Report for Gasoline Range Organics In Situ Chemical Oxidation Treatability Study with Sodium Persulfate and TSI-FSA™ Ferrous Sulfide Activator to Evaluate Loadings and Destruction Efficiency

This report is for an ISCO treatability study for soil contaminated with gasoline. The ISCO treatability study compared the United Initiators (UI) NPS persulfate activated with sodium hydroxide and persulfate activated with four loadings of TSI-FSA™ Ferrous Sulfide Activator. One loading (50 g/L) of persulfate was used for each treatment except the control. The objective was to further evaluate the activator loading, cost, and destruction efficiency for a petroleum hydrocarbon contaminated site.

An earlier study with only spiked tap water had used a loading of 2.1 g/L **TSI-FSA™** (equivalent to 0.15 g/L ferrous sulfide activator assuming 7% ferrous sulfide in the **TSI-FSA™**). The percent removals observed in that treatability study over 28 days are shown below in Table 1. Almost all of the persulfate remained after 28 days in both treatments. Both persulfate treatments (sodium hydroxide or NaOH and TSI-FSA™ removed all of the 1,4-dioxane, benzene, naphthalene, and tetrachloroethene (PCE). The treatment with persulfate and **TSI-FSA™** gave the best treatment of 1,1,1-trichloroethane (1,1,1-TCA). Carbon tetrachloride was reduced by 90.8% with the mackinawite and by 99.8% with persulfate and NaOH.

Table 1. Percent Removals for 50 g/L Persulfate Treatments in Aqueous Only Study

Treatment	Persulfate Consumption %	1,1,1-TCA	1,4-Dioxane	Benzene	Carbon Tetra-chloride	Naph-thalene	PCE
Control		13.8	-30.4	11.8	20.0	16.3	14.3
50 g/L PS 2.1 g/L TSI-FSA™	11.9	99.7	>95.9	>99.97	90.8	>99.96	>99.95
50 g/L PS 0.64 g/L NaOH	9.5	58.6	>95.0	>99.96	99.8	>99.95	>99.94

Persulfate Activation Treatability Study with Gasoline Range Organics in Soil and Groundwater

A total of 15.9 kg of sieved topsoil and 4.1 kg of playground sand was spiked with 20 g of gasoline in 80 g methanol. This spike was added to 900 g of tap water. An additional 1.99 kg of tap water was added. The gasoline-spiked water was mixed with the soil using an auger and electric drill until apparent homogeneity. A Control 0 bottle was prepared with 900 g of the spiked soil and about 500 mL of tap water. The soil was analyzed for benzene, toluene, ethylbenzene, total xylenes (BTEX), cumene, naphthalene, 1,2,4-trimethylbenzene, and 1,3,4-trimethylbenzene and for Gasoline Range Organics (GRO) by EPA Method 8260C and moisture. The spiked water was analyzed for the following parameters: benzene, toluene, ethylbenzene, total xylenes, cumene, naphthalene, 1,2,4-trimethylbenzene, and 1,3,4-trimethylbenzene and for GRO by EPA Method 8260C.

130 Hickman Road – Suite 1 – Claymont – Delaware – 19703
For More Information Call Michael Free at 302-798-9553 or Email: mfree@terrasystems.net

A preliminary study determined the buffer (sodium hydroxide) demands for one loading of sodium persulfate. Four loadings of TSI-FSA™ with persulfate were also evaluated. TSI measured the pH of the soil and groundwater and determined the quantities of 25% sodium hydroxide needed to raise and maintain the pH to 11.0 of 102 g soil (50% by volume) and 60 mL groundwater (50% by volume) for the treatment with 50 g/L UI NPS sodium persulfate and sodium hydroxide. Other treatments included 50 g/L UI NPS and TSI-FSA™ (0.03 g) or a molar ratio of 0.0011 FeS:persulfate; 50 g/L UI NPS and TSI-FSA™ (0.13 g) or a molar ratio of 0.0057 FeS:persulfate; 50 g/L UI NPS and TSI-FSA™ (0.13 g) or a molar ratio of 0.011 FeS:persulfate; 50 g/L UI NPS and TSI-FSA™ (1.25 g) or a molar ratio of 0.055 FeS:persulfate. At the end of the 15-day incubation period, the persulfate was monitored in each treatment.

The control treatment had a pH between 6.9 and 7.1. The treatment with 50 g/L persulfate and sodium hydroxide took 1.1 mL of a 25% NaOH solution to bring the pH to 11.2 on day 0 and it drifted down to 5.5 by Day 2 as the persulfate decomposed to sulfuric acid. A total of 6.0 mL of the 25% NaOH solution was required to maintain the pH above 11 for the 15-day incubation period or about 14.7 g NaOH/kg soil. All of the persulfate was consumed with a soil oxidant demand of >29,412 mg/kg. In the treatments with TSI-FSA™, the pH decreased to as low as 1.9. Residual persulfate decreased on Day 15 as the TSI-FSA™ loading increased with no residual persulfate at the highest loading of 22.8 g/L TSI-FSA™.

A contaminant destruction evaluation was conducted with a control, 50 g/L of UI NPS sodium persulfate activated with TSI-FSA™ at molar ratios of 1:0.0019, 1:0.0080, 1:0.014 and 1:0.040. Two replicates of each oxidant treatment were prepared in 1,010 mL bottles with 858 g soil based upon a density of 2.0 g/cm^3 and about 500 mL groundwater or approximately 50% by volume soil and 50% volume tap water. Three replicates of the control were prepared. The volume of sodium hydroxide required to maintain the pH above 10.5 determined in the initial characterization step was added to the sodium hydroxide amended treatment replicates or 12 g/L. The pH, redox potential, and persulfate of one bottle were recorded over time. Samples of the soil and groundwater from each treatment were collected after 14 and 35 days to be analyzed for BTEX, cumene, naphthalene, TMB, and GRO.

The Control pH ranged between 6.7 and 8 with ORPs between -405 to 272 mV. The pH in the PS + NaOH treatment was initially 13.5 and drifted down to as low as 9.4. On Day 21, 5.0 mL of 25% NaOH solution was added to bring the pH back to 11.2. The pH dropped to 10.2 by Day 35. All of the persulfate was consumed by Day 28 with a soil oxidant demand of >29,487 mg/kg. The pHs in the treatments with mackinawite decreased to as low as 1.6. Highly oxidizing ORPs of 502 to 619 mV were maintained in these treatments. Persulfate persisted in all TSI-FSA™ treatments over 35 days. The soil oxidant demand increased from 23,392 mg/kg for the lowest loading of TSI-FSA™ to 26,167 mg/kg at the highest TSI-FSA™ loading.

Over the 35 day incubation period (Table 2), the aqueous phase benzene was reduced by 35.7% in the Control, 21.4% with PS + NaOH, and by 96.8 to 98.2% with PS + TSI-FSA™ treatments The aqueous phase C6-C10 GRO was reduced by 35.4% in the Control, -15.4% with PS + NaOH (increase compared to Control Day 14), and by 88.5 to 87.7% % with PS + TSI-FSA™ treatments. The aqueous phase total VOCs were reduced by 40.9% in the Control, 24.5 % with PS + NaOH, and by 99.7% with PS + TSI-FSA™ treatments.

Soil treatment removal efficiencies were less than the aqueous phase, but the PS + TSI-FSA™ treatments still outperformed the control or the PS + NaOH treatments.

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On a mass balance basis including both soil and groundwater phases, benzene was reduced by 39.3% in the Control, 18.9% with PS + NaOH, and by 71.9 to 91.9% with PS + TSI-FSA™ treatments The mass balance C6-C10 GRO was reduced by 1.1% in the Control, -4.9% with PS + NaOH, and by 36.4 to 57.5 % with PS + TSI-FSA™ treatments. The mass balance total VOCs were reduced by 24.9% in the Control, 13.6 % with PS + NaOH, and by 43.6 to 79.5% with PS + TSI-FSA™ treatments.

The maximum removal was observed with the high TSI-FSA™ loading of 3.7 g/L of TSI-FSA™ and 50 g/L of persulfate or a ratio of about 0.074:1 of TSI-FSA™:Persulfate.

Table 2. Percent Removals in Aqueous Phase, Soil Phase, and Mass Balances

Sample	Units	Control	PS NaOH	PS Low TSI-FSA™	PS Mod TSI-FSA™	PS High TSI-FSA™	PS V High TSI-FSA™
			12.6 g/L NaOH	0.50 g/L TSI-FSA™	2.1 g/L TSI-FSA™	3.7 g/L TSI-FSA™	10.5 g/L TSI-FSA™
Percent Removal Aqueous Phase from Control 14							
Benzene	mg/L	35.7	21.4	96.8	97.9	97.9	98.2
C6-C10 TPH GRO	mg/L	35.4	-15.4	88.5	88.5	88.5	87.7
Total VOCs	mg/L	40.9	24.5	99.7	99.7	99.7	99.7
Soil Percent Removal from Control 14							
Benzene		40.0	19.1	78.2	68.2	91.1	76.4
C6-C10 TPH GRO		0.0	-4.3	34.8	34.8	56.5	17.4
Total VOCs		24.0	13.2	55.7	41.0	78.6	50.9
Mass Balance % Removal Vs Control 14							
Benzene		39.3	18.9	80.5	71.9	91.9	79.1
C6-C10 TPH GRO		1.1	-4.9	36.4	36.4	57.5	19.5
Total VOCs		24.7	13.6	57.7	43.6	79.5	53.0