

**Contaminated
Soils**

Volume 8

Chemical Oxidation
Heavy Metals
MTBE
Radionuclides
RBCA
Remediation
Risk Assessment
Site Assessment

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CHAPTER 2

Chelated Iron in Fenton-Like Oxidation of BTEX and PAHs in Soils

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ABSTRACT

This study investigated the feasibility of using chelated iron as catalyst in a Fenton-like oxidation of BTEX and PAHs in high acid buffering soils. Three catalysts investigated in this study were native iron (Fe) minerals, chelated native Fe, and Fe-chelate solution. The Fe-chelates selected for the decomposition of hydrogen peroxide consisted of the Fe-polyaminocarboxylate chelates, specifically Fe-ethylene diamine tetraacetic acid (EDTA) and Fe-ethylene triamine pentaacetic acid (DTPA). DTPA is a stronger chelating agent than EDTA and thus expected to be more stable in alkaline conditions. In the systems that utilize chelate to extract Fe from the native soil, significant amounts of other metals such as manganese (Mn), calcium (Ca) and magnesium (Mg) were also detached from mineral surfaces through dissolution and desorption. A series of batch tests was conducted using a BTEX and PAH impacted and high acid buffering capacity soil using aqueous solutions with various concentrations of EDTA and DTPA as well as various concentrations of hydrogen peroxide. The final pH, alkalinity, and concentrations of Fe, Mn, Ca and Mg were determined in the supernatant, and BTEX and PAH concentrations were determined in the soil. The contribution of the chelate catalyst to the generation of free radical oxidants was dependent on the stability of Fe-EDTA and Fe-DTPA complexes. The stability of these Fe-chelates was affected by pH, the activity of oxidants, and the Ca and Mg activity that developed as a result of the formation of anionic complexes with metal ions. Systems to which Fe-chelate was added had significantly greater degradation of PAHs in soil as compared to that observed in systems with Fe-minerals and systems with native chelated Fe as catalyst. In all Fenton-like systems, BTEX was oxidized to non-detectable levels.

can be used to form soluble complexes with free metal ions in solution. In addition, they dissociate exchangeable cations attached to mineral surfaces and also dissolve minerals. The minerals that are dissolved by chelates include iron phases such as ferrihydrite, goethite, and hematite, and carbonates such as calcite, dolomite and siderite (Hill and Evans, 1965; Halvorson et al., 1972; Lindsay, 1979; Stumm and Morgan, 1996). Two mechanisms are discussed in the literature for the dissolution of minerals. One mechanism relates to the formation of anionic complexes with free metal ions, which reduces the activities of the free metal ions in solution. These complexation reactions cause minerals to dissolve and exchangeable ions to dissociate, in order to replenish the ions that are chelated (Lindsay and Norvell, 1978; Lindsay 1979). The other mechanism relates to dislodging metal ions from the lattice of minerals by forming complexes at the surface of minerals (Sposito, 1989). Multidentate ligands such as chelating agents form surface complexes with lattice ions creating a perturbation of the chemical bonds that hold ions in the mineral structure, which results in detachment of the metal ion into the solution (Sparks, 1999).

The objective of this study was to investigate the oxidation of benzene, toluene, ethylbenzene and xylene (BTEX) and PAHs in a soil that possessed high acid buffering capacity using Fenton-like systems. The effectiveness of three catalysts, namely native Fe, chelated native Fe, and Fe-chelate solution, was investigated.

MATERIALS AND METHODS

For this study, contaminated soil obtained from a former manufactured gas plant site was used. The soil sample that was received from the field was thoroughly homogenized. The homogenized sample was analyzed for physical and chemical parameters. All physical parameters were determined according to the respective ASTM standard. The physical properties of the soil are presented in Table 1. The homogenized soil was analyzed ac-

Table 1. Properties of contaminated soil used for this study

Property	Test Method	Value
Grain size distribution	ASTM D 422	% gravel = 1.8 - 15.4 % sand = 50.1 - 65.6 % fines = 32.6 - 34.5
Atterberg limits	ASTM D 4318	Non-Plastic
USCS classification	ASTM D 2488	SM
Water content	ASTM D 2216	7.55%
pH	ASTM D 2974	6.9
Redox potential	ASTM D 2974	186.4 mV

Key Words: oxidation, soils, Fenton's oxidation, PAH, BTEX, EDTA, DTPA

INTRODUCTION

The treatment of recalcitrant compounds such as polycyclic aromatic hydrocarbons (PAHs) in soils and groundwater poses major challenges. The difficulty of treating PAHs in coal tar impacted soils is exacerbated by the high fines content (>20 %) of these soils. Fenton's reagent consisting of a soluble iron (Fe) catalyst and hydrogen peroxide (HP) has been used for the oxidation of PAHs in soils (Kelley et al., 1990; Ravikumar and Gurol, 1992; Pradhan et al., 1997). In the absence of organic compounds, ferrous (Fe(II)) and ferric iron (Fe(III)) initiate the catalytic decomposition of HP to molecular oxygen and water in acidic and neutral media. The free radicals evolving from these reactions include the hydroxyl radical (OH[•]) and the perhydroxyl radical (HO₂[•]). In the presence of oxygen and organic compounds, additional free radicals are produced from the reaction of OH[•] with HP and the organic compounds. The free radicals evolving from the latter reactions include organic radicals (R[•]), organic peroxy radicals (RO₂[•]) and superoxide radicals (O₂^{•-}) (Haber and Willstätter, 1931; Haber and Weiss, 1934). The hydroxyl radical is the predominant radical in neutral and acidic systems and is a relatively non-selective reactant reflected by its reaction rates with organic compounds that range from 10⁷ to 10¹⁰ M⁻¹ s⁻¹ (Buxton et al., 1988; Haag and Yao, 1992).

In case of high acid buffering soils, it is often impractical to reduce the pH of the soil-water system in order for standard Fenton's oxidation of organic compounds to occur. In such cases, Fenton-like oxidation that involves using the iron native to the soil as a catalyst to decompose HP to free radicals is advantageous (Watts et al. 1990, 1997; Tyre et al., 1991; Ravikumar and Gurol, 1994). The native iron available as catalyst in soil-water systems occurs as iron oxide (e.g. Fe₂O₃) or iron oxyhydroxide phases (FeOOH) as well as humic and fulvic organo-iron complexes. Soluble organo-iron complexes that contain carboxylate ligands catalyze the decomposition of HP (Rush and Koppenol, 1987; Rush et al. 1990; Sun and Pignatello, 1992; Voelker et al. 1996, 1997). The catalytic decomposition of HP in an aqueous organo-iron system takes place if a Fe(II)-complex (LFe(II)) is oxidized by HP, and LFe(III) is reduced to LFe(II) by HP. The organic complexes may also act as radical scavengers (Voelker et al. 1996, 1997). Numerous studies have shown that in solutions with near neutral pH, the rate of the reaction of Fe(II)-polyaminocarboxylate complexes with HP is greater by orders of magnitude than the reaction of Fe(II) and its aquo-complexes with HP (Rush et al. 1990).

The polyaminocarboxylate chelates such as ethylene diamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA)

Table 2. TOC and concentrations of organics and selected metals in soil

Organics (mg/kg)	Metals (mg/kg)
TOC ¹	42,720
Total BTEX ²	69
Total PAHs ²	1,493
2-Ring PAHs	659
3-Ring PAHs	329
4-Ring PAHs	383
5-Ring PAHs	89
6-Ring PAHs	33
	Fe
	15,000
	Ca
	38,000
	Mg
	15,000
	Mn
	440

¹ Total organic carbon content

² Total BTEX and total PAH denotes the cumulative concentration of the group of compounds

according to EPA method SW 6020 for metals, EPA method SW 8260 B for BTEX, and EPA method SW 8170 (SIM) for PAHs. The total organic carbon content (TOC) was determined with an element analyzer (Carlo Erba Flash 1112 Series EA). Table 2 shows the TOC, and concentrations of BTEX and PAHs. Table 2 also shows the concentrations of metals investigated in this study.

Initially, the buffering capacity of the soil was determined. Then, batch experiments were conducted to determine both the leachability of metals from soil and the parameters of the aqueous phase that affect Fenton chemistry. Subsequently, the oxidation of selected PAHs as well as BTEX was investigated.

Buffering Capacity Determination

Buffering capacity of soil refers to the capability of soil to neutralize acid. The presence of calcium carbonate or other compounds such as magnesium carbonate or calcium carbonate causes high buffering capacity of the soil. Titration analysis was performed to determine the soil buffering capacity by using 2 M nitric acid as titrant. A soil slurry sample was prepared by mixing 20 g of soil in 200 mL of water. The acid was added incrementally to the slurry, while it was being mixed with a magnetic stirrer. The equilibrium pH of the slurry was measured with a pH meter (Thermo Orion model 720 A).

Metal Leachability Experiments

Batch experiments were conducted using soil slurry samples prepared with 25 g of soil and 100 mL aqueous solution in a conical flask. Stock solutions of the sodium salts of ethylene diamine tetraacetic acid (Na₄-EDTA) and diethylene triamine pentaacetic acid (Na₅-DTPA) were prepared. Na₄-EDTA

and Na₅-DTPA were provided by Akzo Nobel. The pH of the stock solutions was adjusted to that of the soil. Batch tests were conducted with aqueous concentrations ranging from 5 to 40 mM of Na₄-EDTA or Na₅-DTPA. The batch test samples were covered with an all-purpose food service film (Clark Products, Inc) and were shaken for 24 hours on a reciprocating shaker. The final pH of the slurry samples was determined and then the slurry samples were centrifuged. The supernatant was analyzed for Fe, Ca, Mg and Mn using an atomic absorption spectrophotometer (Video 22), and for alkalinity using an electronic titrator (Titronic 96) and a pH meter (Thermo Orion model 720 A) for volumetric analysis. Control batch experiments were also conducted with deionized water and soil.

Oxidation with Chelated Native Iron

The batch experiments for oxidation of organic compounds were also prepared with 25 g of soil and 100 mL aqueous solution in a conical flask. Batch tests were conducted with hydrogen peroxide (HP) to total organic carbon (TOC) mole ratios of 0.25, 0.5, 1 and 2, resulting in HP concentrations of 0.8, 1.6, 3.2 and 6.4 %. The 30 % HP solution purchased from Fisher Scientific was used as stock solution. Batch tests were conducted with the EDTA concentrations ranging from 5 to 40 mM and the DTPA concentrations ranging from 2.5 to 20 mM. The pH of the batch test samples was adjusted to be the same as the initial soil pH. The batch test samples were covered with an all-purpose food service film (Clark Products, Inc) and aluminum foil, and shaken for 24 hours on a reciprocating shaker. Then the final pH of the slurry was determined and the samples were centrifuged. The supernatant was analyzed for Fe, Ca, Mg and Mn using an atomic absorption spectrophotometer (Video 22), and alkalinity was measured using volumetric analysis. Control batch experiments using HP solution alone were also conducted. The treated soil samples were analyzed according to EPA method SW 8260 B for BTEX and EPA method SW 8170 (SIM) for PAHs.

Oxidation with Chelated Iron Solution

Batch experiments were conducted to investigate the effectiveness of adding chelated Fe solutions. Stock solutions with Fe-EDTA and Fe-DTPA were prepared by adding FeSO₄·7H₂O (Fisher Scientific) and Na₄-EDTA or Na₅-DTPA to deionized water. Batch samples were prepared with a Fe-chelate concentration of 1.4 mM and HP concentrations of 0.81 % and 6.4 %. The selected variables for these batch experiments were decided based on the batch test results obtained with chelated native iron that allowed comparison of the test results under similar environmental conditions.

RESULTS

Buffering Capacity

The acid additions required for standard Fenton oxidation are assessed with the determination of the acid buffering capacity. The acid buffering capacity of the aqueous soil slurry with a solids concentration of 8.5 % is 3.7 eq/kg (dry soil) at the inflection point of the titration curve (pH 6.2). Such high acid buffering capacity of the soil makes the standard Fenton oxidation impractical to use.

Leaching Experiments

As shown in Table 3, the aqueous concentrations of Fe, Ca, Mg and Mn increase with chelate concentration. In the lower concentration range of chelates, the aqueous concentration of Fe-DTPA is greater than that of Fe-EDTA. The aqueous Fe concentration ranges from 0.27 to 1.4 mM for the EDTA systems and ranges from 0.51 to 1.33 mM for the DTPA systems for the investigated chelate concentration range (5 mM to 40 mM). The aqueous concentrations of metals decrease in the order $Ca > Mg > Fe > Mn$ for all chelate concentrations. Although the concentrations of Fe and Mg in soil are about the same, the concentration of aqueous Mg is higher than that of aqueous Fe. The concentration of metals in the solution of control samples also decreases in the order $Ca > Mg > Fe > Mn$. The aqueous concentration of Fe is 0.07 mM for the control sample with no chelate.

The mass transfer from the soil into the aqueous phase decreases in the order $Mn > Ca > Mg > Fe$ for the investigated chelate concentration range (see Table 3). The mass transfer is greatest for manganese, despite its low

Table 3. Mass transfer of metals into aqueous phase as a function of chelate concentration

Chelant	concentration (mM)	Fe (%)				Mn
		Ca	Mg	Mn		
DTPA (mM)	40	2.0	2.3	14.0	22.6	
	20	1.6	1.3	9.5	15.9	
	10	1.0	1.6	6.0	13.2	
	5	0.8	2.4	3.2	12.3	
EDTA (mM)	40	2.1	4.9	14.7	23.5	
	20	1.2	1.3	8.5	17.3	
	10	0.8	1.8	5.2	13.2	
	5	0.4	2.1	3.0	12.0	
Control (no chelant)		0.1	0.3	0.1	0.0	

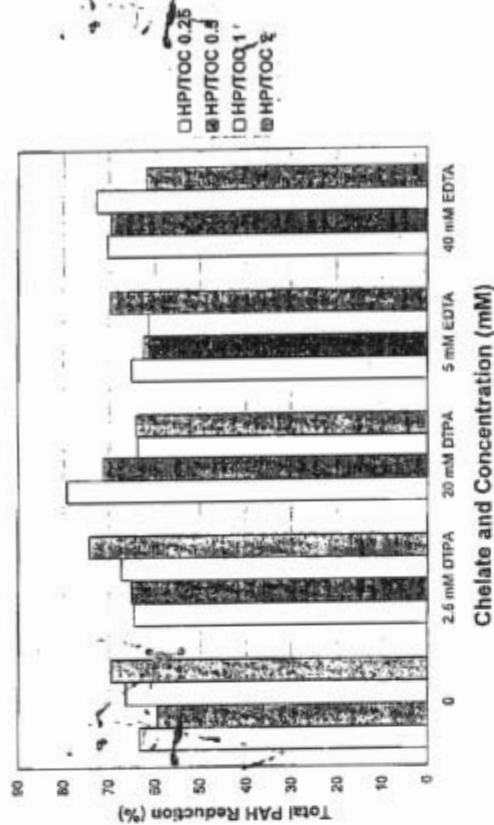


Figure 1. Total PAH Reduction as a function of HP/TOC ratio and chelate concentration

concentration in soil relative to the other three metals. Manganese is not transferred into the aqueous phase of control samples.

In general, the final pH of batch experiments increases with chelate concentration and ranges from pH 7.8 to 8.3. The carbonate alkalinity of the supernatant also increases with chelate concentration, and can be up to 50 times that of the control (no chelate).

Oxidation with Chelated Native Iron

In all of the batch experiments, the BTEX in the soil is oxidized to non-detectable levels. Batch experiments with EDTA, low to intermediate DTPA concentrations as well as batch tests with no chelate showed a total PAH reduction of 60 to 70 %. Figure 1 shows the reduction of total PAH as a function of HP/TOC ratio and chelate concentration. Batch tests with DTPA showed the greatest reduction in PAH for the investigated range of HP concentration (0.8 to 6.4 %). At high chelate concentrations, PAH reduction declines with increasing HP concentration. PAH reduction increases with HP concentration in batch tests with low chelate concentration as well as in tests with no chelate. The batch test with the highest DTPA concentration and the lowest HP concentration showed the greatest reduction in PAH. This test also showed the greatest reduction of 5 and 6-ring PAHs (see Figure 2). At high HP concentrations, the greatest reduction in 5 and 6-ring PAHs occurs at low DTPA concentrations (see Figure 3). In all of the batch

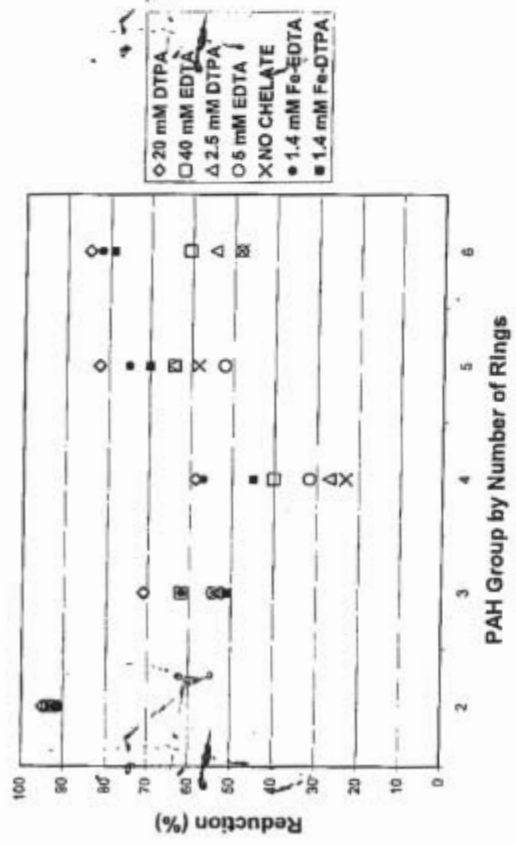


Figure 2. Reduction of PAHs for HP/TOC of 0.25

tests, the 2-ring PAHs are more than 90 % oxidized, and the 4-ring PAHs are the least oxidized group of PAHs (see Figures 2 and 3).

After the completion of oxidation reactions, Fe is non-detectable in the solutions of low chelate systems and increases with chelate concentration. The solution concentration of metals in the systems with high chelate content declines with HP concentration (see Figures 4 and 5). The decline in Fe and Mn concentration is more pronounced for systems with DTPA than for

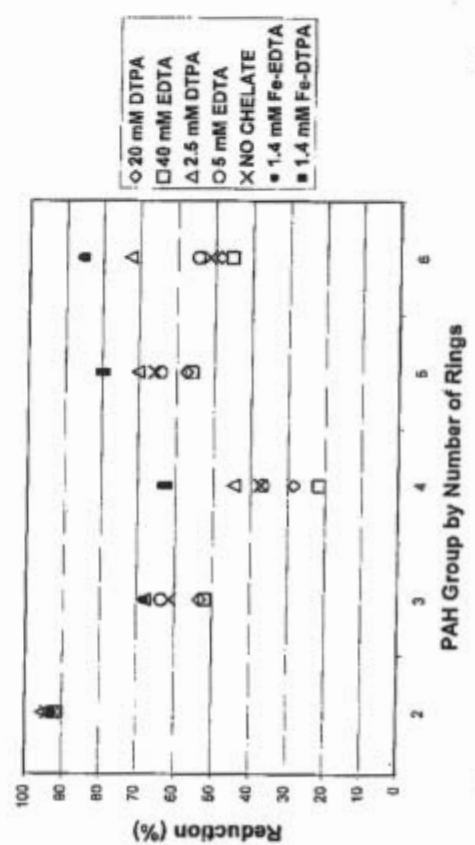


Figure 3. Reduction of PAHs for HP/TOC of 2.0

systems with EDTA. The final pH ranges from pH 6.7 to 7.3 and from pH 7.1 to 7.7 for the systems with low and high chelate concentration, respectively.

Oxidation with Chelated Iron Solution

The Fe-chelate concentration selected for these batch series is the maximum aqueous Fe concentration (1.4 mM) determined from Fe-leaching test. The reduction in total PAH ranges from 69 to 75 % at a HP concentration of 0.8 %, and is 79 % for a HP concentration of 6.4 %. The reduction of PAHs grouped by number of rings is presented in Figures 2 and 3. BTEX is oxidized to non-detectable levels. The final solution pH of systems with 0.8 % and 6.4 % HP is 8.1 and 7.7, respectively. Except for Fe, all of the investigated metals are present in the solution. The metal concentrations increase, whereas the alkalinity decreases with HP concentration.

DISCUSSION

The results of the leaching experiments indicate that carbonate phases in soil dissolve and increase bicarbonate alkalinity. The dissolution of carbonate phases also accounts for the aqueous Ca and Mg activity. The high affinity of EDTA and DTPA for Mn in soils is consistent with the findings of others (Norvell and Lindsay, 1969, 1972; Lindsay and Norvell, 1978). The mass transfer of metals into the aqueous phase reflects both the affinity of the chelates for the respective metal, and the chelate solubility of the respective mineral phases. The lower solution concentration of Fe relative to Ca and Mg may be attributed to both the lower Fe-mineral content of soil relative to carbonates, and the lower chelate solubility of Fe-oxyhydroxide phases relative to that of carbonates (Hill and Evans, 1965).

The chelation of the Fe-catalyst is strongly dependent on solution pH and the solution concentrations of Ca and Mg (Stumm and Morgan, 1996). The leaching of metals from the soil creates the following two solution conditions that decrease the stability of Fe-EDTA and Fe-DTPA: (1) In basic solutions the solubility of Fe is controlled by amorphous Fe(III)-hydroxide (ferrihydrite), which precipitates and diminishes the stability of Fe-EDTA and Fe-DTPA; (2) Ca and Mg at high solution concentrations compete with Fe for chelates (Stumm and Morgan, 1996). The stability of Fe-DTPA is less affected by these solution conditions than that of Fe-EDTA, because of its greater stability constant (Lindsay, 1979).

The degradation of organic compounds in a soil-water system is contingent on both the accessibility of organic compounds to oxidants, and the activity of the free radicals in solution. In contrast to the higher ring PAHs, BTEX and 2-ring PAHs are readily degraded in all of the systems, due to their greater water solubility, which facilitates aqueous phase degradation.

The oxidation of higher ring PAHs seems to be affected by both their low water solubility, and the stability of the Fe-chelate catalyst. The concentration of soluble Fe-catalyst as well as the presence and accessibility of Fe-mineral surfaces (e.g. goethite) control the activity of free radicals. In addition to the aforementioned mechanisms, the hydroxyl ions and radicals that evolve from the reaction of HP with Fe-chelate diminish the solubility of Fe and precipitate it. Moreover, the radicals may oxidize the carbonaceous chelate structure, thereby rendering it incapable of complexing metal ions. The stability of the Fe-catalyst may be affected by the synergism of both the activity of metals competing for chelates and the oxidizing conditions. Diminished Fe solubility invariably results in substitution of Fe by the metals with higher affinity for the chelates. The degradation rate of the organic ligands is contingent on the activity of free radicals.

In systems with chelated native iron as catalyst, the oxidant activity seems to have the predominant influence on Fe-chelate stability. In systems with low oxidant activity and high DTPA concentration, the PAH degradation is greater than in the mineral-catalyzed systems. In contrast, in systems with high oxidant activity and in systems with low oxidant and low EDTA or DTPA concentration the catalytic activity of Fe-chelates is diminished to more or less the same as the catalytic activity of the native Fe-minerals. In the latter systems, the activity of the chelates seems insufficient in overcoming the activity of oxidants and the resulting removal of Fe from the aqueous phase. Either a high concentration of chelate or a low concentration of oxidant maintains an effective aqueous activity of Fe-chelate.

The decline of aqueous metal concentrations in systems with HP relative to systems without HP indicates that the stability of all metal-chelates is affected by the oxidant activity (see Figures 4 and 5). Presumably, all metal-chelates are equally subjected to degradation, since free radicals are non-selective. In systems with moderate to high chelate concentration, the aqueous Fe and Mn concentrations decline with HP concentration, whereas aqueous Ca and Mg concentrations remain more or less the same over the investigated range of HP concentrations. The stability of Fe-chelates, therefore, seems to be predominantly affected by Fe solubility. The concentration differences (more than one order of magnitude) between Ca and Fe or Mg and Fe do not allow the interpretation of trends that would indicate the substitution of Fe by Ca or Mg in chelates.

In systems to which the Fe-chelate is added, the stability of Fe-chelates does not seem to decrease with oxidant activity. The bulk of the Fe-chelate added to the soil-water system seems to remain aqueous, whereas significant amounts of EDTA and DTPA added for leaching of Fe are removed from solution by adsorption to mineral surfaces (Norvell and Lindsay, 1969, 1972). In addition, the dislodging of Fe ions from mineral surfaces by EDTA

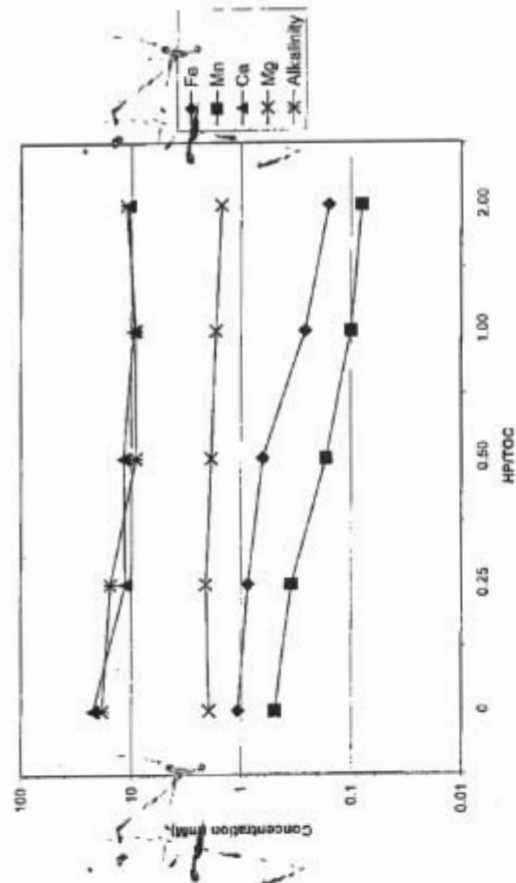


Figure 4. Concentration of metals and carbonate alkalinity in supernatant for 20 mM DTPA

and DTPA may be impeded by the activity of oxidants, i.e. the thermodynamic solution conditions favor the solid over the aqueous phase. The absence of Fe in the solution of system with added Fe-chelate indicates that the chelate structure is eventually degraded by the oxidants.

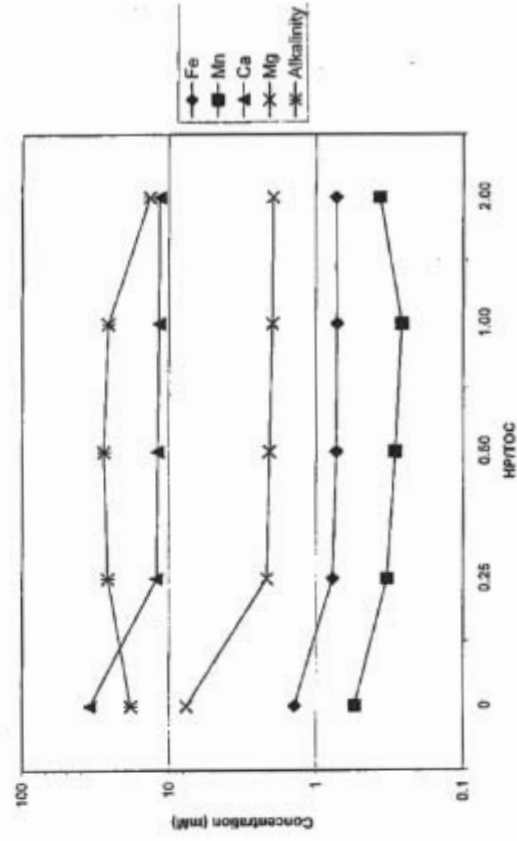


Figure 5. Concentration of metals and carbonate alkalinity in supernatant for 40 mM EDTA

CONCLUSIONS

The catalytic effect of Fe-EDTA and Fe-DTPA is controlled by the stability of these chelates, which in turn is affected by the synergism of the oxidizing conditions created by the degradation products of hydrogen peroxide (i.e. hydroxyl ions and radicals), and the activity of metals competing for chelates. In systems that extract native Fe to generate a Fe-chelate catalyst, the stability of Fe-chelates diminishes with oxidant activity. While metal chelates are degraded by the free radicals, the diminished stability of Fe-chelates can be primarily attributed to the decline in Fe solubility with oxidant concentration. For aqueous Fe-EDTA and Fe-DTPA formed with extracted native Fe to exceed the catalytic effect of native Fe minerals, the chelate concentrations have to compensate both losses from the aqueous phase, due to sorption, and the diminished Fe solubility, due to oxidant activity. Fe-DTPA is the more stable catalyst in systems that utilize native Fe.

Systems with added Fe-chelate have a significantly greater degradation of PAHs than mineral-catalyzed Fenton-like oxidation. The effectiveness of these systems is less affected by sorption to mineral surfaces, and the effect of oxidants on Fe solubility. Significantly less Fe-EDTA and Fe-DTPA are required (1.4 mM) for the catalysis of hydrogen peroxide degradation than EDTA and DTPA are required (40 mM) to generate the same amount of Fe-chelate catalyst with native Fe.

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CHAPTER 3

Thermally Activated Peroxydisulfate Oxidation of Polychlorinated Biphenyls (PCBs)

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ABSTRACT

Polychlorinated biphenyls (PCBs) are a family of man-made chemicals that were used as coolants and lubricants in transformers, capacitors, and other electrical equipment. Due to harmful effects of PCBs, their manufacturing was banned in 1977; however, their nonreactive properties allow PCBs to persist in the environment. Peroxydisulfate ($S_2O_8^{2-}$) is a strong oxidant that can be thermally activated to form the persulfate free radical ($SO_4^{\bullet-}$), an even stronger oxidant. Studies were performed to examine the influence of oxidant strength and time on the ability of peroxydisulfate to degrade PCBs (specifically Aroclor 1242). Aqueous and soil slurry samples were spiked with Aroclor 1242, mixed with sodium peroxydisulfate solutions, and placed in a heated water bath set at 60°C. At specific intervals, samples were removed and placed in an ice bath to stop the reaction. The samples were then extracted with hexane, and analyzed on a GC/ECD to determine the concentration of PCBs remaining. In the aqueous samples spiked with 88.5 µg of Aroclor 1242 and oxidized with a 0.125 M solution of sodium peroxydisulfate, there was a steady decrease in PCB concentration, with 19% degraded after 3 hours, 75% degraded after 12 hours, and all of it degraded after 50 hours. In soil samples spiked with 44 µg of Aroclor 1242 and heated for 5 days at 60°C, the samples with the 0.005 M sodium peroxydisulfate solution contain only 49% of the PCBs found in the control sample; the samples with the 0.052 M sodium peroxydisulfate solution contain only 19% of the PCBs found in the control sample; and the samples with the 0.126 M sodium peroxydisulfate solution contain only 5% of the PCBs found in the control sample.