In Situ Cr(VI) Source and Plume Treatment Using a Ferrous Iron Based Reductant

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Background

- Former ferrochrome production facility in Charleston, S.C.
- 20-acre feet of chromite ore processing residue in saturated zone
- Large dissolved phase Cr(VI) plume migrating toward tidal marsh

Source Zone Groundwater

Cr(VI) 3.0 - 57 mg/L
pH 8.5 - 11.5
D.O. < 1.0 mg/L
conductivity ↳ 15 mS/cm

Source Area

- Pebbly slag, conditioning tower sludge, electrostatic precipitator dust
- Average 3500 mg/kg total Cr in sediments- up to 550 mg/kg as Cr(VI)
- Solid phase exhibits strong pH buffering capacity; high in Mg hydroxides
- Solid phase contains low levels of hydrosulfite (dithionite) reducible iron

Table 1. Reaction of extractants and reductants with slag (LEISB 005 10') for 24 h at 100 rpm at 23°C.

Reagent	pH	Eh (mV)	Cr(VI) (mg L^{-1})
0.025 M $Na_2S_2O_4$	9.72 ± 0.00	132 ± 10	11.8 ± 0.1
0.025 M $Na_2S_2O_4$ + 0.05 M K_2CO_3	10.08 ± 0.00	28 ± 2	12.1 ± 0.1
0.05 M $Na_2S_2O_4$ + 0.10 M K_2CO_3	10.18 ± 0.01	6 ± 5	12.6 ± 0.1
0.025 M $Na_2S_2O_4$ + 0.05 M $KHCO_3$	9.86 ± 0.01	203 ± 5	12.2 ± 0.1
0.05 M $Na_2S_2O_4$ + 0.10 M $KHCO_3$	9.83 ± 0.01	189 ± 3	14.5 ± 0.1
1.0 g Peerless iron	9.82 ± 0.00	254 ± 2	2.9 ± 0.0
0.05 M hydroxylamine sulfate	9.26 ± 0.02	-150 ± 1	0.11 ± 0.01
0.05 M $Na_2S_2O_4$ + 0.05 M $FeCl_2$	9.17 ± 0.00	-213 ± 8	0.00 ± 0.00
0.05 M $Na_2S_2O_4$ + 0.05 M $FeSO_4$	8.62 ± 0.01	-523 ± 1	0.00 ± 0.00
0.05 M $Na_2S_2O_4$ + 0.01 M $FeSO_4$	9.50 ± 0.01	147 ± 7	0.01 ± 0.0
0.01 M $Na_2S_2O_4$ + 0.01 M $FeSO_4$	9.53 ± 0.00	191 ± 3	0.41 ± 0.17
0.05 M citric acid	9.10 ± 0.01	363 ± 3	26.2 ± 0.2
0.05 M citric acid + 0.05 M $FeCl_2$	8.05 ± 0.01	-106 ± 2	22.5 ± 0.9
0.05 M citric acid + 0.05 M $FeSO_4$	8.09 ± 0.00	-115 ± 4	15.6 ± 1.7
0.05 M $Na_2S_2O_4$ + 0.05 M citric acid + 0.05 M $FeSO_4$	8.08 ± 0.01	-151 ± 1	25.1 ± 0.3
0.05 M $FeCl_2$	9.12 ± 0.04	-112 ± 22	0.00 ± 0.00
0.05 M $FeSO_4$	9.00 ± 0.02	-203 ± 21	0.00 ± 0.00
0.05 M $Na_2S_2O_4$ + 0.05 M citric acid + 0.05 M $FeCl_2$	8.11 ± 0.01	-152 ± 4	26.3 ± 0.1

Source Sediment Batch Studies

- Na-dithionite observed to be ineffective
- Ferrous salts (ferrous sulfate/chloride) observed to be highly effective
- Ferrous sulfate in combination with Na-dithionite also observed to be highly effective
- Ferrous sulfate/Na-dithionite blend yields lowest Eh

Reaction of Interest

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \blacklozenge 4Fe_{0.75}Cr_{0.25}(OH)_3 + 4H^+$$

Source Zone Pilot Study

- 4800 gal of a 0.2M ferrous sulfate/0.2M Na-dithionite blend injected into source zone through 2-inch ID PVC well screened 7.5-15 ft bgs
- Reductant blend injected at average flow of 15 gal/min and average pressure of 10 psi


Olin

Source Zone Study Evaluation

- Pre- and post-treatment groundwater samples analyzed for cations, anions, Cr(VI), Fe(II), ORP, pH, DO, and conductivity
- Pre- and post-treatment solid phase analyzed for aqueous, phosphate, and Method 3060 extractable Cr(VI)

	Cr(VI) mg/L	*Total Cr mg/L*	*pH*	*S.C. mS/cm*	*ORP mV*	*Fe(II) mg/L*	*D.O. mg/L*	*Temp. °C*
RM–2 (2.5 ft)								
Pre-Treatment	6.1	6.118		15.0	95	< 0.01	0.08	24.1
48 hrs		0.029	7.49	39.7	-619	92.0	0.42	27.4
144 hrs		<0.003	7.85	38.7	-408	43.5	0.51	28.6
34 days		<0.003	8.23	33.1	-440	>5.0	0.63	29.9
RM-4 (5.0 ft)								
Pre-Treatment	4.6	5.014		16.8	130	<0.01	0.06	24.1
48 hrs		0.011	7.85	31.0	-556	29.7	0.52	24.1
144 hrs		0.008	8.03	30.1	-504	18.5	0.56	26.0
34 days		0.014	8.28	23.4	-417	2.79	0.61	27.4
RM-6 (7.5 ft)								
Pre-Treatment	4.9	4.916		16.8	242	<0.01	0.03	23.4
48 hrs		0.135	8.77	30.4	-403	1.8	0.47	27.6
144 hrs		0.136	8.71	29.7	-388	1.6	0.55	25.7
34 days		0.076	8.75	21.4	-246	0.11	0.65	27.4
RM-8 (10 ft)								
Pre-Treatment	3.4	3.466		20.7	191	<0.01	0.11	23.0
48 hrs		2.241	8.91	28.2	-212	0.11	0.55	24.8
144 hrs		2.700	8.97	25.4	-230	0.06	0.72	23.6
34 days		1.777	8.91	20.1	-174	0.05	0.63	28.6

Parameter	Pre-Treatment	Post-Treatment (24 hours)	Post-Treatment (40 days)
Hexavalent chromium (Cr(VI))	52.0	0.030	< 0.010
Total chromium	48.7	0.003	< 0.003
Total iron (Fe)	< 0.035	55.39	< 0.035
Sodium (Na)	2048	3718	2222
Potassium (K)	3175	1161	2232
Calcium (Ca)	3.580	86.47	25.16
Magnesium (Mg)	5.550	849.7	114.7
Boron (B)	0.759	< 0.021	0.076
Barium (Ba)	< 0.020	0.184	0.173
Manganese (Mn)	< 0.030	15.75	0.357
Antimony (Sb)	0.956	0.049	0.037
Selenium (Se)	0.366	0.119	0.097
Strontium (Sr)	0.171	2.476	0.939
Chloride (Cl^-)	2480	775	1600
Sulfate (SO_4^{2-})	4570	9780	5220
Phosphate (PO_4^{3-})	0.07	0.04	0.03
Alkalinity	660	2100	640
TIC	34.5	10.4	7.12
DIC	24.9	7.96	5.72
TOC	10.1	8.74	7.56
DOC	5.75	5.56	6.98
pH	11.53	7.91	9.63
ORP (mV - uncorrected)	42	- 431	- 190

Source Zone Study Results

- Ferrous iron disseminated out to radius of 8+ ft
- No well clogging observed
- Accessed zones effectively treated based on post-treatment extraction tests
- Treated solid phase acquires residual capacity to treat dissolved phase Cr(VI)

Cr(VI) Plume Study

- Can ferrous iron (in the presence of Na-dithionite) be injected into path of dissolved phase Cr(VI) plume to treat Cr(VI)?
- Will the hydraulic conductivity of the formation be adversely impacted by the injection of ferrous iron?
- How long will the ferrous iron enriched zone remain reactive?

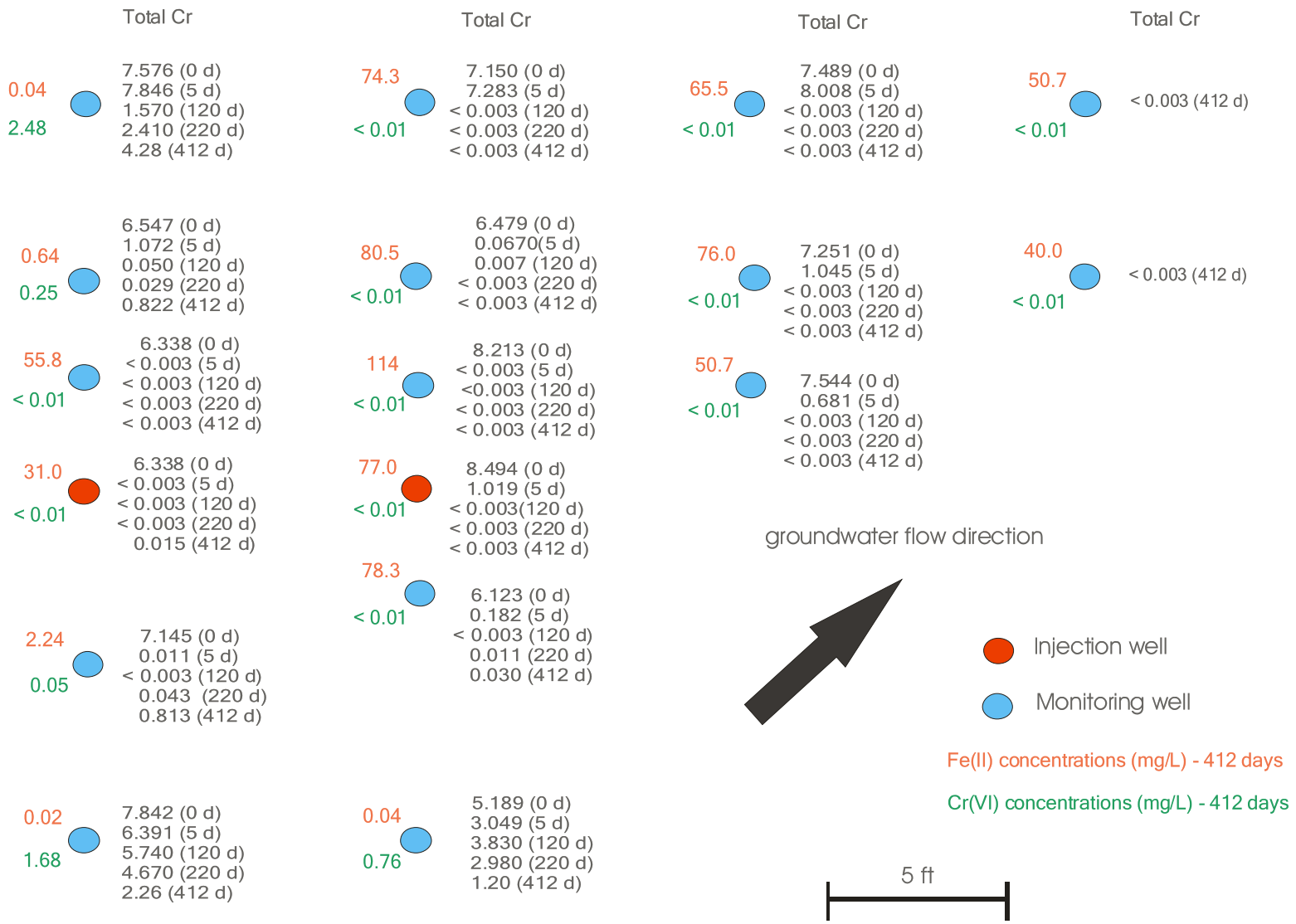

Oil

Cr(VI) Plume Study

- 1300 gallons of 0.2M ferrous sulfate/0.2M Na-dithionite blend injected into each of two 2-inch ID injection wells screened at 10-15 ft bgs and spaced 8 ft apart
- Injection at average 15 gal/min at pressure of 10 psi

Performance Evaluation

- Array of 1-inch ID monitoring wells installed up-gradient and down-gradient of injection wells
- Pre- and post-treatment groundwater samples analyzed for cations, anions, Fe(II), Cr(VI), Eh, pH, DO, conductivity, TOC/DOC



Well configuration for redox zone pilot study at Macalloy Corporation Superfund site.