

## INVESTIGATION OF CHLORINATED METHANES TREATABILITY USING ACTIVATED SODIUM PERSULFATE

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**ABSTRACT:** In situ chemical oxidation is a frequently used remedial approach for the destruction of chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE). However, treatment of more recalcitrant chloroethanes and chloromethanes have challenged traditional oxidation reagents. Recently, new methods of sodium persulfate reagent activation have been developed and these systems have shown promise for improved treatment performance. The new methods of persulfate activation use chelated metals, such as iron (II) ethylenediamine tetraacetic acid [ $\text{Fe}^{+2}(\text{EDTA})$ ], hydrogen peroxide addition or alkaline conditions by addition of base. Both the mixed persulfate/peroxide and the alkaline persulfate reagent systems have shown the ability to treat the more recalcitrant chlorinated methanes and ethanes.

In this study the new methods of persulfate activation have been investigated in bench tests on soil/water mixtures from a site with carbon tetrachloride (CT) and chloroform (CF) contamination. The oxidant systems that were tested included persulfate activated with EDTA chelated iron (II), persulfate and hydrogen peroxide mixtures at mole ratios of 10:1, 1:1 and 1:10 and persulfate at a pH of 11-12 using base addition. The tests were designed to monitor reagent behavior in soil/groundwater mixtures as well as CT and CF treatment effectiveness.

### INTRODUCTION

Persulfate ion ( $\text{S}_2\text{O}_8^{\ominus}$ ) is a strong oxidant capable of oxidizing most organic compounds to carbon dioxide and other mineral products. The standard reduction potential for the half reaction shown below is +2.01 Volts (V). It is on the same order as that for ozone and higher than that for permanganate and hydrogen peroxide, but less than that for the hydroxyl radical ( $\text{OH}\cdot$ ), which is a Fenton's Reagent intermediate.



It is believed that persulfate reacts with organic compounds primarily by the sulfate anion radical, which can be generated in solution by several mechanisms. The sulfate anion radical is a powerful oxidizing species with a standard electrode reduction potential of +2.6 V, which is similar to that for the hydroxyl radical ( $\text{OH}\cdot$ ) species (+2.8 V). The persulfate anion radical in contrast has a longer lifetime in solution and is more selective in its reactions (P. Neta,

1987).



Recently, new methods of persulfate reaction activation with chelated metals, such as iron (II) ethylenediamine tetraacetic acid [ $\text{Fe}^{+2}(\text{EDTA})$ ], hydrogen peroxide addition or alkaline conditions (pH=11-13) by addition of base have been developed (P. Block, 2004). These new methods have shown promise for in situ treatment of more recalcitrant chloroethane and chloromethane compounds and were investigated on soil/groundwater mixtures from a site with CT and CF contamination.

## MATERIALS AND METHODS

**Soil Oxidant Demand (SOD) Tests.** Tests were performed to measure the amount of oxidant consumed in the course of treatment to destroy the target CT and CF compounds. The amount and rate of oxidant consumption is used to determine oxidant dosing and reaction condition requirements for treatment.

Tests were performed using soil/groundwater slurries with a soil to water weight ratio of 1:1.5. Persulfate oxidant systems were tested using an oxidant concentration of 22 g/L. Three molar ratios of persulfate to peroxide were tested for activation of the persulfate and the ratios were 1:10, 1:1 and 10:1. Alkaline activation of persulfate was tested at a pH of 11-12. The pH was established using sodium hydroxide addition and the dose was determined from buffering capacity measurements performed during characterization. For chelated metal activation the iron (II) EDTA complex, [ $\text{Fe}^{+2}(\text{EDTA})$ ] was studied. These tests used an iron concentration of 200 mg/L. Data from these tests were compared to results from similar tests using modified Fenton's Reagent and permanganate.

**Treatment Effectiveness Tests.** Treatment tests were used to evaluate VOC treatment effectiveness over a six-week treatment period. Tests were prepared with zero headspace using 30 grams of soil and 145 milliliter (mL) of groundwater in 160 mL septum bottles for each test condition. Each test bottle was spiked with CT and CF to a target aqueous concentration of 250 mg/L of CT and 50 mg/L of CF to provide the desired concentrations for testing. Four sampling points, 3, 9, 19 and 47 days, were used to collect samples for analysis. Control tests without added oxidant were also run in parallel as a baseline to assess treatment effects due to differences in VOC concentrations.

A 1:1 molar ratio of persulfate to peroxide was tested for peroxide activation at a persulfate concentration of 4 g/L. A lower concentration was used to minimize gas evolution so the test could be performed in a sealed septum vial. Alkaline activation of persulfate was tested at a pH of 11-12 at a persulfate concentration of 22 g/L. The pH was established using trisodium phosphate ( $\text{Na}_3\text{PO}_4$ ) addition to a concentration of 46 g/L, which produced pHs measuring from 11.46 to 12.11 during the test. For chelated metal activation the persulfate concentration was 22 g/L and the  $\text{Fe}^{+2}(\text{EDTA})$  complex was used at an iron

(Fe<sup>+2</sup>) concentration of 200 mg/L.

## RESULTS AND DISCUSSION

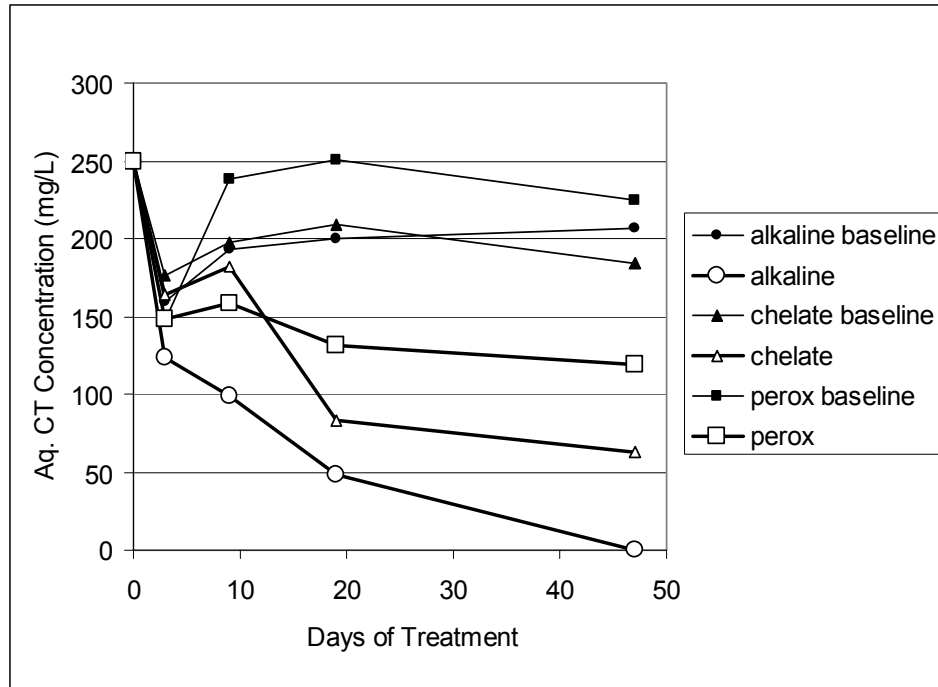
**Soil Oxidant Demand Results.** The peroxide activated persulfate tests showed rapid consumption of both reagents in the presence of site soil. The reagents were consumed at a ratio of between 0.55 to 10 moles of hydrogen peroxide per mole of persulfate until depletion of one or both of the reagents depending on the starting concentrations. For the 10:1 peroxide to persulfate mole ratio test both reagents were essentially depleted within 24 hours. For the 1:1 mole ratio test the peroxide was consumed within 24 hours, but there was a residual persulfate concentration that was relatively stable in the absence of peroxide. For the 1:10 mole ratio test the residual persulfate was stable once the peroxide was consumed. The rapid consumption of reagent for these tests was repeated with consistency over several re-dosings, suggesting that it was due more to reagent decomposition processes than to oxidation of contaminants or soil material.

Three tests, namely the test using persulfate without activation, the alkaline persulfate test and the Fe<sup>+2</sup>(EDTA) complex activated persulfate test were more stable toward persulfate consumption than the peroxide activated persulfate tests. Table 1 shows the initial rates of reagent consumption for these tests assuming a linear relationship with time.

Test Description	Persulfate Consumption Rate [(mg/L)/day]
No activation	185
200 mg Fe <sup>+2</sup> /L as Fe(EDTA)	383
pH=11-12 using NaOH	515

**Table 1. Summary of persulfate initial consumption rates in SOD tests using 22 g/L sodium persulfate and 1:1.5 soil to groundwater.**

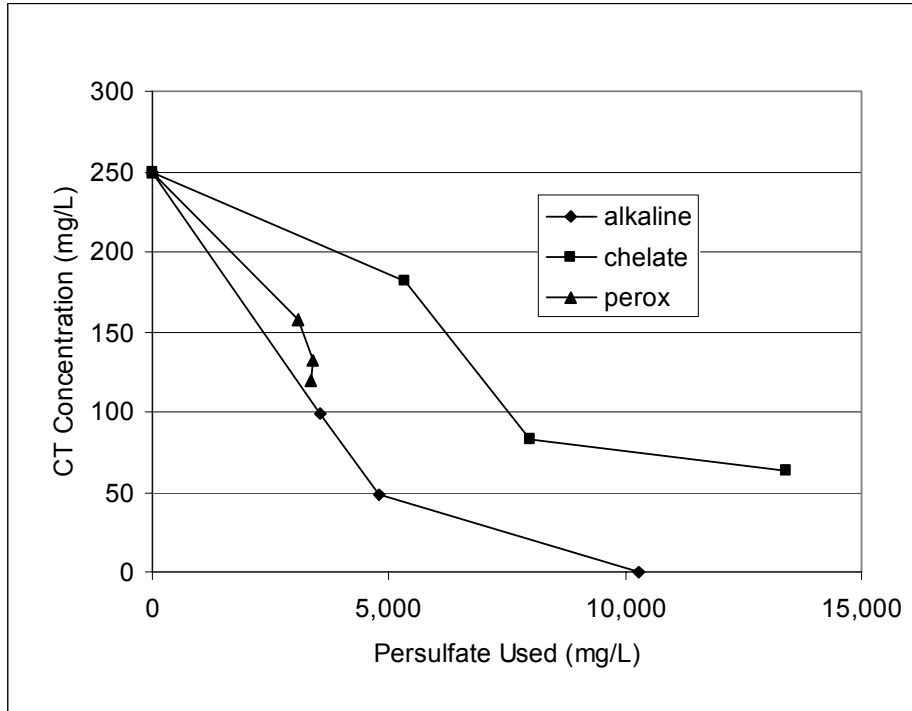
**Treatment Effectiveness Test Results.** Plots of aqueous CT concentration as a function of time (days) for the soil/groundwater treatment tests are shown in Figure 1. The data show that alkaline activated persulfate was most effective in reducing CT concentrations. At the 47-day sampling point the aqueous CT concentration was reduced to 0.051 mg/L. The next most effective treatment based on residual concentration was the Fe<sup>+2</sup>(EDTA) activated persulfate reagent, which reduced the CT concentration to 62.8 mg/L at day 47. The peroxide activated persulfate reagent was not as effective, but the peroxide dose was approximately one-fifth of the other tests. The 47-day CT concentration for this test was 119 mg/L.



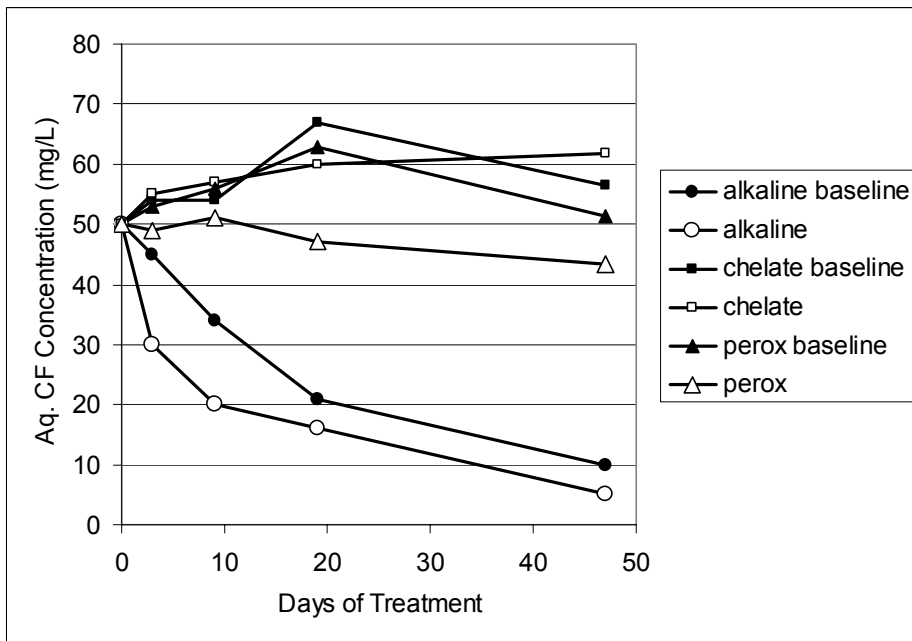
**Figure 1. Carbon tetrachloride treatment results in soil/groundwater mixtures for activated persulfate systems**

Both the alkaline activated persulfate test and the  $\text{Fe}^{+2}$ (EDTA) activated persulfate test retained approximately 50 percent of the persulfate reagent to potentially continue treatment beyond the 47 day time point. The persulfate concentration for the peroxide activated test was less than that for the other tests and by the 9-day sampling point all of the peroxide and 75 percent of the persulfate had been consumed and there was only modest change in CT concentration beyond that point. A plot of CT concentration as a function of persulfate used is shown in Figure 2. This shows that hydrogen peroxide activated persulfate was nearly as effective as the alkaline activated persulfate for treating CT based on the amount of oxidant used, but the rapid consumption of reagent would likely make effective utilization difficult.

Plots of CF concentration as a function of time (days) for the treatment tests are shown in Figure 3. The data show that both the alkaline control and the alkaline activated persulfate tests had a reduction in aqueous CF concentration. The alkaline control had an approximate 80 percent reduction to 9.88 mg/L and the alkaline persulfate test was reduced nearly 90 percent to 5.18 mg/L. The reduction in the control CF concentration is believed to be due to alkaline hydrolysis and this may have also contributed to the reduction in the alkaline activated persulfate test. Chloroform is more readily hydrolyzed by base than either CT or methylene chloride (J. March, 1968). The other tests did not indicate a significant change in CF concentration.



**Figure 2. Aqueous carbon tetrachloride concentration in treatment systems as a function of persulfate used**



**Figure 3. Chloroform treatment results in soil/groundwater mixtures for activated persulfate systems**

## CONCLUSIONS

Activated persulfate systems demonstrated the ability to treat CT concentrations in soil/groundwater mixtures. Persulfate activated by alkaline conditions demonstrated the best performance in reducing aqueous CT concentrations as well as providing the greatest reduction for the amount of oxidant used. Peroxide and  $\text{Fe}^{+2}$ (EDTA) activated persulfate systems also provided reductions in concentration, but not to the same extent as the alkaline activated persulfate.

Alkaline conditions both for the persulfate control test and the persulfate treatment test provided a reduction in CF concentrations with the persulfate treatment providing a slightly lower residual CF concentration. The reduction in control CF concentration was attributed to alkaline hydrolysis of CF, which most likely also contributed to the reduction observed in the persulfate treatment test. Neither the peroxide activated persulfate nor the  $\text{Fe}^{+2}$ (EDTA) activated persulfate systems provided significant treatment.

Peroxide activated persulfate systems were not stable in the presence of site soil. The reagents were typically consumed within 24 hours at rates of 0.5 to 10 moles of peroxide per mole of persulfate until peroxide was depleted and then residual persulfate concentrations were relatively stable. In the absence of site soil the reagent combination was more stable losing less than 50 percent of their concentrations over three weeks.

## REFERENCES

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