Mechanisms of Base, Mineral, and Soil Activation of Persulfate
for Groundwater Treatment

By
Joseph Franklin Corbin III

A dissertation submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Washington State University
Environmental & Natural Resource Sciences
May 2008
To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of JOSEPH FRANKLIN CORBIN III find it satisfactory and recommend that it be accepted.

______________________________  
Chair

______________________________
______________________________
______________________________
ACKNOWLEDGEMENT

I would like to thank my parents, Jennifer Boie, and my committee for all of their help and support. I would like to give a special thanks to Dr. Watts for all of his time and patience.
MECHANISM OF BASE, MINERAL, AND SOIL ACTIVATION OF PERSULFATE FOR GROUND WATER TREATMENT

Abstract

By Joseph Franklin Corbin III, Ph.D.
Washington State University
December 2007

Chair: Richard J. Watts

The purpose of this study was to examine mechanisms of base, mineral, and soil persulfate activation when used for ground water treatment by in situ chemical oxidation.

Four base-activated persulfate systems (adjusting the pH to 12 and using molar ratios of 1:1, 2:1, or 3:1 base to persulfate) were studied using three reaction-specific probe compounds and two radical scavengers. Rapid degradation of oxidative probes occurred at pH 12, but minimal degradation of the reductive probe, carbon tetrachloride, was observed at pH 12. Degradation of all probe compounds occurred in molar ratios systems. The results of this research demonstrate that the reactivity of persulfate formulations increases with increasing base:persulfate ratios.

The potential for 13 minerals to mediate the decomposition of persulfate and generate a reactive oxygen species was investigated. Reactions were conducted at 25°C using 2 g of minerals and 5 ml of 0.5 M sodium persulfate with the addition of oxidative, reductive, and nucleophilic probes. The decomposition of persulfate and the probes by minerals varied extensively. Most of the minerals mediated the decomposition of persulfate, but did not promote the generation of reactive oxygen species, although cobaltite, ilmenite, and pyrite did. The results demonstrate that most of the minerals evaluated do not activate persulfate.
The decomposition of persulfate by 11 soils was investigated in order to observe the impact of these soils on pH and persulfate concentration. Reactions were conducted at 25°C using 10 g of soil and 20 mL of either 0.5 M or 0.1 M persulfate. Reactions were conducted using base:persulfate molar ratios of 1:1, 2:1, or 3:1 over 120 d. Decomposition of persulfate and pH varied greatly between soils, although not between 0.1 M and 0.5 M persulfate. A second set of experiments were conducted in which anisole was used a probe for the overall reactivity of the system. These experiments used 0.5 M persulfate in a 2:1 base:persulfate molar ratio and two soils. The results demonstrated a reduction in anisole destruction when the pH declined. This research demonstrated the importance of pH and soil properties in the use of persulfate treatments.
TABLE OF CONTENTS

SIGNATURE PAGE..............................................................................................................ii
ACKNOWLEDGEMENT......................................................................................................iii
ABSTRACT..........................................................................................................................iv
TABLE OF CONTENTS........................................................................................................v
LIST OF FIGURES...............................................................................................................vii

CHAPTER 1: BACKGROUND AND CURRENT STATE OF PERSULFATE ISCO
  Introduction.......................................................................................................................1
  Theoretical Studies of Activated Persulfate.................................................................5
  Activated Persulfate for Groundwater Remediation....................................................6
  Objectives.......................................................................................................................9
  References......................................................................................................................11

CHAPTER 2: REACTIVITY OF BASE-ACTIVATED PERSULFATE FORMULATIONS
  Abstract.........................................................................................................................13
  Introduction....................................................................................................................14
  Experimental Section....................................................................................................15
    Materials......................................................................................................................15
    Probe compounds.......................................................................................................15
    Hydroxyl radical and sulfate radical scavengers....................................................16
    Experimental procedures...........................................................................................16
    Analysis.......................................................................................................................16
  Results and Discussion.................................................................................................17
    Probe degradation at various pH regime.................................................................17
    Effect of persulfate concentration............................................................................18
    Scavenging of oxidants at pH 12..............................................................................20
    Relative rates of reactive oxygen species generation at high base:persulfate ratios...21
  References......................................................................................................................24
  List of Figures...............................................................................................................26

CHAPTER 3: RATES AND PATHWAYS OF MINERAL ACTIVATED PERSULFATE
  Abstract..........................................................................................................................39
  Introduction....................................................................................................................39
  Experimental Section....................................................................................................40
    Materials......................................................................................................................40
    Probe compounds.......................................................................................................41
    Experimental procedures...........................................................................................42
    Gas chromatography analysis....................................................................................42
  Results and Discussion.................................................................................................43
    Mineral-mediated decomposition of persulfate.......................................................43
    Overview of interaction of mineral-mediated persulfate with probe compounds...44
    Detection of sulfate and hydroxyl radical..............................................................45
    Detection of hydroxyl radicals..................................................................................46
List of Figures

CHAPTER 2: REACTIVITY OF BASE-ACTIVATED PERSULFATE FORMULATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>27</td>
</tr>
<tr>
<td>1b</td>
<td>28</td>
</tr>
<tr>
<td>1c</td>
<td>29</td>
</tr>
<tr>
<td>2a</td>
<td>30</td>
</tr>
<tr>
<td>2b</td>
<td>31</td>
</tr>
<tr>
<td>2c</td>
<td>32</td>
</tr>
<tr>
<td>3a</td>
<td>33</td>
</tr>
<tr>
<td>3b</td>
<td>34</td>
</tr>
<tr>
<td>3c</td>
<td>35</td>
</tr>
<tr>
<td>4a</td>
<td>36</td>
</tr>
<tr>
<td>4b</td>
<td>37</td>
</tr>
<tr>
<td>4c</td>
<td>38</td>
</tr>
</tbody>
</table>

CHAPTER 3: RATES AND PATHWAYS OF MINERAL ACTIVATED PERSULFATE

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>54</td>
</tr>
<tr>
<td>2a</td>
<td>55</td>
</tr>
<tr>
<td>2b</td>
<td>56</td>
</tr>
<tr>
<td>2c</td>
<td>57</td>
</tr>
<tr>
<td>2d</td>
<td>58</td>
</tr>
<tr>
<td>3a</td>
<td>59</td>
</tr>
<tr>
<td>3b</td>
<td>60</td>
</tr>
<tr>
<td>3c</td>
<td>61</td>
</tr>
<tr>
<td>4a</td>
<td>62</td>
</tr>
<tr>
<td>4b</td>
<td>63</td>
</tr>
<tr>
<td>4c</td>
<td>64</td>
</tr>
<tr>
<td>5a</td>
<td>65</td>
</tr>
<tr>
<td>5b</td>
<td>66</td>
</tr>
<tr>
<td>5c</td>
<td>67</td>
</tr>
<tr>
<td>6a</td>
<td>68</td>
</tr>
<tr>
<td>6b</td>
<td>69</td>
</tr>
<tr>
<td>6c</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>71</td>
</tr>
</tbody>
</table>

CHAPTER 4: IMPACT OF SOILS ON PERSULFATE DECOMPOSITION AND PH

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>91</td>
</tr>
<tr>
<td>1b</td>
<td>92</td>
</tr>
<tr>
<td>1c</td>
<td>93</td>
</tr>
<tr>
<td>1d</td>
<td>94</td>
</tr>
<tr>
<td>1e</td>
<td>95</td>
</tr>
<tr>
<td>1f</td>
<td>96</td>
</tr>
<tr>
<td>Figure 2a</td>
<td>97</td>
</tr>
<tr>
<td>Figure 2b</td>
<td>98</td>
</tr>
<tr>
<td>Figure 2c</td>
<td>99</td>
</tr>
<tr>
<td>Figure 2d</td>
<td>100</td>
</tr>
<tr>
<td>Figure 2e</td>
<td>101</td>
</tr>
<tr>
<td>Figure 2f</td>
<td>102</td>
</tr>
<tr>
<td>Figure 3a</td>
<td>103</td>
</tr>
<tr>
<td>Figure 3b</td>
<td>104</td>
</tr>
<tr>
<td>Figure 3c</td>
<td>105</td>
</tr>
<tr>
<td>Figure 3d</td>
<td>106</td>
</tr>
<tr>
<td>Figure 3e</td>
<td>107</td>
</tr>
<tr>
<td>Figure 3f</td>
<td>108</td>
</tr>
<tr>
<td>Figure 4a</td>
<td>109</td>
</tr>
<tr>
<td>Figure 4b</td>
<td>110</td>
</tr>
<tr>
<td>Figure 4c</td>
<td>111</td>
</tr>
<tr>
<td>Figure 4d</td>
<td>112</td>
</tr>
<tr>
<td>Figure 4e</td>
<td>113</td>
</tr>
<tr>
<td>Figure 4f</td>
<td>114</td>
</tr>
<tr>
<td>Figure 5a</td>
<td>115</td>
</tr>
<tr>
<td>Figure 5b</td>
<td>116</td>
</tr>
<tr>
<td>Figure 5c</td>
<td>117</td>
</tr>
<tr>
<td>Figure 5d</td>
<td>118</td>
</tr>
<tr>
<td>Figure 5e</td>
<td>119</td>
</tr>
<tr>
<td>Figure 5f</td>
<td>120</td>
</tr>
<tr>
<td>Figure 6a</td>
<td>121</td>
</tr>
<tr>
<td>Figure 6b</td>
<td>122</td>
</tr>
<tr>
<td>Figure 6c</td>
<td>123</td>
</tr>
<tr>
<td>Figure 6d</td>
<td>124</td>
</tr>
<tr>
<td>Figure 6e</td>
<td>125</td>
</tr>
<tr>
<td>Figure 6f</td>
<td>126</td>
</tr>
<tr>
<td>Figure 7a</td>
<td>127</td>
</tr>
<tr>
<td>Figure 7b</td>
<td>128</td>
</tr>
<tr>
<td>Figure 7c</td>
<td>129</td>
</tr>
<tr>
<td>Figure 7d</td>
<td>130</td>
</tr>
<tr>
<td>Figure 7e</td>
<td>131</td>
</tr>
<tr>
<td>Figure 7f</td>
<td>132</td>
</tr>
<tr>
<td>Figure 8a</td>
<td>133</td>
</tr>
<tr>
<td>Figure 8b</td>
<td>134</td>
</tr>
<tr>
<td>Figure 8c</td>
<td>135</td>
</tr>
<tr>
<td>Figure 8d</td>
<td>136</td>
</tr>
<tr>
<td>Figure 8e</td>
<td>137</td>
</tr>
<tr>
<td>Figure 8f</td>
<td>138</td>
</tr>
<tr>
<td>Figure 9a</td>
<td>139</td>
</tr>
<tr>
<td>Figure 9b</td>
<td>140</td>
</tr>
<tr>
<td>Figure 9c</td>
<td>141</td>
</tr>
<tr>
<td>Figure 9d</td>
<td>142</td>
</tr>
</tbody>
</table>
Chapter 1: Background and Current State of Persulfate ISCO

Introduction

Groundwater contamination from chemical pollutants is a major area of environmental concern. Approximately half of all Americans acquire their water from groundwater sources (Botkin and Keller 1995). Due to poor environmental practices in the past and continued spills and leaks, many aquifers are contaminated with hazardous chemicals. The Environmental Protection Agency (EPA) estimates that 25% of groundwater in the U.S. is contaminated with up to 75% of the groundwater contaminated in some areas (Miller 1999). In New Jersey, for example, every major aquifer is contaminated with hazardous chemicals (Miller 1999). The EPA estimates that 75% of the 175,000 known waste disposal sites in the U.S. may be currently producing toxic plumes (Botkin and Keller 1995). Add this number to the estimated 1 million leaking underground storage tanks (UST) in the U.S. and the severity of the problem becomes apparent (Miller 1999). Although daunting, these numbers could be just the beginning as the EPA expects to identify an additional 294,000 hazardous waste sites in the next 30 years (Williams 2005).

Once contaminated, groundwater is extremely difficult to treat due to a number of reasons. Non-homogeneity, anaerobic conditions, partitioning to soils, and mineralogy are some of the factors that make groundwater so difficult to treat. Even with all of these problems, groundwater remediation was undertaken on a relatively large scale during the 1980s (Watts 1998). Remediation techniques such as air sparging, bioremediation, and pump-and-treat were extensively used in the past. Although these technologies were heralded at the onset, time has shown them to be expensive and relatively ineffective at removing the contamination (EPA
2006). Some problems with these methods are that they are desorption limited, take years for complete remediation if at all, and have a difficult time treating the source.

During the 1990’s a new type of technology was introduced for the remediation of groundwater. This rapidly growing type of treatment injects chemical oxidants, such as hydrogen peroxide ($\text{H}_2\text{O}_2$), permanganate ($\text{MnO}_4^-\text{)}$, and ozone ($\text{O}_3$), directly into the subsurface to clean up groundwater and soil contaminants (EPA 2006). These techniques have become known as in-situ chemical oxidation, or ISCO, and have succeeded when the previous treatment methods have failed. ISCO methods have the ability to rapidly (weeks to months) degrade contaminants, including biorefactory contaminants, to very low levels (EPA 2006). ISCO methods even have the ability to degrade nonaqueous phase liquids (NAPLs), something that the previous remediation methods could not accomplish. All of this has made ISCO the most rapidly growing remedial technology applied at hazardous waste sites (EPA 2006).

The newest chemical oxidant used for ISCO is persulfate. Persulfate, or peroxydisulfate, is a peroxide with the chemical structure; $[\text{O}_3\text{S—O—O—SO}_3^2-]$. The three commercially available salts of persulfate are ammonium, sodium, and potassium (Liang et al. 2003). Of these three salts, sodium persulfate is the salt of choice due to potassium persulfate having a much lower water solubility and ammonium persulfate being less stable (Liang et al. 2003). Persulfate, like hydrogen peroxide and permanganate (the two most commonly injected ISCO oxidants), are solutions that can be directly injected into the subsurface (EPA 2006). Unlike hydrogen peroxide, which rapidly degrades in the subsurface, persulfate is able to last for months (EPA 2006). Persulfate solutions naturally decompose at a slow rate into sulfate radicals (House 1962). The rapid decomposition of persulfate into sulfate radicals is called activation and this can be accomplished by elevated temperatures, transition metals, or high pH values. Like the
hydroxyl radical, the sulfate radical is a strong, relatively non-specific oxidant, with an $E^0 = 2.6$ V. It is a slightly more selective oxidant than the hydroxyl radical (Anipsitakis and Dionysiou 2004). Persulfate is usually activated during ISCO to generate free radicals. These free radicals, many of which last for less than one second, are what account for most of the contaminant destruction in subsurface systems (EPA 2006).

Persulfate can be decomposed by heat to form two sulfate radicals (eq. 1). The rate of decomposition of persulfate increases with increasing heat. Although some autodecomposition occurs at temperatures as low as 25°C, most heat activated persulfate ISCO systems utilize temperatures between 40-99°C (Liang et al. 2003).

$$\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} \quad (1)$$

Activation of persulfate by heat can also lead to other active oxidants when the sulfate radical interacts with organic contaminants. Balazs et al. (2006) have observed organic radicals, hydroxyl radicals, peroxymonosulfate, hydrogen peroxide and nascent oxygen with persulfate activation by heat.

Recent results have shown base activated persulfate to be a viable ISCO technology. Activation at levels practical for ISCO occur at pH regimes above 10. At these basic conditions most of the sulfate radicals are converted to hydroxyl radicals [eq. 2], which can proceed through propagation reactions to give the same reactive species (hydrogen peroxide [eq. 3a], hydroxyl radicals [eq. 4], hydroperoxide [eq. 5], superoxide [eq. 4]) as those that are found in the catalyzed hydrogen peroxide (CHP) systems (Dogliotti and Hayon 1967). These reactive species can be formed through the following reactions:
\[
\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{OH}^- + \text{SO}_4^{2-} \tag{2}
\]
\[
\text{OH}^- + \text{OH}^- \rightarrow \text{H}_2\text{O}_2 \tag{3a}
\]
\[
\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + \text{H}_2\text{O}_2 \tag{3b}
\]
\[
\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \text{O}_2\text{H}^- + \text{OH}' + \text{H}_2\text{O} \tag{4}
\]
\[
\text{H}_2\text{O}_2 + \text{OH}' \leftrightarrow \text{HO}_2^- + \text{H}_2\text{O} \tag{5}
\]

Thus, persulfate may be very similar to CHP. It forms the same free radicals as CHP in addition to generating the sulfate radical. Accordingly, base activated persulfate might be able to treat sites that contain both oxidized and reduced organic contaminants. However, unlike the hydrogen peroxide used in CHP, persulfate is relatively stable in the subsurface and thus has the potential to migrate further down gradient than hydrogen peroxide.

Persulfate is also activated by transition metals. These metals are important to subsurface systems and this activation may be an important factor in the subsurface. Copper, silver, cobalt, platinum, iron, cerium and manganese have all been shown to activate persulfate solutions (Liang et al. 2004). These metals initiate the activation of persulfate through a one-electron transfer reaction in just the same way as the CHP initiation reaction.

\[
\text{S}_2\text{O}_8^{2-} + \text{M}^{2+} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{M}^{3+} \tag{6}
\]

The use of persulfate as an oxidant for ISCO has great potential. We are at a stage where we can use the system, but our knowledge of its interactions in the subsurface is rudimentary at best. With more knowledge comes the ability for greater efficiency and improved reliability, something that is vital in the remediation field. Thus it is paramount that this fundamental knowledge base is increased to a workable level. Initial efforts have provided substantial information over the last few years, but there is still much more that needs to be done.
Several investigators have evaluated the fundamental chemistry of activated persulfate systems. Neta et al. (1977) provided a fundamental study of the reactivity of sulfate radicals with several aromatic compounds. By using radiation pulses in a solution buffered to pH 7, they were able to deduce that electron-withdrawing substituents cause a significant decrease in the reactivity with sulfate radicals. This reduction is due to the electrophilicity of the sulfate radical. Thus, the sulfate radical does not work by addition to the aromatic ring, but they are most likely working by an electron-transfer mechanism. This ability of the sulfate radical to react with aromatic rings was also observed by Elbenberger et al. (1978) in their work. These authors also observed that the reaction of alcohols with sulfate radical proceeded by H abstraction from the C—H bond. Other investigators have studied the reaction of persulfate under varying conditions and with numerous chemicals. George et al. (2001) studied the reaction of persulfate with alcohols, ethers, and esters.

Anipsitakis and Dionysiou (2004) studied the activation of persulfate by nine transition metals. They found that silver (I) had the greatest activation of persulfate. They also found that sulfate and hydroxyl radicals were generated when persulfate was activated by iron (II).

Hayon and McGarvey (1967) found that two radicals were generated when they exposed aerated aqueous solutions of persulfate to flash photolysis at a pH of 5.5. They found the sulfate radical and superoxide in these solutions. These results could explain how persulfate is able to treat highly oxidized compounds such as carbon tetrachloride, which is susceptible to being reduced by superoxide.
Activated persulfate has recently been studied for the remediation of contaminated groundwater. Liang et al. (2003) investigated heat activated persulfate for the remediation of TCE and TCA in soil-groundwater systems. Extensive degradation of TCE and TCA was observed at temperatures of 40°C, 50°C, and 60°C when compared to the 20°C control. Contaminant degradation followed pseudo-first-order reaction rates and degradation increased with increasing temperatures and/or increased persulfate concentration. The authors also studied these reactions in soil slurry systems; results showed that soil constituents such as soil organic carbon exert significant competition for sulfate radicals. Besides being in direct competition for sulfate radicals, the experiments showed that the sulfate radical might react with soil constituents preferably over the contaminant. Thus, persulfate treatments may show a lag time in which the persulfate is destroying soil organic matter before the actual destruction of the contaminant starts.

Nadim et al. (2006) studied the ability of persulfate activated by heat and iron to remediate soil and groundwater contaminated with polycyclic aromatic hydrocarbons (PAHs). The authors looked at the feasibility of degrading 16 U.S. EPA priority PAHs from a Superfund site in Eastern Connecticut with heat and Fe(II)-EDTA catalyzed persulfate reactions. They varied temperature and iron-chelate concentrations and were able to effectively degrade all 16 target PAHs. Although external heat and iron increased treatment efficiency, degradation did occur without the addition of either activator.

Liang et al. (2004) looked at the ability of ferrous ion to activate persulfate for the in situ remediation of trichloroethylene (TCE) and the ability of the reductant thiosulfate to regenerate
the iron in the system. TCE was degraded in their experiments by using various molar ratios of persulfate to iron. However, almost all of the degradation occurred instantaneously and then the reaction stalled and no further degradation occurred. This stalling was believed to be due to the destruction of persulfate by excess Fe$^{2+}$ or the rapid conversion of the activating Fe$^{2+}$ to the non-activating Fe$^{3+}$. Sequential additions of Fe$^{2+}$ were tried to support the authors’ claims that excess Fe$^{2+}$ could cause the system to stall. These experiments showed an improvement in TCE degradation while the overall use of persulfate in the system did not noticeably change, thus supporting the claim. The authors hypothesized that thiosulfate could reduce the Fe$^{3+}$ into Fe$^{2+}$ and that this could keep the system from stalling. Sequential additions of thiosulfate after the initial stalling did increase the overall destruction of TCE and increasing the level of thiosulfate did lead to better destruction of TCE. Further increases of Fe$^{2+}$ and additional thiosulfate additions after the original did not lead to increased degradation.

Huang et al. (2005) investigated the degradation of 59 volatile organic compounds (VOCs) by thermal activated persulfate. The authors used temperatures of 20°C, 30°C, and 40°C. They found that chlorinated ethenes, BTEXs and trichloroethanes were degraded, while compounds with C=C bonds or aromatics with activating functional groups were readily degraded. However, saturated hydrocarbons and halogenated alkanes were not easily degraded. The degradation rate of all compounds increased with increasing temperatures and/or persulfate concentrations. After 72 hours at 40°C, 37 of the 54 VOCs had better than 90% destruction, while no degradation of VOCs was observed at 20°C. Surprisingly, 22 of the VOCs had greater degradation at 30°C than 40°C. These experiments also showed that tetrachloromethane, bromodichloromethane, dibromochloromethane, and bromoform had all been degraded by persulfate. This was an important discovery because these compounds are highly resistant to
oxidation and usually are degraded through reductive pathways. The data show that persulfate systems may be able to generate reductants as CHP does.

Liang et al. (2003) studied persulfate oxidation of dissolved trichloroethylene (TCE) in aqueous and soil slurry systems under a variety of experimental conditions. A chelating agent (citric acid) was used in attempt to manipulate the quantity of ferrous ion in solution by providing an appropriate chelate/Fe$^{2+}$ molar ratio. In an aqueous system a chelate/Fe$^{2+}$ molar ratio of 1/5 (e.g., persulfate/chelate/Fe$^{2+}$/TCE ratio of 20/2/10/1) was found to be the lowest acceptable ratio to maintain sufficient quantities of Fe$^{2+}$ activator in solution resulting in nearly complete TCE destruction after only 20 min. The availability of Fe$^{2+}$ appeared to be controlled by adjusting the molar ratio of chelate/Fe$^{2+}$. In general, high levels of chelated ferrous ion concentrations resulted in faster TCE degradation and more persulfate decomposition. Additionally, the use of citric acid without the addition of supplemental Fe$^{2+}$ in soil slurries, where the citric acid apparently extracted native metals from the soil, appeared to be somewhat effective at enhancing persulfate oxidation of TCE over extended reaction times. A comparison of different chelating agents revealed that citric acid was the most effective. The higher citric acid concentrations used at one level of ferrous ion content resulted in the higher persulfate decomposition. When the Fe$^{2+}$ exceeds the binding ability of the chelate, the overall efficiency of the system is less due to the reaction of the Fe$^{2+}$ with the sulfate radical. In soil slurries Liang et al. (2003) concluded that more efficient oxidation of TCE occurred in soil slurry systems (i.e., requiring less persulfate), but a longer reaction time was needed, what could have been caused by various components of the soil.
Objectives

The proposed research focuses on the following three objectives.

1. To study the radicals generated during base activated persulfate reactions.

   The base activation of persulfate is an ISCO technique that is currently being used in the field, even though the mechanisms of these reactions are not well understood. It is believed that the reactions are proceeding in the same manner as the CHP and thus generating superoxide, hydroperoxide, hydrogen peroxide, hydroxyl radicals and sulfate radicals. The proposed research would confirm if base activated persulfate is generating these species. If base activated systems are generating the same reactive species as CHP, then this system would be able to reduce oxidized compounds such as carbon tetrachloride as well as promote enhanced contaminant desorption by its ability to generate superoxide. Both of these characteristics are very significant in the overall ability of a treatment method to remediate contaminated groundwater. Besides looking at the radicals generated, the research will confirm the major oxidants in this system.

2. To evaluate the ability of minerals to activate persulfate.

   The possibility that minerals may be able to activate persulfate would be of great interest in the application of persulfate ISCO systems. Mineral decomposition of hydrogen peroxide has been shown and it is probable that the same would hold true for persulfate. It has even been shown that certain surfaces may not need any additional catalysts to initiate the CHP reactions. The ability of minerals to catalyze or activate these processes impacts many field design parameters when applying these ISCO methods.

3. To investigate rates of persulfate decomposition in soils of varying characteristics.
Persulfate behavior in relationship to soils and their properties has not yet been studied. The behavior of persulfate in the subsurface needs to be addressed to maximize the effectiveness and efficiency of this ISCO process. How persulfate interacts with soils in these systems could have important consequences to field applications. Some important factors in the interaction between soil and persulfate are the stability and reactivity of the persulfate in different soils and how the carbon content and mineralogy of the soil effect activated persulfate reactions.
References


Chapter 2: Reactivity of Base-Activated Persulfate Formulations

Abstract

Four base-activated persulfate systems (adjusting the pH to 12 and using molar ratios of 1:1, 2:1, or 3:1 base to persulfate) were studied using three reaction-specific probe compounds and two radical scavengers. Anisole was used as a probe compound to detect both hydroxyl radicals and sulfate radicals, and nitrobenzene was used to detect only hydroxyl radicals. Carbon tetrachloride was used as a general reductant probe. tert-Butyl alcohol was used to scavenge hydroxyl radicals, and isopropanol was used to scavenge both hydroxyl and sulfate radicals.

Reactions were conducted at pH 2, 7, and 12; no probe compound degradation occurred at pH 2 or 7, demonstrating minimal generation of reactive oxygen species. Rapid degradation of anisole and nitrobenzene occurred at pH 12, but no degradation of carbon tetrachloride was observed at pH 12.

The degradation of all probe compounds occurred in activated persulfate systems with 1:1, 2:1, and 3:1 base:persulfate molar ratios. The cumulative generation of sulfate and hydroxyl radicals detected through anisole degradation increased with increasing base:persulfate molar ratios; however, minimal differences were found in hydroxyl radical generation rates through the oxidation of nitrobenzene at all three molar ratios. Carbon tetrachloride degradation was proportional to the base:persulfate ratio indicating that reductants are generated at higher base:persulfate ratios. The results of this research demonstrate that the reactivity of persulfate formulations increases with increasing base:persulfate ratios, providing widespread reactivity through the generation of a range of reactive oxygen species.
Introduction

*In situ* chemical oxidation (ISCO) is an increasingly popular method for the remediation of organic contaminants in soils and groundwater. The most common ISCO processes, catalyzed H₂O₂ propagations (i.e. modified Fenton’s reagent), permanganate, and activated persulfate, have the potential to rapidly oxidize biorefractory contaminants, such as perchloroethylene (PCE) and trichloroethylene (TCE), at rates that are orders of magnitude faster than bioremediation or natural attenuation (U.S. EPA, 2007). Activated persulfate is the newest ISCO treatment technology. Persulfate, like hydrogen peroxide and permanganate, are prepared as solutions that can be directly injected into the subsurface. Unlike hydrogen peroxide, which rapidly decomposes in the subsurface, persulfate is stable for months (Brown, 2003). Aqueous solutions of persulfate naturally decompose at a slow rate into sulfate radicals (House, 1962). The rapid decomposition of persulfate into sulfate radicals through activation can be promoted by elevated temperatures, transition metals, or high pH. Activated persulfate is currently being implemented in the field successfully, even though there is limited information on its reactivity and mechanisms in the subsurface.

Base activated persulfate is one of the most common methods for activating persulfate, with two formulations commonly used. These formulations include adjusting the pH to 12 and using a molar ratio of base to persulfate. The pH 12 system has the advantage of initially requiring small amounts of base to activate the persulfate. The disadvantage is that *in situ* applications require additional amounts of base over time because the buffering capacity of the subsurface solids results in a significant drop in pH. Molar ratios of 2:1 and 3:1 base:persulfate are capable of maintaining the subsurface pH above 12 by overcoming the buffering capacity and the sulfuric acid generated through the activation of persulfate.
Persulfate activation results in the generation of free radicals, which are short lived but account for most of the contaminant destruction (U.S. EPA, 2007). There are no published reports on the reactivity and mechanisms of base-activated persulfate systems. The most likely mechanism for base-activated persulfate is the base catalyzed hydrolysis of persulfate to generate hydroperoxoide with subsequent decomposition to reactive oxygen species.

The presence of hydroxyl radical has been observed at high pH by Couttenye et al. (2002), and its activity may be predominant in persulfate systems. The purpose of this research was to evaluate the relative activities of different reactive oxygen species in basic persulfate formulations through the use of reaction-specific probe compounds.

**Experimental Section**

**Materials.** Sodium persulfate (≥98%), anisole (99%), carbon tetrachloride (99.9%) and sodium phosphate monobasic monohydrate (98%) were purchased from Sigma-Aldrich. Sodium hydroxide (99%), tert-butyl alcohol (99.8%), sulfuric acid (97%), hexanes (HPLC grade), isopropanol (99+) and nitrobenzene (99%) were obtained from J. T. Baker. Sodium thiosulfate (99+) was purchased from Fisher Scientific. Double-deionized water (>18 MΩ•cm) was purified with a Barnstead Nanopure II Ultrapure system.

**Probe compounds.** The probe compounds were selected based on reactivities with each of the reactive oxygen species (ROS). Anisole \(k_{\text{OH}^+} = 5.4 \times 10^9 \text{M}^{-1}\text{s}^{-1}; k_{\text{SO}_4^{2-}} = 4.9 \times 10^9 \text{M}^{-1}\text{s}^{-1}\) was used because of its high reactivity with both hydroxyl radicals and sulfate radicals (Buxton et al., 1988; O’Neill et al., 1975). Nitrobenzene \(k_{\text{OH}^+} = 3.9 \times 10^9 \text{M}^{-1}\text{s}^{-1}; k_{\text{SO}_4^{2-}} = \leq 10^6\) was selected to detect only hydroxyl radicals (Buxton et al., 1988; Neta et al., 1977). Carbon tetrachloride \(k_{\text{OH}^+} = < 2 \times 10^6 \text{M}^{-1}\text{s}^{-1}; k_{c} = 1.3 \times 10^{10} \text{M}^{-1}\text{s}^{-1}\) was used as a general reductant.
probe (Haag and Yao, 1992; Afanassiev et al., 1979). The initial concentration of all probe compounds was 1 mM.

**Hydroxyl radical and sulfate radical scavengers.** tert-Butyl alcohol \[k_{\text{OH}^\bullet} = 5.2 \times 10^8 \text{M}^{-1}\text{s}^{-1}; k_{\text{SO}_4^\bullet} = 8.4 \times 10^5 \text{M}^{-1}\text{s}^{-1}\] was used to scavenge hydroxyl radicals, and isopropanol \[k_{\text{OH}^\bullet} = 1.9 \times 10^9 \text{M}^{-1}\text{s}^{-1}; k_{\text{SO}_4^\bullet} = 8.2 \times 10^7 \text{M}^{-1}\text{s}^{-1}\] was used to scavenge both hydroxyl and sulfate radicals (Buxton et al., 1988; Clifton and Huie, 1989). The scavenger:probe molar ratio was 1000:1.

**Experimental procedures.** All solutions were prepared using double-deionized water and all reactions were conducted at 25° C in a thermally controlled water bath. Reactions using anisole and nitrobenzene as probe compounds were conducted in 1 L borosilicate glass bottles and reactions using carbon tetrachloride as a probe compound were conducted in sealed 200 mL borosilicate glass bottles to minimize volatilization. Sodium hydroxide (6 M) or sulfuric acid (5 M) were used to maintain the desired pH as the reactions proceeded. Experiments conducted at pH 12 were buffered using 0.01 M sodium phosphate monobasic monohydrate. Aliquots of 15 mL were collected periodically from the reactors and were extracted with hexane; the extracts were analyzed by gas chromatography.

**Analysis.** Extracts containing anisole and nitrobenzene were analyzed on a Hewlett-Packard 5890 gas chromatograph with a 15 m x 0.53 mm (i.d.) SPB-5 capillary column fitted with a flame ionization detector (FID). The injector port and detector port temperatures were 200°C and 250°C, respectively. The initial oven temperature was 70°C. The program rate was 20°C min⁻¹, and the final temperature was 210°C. Extracts containing carbon tetrachloride were analyzed on a Hewlett-Packard 5890A gas chromatograph with a 15 m x 0.53 mm (i.d.) Equity-5 capillary column and electron capture detection (ECD). The injector port and detector port
temperatures were 200°C and 250°C, respectively. A split flow was used with the initial oven temperature at 50°C. The program rate was 30°C min⁻¹, and the final temperature was 170°C. Persulfate concentrations were measured by iodometric titration with 0.01 N sodium thiosulfate. Solution pH was measured using with a Fisher Accument pH meter 900.

Results and Discussion

Probe degradation at various pH regimes. The degradation of the sulfate radical-hydroxyl radical probe anisole by persulfate at various pH regimes is shown in Figure 1a. These results illustrate that pH had a significant effect on the generation of sulfate radicals and/or hydroxyl radicals. Anisole oxidation was minimal at pH 2 and pH 7, indicating that sulfate and hydroxyl radical generation was eligible at these pH regimes. At pH 12, >99% of the anisole was oxidized over 30 min. Anisole is characterized by a high reactivity with both sulfate radical ($k_{SO_4^•-} = 4.9 \times 10^9$ M⁻¹s⁻¹) and hydroxyl radical ($k_{OH^•} = 5.4 \times 10^9$ M⁻¹s⁻¹); therefore, the generation of one or both of these radicals is responsible for anisole degradation at pH 12 (O’Neill et al., 1975; Buxton et al., 1988).

Trends in the oxidation of the hydroxyl radical probe nitrobenzene by persulfate at pH regimes of 2, 7, and 12 are similar to those observed for anisole (Figure 1b). Oxidation of nitrobenzene at pH 2 and 7 was not significantly different from rates in parallel control systems; however, >60% oxidation of nitrobenzene occurred over 600 min at pH 12. Nitrobenzene exhibits minimal reactivity with sulfate radical ($k_{SO_4^•-} \leq 10^6$ M⁻¹s⁻¹), but reacts rapidly with hydroxyl radical ($k_{OH^•} = 3.9 \times 10^9$ M⁻¹s⁻¹) (Neta et al., 1977; Buxton et al., 1988). Therefore, the data shown in Figure 1b strongly suggest that hydroxyl radical is generated in base-activated persulfate systems.
Carbon tetrachloride, a highly oxidized compound, was used as a probe compound for reducing and nucleophilic species (Figure 1c). Potential reductants and nucleophiles generated in activated persulfate systems include alkyl radicals (Peyton et al., 1995) and superoxide, which is unreactive in deionized water but is characterized by increased activity in water–cosolvent systems (Smith et al., 2004). Carbon tetrachloride degradation was negligible relative to control systems at each of the three pH regimes; demonstrating that reductants and nucleophiles were not generated at any of the three pH regimes. The loss of carbon tetrachloride observed in all reactions and control systems was likely due to volatilization.

The results of Figures 1a-c demonstrate the influence of pH on the generation of reactive oxygen species in base-activated persulfate systems. The increase in the rate of generation of reactive oxygen species maybe due to an increased rate of base-catalyzed hydrolysis at pH 12:

\[
S_2O_8^{2-} + H_2O \rightarrow HO_2^- + 2SO_4^{2-} + H^+ \quad (1)
\]

\[
HO_2^- + H^+ \leftrightarrow H_2O_2 \quad pK_a = 11.7 \quad (2)
\]

After hydrolysis of persulfate to hydrogen peroxide occurs, the hydrogen peroxide can potentially proceed through propagation reactions similar to those of catalyzed hydrogen peroxide (CHP) systems:

\[
H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \quad (3)
\]

\[
HO_2\cdot \rightarrow O_2\cdot^- + H^+ \quad pK_a = 4.8 \quad (4)
\]

\[
HO_2\cdot + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \quad (5)
\]

**Effect of persulfate concentration.** The effect of persulfate concentration on the degradation of the hydroxyl radical-sulfate radical probe anisole is shown in Figure 2a. Increases in persulfate concentration resulted a greater flux of hydroxyl radical and sulfate radical quantified by the degradation of anisole. Loss of anisole with 0.025 M persulfate was
negligible relative to the control. However, doubling the persulfate concentration to 0.05 M resulted in 80% loss of the probe compound over 180 min. Higher persulfate concentrations promoted significantly higher rates of anisole loss; 0.25 M persulfate promoted 97% anisole loss within 60 min, and 0.5 M persulfate provided >99.9% anisole loss in <60 min.

Degradation of the hydroxyl radical probe nitrobenzene by persulfate concentrations of 0.025 M, 0.05 M, 0.25 M, and 0.5 M at pH 12 is shown in Figure 2b. Loss of nitrobenzene was negligible using 0.025 and 0.05 M persulfate. However, solutions containing 0.25 M and 0.5 M persulfate promoted nitrobenzene losses of 42% and 68% over 600 min, respectively. Because sulfate radicals are unreactive with nitrobenzene, the results of Figure 2b suggest that hydroxyl radicals have a major role in base-activated persulfate oxidations.

Degradation of the reductant probe carbon tetrachloride in systems containing the same four concentrations of persulfate is shown in Figure 2c. Degradation of carbon tetrachloride was negligible relative to the control for all four persulfate concentrations, and the loss of carbon tetrachloride that did occur was likely due to volatilization. These results demonstrate that there is negligible generation of reactive oxygen species capable of degrading highly oxidized compounds such as carbon tetrachloride in base-activated persulfate systems at pH 12.

The results shown in Figures 2a-c demonstrate some important aspects of persulfate systems maintained at pH 12. Higher persulfate concentrations promoted increased degradation of compounds susceptible to attack by hydroxyl and sulfate radicals, but did not increase the degradation rate of oxidized compounds, such as carbon tetrachloride. These results are in agreement with those of Liang et al. (2003, 2004, 2004) and Huang et al. (2002, 2005), who also found greater contaminant oxidation rates with higher persulfate concentrations in heat- and Fe(II)-activated persulfate systems.
Negligible carbon tetrachloride degradation in a heat-activated persulfate system was also observed by Huang et al. (2004). Carbon tetrachloride degradation in activated persulfate systems may be due to reduction by alkyl radicals (Peyton et al., 1995) or by superoxide in the presence of electrolytes that lower the polarity of water (Smith et al., 2004). Alkyl radicals would not be present in the deionized water-persulfate-base system used, but superoxide can be potentially generated via equation 4; however, the concentration of base present in the reactions at pH 12 may not be sufficient to drive the base-catalyzed hydrolysis of persulfate. Therefore, no detectable degradation of carbon tetrachloride would be expected in the base-activated persulfate system at pH 12.

**Scavenging of oxidants at pH 12.** The degradation of anisole at pH 12 in the presence of the hydroxyl radical scavenger tert-butyl alcohol and the hydroxyl radical-sulfate radical scavenger isopropanol is shown in Figure 3a. Anisole was degraded >90% within 15 min in the persulfate system at pH 12, compared to negligible degradation in the control. When sulfate and hydroxyl radicals were scavenged from the base-activated persulfate system by the addition of excess isopropanol, anisole loss was similar to the control. Addition of the hydroxyl radical scavenger tert-butyl alcohol resulted in a 30% decrease in the loss of anisole after 60 min, demonstrating that hydroxyl radicals are the predominant oxidant in base-activated persulfate systems at pH 12. These results suggest that the generally held assumption that sulfate radicals predominate in base-activated persulfate systems at pH 12 may be incorrect.

Degradation of the hydroxyl radical probe nitrobenzene in base-activated persulfate systems at pH 12 with the addition of scavengers is shown in Figure 3b. Minimal loss of nitrobenzene occurred in the presence of both isopropanol and tert-butyl alcohol, confirming that hydroxyl radical is the dominant oxidant in base-activated persulfate systems at pH 12.
The loss of carbon tetrachloride in persulfate systems at pH 12 containing the scavengers isopropanol and tert-butyl alcohol is shown in Figure 3c. There was no significant difference in carbon tetrachloride degradation between base-activated persulfate systems with and without scavenging by tert-butyl alcohol. However, the addition of the cumulative sulfate radical-hydroxyl radical scavenger isopropanol increased the degradation of carbon tetrachloride to non-detectable levels within 600 min. This increased carbon tetrachloride degradation may be a result of increased persulfate activation by the presence of isopropanol, which is oxidized to acetone (a documented activator of persulfate) in the presence of persulfate (Montgomery, 1974).

Relative rates of reactive oxygen species generation at high base:persulfate ratios.

The relative rates of sulfate radical and hydroxyl radical generation, quantified through the degradation of anisole, in base-activated persulfate systems containing 1:1, 2:1, and 3:1 base:persulfate molar ratios are shown in Figure 4a. Cumulative sulfate and hydroxyl radical generation rates increased as a function of the base:persulfate ratio. The sulfate and hydroxyl radical generation rates were proportional to the base:persulfate ratio, which indicates that hydroxide has a significant role in the activation of persulfate to generate sulfate and hydroxyl radicals.

Relative rates of hydroxyl radical generation, quantified through the loss of nitrobenzene, with base:persulfate ratios of 1:1, 2:1, and 3:1 are shown in Figure 4b. These results show only small differences in hydroxyl radical generation rates compared to the data shown in Figure 4a. Unlike anisole, there was no apparent difference between the 2:1 and 1:1 systems; >90% of the nitrobenzene was degraded in approximately 300 min in both of these systems. These results suggest that increasing the base:persulfate ratio may increase the generation of sulfate radical compared to that of hydroxyl radical.
The degradation of the reductant probe carbon tetrachloride in activated persulfate systems with 1:1, 2:1, and 3:1 base:persulfate molar ratios is shown in Figure 4c. Carbon tetrachloride loss was evident in all three systems and increased as a function of the base concentration. Carbon tetrachloride degradation may be due to the formation of alkyl radicals or superoxide in the presence of electrolytes (Smith et al., 2004). Because no organic compounds other than carbon tetrachloride were present in the system to form alkyl radicals, carbon tetrachloride was likely degraded by superoxide.

The data shown in Figures 4a-c demonstrate that higher molar ratios of base:persulfate significantly increase persulfate reactivity and result in a change in degradation pathways compared to systems that are simply adjusted to pH 12. The increased reactivity is likely due to an increase in the base-catalyzed hydrolysis of persulfate to form hydrogen peroxide and its conjugate base hydroperoxide. Subsequent propagation reactions may then proceed, resulting in the generation of superoxide, which has the potential to degrade carbon tetrachloride in the presence of electrolytes.

The results of this research demonstrate that base-activated persulfate is characterized by varied reactivity under different basic conditions. When the pH is simply adjusted to pH 12, a significant flux of hydroxyl radical is generated, with minimal net generation of sulfate radical. Furthermore, minimal generation of species capable of degrading the oxidized compound carbon tetrachloride occurred at pH 12. However, when increasingly higher concentrations of base were used in persulfate systems, rates of sulfate radical generation increased in proportion to the molar ratio of base added to the persulfate formulations. However, the relative hydroxyl radical reactivity did not increase significantly as the base:persulfate ratios increased from 1:1 to 3:1. Furthermore, relative rates of reductant production quantified with the oxidized probe carbon
tetrachloride increased in parallel to hydroxyl radical activity. In summary, increased
centrations of base in persulfate formulations increases its oxidant and reductant reactivity.
These results demonstrate that high base:persulfate ratios can be an important ISCO technology.
And even greater contaminant degradation may occur in the presence of subsurface solids.
References


List of Figures

Figure 1a. Loss of the cumulative sulfate + hydroxyl radical probe anisole at pH 2, 7, and 12

Figure 1b. Loss of the hydroxyl radical probe nitrobenzene at pH 2, 7, and 12

Figure 1c. Loss of reductant probe carbon tetrachloride at pH 2, 7, and 12

Figure 2a. Relative rates of cumulative sulfate + hydroxyl radical generation measured by loss of the the probe anisole with four persulfate concentrations

Figure 2b. Relative rates hydroxyl radical generation measured by loss of the the probe nitrobenzene with four persulfate concentrations

Figure 2c. Relative rates reductant generation measured by loss of the the probe carbon tetrachloride with four persulfate concentrations

Figure 3a. Effect of scavenging of hydroxyl radical using tert-butyl alcohol and sulfate + hydroxyl radical using isopropanol cumulative sulfate + hydroxyl radical generation measured by loss of the the probe anisole at pH 12

Figure 3b. Effect of scavenging of hydroxyl radical using tert-butyl alcohol and sulfate + hydroxyl radical using isopropanol hydroxyl radical generation measured by loss of the the probe nitrobenzene at pH 12

Figure 3c. Effect of scavenging of hydroxyl radical using tert-butyl alcohol and sulfate + hydroxyl radical using isopropanol reductant generation measured by loss of the the probe carbon tetrachloride at pH 12

Figure 4a. Relative rates of cumulative sulfate + hydroxyl radical generation measured by loss of the the probe anisole under three hydroxide:persulfate molar ratios

Figure 4b. Relative rates of hydroxyl radical generation measured by loss of the the probe nitrobenzene under three hydroxide:persulfate molar ratios

Figure 4c. Relative rates of reductant generation measured by loss of the the probe carbon tetrachloride under three hydroxide:persulfate molar ratios
Figure 1a

Anisole (mM)

Time (min)
Figure 1b

- pH 2 Control
- pH 7 Control
- pH 12 Control
- pH 2 Reaction
- pH 7 Reaction
- pH 12 Reaction

Nitrobenzene (mM) vs. Time (min)
Figure 1c

Carbon Tetrachloride (mM)

Time (min)

- pH 2 Control
- pH 7 Control
- pH 12 Control
- pH 2 Reaction
- pH 7 Reaction
- pH 12 Reaction
Figure 2b

Nitrobenzene (mM)

pH 12 Control
0.025 M Persulfate
0.05 M Persulfate
0.25 M Persulfate
0.5 M Persulfate

Time (min)
Figure 2c

Carbon Tetrachloride (mM)

Time (min)

- pH 12 Control
- 0.025 M Persulfate
- 0.05 M Persulfate
- 0.25 M Persulfate
- 0.5 M Persulfate
Figure 3a

- pH 12 Control
- pH 12 Reaction, No Scavenging
- pH 12 Reaction, Scavenging by Isopropanol
- pH 12 Reaction, Scavenging by tert-Butyl Alcohol
Figure 3b

0 100 200 300 400 500 600

Nitrobenzene (mM)

0 0.2 0.4 0.6 0.8 1

Time (min)

- pH 12 Control
- pH 12 Reaction, No scavenging
- pH 12 Reaction, Scavenging by Isopropanol
- pH 12 Reaction, Scavenging by tert-Butyl Alcohol
Figure 3c

- pH 12 Control
- pH 12 Reaction, No Scavenging
- pH 12 Reaction, Scavenging by Isopropanol
- pH 12 Reaction, Scavenging by tert-Butyl Alcohol
Anisole (mM)

Figure 4a

1:1 Control
2:1 Control
3:1 Control
1:1 Reaction
2:1 Reaction
3:1 Reaction
Figure 4b

Nitrobenzene (mM) vs. Time (min)

- 1:1 Control
- 2:1 Control
- 3:1 Control
- 1:1 Reaction
- 2:1 Reaction
- 3:1 Reaction
Chapter 3: Rates and Pathways of Mineral-Activated Persulfate

Abstract

The potential for 13 naturally occurring minerals to mediate the decomposition of persulfate and generate a range of reactive oxygen species was investigated in order to provide fundamental information on activation mechanisms when persulfate is used for \textit{in situ} chemical oxidation (ISCO). Reactions were conducted at 25°C using 2 g of minerals and 5 mL of 0.5 M sodium persulfate with the addition of one of four probe compounds: anisole (to detect cumulative generation of sulfate and hydroxyl radicals), nitrobenzene (to detect hydroxyl radical), 1, 3, 5-trinitrobenzene (to detect hydroperoxide), and carbon tetrachloride (to detect reductants). The interactions of persulfate with minerals demonstrated everything from a hindering of the decomposition of persulfate to a rapid decomposition of persulfate. The interaction of the mineral-persulfate systems varied with each of the probe systems. Most of the minerals mediated the decomposition of persulfate, but did not promote the generation of reactive oxygen species. Three minerals, cobaltite, ilmentite, and pyrite, did promote the generation of reactive oxygen species. The results of this research demonstrate that the majority of minerals evaluated do not activate persulfate to generate reactive oxygen species, and other mechanisms of activation are necessary to promote contaminant degradation in the subsurface.

Introduction

The use of activated persulfate for the remediation of contaminated soils and groundwater by \textit{in situ} chemical oxidation (ISCO) has been the subject of increased attention. Four ISCO reagents (hydrogen peroxide, permanganate, ozone, and persulfate) have been used to date at numerous locations (Watts and Teel, 2006). Persulfate, like hydrogen peroxide, is a peroxygen; however unlike hydrogen peroxide, which rapidly decomposes in the subsurface, persulfate can...
be stable for months (EPA, 2006). Aqueous solutions of persulfate decompose at a slow rate to sulfate radicals (House, 1962). However, persulfate used for ISCO, is usually activated by elevated temperatures, transition metals, or high pH to generate reactive oxygen species (ROS) including the sulfate and hydroxyl radical. Like hydroxyl radical, the sulfate radical is a strong, relatively non-specific oxidant, with an $E^\circ = 2.6$ V (Eberson, 1987). However, hydroxyl radicals generated through propagation reactions appear to be more significant than sulfate radicals in activated persulfate systems (Corbin III and Watts, 2007).

Although a modicum of fundamental information is known about activated persulfate in relatively pure aqueous systems, its subsurface chemistry has received little attention. Historical development of ISCO technologies has demonstrated that the subsurface chemistry is a major factor in the effectiveness of these technologies. For example, minerals are known to decompose hydrogen peroxide leading to the formation of reactive oxygen species catalyzed $\text{H}_2\text{O}_2$ propagation (CHP) systems, resulting in more rapid decomposition of hydrogen peroxide in the subsurface (Watts et al., 1997). Minerals are usually so effective in decomposing $\text{H}_2\text{O}_2$ that the addition of soluble iron as a catalyst is usually not required.

The mineral-catalyzed decomposition of persulfate may potentially generate reactive oxygen species by mechanisms similar to CHP systems. However, the reactivity of persulfate is lower than hydrogen peroxide, and the reactive pathways may be different. The objective of this research was to study the rates of mineral-catalyzed decomposition and activation of persulfate.

**Experimental Section**

**Materials.** Minerals collected from sites throughout North America were purchased from DJ Minerals (Butte, MT). Thirteen minerals were used: anatase [TiO$_2$], bauxite [Al(OH)$_3$], calcite [CaCO$_3$], cobaltite [CoAsS], cuprite [Cu$_2$O], hematite [Fe$_2$O$_3$], ilmenite [FeTiO$_3$],
magnesite [MgCO$_3$], malachite [Cu$_2$(CO$_3$)(OH)$_2$], pyrite [FeS$_2$], pyrolusite [MnO$_2$], siderite [FeCO$_3$], willemite [Zn$_2$SiO$_4$]. The minerals, which were received as cubes approximately 1 cm x 1 cm x 1 cm, were crushed to a fine powder using a 150 mL capacity Spex shatter box with hardened steel as a grinder. Surface areas were determined by Brunauer, Emmett, Teller (BET) analysis under liquid nitrogen on a Coulter SA 3100 (Carter et al. 1986). The surface areas for the minerals were: anatase [11.7 ± 0.2 m$^2$/g], bauxite [28.8 ± 0.2 m$^2$/g], calcite [38.0 ± 0.2 m$^2$/g], cobaltite [2.21 ± 0.03 m$^2$/g], cuprite [49.5 ± 0.08 m$^2$/g], hematite [28.2 ± 0.2 m$^2$/g], ilmenite [1.7 ± 0.04 m$^2$/g], magnesite [38.0 ± 0.3 m$^2$/g], malachite [3.65 ± 0.03 m$^2$/g], pyrite [2.12 ± 0.01 m$^2$/g], pyrolusite [1.39 ± 0.04 m$^2$/g], siderite [6.8 ± 0.4 m$^2$/g], willemite [1.8 ± 0.02 m$^2$/g]. Sodium persulfate (≥98%), anisole (99%) and carbon tetrachloride (99.9%) were purchased from Sigma-Aldrich. Nitrobenzene (99%) was obtained from J. T. Baker and 1, 3, 5- Trinitrobenzene (TNB) (99%) was purchased from Chem Service and HPLC grade hexanes from Fisher. Double-deionized water (>18 MΩ•cm) was purified using a Barnstead Nanopure II Ultrapure system.

**Probe compounds.** The probe compounds were selected based on their reactivities with each of the reactive oxygen species. Anisole [$k_{\text{OH}^*} = 5.4 \times 10^9$ M$^{-1}$s$^{-1}$; $k_{\text{SO}_4^{2-}*} = 4.9 \times 10^9$ M$^{-1}$s$^{-1}$] was used because of its high reactivity with both hydroxyl radicals and sulfate radicals (O’Neill et al., 1975; Buxton et al., 1988). Nitrobenzene [$k_{\text{OH}^*} = 3.9 \times 10^9$ M$^{-1}$s$^{-1}$; $k_{\text{SO}_4^{2-}*} = \leq 10^6$] was used because it is highly reactive with hydroxyl radicals, but is unreactive with sulfate radicals, allowing a comparison between the two radicals (Neta et al., 1977, Buxton et al., 1988). Carbon tetrachloride [$k_{\text{OH}^*} = \leq 2 \times 10^6$ M$^{-1}$s$^{-1}$] was used to confirm the presence of reductants in the system (Haag and Yao, 1992). 1, 3, 5- Trinitrobenzene, a highly oxidized nitroaromatic compound resistant to oxidation, was used as a probe for hydroperoxide.
Experimental procedures. All reactions were conducted in 20 ml borosilicate volatile organics analysis (VOA) vials with 2 g of mineral and 5 ml of solution at 25°C. A sodium persulfate concentration of 0.5 M, which is commonly employed in field applications, was used and the pH of the solutions was allowed to drift downward as it would in a natural groundwater system. Probe and persulfate concentrations were analyzed at selected time points. Probe concentrations were measured by extracting each VOA vial with 3 ml of hexane and then analyzing the extract by gas chromatograph; persulfate concentrations were quantified using idometric titrations with 0.01 N sodium thiosulfate (Kolthoff and Belcher, 1957). Solution pH was measured using a Fisher Accument pH meter 900.

Gas chromatography analysis. Extracts containing anisole, nitrobenzene and 1, 3, 5-trinitrobenzene were analyzed on a Hewlett-Packard 5890 gas chromatograph fitted with a 15 m x 0.53 mm (i.d.) SPB-5 capillary column and a flame ionization detector (FID). The injector port and detector port temperatures for anisole and nitrobenzene were 200°C and 250°C, respectively. The initial oven temperature was 70°C. The program rate was 20°C min\(^{-1}\), and the final temperature was 210°C. Gas chromatograph conditions for the analysis of 1, 3, 5-trinitrobenzene included an initial oven temperature of 160°C and a final temperature of 190°C. The program rate was 10°C min\(^{-1}\), the injector temperature was 200°C, and the detector temperature was 250°C. Extracts containing carbon tetrachloride were analyzed on a Hewlett-Packard 5890A gas chromatograph fitted with a 15 m x 0.53 mm (i.d.) Equity-5 capillary column and an electron capture detector (ECD). The injector port and detector port temperatures were 100°C and 250°C, respectively. A split flow was used with the initial oven temperature at 50°C; the program rate was 30°C min\(^{-1}\), and the final temperature was 170°C.
Results and Discussion

Mineral-mediated decomposition of persulfate. The decomposition of persulfate mediated by 13 trace minerals is shown in Figure 1. The rates of mineral-mediated persulfate decomposition ranged substantially; therefore, the minerals were classified into four distinct groups based on the rates at which they promoted the decomposition of persulfate. The group of minerals that promoted rapid persulfate decomposition (cobaltite and pyrite) was characterized by >90% decomposition of persulfate within 12-36 hr. The minerals classified as slowly decomposing persulfate (ilmenite and siderite) promoted the decomposition of persulfate over approximately 20 d. The control group (pyrolusite and hematite) was characterized by an undetectable change in persulfate decomposition compared to aqueous controls. The fourth group of minerals (calcite, anatase, bauxite, cuprite, magnesite, malachite, willemite) demonstrated persulfate decomposition rates that were slower than that of persulfate decomposition in deionized water controls.

Most of the minerals retarded or had minimal effect on the rate of persulfate decomposition, while four minerals (pyrite, cobaltite, ilmenite, and siderite) increased the rate of persulfate decomposition. There was no correlation found between mineral surface areas and rates of persulfate decomposition. In addition, the metal composition of the minerals appeared to be a weak predictor of the potential for a mineral to decompose persulfate. For example, ilmenite, pyrite, and siderite are Fe (II) minerals. Ilmenite and siderite were slow in decomposing persulfate, whereas pyrite was rapid. Persulfate decomposition mediated by Fe (II)-based minerals was no greater than hematite-mediated persulfate decomposition (hematite was the only Fe (III) mineral evaluated). Unlike the iron minerals, the copper-based minerals
showed no difference in persulfate decomposition rates between the Cu (I) of cuprite and the Cu (II) of malachite.

**Overview of interactions of mineral-mediated persulfate with probe compounds.**

Anisole degradation studies were conducted over 24 hr. The cumulative sulfate and hydroxyl radical probe compound anisole demonstrated a loss of 60% in persulfate systems containing no minerals. Mineral-mediated persulfate decomposition rates correlated well with corresponding rates of sulfate and hydroxyl radical generation, which was quantified by the oxidation of anisole. However, a few exceptions were found. Cobaltite promoted the most rapid decomposition of persulfate, but slowed the relative rate of sulfate and hydroxyl radical generation (measured by anisole loss) by 20%. Conversely, malachite mediated minimal decomposition of persulfate, but promoted rapid generation of sulfate and hydroxyl radicals.

Relative rates of hydroxyl radical generation (quantified by nitrobenzene oxidation) are shown in Figure 2b. Minimal loss of nitrobenzene occurred in nitrobenzene-deionized water systems, and nitrobenzene loss was 40% in persulfate-deionized water systems. Similar to the data shown in Figure 2a, relative hydroxyl radical generation rates usually correlated with persulfate decomposition rates. Cobaltite and pyrolusite-mediated persulfate systems promoted less hydroxyl radical generation relative to persulfate decomposition compared to the other 11 minerals.

Relative rates of hydroperoxide generation, quantified by the loss of TNB, in mineral-persulfate systems are shown in Figure 2c. Cobaltite-, cuprite-, ilmenite-, and magnesite-persulfate systems promoted the generation of hydroperoxide more rapidly than persulfate-deionized water systems. Conversely, pyrite-, and siderite-persulfate systems promoted lower rates of hydroperoxide generation relative to persulfate-deionized water systems. Relative
hydroperoxide generation rates for anatase, bauxite, calcite, pyrolucite, malachite and willemite were not significantly different from hydroperoxide generation rates in persulfate-deionized water systems. These results demonstrate that pyrite-mediated decomposition of persulfate is proceeding through oxidative pathways, and not generating a significant flux of nucleophiles. Although cobaltite rapidly promotes the decomposition of persulfate, it slowly generates hydroperoxide.

The relative generation of reductants, such as superoxide, using carbon tetrachloride as a reductant probe, is shown in Figure 2d. Calcite-, ilmenite-, magnesite-, and pyrolucite-persulfate systems promoted the generation of reductants at rates exceeding that of persulfate-deionized water systems. The nine other minerals promoted the generation of reductants at rates lower than or equal to that of the persulfate-deionized water system.

The results of Figures 2a-d suggest that numerous mechanisms may be occurring in mineral-persulfate systems. Ilmenite- and magnesite-persulfate systems do not promote the generation of sulfate and hydroxyl radicals, but promote the generation of nucleophiles and reductants. In contrast, pyrite-persulfate systems promote the rapid generation of sulfate and hydroxyl radical, but do not promote the generation of nucleophiles and reductants.

**Detection of sulfate and hydroxyl radical.** Pyrite, ilmenite, and calcite were used as representative minerals of those that decompose persulfate rapidly, slowly, and less than persulfate-deionized water systems. The capacity of these three minerals to promote the degradation of anisole was studied as a basis for quantifying relative cumulative generation rates of sulfate and hydroxyl radicals.

The calcite-mediated degradation of anisole is shown in Figure 3a. Loss of anisole in the calcite-persulfate system was not significantly different than its loss in the persulfate-deionized
system. The minimal degradation of anisole in the persulfate-deionized water system is likely due to the direct oxidation of anisole by persulfate \( (E^0 = 2.01 \text{ V}) \) (Latimer, 1952). These results demonstrate that calcite does not activate persulfate and, thus, sulfate and hydroxyl radicals are not generated in the calcite-persulfate system. Although carbonates are known scavengers of the sulfate \( (k_{\text{SO}_4}^- = 9.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}) \) and hydroxyl radicals \( (k_{\text{OH}}^- = 1.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}) \), no scavenging effects were observed (Dogliotti and Hayon, 1967; Watts, 1997). These results suggest that carbonate concentrations were not high enough to scavenge sulfate or hydroxyl radicals. The pH of these systems was <4; the pK\(_a\) of bicarbonate-carbonic acid is 4.5. Therefore, any dissolved calcite likely escaped from the system as carbon dioxide.

Relative rates of sulfate and hydroxyl radical generation in ilmenite-persulfate systems is shown in Figure 3b. Over 99% anisole degradation in the ilmenite-persulfate system within 40 min demonstrates a significant generation rate of sulfate and hydroxyl radicals.

The pyrite-mediated degradation of anisole in persulfate systems is shown in Figure 3c. Anisole degradation was significantly higher in the presence of pyrite (>90% degraded) compared to systems containing only persulfate (<10% anisole degraded). These results demonstrate rapid generation of sulfate and hydroxyl radicals in pyrite-persulfate systems.

**Detection of hydroxyl radicals.** The detection of hydroxyl radical was evaluated through the oxidation of the hydroxyl radical probe nitrobenzene in persulfate systems containing pyrite, ilmenite and calcite.

Nitrobenzene was oxidized more slowly in calcite-persulfate systems than in persulfate-deionized water systems (Figure 4a). In the persulfate-deionized water systems >99% of the nitrobenzene was oxidized within 144 hr while only 60% of the nitrobenzene was oxidized in calcite-persulfate systems. Unlike the data of Figure 3a, these results suggest that calcite is
scavenging hydroxyl radicals. Scavenging may be occurring in the nitrobenzene system, while not the anisole system, because the nitrobenzene systems react longer allowing for more dissolution of carbonates. Hydroxyl radical generation was promoted in the ilmenite-persulfate system compared to systems containing only persulfate and deionized water (Figure 4b). Over 72 hr, >99% of the hydroxyl radical probe nitrobenzene was oxidized in ilmenite-persulfate systems, while approximately 50% of the nitrobenzene was oxidized in persulfate-deionized water systems.

Relative rates of hydroxyl radical generation measured by the oxidation of nitrobenzene in pyrite-persulfate systems are shown in Figure 4c. Approximately 90% of the nitrobenzene was degraded in pyrite-persulfate systems over 11 hr compared to <10% in persulfate-deionized water systems. These results demonstrate that pyrite can promote the rapid generation of hydroxyl radical in persulfate systems.

The results of Figures 4a-d demonstrate that the trace minerals pyrite and ilmenite promote the generation of hydroxyl radical in persulfate slurries. Generation of hydroxyl radical in pyrite slurries is rapid, which is likely due to dissolution of the pyrite, providing soluble iron (II) to activate persulfate:

$$\text{FeS }\leftrightarrow\text{ Fe}^{2+} + \text{ S}^{-}$$

Hydroxyl radical generation was slower in ilmenite systems. The mechanism of activation of persulfate in the presence of these minerals is unknown, but may involve the dissolution of the metal oxides or heterogeneous catalysis on the mineral surfaces.

Detection of nucleophiles. Degradation of the nucleophile probe TNB in calcite-persulfate systems is shown in Figure 5a. The addition of calcite to the persulfate system had no observable impact on the degradation of TNB. Approximately 90% of the TNB was degraded
over 216 hr in both the persulfate-deionized water systems and the calcite-persulfate systems. Approximately 40% of the TNB loss occurred in the first hr.

A large portion (40%) of the TNB degradation occurred within the first hr; thereafter, TNB degraded slowly, and after 120 hr there was a >90% loss of TNB in ilmenite-persulfate systems (Figure 5b). TNB loss in persulfate-deionized water systems also declined rapidly over the first hr, followed by a slow reaction; 90% loss of the TNB then occurred over 220 hr.

The degradation of TNB by pyrite is shown in Figure 5c. Dissolution of pyrite may be increasing the extraction efficiency during the analysis of the TNB, resulting in an apparent increasing concentration of TNB. Nonetheless, the persulfate-pyrite system showed significant loss relative to the control systems, demonstrating the generation of nucleophiles in pyrite-persulfate systems.

**Detection of reductants.** Carbon tetrachloride was used as probe for superoxide, a reductant generated in CHP systems and likely generated in activated persulfate systems as well. In CHP systems superoxide is responsible for degrading highly oxidized compounds, and it is also important in the enhanced desorption of hydrophobic organic contaminants (Corbin et al., 2007).

Degradation of carbon tetrachloride in calcite-persulfate systems is shown in Figure 6a; >80% carbon tetrachloride degradation was observed in both calcite-deionized water and calcite-persulfate systems after 8 hr. Approximately 70% of the carbon tetrachloride degradation occurred within the first hour, after which the rate slowed significantly. Most of the carbon tetrachloride loss was likely due to volatilization; therefore, calcite-persulfate systems do not promote the generation of reductants.
Loss of carbon tetrachloride in ilmenite-persulfate systems is shown in Figure 6b. Reductant activity was lower in ilmenite-persulfate systems than in persulfate-deionized water systems and, therefore, reductant generation in negligible in ilmenite-persulfate systems.

Degradation of carbon tetrachloride in pyrite-persulfate slurries is shown in Figure 6c. Carbon tetrachloride degradation in pyrite-persulfate systems was less than that of the persulfate-deionized water systems; these data demonstrate that no reductants are generated in pyrite-persulfate slurries. Furthermore, minimal generation of reductants was observed in any of the mineral-persulfate systems evaluated.

All of the mineral persulfate systems exhibited lower reactivity with carbon tetrachloride than the persulfate-deionized water control systems, denoting lower generation rates for reductants. A significant trend can be found between the total oxidant (sulfate and hydroxyl radical) generation and reductant generation in mineral-persulfate systems. The relative rate of total oxidant generation was inversely proportional to the relative rate of reductant generation.

The degradation of anisole, nitrobenzene, TNB and carbon tetrachloride in 13 mineral-persulfate systems compared to corresponding persulfate-deionized water systems over 4 hr, 24 hr, 48 hr, 120 hr, is shown in Figure 7. The probe compounds were degraded at rates slower than persulfate-deionized water controls in most of the mineral-persulfate systems. These results suggest that, in most cases, the minerals scavenge the reactive oxygen species or inhibit activation of persulfate.

The results of this research demonstrate that most trace minerals promote the decomposition of persulfate; however, the decomposition of persulfate appears to have varied consequences in the generation of reactive oxygen species with some minerals increasing reactivity and others lowering the reactivity of the persulfate.
References


List of Figures

Figure 1: Degradation of 0.5 M sodium persulfate by 13 various trace minerals with the temperature maintained at 25°C ± 1°C

Figure 2a: Degradation of the cumulative sulfate + hydroxyl radical probe anisole remaining after degradation by 0.5 M sodium persulfate coupled with trace minerals after 24 hr with the temperature maintained at 25°C ± 1°C

Figure 2b: Degradation of the hydroxyl radical probe nitrobenzene remaining after degradation by 0.5 M sodium persulfate coupled with trace minerals after 48 hr with the temperature maintained at 25°C ± 1°C

Figure 2c: Degradation of the hydroperoxide probe 1,3,5-trinitrobenzene remaining after degradation by 0.5 M sodium persulfate coupled with trace minerals after 120 hr with the temperature maintained at 25°C ± 1°C

Figure 2d: Carbon tetrachloride remaining after degradation by 0.5 M sodium persulfate coupled with trace minerals after 4 hr with the temperature maintained at 25°C ± 1°C

Figure 3a: Degradation of the cumulative sulfate + hydroxyl radical probe anisole by calcite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 3b: Degradation of the cumulative sulfate + hydroxyl radical probe anisole by ilmenite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 3c: Degradation of the cumulative sulfate + hydroxyl radical probe anisole by pyrite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 4a: Degradation of the hydroxyl radical probe nitrobenzene by calcite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 4b: Degradation of the hydroxyl radical probe nitrobenzene by ilmenite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 4c: Degradation of the hydroxyl radical probe nitrobenzene by pyrite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 5a: Degradation of the hydroperoxide probe 1,3,5-trinitrobenzene by calcite-persulfate systems with the temperature maintained at 25°C ± 1°C

Figure 5b: Degradation of the hydroperoxide probe 1,3,5-trinitrobenzene by ilmenite-persulfate systems with the temperature maintained at 25°C ± 1°C.

Figure 5c: Degradation of the hydroperoxide probe 1,3,5-trinitrobenzene by pyrite-persulfate systems with the temperature maintained at 25°C ± 1°C.
Figure 6a: Degradation of the reductant probe carbon tetrachloride by calcite-persulfate systems with the temperature maintained at 25°C ± 1°C.

Figure 6b: Degradation of the reductant probe carbon tetrachloride by ilmenite-persulfate systems with the temperature maintained at 25°C ± 1°C.

Figure 6c: Degradation of the reductant probe carbon tetrachloride by pyrite-persulfate systems with the temperature maintained at 25°C ± 1°C.

Figure 7: Degradation of the four probes as relative to corresponding control systems. Duration of reactions was probe-specific: anisole over 24 hr; nitrobenzene over 48 hr; 1, 3, 5-trinitrobenzene over 120 hr; carbon tetrachloride over 4 hr.
Figure 1

Persulfate (C/C₀) vs. Time (Days)

- Antase
- Cuprite
- Pyrite
- Bauxite
- Hematite
- Pyrolusite
- Calcite
- Ilmenite
- Siderite
- Cobaltite
- Magnesite
- Willemite
- Control
- Malachite
Figure 2a

Anisole Remaining after Degradation by Various Minerals over 24 Hours
Figure 2b

Nitrobenzene Remaining after Degradation by Various Minerals over 48 Hours

Nitrobenzene (mM)

Antase
Bazulte
Calcite
Cobaltite
PS-DI Control
Cuprite
Hematite
Ilmenite
Pyrolusite
Pyrite
Malachite
Magnesite
Siderite
Willemite
DI Control
Figure 2c

1, 3, 5-Trinitrobenzene Remaining after Degradation by Various Minerals over 120 Hours
Figure 2d

Carbon Tetrachloride Remaining after Degradation by Various Minerals over 4 Hours
Figure 3a

Anisole (mM) vs. Time (hr)

- Persulfate-Deionized Water
- Calcite-Deionized Water
- Calcite + Persulfate
Figure 3b

Persulfate-Deionized Water
Ilmenite-Deionized Water
Ilmenite + Persulfate

Anisole (mM) vs. Time (hr)

---

60
Figure 3c

Anisole (mM) vs Time (hr)

- Persulfate-Deionized Water
- Pyrite-Deionized Water
- Pyrite + Persulfate
Figure 4a

Persulfate-Deionized Water
Calcite-Deionized Water
Calcite + Persulfate

Nitrobenzene (mM) vs Time (hr)

0 24 48 72 96 120 144
Figure 4b

Nitrobenzene (mM) vs. Time (hr)

- Persulfate-Deionized Water
- Ilmenite-Deionized Water
- Ilmenite + Persulfate
Figure 4c

Persulfate-Deionized Water
Pyrite-Deionized Water
Pyrite + Persulfate

Nitrobenzene (mM) vs. Time (hr)
Figure 5a

1, 3, 5-Trinitrobenzene (mM)

Time (hr)

- Persulfate-Deionized Water
- Calcite-Deionized Water
- Calcite + Persulfate
Figure 5b

[Graph showing the degradation of 1,3,5-trinitrobenzene (mM) over time (hr) under different conditions: Persulfate-Deionized Water, Ilmenite-Deionized Water, and Ilmenite + Persulfate.]
Figure 5c

Persulfate-Deionized Water
Pyrite-Deionized Water
Pyrite + Persulfate

1, 3, 5-Trinitrobenzene (mM)

Time (min)
Figure 6a

- Volatilization
- Persulfate-Deionized Water
- Calcite-Deionized Water
- Calcite + Persulfate

Carbon Tetrachloride (mM) vs. Time (hr)
Figure 6b

Carbon Tetrachloride (mM) vs. Time (hr)

- Volatilization
- Persulfate-Deionized Water
- Ilmenite-Deionized Water
- Ilmenite + Persulfate

Figure illustrating the decrease in Carbon Tetrachloride concentration over time for different treatments.
Figure 6c

- Volatilization
- Persulfate-Deionized Water
- Pyrite-Deionized Water
- Pyrite + Persulfate

Carbon Tetrachloride (mM) vs. Time (hr)

0 1 2 3 4 5 6 7 8

0.2 0.4 0.6 0.8 1.0
Figure 7

% Decreasing Degradation

% Increasing Degradation

Anisole
Nitrobenzene
1, 3, 5-Trinitrobenzene
Carbon Tetrachloride

Antase
Bazuite
Calcite
Cobaltite
Cuprite
Hematite
Ilmenite
Pyrolusite
Pyrite
Malachite
Siderite
Willemite
Chapter 4: Impact of Soils on Persulfate Decomposition and pH

Abstract

The decomposition of persulfate by 11 soils was investigated in order to observe the impact of these soils on pH and persulfate concentration. Reactions were conducted at 25°C using 10 g of soil and 20 mL of either 0.5 M or 0.1 M persulfate. Reactions were conducted using base:persulfate molar ratios of 1:1, 2:1, or 3:1 over 120 d. Decomposition of persulfate and pH varied greatly between soils. Minimal discrepancies were observed between 0.1 M and 0.5 M persulfate. A second set of experiments were conducted in which anisole was used a probe for the overall reactivity of the system. These experiments were conducted in the same manner as the previous, but only using 0.5 M persulfate in a 2:1 base:persulfate molar ratio and with only two soils. These experiments were conducted at 0, 5, 10, 15 and 20 d. The results of these experiments demonstrated the importance of the pH in these systems as anisole destruction declined when the pH declined. This research demonstrated the importance of pH and soil properties in the use of persulfate for ISCO treatments.

Introduction

In situ chemical oxidation (ISCO) is an increasingly popular method for the remediation of organic contaminants in soils and groundwater. Activated persulfate is the newest ISCO treatment technology in which elevated temperatures, transition metals, H₂O₂, or high pH are used to promote the rapid decomposition of persulfate into reactive oxygen species (Watts and Teel, 2006). Activated persulfate is currently being implemented in the field successfully, even though there is limited information on its subsurface reactivity and mechanisms (Watts and Teel, 2006).
A common method for the activation of persulfate in ISCO systems is by the addition of base to the system. Two modes of base activation include adjusting the pH to 12 and using a molar ratio of base to persulfate. Although systems at pH 12 only require a small input of base to activate the system, the pH continually declines \textit{in situ} due to the buffering capacity of the subsurface solids and the generation of sulfuric acid through the decomposition of persulfate. The drop in pH renders the system ineffective unless additional inputs of base are subsequently added. Molar ratios of 2:1 and 3:1 base:persulfate may have the potential to maintain the subsurface pH above 12 by overcoming the buffering capacity of the soils and the sulfuric acid generated.

The activation of persulfate results in the generation of sulfate radicals:

\[
\text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} \quad (1)
\]

In addition to sulfate radicals, other reactive oxygen species (ROS) have been observed in activated persulfate systems including hydrogen peroxide, superoxide, and hydroxyl radicals. Hydroxyl radicals are the main oxidant in catalyzed hydrogen peroxide (CHP) systems; they are also formed through the reaction of sulfate radicals with hydroxide (Eq. 2).

\[
\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{OH}^- + \text{SO}_4^{2-} \quad (2)
\]

Thus, base activated persulfate systems deliver two powerful ROS in sulfate and hydroxyl radicals.

In addition to providing buffering capacity to the subsurface, soils have other important characteristics when applying ISCO treatments. Soils may activate persulfate through activation by minerals or organic matter, or they may retard the decomposition of persulfate through the presence of carbonates that scavenge the sulfate (\(k_{\text{SO}_4^{2-}} = 9.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}\)) and hydroxyl radicals (\(k_{\text{OH}^-} = 1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}\)) (Dogliotti and Hayon, 1967; Watts, 1997; Corbin and Watts, 2008).
The purpose of this research was to evaluate the decomposition of persulfate at various base:persulfate molar ratios in a series of soils and to study how the interaction between the soil and persulfate impacts the capacity of the system to degrade anisole, a cumulative sulfate and hydroxyl radical probe compound.

**Experimental Section**

**Materials.** Sodium persulfate (≥98%) and Anisole (99%) was purchased from Sigma-Aldrich, and hexanes (HPLC grade), sodium hydroxide (99%) and sand (purified, acid washed and ignited) were obtained from J. T. Baker. Soil samples and well cuttings were collected by the author’s lab through various means. Double-deionized water (>18 MΩ•cm) was purified with a Barnstead Nanopure II Ultrapure system.

**Experimental procedures.** Persulfate decomposition reactions were conducted in 40 mL borosilicate volatile organics analysis (VOA) vials with 10 g of soil and 20 mL of solution at 25°C in a thermally controlled water bath. Initial persulfate concentrations of 0.25 M and 0.1 M were paired in molar base:persulfate ratios of 1:1, 2:1, and 3:1.

Reactions in which anisole was used as a sulfate and hydroxyl radical probe were conducted using a molar base:persulfate ratio of 2:1 with 0.5 M persulfate to observe the impacts of the soil on contaminant degradation. Anisole \( [k_{\text{OH}^\bullet} = 5.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}; k_{\text{SO}_4^\bullet^\cdot} = 4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}] \) was used as a probe molecule because of its high reactivity with both hydroxyl radicals and sulfate radicals (Buxton et al., 1988; O’Neill et al., 1975). The 2:1 ratio was used because it provides sufficiently basic conditions to activate persulfate, while usually allowing the pH to return to near neutral. Persulfate concentrations of 0.5 M were used to replicate ISCO field
Application and soils H and J were chosen because they are the same soil, but from different horizons, thus differing only in soil organic carbon. Experiments were conducted by the same procedure as the persulfate decomposition reactions, with the exception that 18 ml of solution was used instead of 20 mL. The reactions were started, and placed into a water bath at which selected times 2 mL of 10 mM anisole solution were added to evaluate the flux of sulfate and hydroxyl radicals. At selected time points the entire vial contents were extracted with 3 mL of hexane, and the extracts were analyzed by gas chromatography.

**Analysis.** Extracts were analyzed on a Hewlett-Packard 5890 gas chromatograph fitted with a 15 m x 0.53 mm (i.d.) SPB-5 capillary column and a flame ionization detector (FID). The injector port and detector port temperatures were 200°C and 250°C, respectively. The initial oven temperature was 70°C. The program rate was 20°C min⁻¹, and the final temperature was 210°C. Persulfate concentrations were measured by iodometric titration with 0.01 N sodium thiosulfate. Solution pH was measured using a Fisher 900 Accumet pH meter.

**Results and Discussion**

**Decomposition of persulfate in soil-persulfate slurries.** Decomposition of persulfate by three base:persulfate molar ratios was conducted without soils for both 0.25 M and 0.1 M persulfate in parallel to reactions in soil-persulfate system. Decomposition of persulfate occurred at all base:persulfate molar ratios in 0.5 M persulfate systems (Figures 1a-c). Approximately 32% of the persulfate decomposed in the 3:1 system (Figure 1a). Approximately 12% of the persulfate decomposed in the 2:1 system (Figure 1b) and the 1:1 system (Figure 1c) decomposed approximately 12% of the persulfate. The pH in all of the 0.25 M persulfate systems remained relatively stable near 13. Systems containing 0.1 M persulfate (Figures 1d-e) did not decompose.
as rapidly as the 0.25 M persulfate systems. As with the 0.25 M persulfate systems, the pH remained near 13. The decomposition of persulfate is probably due to the base catalyzed hydrolysis of the persulfate promoted by the higher base concentrations in the 0.25 M persulfate system.

The decomposition of persulfate mediated by sand was conducted as a control for both the 0.25 M persulfate (Figures 2a-c) and 0.1 M persulfate systems (Figures 2d-f). Persulfate decomposition in systems with 0.25 M persulfate increased with increasing base:persulfate molar ratio, while the pH was parallel to that of the control. The largest persulfate decomposition (approximately 25%) occurred in the 3:1 base:persulfate system (Figure 2a). The 2:1 base:persulfate system (Figure 2b) decomposed 12% of the persulfate while the no observable decomposition occurred in the 1:1 system (Figure 2c). Negligible persulfate decomposition was not observed in 0.1 M systems (Figures 2d-f) and the initial pH of 13 did not vary significantly.

The decomposition of persulfate mediated by soil A is shown in Figures 3a-f. In the 0.25 M base:persulfate 3:1 system (Figure 3a) approximately 85% of the persulfate decomposed over 120 d, which was accompanied by a pH drop down to 9.4. Most of the persulfate decomposition occurred within the first 2 d, and >90% of the decomposition occurred within 40 d. Most of the pH drop occurred within the first 10 d. Persulfate and pH both dropped in the 2:1 base:persulfate system (Figure 3b), with 32% persulfate loss and a final pH of 7. The 1:1 base:persulfate system was characterized by the greatest decline in pH coupled with the lowest decomposition of persulfate (Figure 3c). After 120 d, 52% of persulfate remained, and the final pH was 4. Similar to the 0.25 M persulfate systems, the systems containing 0.1 M persulfate were also characterized by loss of persulfate and a drop in pH for all base:persulfate ratios. In the 3:1 base:persulfate system (Figure 3d) the pH declined to approximately 8, and 32% of the persulfate
remained. In the 2:1 base:persulfate system (Figure 3e), 20% of the persulfate decomposed with a final pH of 7; however in the 1:1 base:persulfate system (Figure 3f) 10% of the persulfate decomposed and the final pH was 4.5. Experiments conducted with soil A substantially decreased pH and increased decomposition when compared to controls.

The decomposition of persulfate and change in pH for soil B persulfate systems are shown in Figures 4a-f. Similar trends were found in both the 0.25 M 3:1 base:persulfate system (Figure 4a) and the 0.25 M 2:1 base:persulfate system (Figure 4b). Persulfate loss was 32% in the 3:1 base:persulfate system and 24% for the 2:1 base:persulfate system; the pH remained at 13 through the course of the reactions. The 1:1 base:persulfate system was characterized by smaller loss of persulfate and a greater drop in pH (Figure 4c). The persulfate loss was 15%, and the final pH was approximately 12, a full unit lower than in the 0.25 M persulfate system. As in the 0.25 M persulfate systems, the 0.1 M systems of 3:1 and 2:1 were similar while the 1:1 system differed significantly. The 3:1 base:persulfate system (Figure 4d) and the 2:1 base:persulfate system (Figure 4e) demonstrated no significant decrease in pH. The 3:1 base:persulfate system promoted 30% persulfate decomposition compared to 20% persulfate decomposition in the 2:1 base:persulfate system. The 1:1 base:persulfate system decomposed 20% of the persulfate, which was similar to the other 0.1 M persulfate systems; but unlike those systems a large pH drop of 5 was observed.

The influence of soil C on pH and the decomposition of persulfate in 0.25 M and 0.1 M persulfate systems activated by base:persulfate molar ratios of 3:1, 2:1, and 1:1 is shown in Figures 5a-f. The decomposition of persulfate in 0.25 M persulfate systems decreased with decreasing base:persulfate ratios while the pH only varied slightly from the initial value of 13. In the 3:1 base:persulfate system (Figure 5a), 32% persulfate loss occurred and 16% persulfate
and 4% persulfate was lost in the 2:1 base:persulfate system and 1:1 base:persulfate system, respectively. There was minimal difference between each of the three base:persulfate molar ratios (Figures 5d-f). For example, the pH varied by only 0.6 and the persulfate concentration varied by <9%. The decomposition of persulfate in these systems did not significantly differ from those of the controls, demonstrating that soil C did not activate persulfate in these systems.

The decomposition of persulfate 0.25 M and 0.1 M systems containing soil D activated by base:persulfate molar ratios of 3:1, 2:1, and 1:1 along with corresponding pH values are shown in Figures 6a-f. A range of persulfate and pH responses was observed in systems containing 0.25 M persulfate. In the 3:1 base:persulfate system (Figure 6a) approximately 75% of the persulfate was decomposed, and the pH dropped to approximately 11 over 120 d. Over half of the persulfate decomposition occurred within the first 2 d. As in the 3:1 system, the 2:1 system was characterized by > 50% persulfate loss in the first 2 d; the persulfate then decomposed by 68% over 120 d (Figure 6b). The final pH for the 2:1 system was 7.5, a 3.5 unit decrease from the 3:1 system. Persulfate concentrations in the 1:1 base:persulfate system (Figure 6c) decomposed by approximately 40% of the persulfate in the 2 d., and the pH decreased from 13.5 to 3.7 in 120 d. The 0.1 M persulfate systems also demonstrated a wide variety of responses depending on the molar concentration of base. The 3:1 base:persulfate system (Figure 6d) degraded 80% of the persulfate and the pH declined to 9.9. The 2:1 base:persulfate system (Figure 6e) and the 1:1 base:persulfate system (Figure 6f) also demonstrated persulfate degradation accompanied by declining pH values. The 2:1 base:persulfate system decomposed 72% of the persulfate while the 1:1 base:persulfate system degraded 60%; and the final pH for the systems was 7.4 and 5.2 for, respectively. Systems with the same base:persulfate ratios were very comparable regardless of the initial persulfate concentration.
The influence of soil E on the pH and degradation of persulfate in base activated systems is shown in Figures 7a-f. Soil E was efficient at promoting the degradation of 0.25 M persulfate when coupled with a base:persulfate ratio of 3:1 (Figure 7a). After 120 d only 20% of the persulfate remained and the pH was at 12.3. The 2:1 base:persulfate system (Figure 7b) degraded 68% of the persulfate while the pH declined to 7.5, almost 5 lower than the 3:1 base:persulfate system. The 1:1 base:persulfate system (Figure 7c) decomposed persulfate down to 66% while the pH decline down to 2.8. Soil E was also efficient at decomposing persulfate systems with 0.1 M persulfate. The 3:1 base:persulfate system (Figure 7d) demonstrated a persulfate loss of 80% and had a final pH of 10.2, while the 2:1 base:persulfate system (Figure 7e) decomposed 60% of the persulfate resulting in a final pH of 8. The 1:1 base:persulfate system (Figure 7f) pH declined to 4.5 while 40% of the persulfate was lost.

The degradation of 0.1 M and 0.25 M persulfate by soil F when activated by various molar base:persulfate ratios is shown in Figures 8a-f. Persulfate decomposition by soil F in the 0.25 M persulfate system resulted in a loss of 80% of the persulfate and a decline in pH to 12.4 (Figure 8a). The 2:1 base:persulfate system (Figure 8b) and the 1:1 base:persulfate system (Figure 8c) degraded 72% and 52% of the persulfate and had pH declines of 8 and 10, respectively. The soil F persulfate systems containing 0.1 M persulfate decomposed persulfate efficiently while demonstrating a lower decline in pH than observed in most 0.1 M persulfate systems. The 3:1 base:persulfate system (Figure 8d) decomposed approximately 90% of the persulfate while the pH decline to 10.5. The 2:1 base:persulfate system (Figure 8e) lost approximately 75% of the persulfate while the pH was lowered to 8. The 1:1 base:persulfate system had a reduction of persulfate down to 0.55 M with a corresponding pH of 4.8 (Figure 8f).
The degradation of 0.1 M and 0.25 M persulfate solution by soil G is shown in Figures 9a-f. Soil G, at both the 0.25 M and the 0.1 M level, displayed some of the lowest pH values and largest decomposition of persulfate for any soil tested. The 0.25 M persulfate system with a molar base:persulfate ratio of 3:1 decomposed over 99% (70% in the first 2 d) of the persulfate and had a pH value of 8.5 at the end of 120 d (Figure 9a). The 2:1 base:persulfate system (Figure 9b) also was efficient at decomposing persulfate and as with the 3:1 base:persulfate system a large part of the decomposition occurred within 2 d. At the end of 120 d the 2:1 base:persulfate system had decomposed 84% of the persulfate and had a corresponding pH of 5.3. The 1:1 base:persulfate system lacked the large initial decline in persulfate, but it did demonstrate a relatively large decline in pH over the first 2 d (Figure 9c). The 1:1 base:persulfate system decomposed 68% of the persulfate and decreased the pH from 13.5 to 3.

Most of the observations seen in the 0.25 M persulfate systems were observed in the 0.1 M persulfate systems. Both the 3:1 base:persulfate system (Figure 9d) and the 2:1 base:persulfate system (Figure 9e) demonstrated large decreases in persulfate over 2 d. As in the 0.25 M persulfate system, the 0.1 M persulfate system coupled with the 1:1 base:persulfate ratio did not display the large drop in persulfate, but it did have a significant drop in pH over the initial 2 d (Figure 9f). Final persulfate concentrations were 0.01, 0.02, and 0.03 M persulfate with corresponding pHs of 8.0, 5.8, and 3.7 for the 3:1, 2:1, and 1:1 base:persulfate ratios, respectively.

Base activated persulfate systems containing soil H are shown in Figure 10a-f. Soil H systems containing 0.25 M persulfate were comparable to other rapid decomposers of persulfate. The 3:1 base:persulfate system (Figure 10a) decomposed >90% of the persulfate while the pH declined to approximately 8. The 2:1 (Figure 10b) and 1:1 (Figure 10c) base:persulfate systems
both decomposed persulfate and demonstrated pH declines. The final pHs for these two systems was 6.5 and 2.8, respectively. In the end, the 2:1 system decomposed 80% of the persulfate while the 1:1 system decomposed 64% of the persulfate. The 0.1 M persulfate systems (Figures 10d-f) had pH and persulfate values that did not significantly differ from the 0.25 M persulfate system.

The interaction of soil J with 0.1 M and 0.25 M persulfate systems is shown in Figures 11a-f. Although not a rapid decomposer of persulfate, the 3:1, 2:1 and 1:1 base:persulfate systems were able to decompose 48%, 44%, and 36% of the persulfate over 120 d, respectively. The pH in these systems each declined to 12.4, 10.3 and 6.6 for the three above mentioned systems, respectively. The 0.1 M persulfate systems (Figures 11d-f) decomposition of persulfate did not significantly differ from that of the 0.25 M persulfate systems, although there were some differences in the pH. The final values for the pH were 10.5 for the 3:1 base:persulfate system (Figure 11d), 8.6 for the 2:1 base:persulfate system (Figure 11e) and 7.0 for the 1:1 base:persulfate system (Figure 11f).

The addition of soil K to 0.1 M and 0.25 M persulfate systems activated by molar ratios of base:persulfate promoted the degradation of persulfate and decline of pH (Figures 12a-f). Systems containing soil K and 0.5 M persulfate decomposed 68%, 56%, and 48% of the persulfate while the pH fell to 11.2, 9.4, and 6.0 for the 3:1 base:persulfate system (Figure 12a), the 2:1 base:persulfate system (Figure 12b) and the 1:1 base:persulfate system (Figure 12c), respectively. As with soil J, the persulfate decomposition did not significantly differ between the 0.5 M persulfate systems and the 0.1 M persulfate systems, but the pH did. Values for the 3:1 base:persulfate system (Figure 12d), the 2:1 base:persulfate system (Figure 12e), and the 1:1 persulfate system (Figure 12f) were 10, 8, and 5 respectively.
**Detection of sulfate and hydroxyl radicals.** The degradation of the cumulative sulfate and hydroxyl radical probe anisole by 0.25 M persulfate systems with a base:persulfate ratio of 2:1 coupled in soils H and J is shown in Figure 13a. Both soils demonstrated an increase in anisole degradation over that of the control. The initial persulfate concentration in these reactions of 0.25 M the pH was 13.5. Enhanced degradation of anisole is likely due to a rapid conversion of persulfate to ROS by either minerals or organic materials found in the soils. Soil J is initially faster than soil H at degrading anisole, but both systems are relatively equal after 2 hr at approximately 85% degradation compared to only approximately 20% degradation for the control. All reactions degraded >90% of the anisole in 5 hr.

After 5 d relative rates of sulfate and hydroxyl radicals changed (Figure 13b). The initial persulfate concentration in soil H was 0.13 M, and the pH was 10.2 while the persulfate concentration in soil J was 0.21 M and the pH was 13.2. Under these conditions, the rates of anisole oxidation was less than that of the control system. Soil H systems demonstrated minimal anisole degradation over 24 hr probably due to the already low initial pH of the system. When soil J was added to the system the degradation of the anisole slowed noticeably from the control although the system did degrade approximately 85% of the anisole over 24 hr.

The reactions of soil H and soil J with anisole after 10 d are shown in Figure 13c, while the reactions of soil H and J after 15 d are shown in 13d. After 10 d soil H had a persulfate concentration of 0.11 M coupled with a pH of 8.1, while the soil J system had a persulfate concentration of 0.18 M with a pH of 12.1. The slurry characteristics were nearly the same after 15 d. After 15 d, soil H had a persulfate concentration of 0.11 M and a pH of 7.6, while soil J had a persulfate concentration of 0.18 M and a pH of 12.1. With such large variation between pH of the two systems, the data shown in Figure 13c and 13d are similar. The addition of soil H
does increase the degradation of anisole slightly over that of the control, while the addition of soil J does not increase the degradation of anisole, which degrades approximately 90% of the anisole over 24 hr.

The reactions between soil H and soil J with anisole after 20 d are shown in Figure 13e. Soil H was characterized by an initial persulfate concentration of 0.10 M coupled with a pH of 7.5, while the soil J system had a persulfate concentration of 0.17 M with a pH of 11.8. Although these values are close to those of the 10 d and 15 d systems, the reaction characteristics were different. Additions of soil H caused a 20% increase in the degradation of anisole; an increase larger than observed in either of the 5 d, 10 d, or 15 d reactions. This may be due to a loss of soil organic matter by persulfate, which can act as ROS scavengers. Alternatively, the reaction containing soil J was the least effective soil J system at degrading anisole. Again, this can probably be explained best by a reduction of activating organic material.

In general, most soils increased the decomposition of persulfate in base activated persulfate systems with molar ratios of 3:1, 2:1, and 1:1 when coupled with 0.1 M and 0.25 M persulfate over the controls. The enhanced decomposition of persulfate is probably due to minerals and organic matter present in the soils. Although soils can enhance the decomposition of persulfate, this does not necessarily equal an increase in the systems capacity to degrade contaminants.
References


List of Figures

Figure 1a: Reactions of 20 mL, 0.25 M persulfate coupled with a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 1b: Reactions of 20 mL, 0.25 M persulfate coupled with a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 1c: Reactions of 20 mL, 0.25 M persulfate coupled a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 1d: Reactions of 20 mL, 0.1 M persulfate coupled a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 1e: Reactions of 20 mL, 0.1 M persulfate coupled with a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 1f: Reactions of 20 mL, 0.1 M persulfate coupled with a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 2a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 2b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 2c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 2d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 2e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 2f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of sand and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 3a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 3b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 2:1 at a temperature of 25°C.
Figure 3c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 3d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 3e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 3f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil A and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 4a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 4b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 4c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 4d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 4e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 4f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil B and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 5a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 5b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 5c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 5d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 5e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 2:1 at a temperature of 25°C.
Figure 5f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil C and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 6a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 6b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 6c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 6d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 6e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 6f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil D and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 7a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 7b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 7c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 7d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 7e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 7f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil E and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 8a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 8b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 2:1 at a temperature of 25°C.
Figure 8c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 8d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 8e: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 8f: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil F and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 9a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 9b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 9c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 9d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 9e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 9f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil G and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 10a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 10b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 10c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 10d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 10e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 2:1 at a temperature of 25°C.
Figure 10f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil H and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 11a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 11b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 11c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 11d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 11e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 11f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil J and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 12a: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 12b: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 12c: Reactions of 20 mL, 0.5 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 12d: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 3:1 at a temperature of 25°C.

Figure 12e: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 2:1 at a temperature of 25°C.

Figure 12f: Reactions of 20 mL, 0.1 M persulfate coupled with 10 g of soil K and a base:persulfate ratio of 1:1 at a temperature of 25°C.

Figure 13a: Reactions of 20 mL, persulfate solution coupled with 10 g of soil H or soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C. Initial anisole concentration of 0.1 mM added at 0 d. Controls were reaction replicates without addition of soils. Initial persulfate concentration and pH were equal to experimental values obtain in previous experiments.
Figure 13b: Reactions of 20 mL, persulfate solution coupled with 10 g of soil H or soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C. Initial anisole concentration of 0.1 mM added at 5 d. Controls were reaction replicates without addition of soils. Initial persulfate concentration and pH were equal to experimental values obtain in previous experiments.

Figure 13c: Reactions of 20 mL, persulfate solution coupled with 10 g of soil H or soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C. Initial anisole concentration of 0.1 mM added at 10 d. Controls were reaction replicates without addition of soils. Initial persulfate concentration and pH were equal to experimental values obtain in previous experiments.

Figure 13d: Reactions of 20 mL, persulfate solution coupled with 10 g of soil H or soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C. Initial anisole concentration of 0.1 mM added at 15 d. Controls were reaction replicates without addition of soils. Initial persulfate concentration and pH were equal to experimental values obtain in previous experiments.

Figure 13e: Reactions of 20 mL, persulfate solution coupled with 10 g of soil H or soil J and a base:persulfate ratio of 2:1 at a temperature of 25°C. Initial anisole concentration of 0.1 mM added at 20 d. Controls were reaction replicates without addition of soils. Initial persulfate concentration and pH were equal to experimental values obtain in previous experiments.
Figure 1a

Persulfate (M)

pH

Time (Days)

Persulfate

pH
Figure 1b

Persulfate (M) vs. Time (Days)

- Open circles represent Persulfate concentration.
- Squares represent pH values.

The graph shows the decrease in Persulfate concentration and the change in pH over time.
Figure 1e

Persulfate (M) vs. Time (Days)

- Persulfate
- pH

Persulfate concentration and pH over time.
Figure 1f

Persulfate (M)

Time (Days)

Persulfate

pH

0 20 40 60 80 100 120
0 0.02 0.04 0.06 0.08 0.1 0.12
0 2 4 6 8 10 12 14

Hd
Figure 2a

Persulfate (M) vs. Time (Days)

Persulfate

pH
Figure 2b

Persulfate (M) vs. Time (Days)

- Persulfate
- pH

0 20 40 60 80 100 120

0 0.05 0.1 0.15 0.2 0.25 0.3

0 2 4 6 8 10 12 14
Figure 2c

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 2e

Persulfate (M) vs. Time (Days)

Persulfate

pH
Figure 2f

Persulfate vs. Time (Days)

- Persulfate (M)
- pH

Time (Days)

Persulfate (M)

Hd
Figure 3a
Figure 3b

Persulfate (M) vs. Time (Days) for pH and Persulfate.
Figure 3c

Persulfate (M) vs. Time (Days)

Persulfate

pH

Time (Days)
Figure 3d

Persulfate (M) vs. pH over time (in days).
Figure 3e

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 3f
Figure 4a

Persulfate (M) vs. Time (Days)

Persulfate

pH
Figure 4d

Persulfate (M) vs. Time (Days)

Persulfate
pH
Figure 4e

Persulfate (M)

Time (Days)

Persulfate

pH

0.02
0.04
0.06
0.08
0.1
0.12
0
20
40
60
80
100
120
Figure 4f

Persulfate vs. pH over time (days).

- Persulfate (M) axis ranges from 0 to 0.12.
- pH axis ranges from 0 to 14.
- Time (Days) axis ranges from 0 to 120.

Lines and markers indicate the decrease in Persulfate and pH over time.
Figure 5c

Persulfate (M) vs. Time (Days) for different pH levels.
Figure 5d

Persulfate (M)

Time (Days)

Persulfate

pH

0 20 40 60 80 100 120

0 0.02 0.04 0.06 0.08 0.1 0.12

0 2 4 6 8 10 12 14
Figure 5e

Persulfate vs. pH over time (days).

- Persulfate (M)
- pH

Time (Days)
Figure 5f

Persulfate (M) vs. Timer (Days)

- Persulfate
- pH
Figure 6a

![Graph showing Persulfate (M) and pH over time (Days)]

- **Persulfate**
  - Initial value: 0.25
  - Decreases over time
- **pH**
  - Initial value: 14
  - Decreases to 10 over time

**Axes:**
- **Y-axis:** Persulfate (M) and pH
- **X-axis:** Time (Days)
Figure 6b

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 6c

Persulfate (M)

Time (Days)

Persulfate

pH

Hd

0 20 40 60 80 100 120

0 0.05 0.1 0.15 0.2 0.25

0 4 8 12 14
Figure 6d
Figure 6e

Persulfate (M) vs. Time (Days) for pH (Hd)
Figure 6f

Persulfate (M) vs. Time (Days)

- Open circles: Persulfate
- Solid squares: pH

Persulfate and pH concentrations decrease over time.
Figure 7b

Persulfate (M) vs. Time (Days)

Persulfate

pH

Hd
Figure 7c

The graph shows the decrease in persulfate (M) and pH over time (days). The x-axis represents time in days, ranging from 0 to 120, while the y-axis represents persulfate (M) and pH, ranging from 0 to 0.25 for persulfate and 0 to 14 for pH.

- **Persulfate (M)**: The concentration of persulfate decreases significantly over time, starting from a higher value and stabilizing at a lower level by day 120.
- **pH**: The pH decreases from an initial value, stabilizing at a lower level by day 120.

The data points are marked with error bars, indicating the variability in the measurements.
Figure 7d

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 7e

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 8b

Persulfate (M) vs. Time (Days)

Persulfate

pH

Time (Days)
Figure 8c

The graph illustrates the change in persulfate concentration (M) and pH over time (days). The persulfate concentration decreases sharply in the first few days, followed by a more gradual decrease. The pH shows a general increase over time, indicating the formation of alkaline conditions. The data points and error bars suggest variability in the measurements over the duration of the experiment.
Figure 8e

Persulfate (M) vs. Time (Days)

Persulfate

pH
Figure 8f

Persulfate (M) vs. Timer (Days)

Persulfate

pH
Figure 9a

Persulfate (M)

Time (Days)

0 20 40 60 80 100 120

Persulfate

pH
Figure 9c

Persulfate (M) vs. pH over time (days) for various conditions.

- **Persulfate** (open circles)
- **pH** (filled squares)

The graph shows the decrease in persulfate concentration and pH with increasing time.
Figure 9d

Persulfate (M) vs. Time (Days)

- Persulfate
- pH

0 204 0 608 0 100 120

0 0.02 0.04 0.06 0.08 0.1 0.12

0 2 4 6 8 10 12 14
Figure 9e

Persulfate (M)

Time (Days)

Persulfate

pH
Figure 9f

Persulfate (M) vs. Time (Days)

- **Persulfate**
- **pH**

0 204 0 608 0 100 120

0 0.02 0.04 0.06 0.08 0.1 0.12

0 2 4 6 8 10 12 14
Figure 10a

Persulfate (M)

Time (Days)

Persulfate

pH
Figure 10b

Persulfate (M) vs. Time (Days)

- **Persulfate**
- **pH**
Figure 10d

Persulfate (M) vs. Time (Days)

Persulfate

pH

Hd

0 20 40 60 80 100 120

0 0.02 0.04 0.06 0.08 0.1 0.12

0 2 4 6 8 10 12 14
Figure 10f

Persulfate (M) vs. Time (Days)

Persulfate

pH
Figure 11b

Persulfate (M) vs. Time (Days)

- Persulfate
- pH
Figure 11c

Persulfate (M) vs. Time (Days) for pH

- Persulfate
- pH
Figure 11d
Figure 11e

Persulfate

pH

Persulfate (M)

Time (Days)

0 20 40 60 80 100 120

0 0.02 0.04 0.06 0.08 0.1 0.12

0 2 4 6 8 10 12 14

Hd

Persulfate

pH

0 2 4 6 8 10 12 14

0 0.02 0.04 0.06 0.08 0.1 0.12

Time (Days)
Figure 11f

Persulfate (M)

Time (Days)

Persulfate

pH
Figure 12a

The graph shows the change in persulfate concentration (M) and pH over time (days). The persulfate concentration decreases significantly in the first 20 days and then stabilizes, while the pH remains relatively constant throughout the observed time period. The x-axis represents time in days, ranging from 0 to 120, and the y-axis represents persulfate concentration in M, ranging from 0 to 0.25. The pH values are indicated by the legend, with persulfate depicted by open circles and pH by closed squares.
Figure 12b

Persulfate (M) vs. Time (Days)

- **Persulfate**
- **pH**

Time (Days): 0 20 40 60 80 100 120

Persulfate (M): 0 0.05 0.1 0.15 0.2 0.25

pH: 0 2 4 6 8 10 12 14
Figure 12e

Persulfate (M)

Time (Days)

Persulfate

pH
Figure 12f

Persulfate (M) vs Time (Days)

Persulfate (M) decreases over time. The pH shows a slight decrease as well.
Figure 13a

Anisole (mM) vs. Time (hr) for different soil reaction types:
- Soil H/J Control
- Soil H Reaction
- Soil J Reaction
Figure 13b

Soil H Control
Soil J Control
Soil H Reaction
Soil J Reaction

Anisole (mM)

Time (hr)
Figure 13c

Soil H Control
Soil J Control
Soil H Reaction
Soil J Reaction

Anisole (mM) vs Time (hr)

- Soil H Control
- Soil J Control
- Soil H Reaction
- Soil J Reaction
Figure 13d

Soil H Control
Soil J Control
Soil H Reaction
Soil J Reaction

Anisole (mM)

Time (hr)

Soil H Control
Soil J Control
Soil H Reaction
Soil J Reaction
Figure 13e

Soil H Control
Soil J Control
Soil H Reaction
Soil J Reaction

Anisole (mM)
Time (hr)