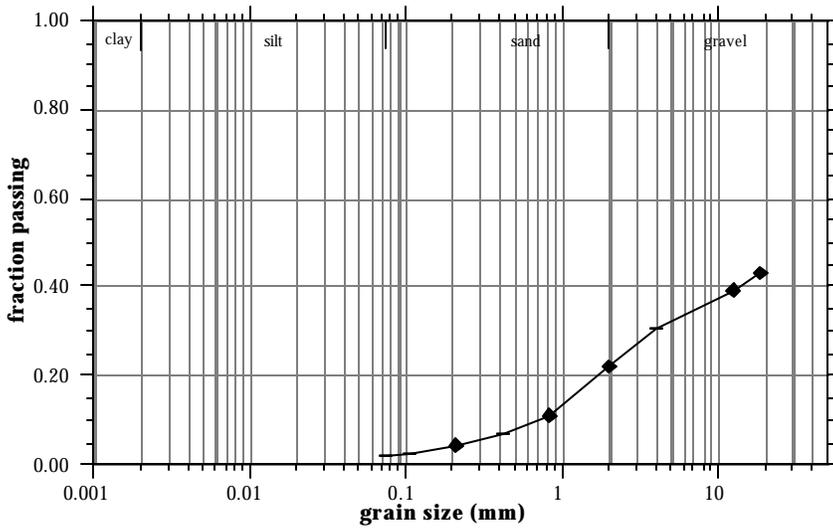
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.50455 |
| 12.5 | 0.39174 |
| 4 | 0.28182 |
| 2 | 0.18145 |
| 0.85 | 0.10911 |
| 0.425 | 0.08404 |
| 0.212 | 0.06 |
| 0.106 | 0.03889 |
| 0.075 | 0.03092 |
| 0.05156 | 0.03092 |
| 0.02977 | 0.03092 |
| 0.0164 | 0.02617 |
| 0.00955 | 0.01903 |
| 0.00681 | 0.01189 |
| 0.00556 | 0.01189 |
| 0.00481 | 0.01189 |
| 0.0014 | 0.00714 |

Well INJ-1, 30-30.5' FHC Sieve and Hydrometer



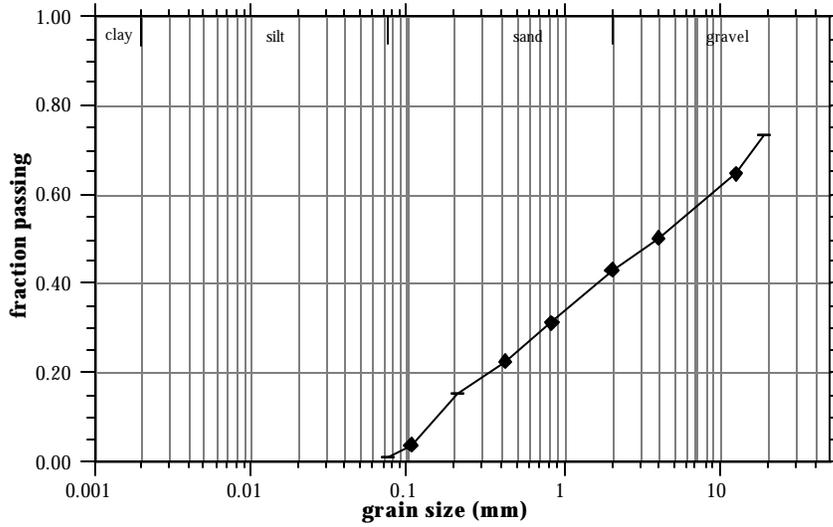
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.66422 |
| 12.5 | 0.47382 |
| 4 | 0.34074 |
| 2 | 0.27386 |
| 0.85 | 0.14425 |
| 0.425 | 0.06809 |
| 0.212 | 0.03668 |
| 0.106 | 0.02082 |
| 0.075 | 0.01577 |
| 0.05301 | 0.01577 |
| 0.03061 | 0.01577 |
| 0.01681 | 0.01052 |
| 0.00971 | 0.01052 |
| 0.00688 | 0.00526 |
| 0.00562 | 0.00526 |
| 0.00487 | 0.00526 |
| 0.0014 | 0.00526 |

Well INJ-1, 35.5-36' FHC Sieve



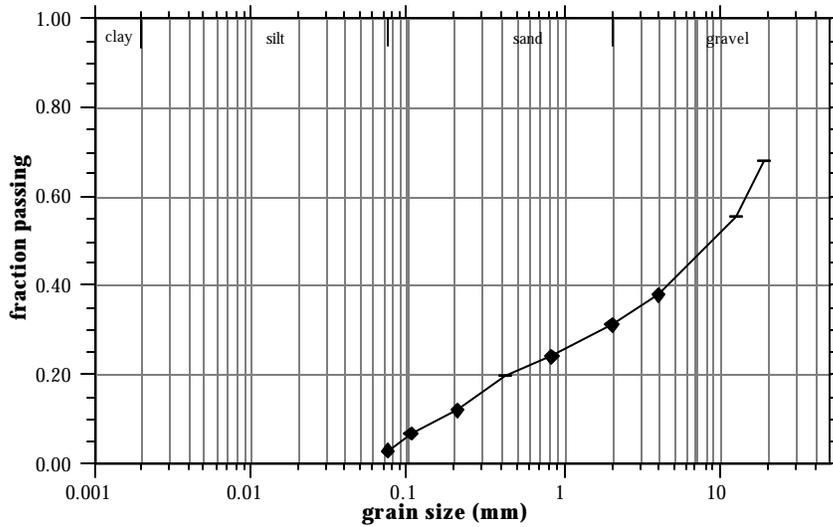
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.42969 |
| 12.5 | 0.39425 |
| 4 | 0.30654 |
| 2 | 0.21887 |
| 0.85 | 0.10874 |
| 0.425 | 0.067412 |
| 0.212 | 0.042241 |
| 0.106 | 0.024834 |
| 0.075 | 0.018083 |

Well INJ-1, 41.5-42' FHC Sieve

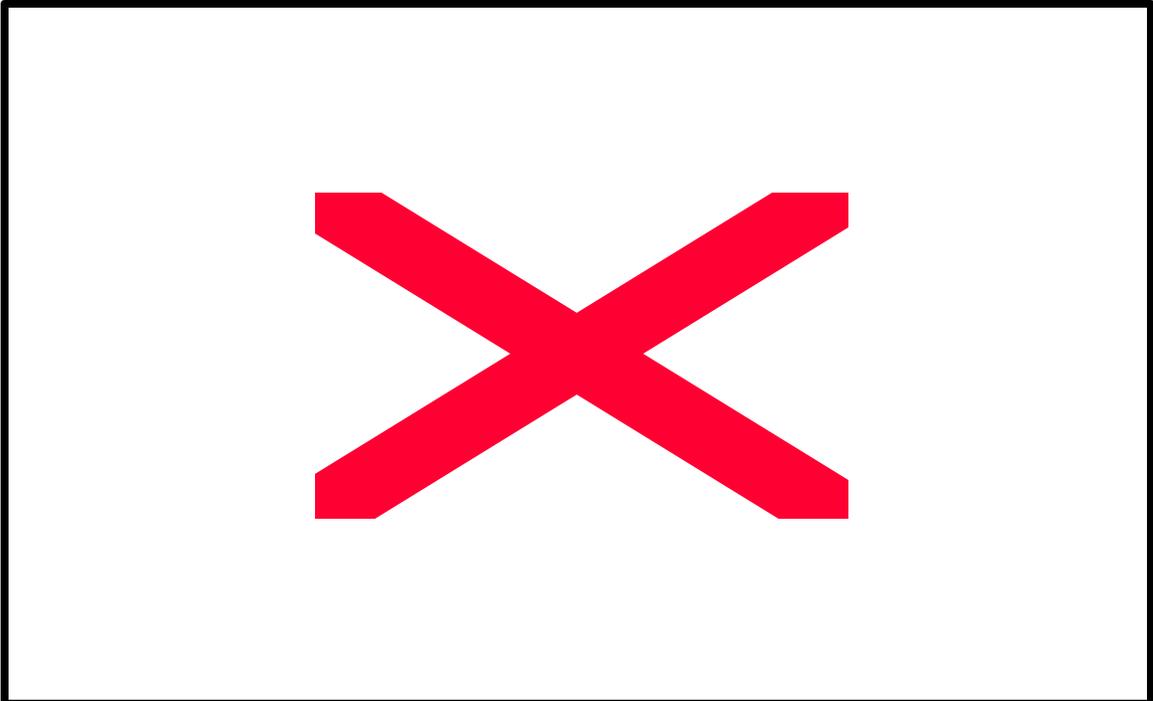
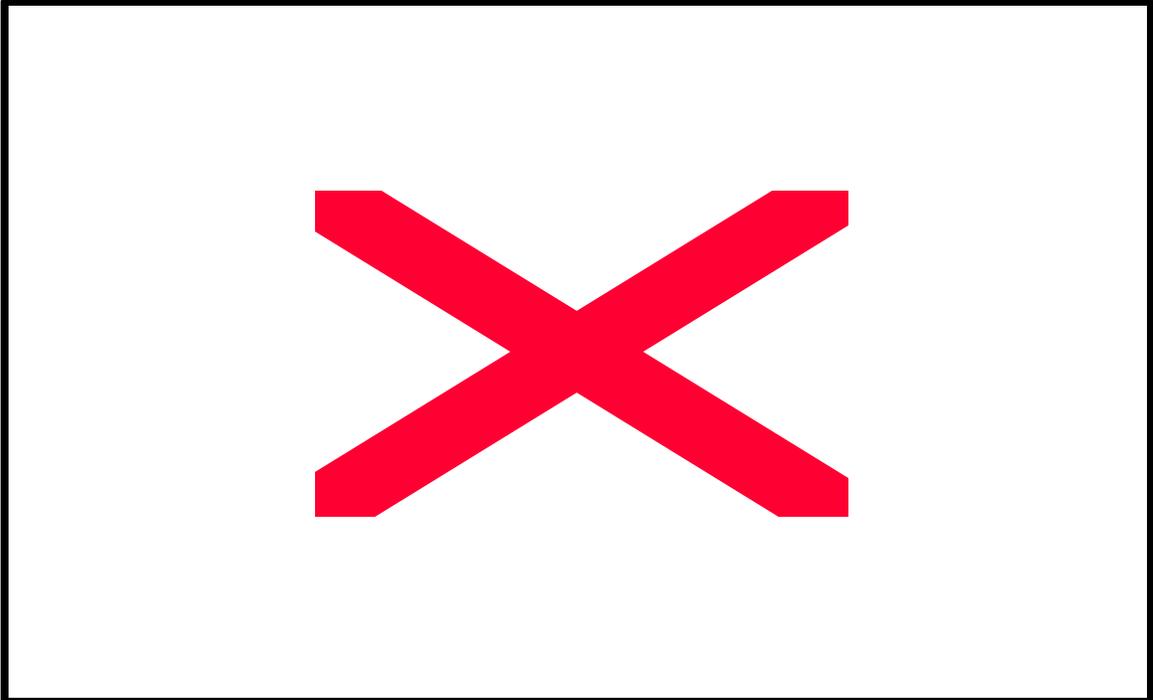


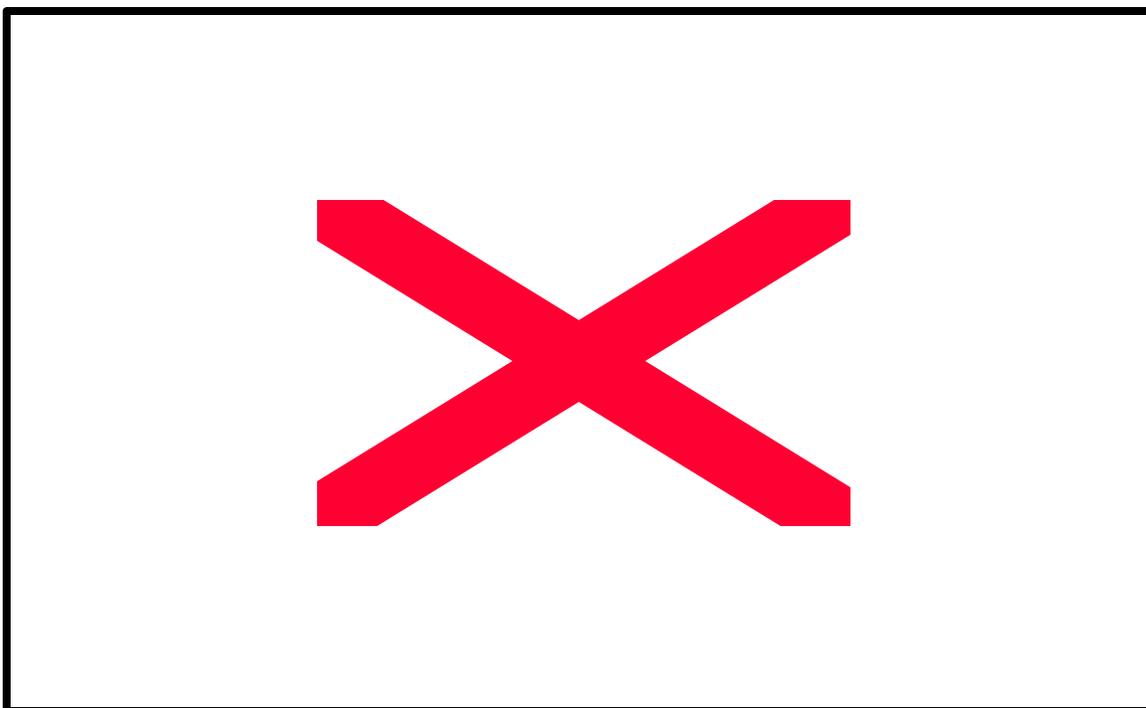
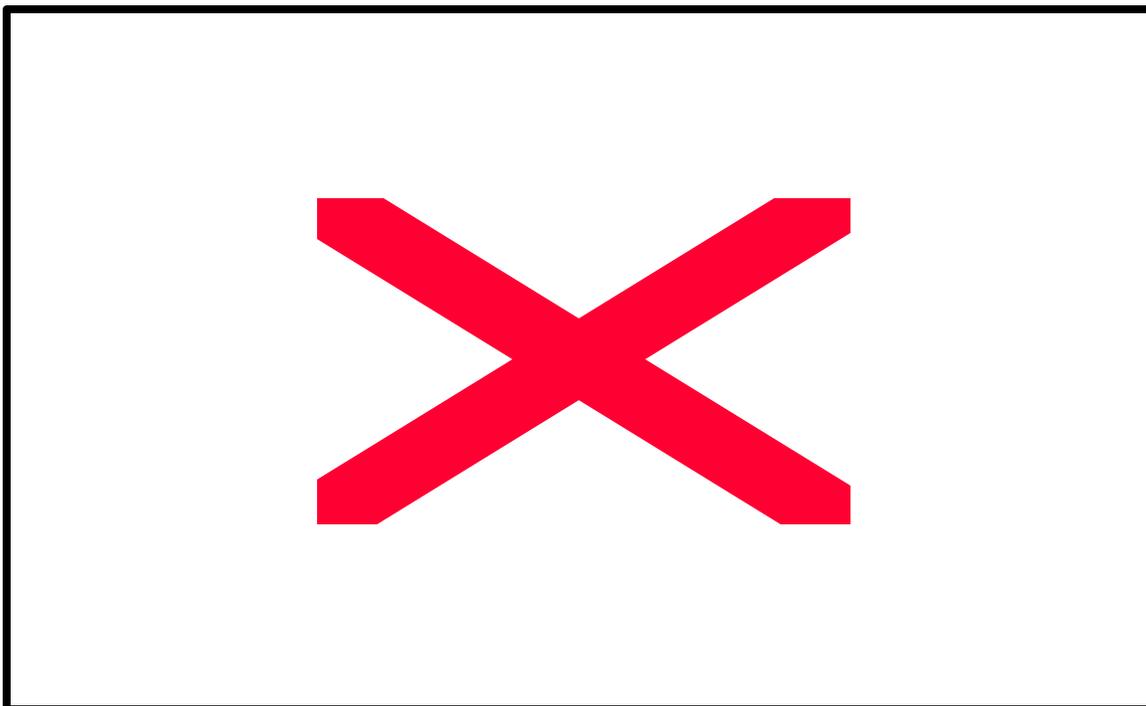
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.73325 |
| 12.5 | 0.64596 |
| 4 | 0.50326 |
| 2 | 0.42961 |
| 0.85 | 0.31187 |
| 0.425 | 0.22587 |
| 0.212 | 0.15508 |
| 0.106 | 0.04078 |
| 0.075 | 0.00836 |

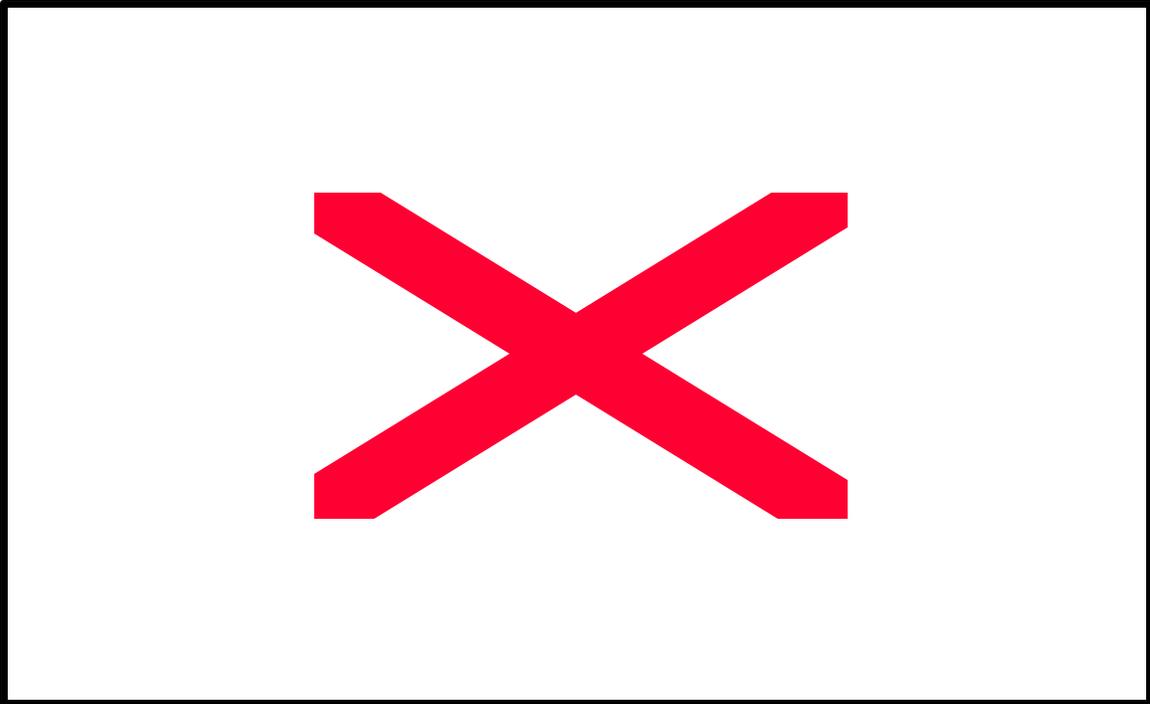
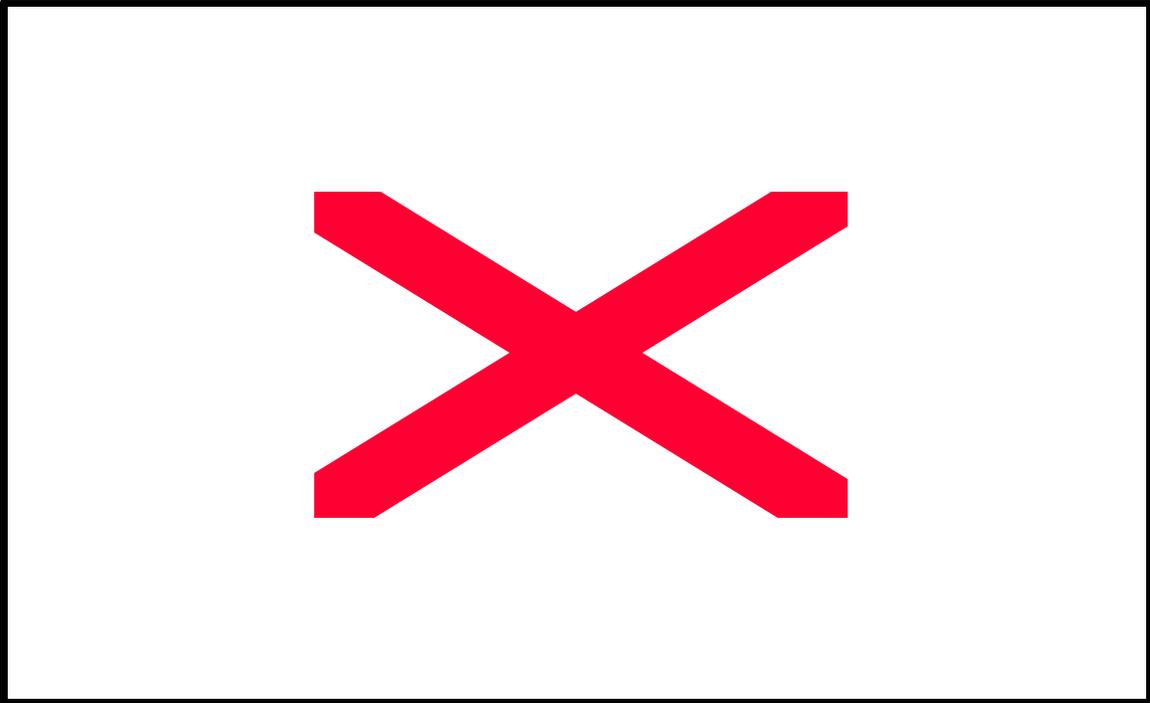
Well MW-7, 26.5-27' FHC Sieve



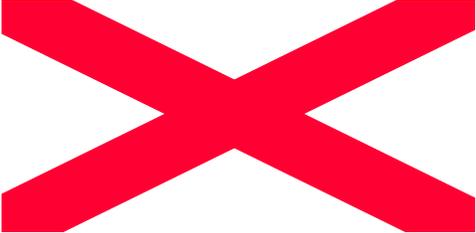
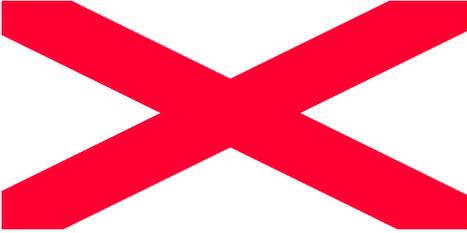
| grain size (mm) | passing (fraction) |
|-----------------|--------------------|
| 19 | 0.67918 |
| 12.5 | 0.55489 |
| 4 | 0.38055 |
| 2 | 0.31362 |
| 0.85 | 0.24056 |
| 0.425 | 0.19819 |
| 0.212 | 0.11793 |
| 0.106 | 0.06881 |
| 0.075 | 0.03154 |







Appendix B – Data from Frontier Sediment Reduction Experiments

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Appendix C – Data from Frontier Sediment Oxidation Experiments

