

Novel Activation Technologies for Sodium Persulfate *In Situ* Chemical Oxidation

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ABSTRACT: Persulfate oxidation chemistry is an emerging technology for the *in situ* chemical oxidation of chlorinated and non-chlorinated organics. Activation of persulfate to form sulfate radicals is a potent tool for the remediation of a wide variety of contaminants, including chlorinated solvents (ethanes, ethanes and methanes), BTEX, MTBE, 1,4-dioxane, PCB's and PAH's. Several new activation technologies now exist to catalyze the formation of sulfate radicals, including persulfate combined with chelated-metal complexes, persulfate combined with hydrogen peroxide and alkaline persulfate. The breadth of activator systems allows for the proper choice of persulfate technology for given contaminants and site conditions.

Introduction

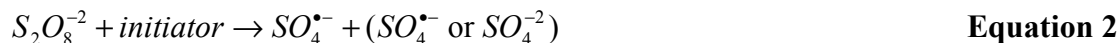
Persulfates (specifically dipersulfates) are strong oxidants that have been widely used in many industries for initiating emulsion polymerization reactions, clarifying swimming pools, hair bleaching, micro-etching of copper printed circuit boards, and TOC analysis. In the last few years there has been increasing interest in sodium persulfate as an oxidant for the destruction of a broad range of soil and groundwater contaminants. Persulfates are typically manufactured as the sodium, potassium, and ammonium salts. The sodium form is the most commonly used for environmental applications.

The persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants used in remediation. The standard oxidation – reduction potential for the reaction



is 2.1 V, as compared to 1.8 V for hydrogen peroxide (H₂O₂) and 1.4 V for the peroxymonosulfate anion (HSO₅⁻). This potential is higher than the redox potential for the permanganate anion (MnO₄⁻) at 1.7 V, but slightly lower than that of ozone at 2.2 V.

In addition to direct oxidation, sodium persulfate can be induced to form sulfate radicals, thereby providing free radical reaction mechanisms similar to the hydroxyl radical pathways generated by Fenton's chemistry. The generation of sulfate radicals is



The sulfate radical is one of the strongest aqueous oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical, 2.7 V.

In addition to its oxidizing strength, persulfate and sulfate radical oxidation has several advantages over other oxidant systems. First, it is kinetically fast. Second, the sulfate radical is more stable than the hydroxyl radical and thus able to transport greater

distances in the sub-surface. Third, persulfate has less affinity for natural soil organics than does the permanganate ion (Brown 2003) and is thus more efficient in high organic soils. These attributes combine to make persulfate a viable option for the chemical oxidation of a broad range of contaminants.

Conventional Persulfate Activation

In the early 1960's, a significant body of work examined the kinetics and mechanisms associated with persulfate oxidation (House, 1962 and Haikola, 1963). While the persulfate anion by itself was found to be a strong oxidizer, its reaction rates are kinetically slow for the more recalcitrant contaminants, such as trichloroethylene. However, the kinetics of persulfate oxidation can be significantly enhanced by the generation of sulfate radicals.

Sulfate radical initiation (Equation 2) can be achieved through the application of heat, transition metal catalysts or UV radiation. These processes are reviewed in several references (House, 1962; Behrman, 1980; Balazs, 2000). With transition metal activation, Balazs points out that while the mechanism is dependent on catalyst type, organic substrate and oxidant concentration, the rate equation can be generally stated as:

$$d[S_2O_8^{2-}]/dt = -k[S_2O_8^{2-}]^x [catalyst]^y \quad \text{Equation 3}$$

where $\frac{1}{2} < x < \frac{3}{2}$ and $0 < y < \frac{3}{2}$. This suggests that the reaction rate is independent of the contaminant loading. Several recent patents have specifically disclosed the activation of persulfate for the oxidation of organic contaminants by either heat or transition metals. Pugh (1999) discusses both metal catalysis and heat activation, at temperatures above 20°C, to oxidize organic contaminants. Hoag (2000, 2002) discusses divalent metal catalysis and the application of heat in the range of 40 to 99°C to oxidize VOCs. This body of literature basically leads one to conclude that the effective use of persulfate for environmental applications necessitates the use of either heat activation or the addition of iron II.

In the laboratory, heat-activated persulfate has been demonstrated in aqueous systems to be applicable to a wide range of contaminants. The activation temperature required varies by compound. Table 1 lists the oxidation of various compounds as a function of temperature. At 45°C and above all the compounds tested were oxidized. Bruell (2001) has shown that heat-catalyzed persulfate oxidation of organics in a soil environment requires higher temperatures than in aqueous systems.

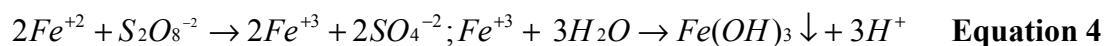
For activation by transition metal catalysis, ferrous iron (Fe⁺²) is the most common and readily available activator, with common forms being ferrous sulfate (FeSO₄) and ferrous chloride (FeCl₂). Generally, 100 to 250 mg / L of iron is required to effectively activate persulfate. Additions of ferrous iron in excess, greater than 750 mg / L, can lead to the rapid decomposition of persulfate and a loss

Table 1
List of Contaminants With > 90% Decomposition Treated with Persulfate @ 20^o C
Toluene, Ethylbenzene; Xylene; 1,1-DCE; 1,2-Dichlorobenzene; 1,3-Dichlorobenzene, 1,2,4-Trichlorobenzene
List of Additional Contaminants With > 90% Decomposition Treated with Persulfate @ 35^o C
1,2-DCE, PCE, TCE, Vinyl Chloride, Carbon Tetrachloride, 1,1-DCA; 1,2-DCA, Benzene, Chlorobenzene, MTBE
List of Additional Contaminants With > 90% Decomposition Treated with Persulfate @ 45^o C
Methylene Chloride, Chloroform, 1,1,1-TCA

in remediation performance. If significant amounts of reduced metals are available in the subsurface, addition of metal catalysts may not be necessary to catalyze the persulfate. Divalent iron activated persulfate effectively oxidizes many of the compounds susceptible to the heat-activated persulfate, including BTEX, chlorobenzene, dichlorobenzene, DCE, TCE, and PCE. However, its effectiveness against chlorinated ethanes, such as TCA, and chlorinated methanes, such as chloroform, is limited.

While heat and iron II activation of persulfate are effective in bench scale oxidation studies, they both have limitations for field application. Heat activation requires installation of a parallel heating system to heat the aquifer matrix to the desired temperature. This entails both capital expenditures as well as additional operating expense. The options for *in situ* heating include steam or hot air injection, electrical resistance (joule) heating, or radio frequency heating. Generally heating is best applied for source treatment where the target area is limited. *In situ* heating, with an external heating source, is impractical for treating large groundwater plumes.

The problem with the use of iron II as an activator is its transportability. Iron II is eventually oxidized by the persulfate to iron III, which, at a pH above 4, is insoluble. The net reaction is:



Meyers (Meyers, 2002) discussed the affect of the precipitation of iron on the loss of persulfate activation in field applications. As an example, in a pilot treatment test of TCE with persulfate, a persulfate and iron mixture (10% sodium persulfate and 174 mg/L of available Fe^{+2}) was injected into a sandy silt. Nine days after the injection, a monitoring point 1.5 M down-gradient of the injection point was sampled, and the iron concentration was found to be 0.3 mg/L, and the TCE concentration was 9.3 mg/L. Groundwater samples from the monitoring point were collected and re-dosed with either iron alone or with persulfate without additional iron. After 7 days the re-dosed samples were reanalyzed for TCE. The results are shown in Table 2. Greater reduction in TCE levels was achieved when additional Fe^{+2} was added, as compared to when only additional persulfate was added, suggesting a lack of available catalyst, and not oxidant, in the subsurface at the down-gradient monitoring point.

Dosing Material	TCE, µg/L
Control – no dose	8,700
1 g/L Persulfate	7,500
250 mg/L Fe^{+2}	4,240

Novel Activation Technologies

Practical constraints in sulfate radical formation by heating or addition of ferrous iron indicate a need for improved persulfate activation systems. Such technologies should:

- be transportable in a groundwater system
- increase the reactivity of persulfate with a broad range of organic contaminants
- be easy to apply in a variety of subsurface conditions.

Several new persulfate activation systems have recently been developed (FMC - ERM, 2002; FMC - Orin, 2003) that address these issues. A few of these technologies use non-

metal routes to generate sulfate radicals. The following is a discussion of these novel activators.

A. Chelated Metal Catalysts

Chelated metal catalysts are complexes of transition metals bound to strong chelating agents. Examples of chelating agents include: ethylenediaminetetraacetic acid (EDTA), citrate, polyphosphate, glycolic acid, catechol, nitrotriacetic acid (NTA), Tetrahydroquinine (THQ) and others in this class of materials. Previous work (Pignatello, 1992) demonstrated the benefit of chelated iron complexes to activate hydrogen peroxide for the destruction of complex pesticides. Chelated trivalent iron (Fe^{+3}), in addition to Fe^{+2} , was found to have excellent oxidation performance.

Laboratory tests were conducted to test the efficacy of chelated iron catalysts for persulfate activation utilizing several different iron – chelant complexes. The best performing complex, Fe(III) – EDTA will be highlighted for discussion purposes. All samples were prepared as aqueous solutions in VOA bottles with zero headspace. A standard contaminant mixture was used: twenty-eight different VOCs were dissolved in DI water to attain individual VOC concentrations of 10-20 mg/L. The Fe-EDTA complex was generated by reacting equimolar concentrations of ferric chloride and EDTA. The Fe-EDTA complex was dosed to provide 550 mg / L of available iron to the solution. An oxidant dosage level of 10 % sodium persulfate was used. Samples were taken at time zero, and at 7, 14 and 21 days and analyzed via GC-MS. All studies were conducted at room temperature and ambient pH.

The 21-day results are shown in Table 3, which compares persulfate alone and persulfate with: iron II (unchelated), Fe(III) (unchelated), and Fe(III)-EDTA. A DI water control was also run. The table displays the results for different classes of contaminants. Several

µg / L	Control	Persulfate	Persulfate Fe(II)	Persulfate Fe(III)	Persulfate Fe(III)-EDTA
Chloromethanes	35000	34000	29100	35000	32000
Chloroethanes	50000	52000	37600	50000	48000
Chloroethenes	32700	9830	0	660	0
Chlorobenzenes	34800	9300	0	3100	360
BTEX	43700	1370	0	0	0
Oxygenates	46000	44000	830	17600	3550
pH	6.9	2.2	2.3	2.3	2.2

observations can be made from the data. First, none of the persulfate / iron catalysts are effective with the chloroethanes or chloromethanes. Second, all persulfate solutions resulted in a low pH. Third, Fe(II) was the most effective catalyst. The second best performing catalyst was the Fe-EDTA complex. Fourth, BTEX oxidation was effective with persulfate alone. And fifth, Fe(III), at a low pH, is a moderately effective catalyst. It should be noted that the results in Table 3 are at a pH of 2, where metal solubility and activity is not an issue.

Under the neutral pH conditions that may be found in the field, chelating the transition metal catalyst provides protection from hydration and subsequent precipitation (see Eq. 4). Table 4 shows the results for different iron catalysts with persulfate at a controlled pH of 7-8. The experimental conditions were similar to those used to generate Table 3, except: 1) a commercial Fe (III) -EDTA (Aldrich) was used with the dosing

level at 100 mg/L iron, and 2) the persulfate concentration was 2.5% (instead of 10%). As can be seen from Table 4, at a pH of 7 - 8, only the Fe-EDTA catalyst with persulfate was effective; whereas the un-chelated iron catalysts had reduced activity.

µg / L	Control	Persulfate Ctrl pH	Fe (II) Amb pH	Fe (II) Ctrl pH	Fe (III) Ctrl pH	Fe-EDTA Ctrl pH
Ethenes	34,083	32,606	0	27,730	31,230	9,870
Ethanes	67,115	62,379	61,908	63,702	64,756	50,246
Methanes	51,983	48,180	42,261	45,597	49,664	44,900
BTEX	40,119	3,963	0	13,538	13,560	647
Chlorobenzenes	56,089	36,990	0	31,824	34,662	7,428
Oxygenates	60,908	53,923	11,639	56,444	57,187	26,931
pH	6.7	8.5	2	7.5	8	7.6

The solubility and availability of the transition metal catalysts are critical factors in the activation of persulfate. Chelation is an effective means of maintaining metal activity at neutral or alkaline groundwater conditions.

B. Dual Oxidant System: Sodium Persulfate & Hydrogen Peroxide

Hydrogen peroxide technology, known as Fenton's reagent, has been widely applied in treating groundwater contaminants with varying results. In general, it is highly reactive and is able to oxidize a wide range of contaminants. However, the limitation of peroxide is its stability in some soil matrixes, where it rapidly decomposes, limiting its transport and effectiveness. A dual oxidant system (FMC - Orin, 2003) utilizing hydrogen peroxide and sodium persulfate has been developed that combines the reactivity of peroxide in the reduction of compounds of concern with the enhanced stability of persulfate. It is hypothesized that hydrogen peroxide and persulfate may have several synergistic attributes. First, hydroxyl radicals can initiate persulfate radical formation. Similarly, sulfate radicals can stimulate formation of hydroxyl radicals. Secondly, hydrogen peroxide may react with a significant portion of the more reactive contaminants, allowing the sulfate radicals to destroy the more recalcitrant compounds of concern. Finally, a combination of peroxide and sulfate radicals may provide a multi-radical attack mechanism, yielding either a higher efficiency in destroying contaminants, or allowing for recalcitrant compounds to be more readily degraded.

Initial laboratory testing by Orin RT (FMC - Orin, 2003) was performed by adding chlorinated solvents to an aqueous solution at room temperature. Two grams of sodium persulfate and 8 mL of 12.5% hydrogen peroxide were added per 100 grams of contaminated solution. Samples were taken on Day 8 and analyzed by GC-MS. Table 5 displays the results from the study. Significant reductions were measured not only for chlorinated ethenes, but chlorinated ethanes as well.

(mg/L)	Time 0	Day 8
1,1-DCE	4.5	0.1
TCE	2.8	non-detectable
1,1-DCA	1.1	non-detectable
1,1,1-TCA	12.0	0.6

A second laboratory study was run using soils from an MGP site. A slurry was made using 400 g of processed soil and 1.08 L of distilled water. Sodium persulfate was then added to a concentration of 11.5 g/L and allowed to mix. 120 mL of 50% peroxide was then added. The slurry was then analyzed via GC-MS. The results are pictured in

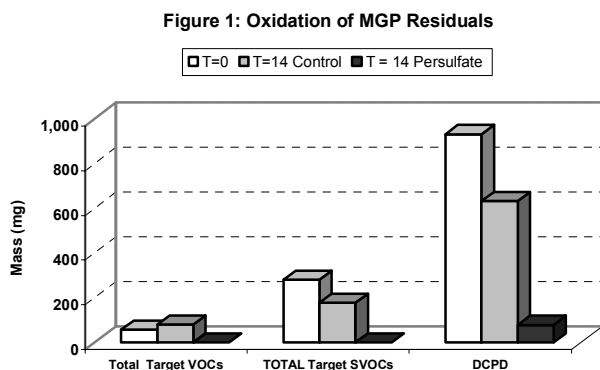


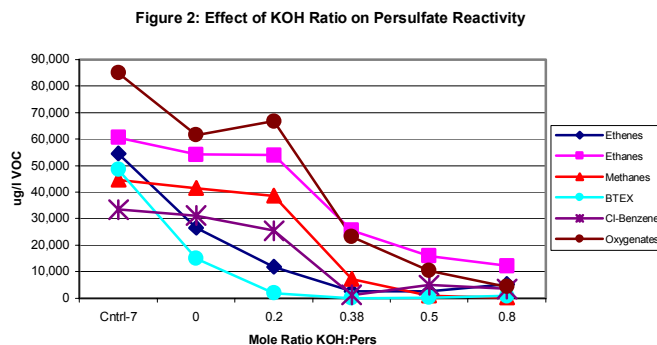
Figure 1. The VOCs present were BTEX and styrene. The SVOCs were 3 to 5 ring PAHs. Dicyclopentadiene (DCPD) was present as the major constituent. As can be seen from Figure 1, the combined peroxide-persulfate system was effective against all of these contaminants.

The combined peroxide-persulfate reaction system appears to have a broad range of applicability. It not only oxidizes compounds generally amenable to persulfate oxidation, but also oxidizes compounds not readily oxidized by conventional persulfate technology.

D. Alkaline Persulfate

Persulfate is known to be highly reactive at low pH (<3), but it is also highly reactive at pH's greater than 10. It should thus be possible to "activate" persulfate by increasing the pH to high values. Initial laboratory testing indicated the persulfate oxidation of contaminants was not just a matter of high pH, but of the buffering capacity as well (mole ratio of pH modifier to persulfate).

Studies were conducted in VOA vials with zero headspace. While a variety of pH modifiers were observed to activate persulfate, KOH will be used for discussion. Samples were prepared by adding persulfate at a concentration of 25 g/L and KOH to achieve mole ratios of 0.2, 0.4, 0.5 and 0.8 KOH : persulfate. The samples were analyzed after 7 days by GC-MS. A control with no persulfate or KOH was also run. No other catalysts were added to the samples. The activation of persulfate that was observed is solely due to the added base. The results of these studies are pictured in Figure 2. The data are grouped by class of contaminant.



Several observations can be made from these results. First persulfate reactivity increases with increasing levels of KOH. Second, there appears to be a threshold effect in the oxidation of some chlorinated VOCs. The mole ratio needs to be 0.4 or above for the persulfate to effectively react with the recalcitrant chlorinated VOCs (ethanes and methanes). The effect of the amount of KOH on the oxidation of

BTEX and oxygenates (MTBE, TBA, 1,4-dioxane) is more gradual. The amount oxidized increases with increasing KOH.

Table 6 lists the pH observed at 7 and 14 days for the different mole ratios of KOH and persulfate. The pH appears to have a breakpoint similar to that observed for the reactivity. A mole ratio of 0.4 or above is needed to achieve a pH above 10.0.

Mole Ratio	pH, 7-days	pH, 14-days
0	1.3	0.5
0.2	4.3	4.5
0.38	11.5	10.4
0.5	11.5	10.5
0.8	12.2	13

An interesting result for this study is the effect of the alkaline pH on historically difficult to destroy compounds, such as chlorinated ethanes and methanes. Table 7 displays

the 14 day results from the study for a selection of compounds for two different KOH : persulfate mole ratios. In most cases, there was complete destruction of these compounds

µg / L	Control Day 14	0.5 mol KOH : Persulfate	0.8 mol KOH : Persulfate
1,1,1-TCA	19,000	14,400	3,400
1,1,2-TCA	25,000	ND	ND
1,2-DCA	22,000	ND	ND
1,1-DCA	17,000	1,600	ND
Carbon Tetrachloride	18,000	ND	ND
Methylene Chloride	20,000	ND	ND
Vinyl Chloride	195	ND	ND
	ND – non detect		

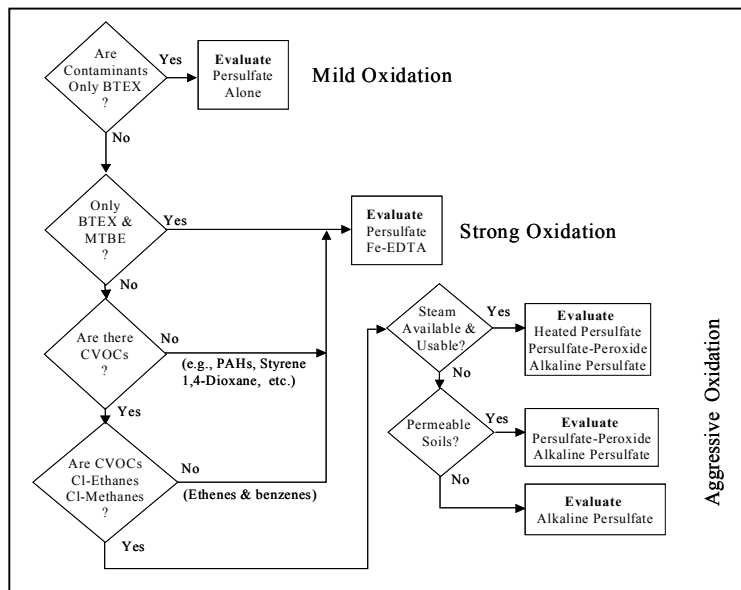
A number of conclusions can be drawn from these studies. First, alkaline persulfate has a broad reactivity. Second, the alkaline activation of persulfate appears to be possible with a number of different bases. Each base may have a different optimal ratio and/or breakpoint. Third, in applying the alkaline-persulfate activator technology it is important to add sufficient base (excess buffering capacity). The quantity of base needs to take into account any acidity in the soil. Fourth, there are reaction pathways for persulfate that are not currently well understood and can potentially be further optimized. The reaction of persulfate under basic conditions is a novel technology deserving further study.

Summary

Persulfate oxidation chemistry is an emerging technology for the *in situ* chemical oxidation of chlorinated and non-chlorinated organics. Activation of persulfate to form sulfate radicals yields a very potent tool for the remediation of a wide variety of contaminants, including chlorinated solvents (ethenes, ethanes and methanes), BTEX, MTBE, 1,4-dioxane, PCB's and polyaromatic hydrocarbons.

There now exists a

Figure 3: Choosing the Right Activator



variety of chemistries from which to choose to catalyze the formation of sulfate radicals. Choosing which activator system to use is key to maximizing the efficacy of persulfate oxidation. Figure 3 provides a logic-flow for assessing the different activator systems. There are three levels of persulfate activators that can be used. These include “Mild Oxidation,” in which persulfate alone is used. This may be appropriate for BTEX sites. If MTBE is present, then the “Strong Oxidation” system, which is persulfate activated with Fe-EDTA, is appropriate. This “Strong Oxidation” system is also appropriate for sites with only chlorinated ethenes (PCE, TCE, DCE) or chloro-benzenes. If there are chlorinated ethanes or methanes present that need treatment, then the “Aggressive Oxidation” systems should be evaluated. These include the alkaline-persulfate, combined peroxide and persulfate, and heated persulfate. These aggressive activation chemistries may be applied also for BTEX and chlorinated ethene sites if faster remediation is desired, or if there is a high contaminant load.

Proper evaluation of the site conditions is also needed for the effective application of the appropriate persulfate technology. Site geology, hydrogeology, soil properties, soil oxidant demand, and the remedial goals are all key factors to evaluate. Persulfate technology is not a “one-size-fits-all” technology. There is a rich and varied chemistry that can be brought to bear on a wide variety of contaminant problems.

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