In Situ Reclamation by Chemical Means: A Feasibility Study

Gary R. Peyton,
Mary H. LeFaivre,
Michelle A. Smith

Illinois State Water Survey
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A Feasibility Study

by

Gary R. Peyton, Mary H. LeFaivre and
Michelle A. Smith

Aquatic Chemistry Section
Illinois State Water Survey
Champaign, Illinois 61820

Printed September 1988
IN SITU AQUIFER RECLAMATION BY CHEMICAL MEANS:
A FEASIBILITY STUDY

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Illinois State Water Survey
Champaign, Illinois 61820

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CONTENTS

List of Tables................................................................. v
List of Figures............................................................................... vi
Acknowledgements........................................................................ vii
Abstract........................................................................................ ix
Executive Summary.......................................................................... xi
  Introduction.................................................................................. xi
  Findings..................................................................................... xi
  Conclusions................................................................................ xiii
  Recommendations.......................................................................... xii
Section 1. Background.................................................................... 1
  Aquifer Reclamation....................................................................... 1
  In Situ Treatment.......................................................................... 1
  Chemical Reaction Kinetics.......................................................... 4
    First- and Second-Order Reactions............................................... 4
  Chemical In Situ Aquifer Reclamation Using Oxy-Radicals............. 6
    Selection of Candidate Reagents for In-Situ Generation of Oxy-Radicals.......................................................... 6
    Possible Means of Generating Candidate Oxy-Radicals................. 9
      Hydroxyl Radical.................................................................. 9
      Sulfate Radical Anion (SRA).................................................. 11
    Selection of Model Organic Substrate........................................ 13
Section 2. Experimental Procedures............................................... 15
  Summary of Experiments Performed............................................ 15
  Materials.................................................................................... 15
    Sand....................................................................................... 15
    Reagents................................................................................ 16
    Apparatus............................................................................... 16
      Glassware.............................................................................. 16
      Water Bath........................................................................... 17
      Constant-Temperature Box.................................................... 17
  Methods..................................................................................... 17
    Analytical Procedures............................................................. 17
      Persulfate Analysis.................................................................. 17
      Benzene Determinations........................................................ 18
    Preparation.............................................................................. 18
      Sand Preparation................................................................... 18
      Preparation of Apparatus....................................................... 19

(concluded on next page)
## CONTENTS (concluded)

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Experimental Results</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Notation</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Experiments 1 and 2</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Experiment 3</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Experiment 4</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Experiment 5</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Experiment 6</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Experiment 7</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Experiment 8</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Experiment 9</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Experiment 10</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Experiment 11</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Observations</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Experiment 12</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Experiment 13</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Experiment 14</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>Discussion</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Project Objectives</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Candidate Reagents</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Batch Kinetics of SRA</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Kinetics of Organic Compound Destruction</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Prediction of Sand Column Results from Kinetic Data</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Feasibility of Oxidative In Situ Degradation</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>Conclusions</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
<td>Recommendations</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>77</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>First- and Second-Row Nonmetals Plus the Halogens</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Oxy-Radicals of First- and Second-Row Nonmetal Elements</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Methods of Sand Preparation</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Rate Constants and Stoichiometric Ratios for Kinetic Experiments</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Initial Reaction Rates in Experiment 8</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>Experimental Matrix for Site P Sand Column, Experiment 10</td>
<td>45</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>Figure Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene and persulfate disappearance at 90°C</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>Comparison of determined rate constants with literature values</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>Disappearance curves, experiment 4 (70°C)</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Effect of phosphate buffer on benzene disappearance at 70°C</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>Effect of phosphate buffer on persulfate disappearance at 70°C</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>Benzene and persulfate disappearance curves for experiment 6, 70°C</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>Disappearance curves, experiment 7</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>Disappearance of persulfate at 50°C, experiment 8</td>
<td>39</td>
</tr>
<tr>
<td>9</td>
<td>Benzene removal by persulfate at 50°C, experiment 8</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>Persulfate disappearance at 32°C, experiment 9</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Persulfate decomposition in 33°C small-column experiments using Site P sand</td>
<td>46</td>
</tr>
<tr>
<td>12</td>
<td>Benzene removal in 30°C small-column experiments using Site P sand</td>
<td>48</td>
</tr>
<tr>
<td>13</td>
<td>Benzene elution curves, experiment 11</td>
<td>52</td>
</tr>
<tr>
<td>14</td>
<td>Persulfate concentrations eluting from columns, experiment 11</td>
<td>53</td>
</tr>
<tr>
<td>15</td>
<td>Benzene losses due to different factors present in column experiments</td>
<td>56</td>
</tr>
<tr>
<td>16</td>
<td>Benzene and persulfate removal during experiment 13</td>
<td>58</td>
</tr>
<tr>
<td>17</td>
<td>Persulfate disappearance, experiment 14</td>
<td>60</td>
</tr>
<tr>
<td>18</td>
<td>Benzene disappearance, experiment 14</td>
<td>62</td>
</tr>
<tr>
<td>19</td>
<td>Cumulative stoichiometric ratio for experiment 14</td>
<td>67</td>
</tr>
</tbody>
</table>
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ABSTRACT

Cleanup of ground water contaminated by organic chemicals that adsorb to aquifer solids may require decades if the water is pumped to the surface to be treated by conventional technologies. In situ treatment means treatment of the contaminant while it is still in the aquifer. It could conceivably take place at the rate at which the treatment can be transported to the contaminant. Although in situ biotic processes appear promising in many aquifer reclamation applications, chemical in situ reclamation using free-radical processes represents a complementary, and in some respects more general, method of destroying organic contaminants in aquifers.

This feasibility study has demonstrated that chemical in situ aquifer reclamation can be feasible in at least some situations. In one experiment, 58 ppm (in the pore water) of benzene, used as the model contaminant, was 62% destroyed when the experiment was terminated at the end of two months. Reactive free radicals were generated from more stable water-soluble reagents which are pumped to the contamination region. The rate of generation of free radicals was not predictable from batch solution kinetic studies, but was accelerated, apparently due to the presence of promoter substances formed in the reaction of free radicals with soil material. The presence of 50 ppm alkalinity had no detrimental effect on the process.
EXECUTIVE SUMMARY

INTRODUCTION

Contamination of ground water by organic chemicals is one of the most widespread environmental problems in the United States. The public has demanded cleanup of contaminated aquifers, and the legislation is in place to enforce those demands. However, removal or destruction of organic contaminants in an aquifer is a difficult task.

Most current cleanup technologies rely on relocating the material to a more secure site, or pumping the water to the surface and treating it by an adaptation of some existing water treatment technology. Many of these "pump and treat" schemes, such as air stripping or activated carbon adsorption, can merely trade one pollution problem for another by transferring the pollutant from one phase (water) to another (gas or solid). This type of cleanup may require decades if the contaminant is strongly adsorbed to the aquifer material.

In situ treatment means treatment of the contaminant while it is still in the aquifer. It would conceivably take place at the rate at which the treatment can be transported to the contaminant. Although in situ biotic processes appear promising in many aquifer reclamation applications, chemical in situ reclamation using free radical processes represents a complementary, and in some respects more general, method of destroying organic contaminants in aquifers. Free-radical processes are capable of converting organic compounds completely to carbon dioxide and water, and are therefore potentially very "clean" treatment processes.

The objectives of the current feasibility study were to determine if this type of reclamation process did show promise of feasibility, and if so, to determine if the free-radical generation and reaction rates were predictable from batch-kinetic data from the free-radical literature. Kinetic control of the reaction will be a major question in actual implementation of the process. It will be necessary to couple hydrogeologic modeling/control with kinetic control in order to transport the radical-generating reagent to the contaminant and to generate the radicals at the appropriate rate.

FINDINGS

From information obtained during a literature survey, the most favorable method of free-radical generation was found to be the generation of sulfate radical anion from potassium peroxydisulfate. This choice was based on availability and economics of starting materials, toxicity of by-products, and probability of success in efficiently generating and utilizing free radicals.
Experiments were run using actual sandy soil taken from a location adjacent to a Superfund site in Illinois, and solutions of benzene as a model contaminant. The rate of free-radical generation in the presence of this soil was found to be much faster than that predicted by solution kinetic data which was reported in the literature and verified in this study. This faster reaction rate is advantageous in the context of the present application since reaction times (and thus expected cleanup times) may be on the order of weeks to months rather than years. In one experiment, benzene was reduced from 58 mg/L in the pore water to 22 mg/L during the 67-day period before the experiment was terminated. At the end of the experiment there was still a free-radical-generating reagent present, and benzene destruction was still occurring. Destruction of benzene proceeded at the same rate in a parallel experiment that was identical except for the addition of 50 ppm of alkalinity.

Free-radical generation was catalyzed in the presence of the sandy soil used. Apparently, promoters are produced by reaction of free radicals with some material (presumably organic matter) in the soil. The reaction was much slower in soil from which the organic matter has been removed by prior oxidation. This implies that radical-generation kinetics may be specific to the soil used.

CONCLUSIONS

1) Abiotic oxidative in situ degradation of organic pollutants, using sulfate radical anion generated from persulfate, appears to be feasible in some cases.

2) Below about 50°C the kinetics of the radical-generating reaction appear to be dominated by the nature of the promoters present in, or generated from, the natural organic material, as well as perhaps the pollutant degradation products. This promoted reaction was at least an order of magnitude faster than the thermal reaction. Since it is probably system-specific, it must presently be determined by experiment until it is understood well enough to be modeled.

3) Persulfate decomposition, and thus radical generation, is in general faster in the presence of natural sand than in the presence of the same sand after the organic matter has been removed.

4) The equivalent of 50 mg/L of alkalinity had no detrimental effect on the process, even though bicarbonate is a known free-radical scavenger.

RECOMMENDATIONS

Several aspects of this work should be investigated further. In particular:
1) More needs to be known concerning the nature of the promoters, both those present in the natural organic material and those formed as organic substrate reacts.

2) Further testing is needed, using actual soil/sands and ground water rather than synthetic ground water.

3) The role of adsorbed versus dissolved substrate should be carefully considered.

4) Development and verification of a kinetic model of the process is needed, in order to better understand and optimize conditions for the process.

5) To the extent possible, the products of the reaction should be investigated in order to better understand their competitive and catalytic function. This may be better done by high pressure liquid chromatography methods than by coupled gas chromatography/mass spectrometry because the products are probably not particularly volatile or stable.
AQUIFER RECLAMATION

Contamination of ground water by organic chemicals is currently one of the most widespread environmental problems in the United States, and one that is very much in the public eye. The public has demanded the cleanup of contaminated aquifers that contain potable water, and legislation is in place to enforce those demands. However, removal or destruction of the contaminants is a very difficult task. The broad subject of aquifer reclamation has been covered in an extensive review by Knox et al. (1986), but it is a characteristic of this fast-moving field that the review was in many respects outdated by the time it was published.

In the past, "cleanup" has frequently consisted merely of removing source material at the surface and relocating that material to a "secure" landfill. In some cases, "pump and treat" (PAT) technology has been used to clean the ground water. In this type of treatment, water is pumped to the surface and then treated with a conventional technology, such as air stripping for volatile organic compounds, or activated carbon adsorption. A major drawback to all of the above technologies (i.e., relocation, stripping, and adsorption) is that after treatment, a pollution problem still exists. A method of absolute cleanup is needed, which does not simply transfer the problem from one place to another.

IN SITU TREATMENT

In situ treatment of ground water means treatment of the ground water without removing it from the ground. An organic compound traveling in a ground-water aquifer generally moves more slowly than the formation water, due to adsorption of the compound to the stationary formation material (Jury et al., 1983). The extent of retardation varies greatly with the polarity and hydrophobicity of the solute (Sutton and Barker, 1985; Griffin and Chou, 1980); the organic content of the solid aquifer material (Schwarzenbach and Westall, 1981; Briggs, 1981; Karickhoff et al., 1979); and the extent to which sorption of the solute to moving particulate or macromolecular material occurs (Gschwend and Wu, 1985). In the case of hydrophobic solutes, movement of the major portion of a contaminant may be very slow relative to the ground water, with only a small amount of the solute partitioning the aqueous phase (Griffin and Chou, 1980). This is an unfavorable
situation for "pump-and-treat" (PAT) rehabilitation schemes, since even with artificially enhanced gradients over small regions it may take decades to desorb and remove all of the organic compound. In situ aquifer rehabilitation methods treat the contaminant while it is in place in the aquifer. Thus, a major advantage of in situ rehabilitation methods over PAT schemes is that the treatment process is transported to the concentrated contaminant at the velocity of the ground water.

A great deal of work has been done on biotic in situ treatment methods (Wilson and Wilson, 1985; Bouwer et al., 1981) for the removal of organic compounds from ground water. The major problem in many cases is the lack of an adequate oxygen supply for aerobic removal processes to occur to an appreciable extent. Attempts to overcome this problem include aeration of water pumped into the formation (Smith et al., 1984) and/or addition of substances such as hydrogen peroxide, which later release oxygen in the aquifer (Brown and Norris, 1984). Much of the development work on biotic processes has been of a commercial nature, with proprietary information not being published in the open literature for general use.

Some drawbacks to biotic reclamation are that the indigenous bacteria may require long adaptation times for some organic compounds, may be killed by the organic compound, or simply may not degrade the compound under the existing conditions. The concept of introducing foreign or genetically altered bacteria should await careful scrutiny before being tried in the field. Nonetheless, biological in situ reclamation remains an attractive prospect for aquifer reclamation in the future.

Although they represent an important and complementary alternative to biotic in situ reclamation, abiotic processes have received considerably less attention than has biodegradation. Many abiotic processes have focused on inorganic substances, or on immobilization by precipitation (Hallberg and Martinell, 1976) rather than on actual cleanup. It is desirable, however, to develop cleanup technology which has some general applicability to broad classes of toxic organic compounds which may be refractory to biological degradation. Some above-ground unit processes, such as the combination of ozone and ultraviolet light (Peyton et al., 1982; Peyton and Smith, 1986; Glaze et al., 1980, 1982, 1984) are highly effective in destroying virtually any organic compound in water. These processes owe their treatment power to the generation of very highly oxidizing species such as hydroxyl radical. This radical can abstract either a hydrogen atom or an electron from any organic compound, but does not react with water in any consumptive manner. Such a powerful reagent would be of value in the rapid destruction of a wide variety of organic pollutants in ground water. However, the very property of reactivity makes it impossible to directly transport these substances to the reaction site in an aquifer.
As photolytic generation of these species in ground water is not practical, other means must be found by which the "timed release" of these or other radicals can be achieved.

Hydroxyl radical is a member of the family of species called oxy-radicals. These radicals are potentially very useful for the destruction of organic compounds in water. They owe their reactivity to the fact that they are "open shell" species, that is, they do not have a complete octet (closed shell) of electrons in their outer shell. Thus, removal of an electron from hydroxide ion (I) generates hydroxyl radical (II):

\[
\begin{align*}
\text{H}_2\text{O}^- & \xleftrightarrow{\text{e}^-} \text{H}_2\text{O}^+ \\
\text{H}_2\text{O}^- & \xrightarrow{\text{e}^-} \text{H}_2\text{O}^+ \\
\end{align*}
\]

The driving force to complete the electron octet around the oxygen atom is even stronger than that for carbon atoms, so oxy-radicals participate in addition, electron transfer, and hydrogen atom abstraction reactions which transfer the "hole" in the outer shell to a carbon atom, e.g.,

\[
\begin{align*}
\text{CH}_3\text{OH} + \cdot\text{OH} & \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
\end{align*}
\]

These reactions proceed until the organic molecule is so "oxygenated" at a particular site that it becomes unstable, whereupon it decomposes to form carbon dioxide and a smaller organic molecule. Eventually, all organic compounds are transformed to carbon dioxide by this process.

Processes of this type are in general energetically favorable for reaction of most oxy-radicals with most carbon compounds. In some cases the reaction may not proceed at a rate which is fast enough to be of value in a water treatment process. The study of the rates at which chemical reactions proceed is called chemical reaction kinetics. This subject warrants some discussion, since the relative rate of competing reactions is often the determining factor in the viability of oxy-radical treatment processes.
CHEMICAL REACTION KINETICS

Since chemical reaction kinetics is the basis for many arguments in this report, the fundamental concepts are summarized below. This information is discussed in greater detail in any basic kinetics text, such as that by Moore and Pearson (1981).

First- and Second-Order Reactions

Most elementary reaction steps are either first- or second-order. A first-order reaction is one in which the reaction rate is proportional to the first power of the concentration of the reactant:

\[
\text{Rate} = \frac{d[C]}{dt} = -k[C]
\]

where \([C]\) is the concentration of the reactant, and \(k\) is called the first-order rate constant, which has units of \(\text{time}^{-1}\). Reactions which are first-order are generally those which do not require the participation of another reactant. The most important example of a first-order reaction for the present application is a unimolecular decomposition:

\[
A \rightarrow \text{products}
\]

Similarly, the most important example of a second-order reaction is when two species, \(A\) and \(B\), react to form products:

\[
A + B \rightarrow \text{products}
\]

In this case, the reaction rate is proportional to the concentration of both reactants, reflecting the fact that increasing the concentration of either reactant increases the probability of an encounter between them and thus of reaction. The corresponding rate expression is

\[
\text{Rate} = \frac{d[C_A]}{dt} = \frac{d[C_B]}{dt} = -k[C_A][C_B]
\]

In this expression, \(k\) is the second-order rate constant for the reaction between \(A\) and \(B\), and usually has units of \(\text{L} \cdot \text{mol}^{-1} \cdot \text{time}^{-1}\). It should be noted that while equation 6 is second-order overall, it is first-order in each component, \(A\) and \(B\).
Almost all elementary reaction steps of interest are either first- or second-order. The complex or fractional orders sometimes seen in physical chemistry textbooks are the result of determining a reaction order for a chemical conversion which is actually a series of reactions.

It is sometimes convenient to design laboratory experiments such that one component of a second-order reaction is present in great excess, so that its concentration does not change significantly during the course of the reaction. In this case, the (constant) concentration of that component (e.g., B) can be grouped with the second-order rate constant to form a pseudo-first-order rate constant (k'), by analogy with equation 3:

\[
\text{Rate} = \frac{d[C_A]}{dt} = -k[C_A][C_B] = -k'[C_A]
\]

(7)

It is sometimes convenient to analyze kinetic data graphically. Integration of equation 3 from \(C = C_0\) at \(t = 0\) to some concentration \(C\) at time \(t\) gives

\[
C = C_0e^{-kt}
\]

(8)

Taking the natural logarithm of both sides yields

\[
\ln C = \ln C_0 - kt
\]

(9)

or

\[
\ln \left(\frac{C}{C_0}\right) = -kt
\]

(10)

Thus, a plot of \(\ln C\) or \(\ln(C/C_0)\) versus \(t\) should be a straight line with slope equal to \(k\). Equation 10 is used if the value of \(C_0\) is well known. Otherwise, equation 9 can be used to estimate \(C_0\).

Integration of the second-order equation (6) gives

\[
(B_0 - A_0)^{-1} \ln(A_0B/B_0A) = kt
\]

(11)
where \( A_0 \) and \( A \) are the concentrations of species \( A \) initially and at time \( t \), etc. Other expressions have been developed as well, some of which are specific to the means of reactant or product measurement, such as spectroscopic methods (Moore and Pearson, 1981). The use of pseudo-first-order conditions can simplify data analysis for second-order reactions.

The utility of the kinetic approach is that the rate "constants" really are constant, to the extent that they can be tabulated in the literature for use by other investigators. One check that investigators using kinetic methods frequently employ is to run some experiments under conditions identical to those used by previous investigators, in order to compare reaction rate constants before extending the work to untried systems. Agreement of the data with the literature gives investigators confidence that their results are representative of the system they are trying to study, and are not the result of an artifact or catalytic reagent impurity.

CHEMICAL IN SITU AQUIFER RECLAMATION USING OXY-RADICALS

Selection of Candidate Reagents for In Situ Generation of Oxy-Radicals

In order to narrow the possibilities for candidate reagents for oxy-radical generation, it was convenient to start with known oxy-radicals and eliminate inappropriate species. Oxy-radicals were selected from the larger set of all radicals, since they revert to common anions upon gaining an electron, i.e., upon acting as an oxidizing agent, and because they react with carbon compounds in general. The choice was further narrowed to the anions of the first- and second-row nonmetals for reasons of toxicity and cost of the reagents. These elements are indicated in Table 1. The corresponding radical anions are given in Table 2. Of these, \( \text{H}_2\text{BO}_3^- \) was not found in the course of the literature survey, and in any case boron and nitrate would be undesirable solutes to place in potable aquifers. Carbonate and silicate radical anions are too unreactive with most organic compounds (Kuzmin, 1972; Ross and Neta, 1979) to be of much value in aquifer reclamation, although carbonate radical anion has been shown to be quite reactive with certain types of compounds such as anilines (Larson and Zepp, 1986), indole, and tryptophane (Chen and Hoffman, 1974). In actual application of oxy-radicals to in situ reclamation, carbonate and perhaps silicate radical anions will be formed by the action of stronger oxy-radicals on bicarbonate and silicate which are present naturally. Therefore, their chemistry is of interest in the present ground-water application, even though they were eliminated as reagent candidates. The complications introduced by their presence are currently being studied at the Illinois State Water Survey (Peyton, 1986).
Table 1. First- and Second-Row Nonmetals Plus the Halogens (a)

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O(b)</th>
<th>F</th>
<th>Ne</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>Ar</th>
<th>As</th>
<th>Se</th>
<th>Br</th>
<th>Kr</th>
<th>I</th>
<th>Xe</th>
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</tr>
</tbody>
</table>

(a) Symbols in box represent those that may be of interest.
(b) The anions of oxygen are unstable in water, except for \(-\text{OH},\) which is taken into consideration as a pH effect.
Table 2. Oxy-Radicals of First- and Second-Row Nonmetal Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxy-Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>( \cdot H_2BO_3 ) (a)</td>
</tr>
<tr>
<td>Carbon</td>
<td>( \cdot HCO_3/\cdot CO_3^- )</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>( \cdot NO_3 )</td>
</tr>
<tr>
<td>Oxygen</td>
<td>( \cdot OH, O^-, O_2, O_2^-, O_3, O_3^- )</td>
</tr>
<tr>
<td>Silicon</td>
<td>( \cdot SiO_3^- )</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>( \cdot H_2PO_4/\cdot HPO_4^-/\cdot PO_4^{2-} )</td>
</tr>
<tr>
<td>Sulfur</td>
<td>( \cdot SO_3^-/\cdot SO_4^- ) (b)</td>
</tr>
</tbody>
</table>

(a) Although perborate, \( BO_3^- \), exists, it is not known whether \( H_2BO_3 \) does.
(b) There are also other sulfur oxy-radicals corresponding to other oxidation states of sulfur.
Of the oxygen radicals, $O_3$ and $O_3^-$ are too short-lived (Hoigne and Bader, 1976; Bühler et al., 1984) to survive the travel times required for in situ reclamation; $O_2$ and $O_2^-$ are too unreactive (kinetically slow) (Bielski et al., 1985) to be of practical importance; and $O^-$ exists only at very high pH values (Farhataziz and Ross, 1977), leaving hydroxyl radical, $\cdot OH$, as a candidate.

The phosphorus radical anions are reactive enough (Maruthamuthu and Neta, 1977; Ross and Neta, 1979) to be of value in destroying organic compounds, but no suitable method of generating them in situ has been found. Even the use of a more powerful radical is inefficient (Maruthamuthu and Neta, 1977). The usual methods of generating oxy-radicals in the laboratory are pulse-radiolysis (Maruthamuthu, 1985) or flash photolysis (or catalyzed decomposition) (Huber and Hayon, 1968) of the corresponding peroxy compound. In the case of the phosphate radical anion, the peroxy compound was not found to be available from laboratory supply houses, but is said (Maruthamuthu and Neta, 1977) to be available from FMC Corporation, a major industrial producer of hydrogen peroxide. However, it has usually been produced electrolytically in laboratory studies.

Of the sulfur radicals, sulfite is a reducing agent and would thus counteract the desired effect, i.e., oxidation. Sulfate radical anion is, however, a good candidate species since, in addition to being a powerful oxidizing radical, acting by electron transfer (Eberhardt, 1981; Neta et al., 1977), hydrogen abstraction (Davies et al., 1985), and radical addition, it is also easily produced from a commercially available peroxy salt, potassium peroxodisulfate (Ross and Neta, 1979).

In summary, two oxy-radicals, hydroxyl radical ($OH$) and sulfate radical anion ($SRA$), were selected as candidate reagents, based on oxidizing power, commercial availability of starting material, and toxicity of reaction by-products.

Possible Means of Generating Candidate Oxy-Radicals In Situ

Most of the means commonly used to generate oxy-radicals in the laboratory are unsuitable for in situ generation. The following sections discuss the possible means of in situ radical generation which might have promise, and address their feasibility.

**Hydroxyl Radical.** Practically all means of hydroxyl radical generation which are not driven by radiation or photochemical reactions utilize peroxides as the radical precursor. Almost all peroxide-based methods are metal-catalyzed, involving oxidation of the metal:

$$M^{+n} + H_2O_2 \rightarrow M^{+n+1} + ^{-}OH + \cdot OH$$  \hspace{1cm} (12)
Although there are a myriad of metal-catalyzed reactions of this type (Sheldon and Kochi, 1981), most can be eliminated for purposes of in situ reclamation on the basis of the toxicity of the metal catalyst. Two notable exceptions are the titanium (III) and iron (II) reactions.

The product of the titanium reaction, Ti(IV), is converted to titanium dioxide in aqueous solution (Cotton and Wilkinson, 1962). Titanium dioxide is presently the most commonly used commercial white paint pigment, largely because of its lack of toxicity. Since the metal in its reduced state is actually not a catalyst but is consumed in the reaction, stoichiometric rather than "catalytic" quantities would be required, so that the cost would be prohibitive.

The cost of laboratory-grade (not reagent-grade) Ti(III) chloride was found (Alfa Products, 1982) to be twice the cost of Fe(II) chloride, which was in turn almost three times the cost of Fe(II) sulfate. The cost of titanium(III) sulfate was not found. There are, however, even worse problems with the use of titanium in this regard. Dry TiCl₃ is pyrophoric (ignites spontaneously) in air. Furthermore, the product of oxidation followed by hydrolysis, TiO₂, is quite insoluble in water and would thus tend to block the pores of the aquifer material, reducing its permeability.

The other candidate metal ion, iron (II), is attractive because of its low cost and relatively low toxicity. The iron (II)/hydrogen peroxide system is known as Fenton's reagent, and has been studied extensively (Walling, 1975). Despite the volume of papers which have been published on Fenton's reagent, there was disagreement as to the mechanism of the reaction as lately as 1975 (Walling, 1975, ref. 16), due to the complexity of the reaction. This complexity makes the reaction more difficult to control and less predictable under poorly defined circumstances.

A second rather serious flaw of Fenton's reagent is the low efficiency of conversion of organic compounds, due in part to the fact that ferrous ion must be regenerated by reaction of iron (III) with intermediate radicals (R•). In addition, hydroxyl radical may react with iron (II):

\[
\begin{align*}
H₂O₂ + Fe^{+2} & \rightarrow Fe^{+3} + \cdot OH + \cdot OH & (13) \\
R• + Fe^{+3} & \rightarrow R^+ + Fe^{+2} & (14) \\
Fe^{+2} + \cdot OH & \rightarrow Fe^{+3} + \cdot OH & (15)
\end{align*}
\]

These problems are particularly serious in the case of aquifer restoration, where the concentration of organic target compound may be on the order of millimolar or less.
Finally, in near-neutral solutions, iron forms a gelatinous precipitate of the hydrous hydroxide, which would block pores in the aquifer material.

Hydroxyl radical can also be generated by the reaction of sulfate radical anion (SRA, discussed in the next section) with water or hydroxide ion:

\[
\cdot\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot\text{OH} \quad (16)
\]

\[
\cdot\text{SO}_4^- + \cdot\text{OH} \rightarrow \text{SO}_4^{2-} + \cdot\text{OH} \quad (17)
\]

However, \(k_{16}[\text{H}_2\text{O}] < 3 \times 10^3 \text{ s}^{-1}\) and \(k_{17} = 6.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}\) (Hayon et al., 1972), so that the pseudo-first-order rate constants for SRA are \(k_{16}[\text{H}_2\text{O}] = < 3 \times 10^3 \text{ sec}^{-1}\) and \(k_{17} \times 10^{-14} + \text{pH} = 6.5 \times 10^7 = \text{sec}^{-1}\) at \(\text{pH} \leq 8\) or below. Typical SRA rate constants for reaction of SRA with organic compounds are in the range of \(k \sim 10^7 \text{ M}^{-1}\text{sec}^{-1}\), so that for millimolar organic concentrations, the pseudo-first-order rate constant is \(k \sim 10^7 \text{ M}^{-1}\text{sec}^{-1} \times 10^{-3} \text{ M} = 10^4 \text{ sec}\). Comparison of this value to those of hydroxyl radical generation by equations 16 and 17 indicates that the majority of sulfate radical anion formed would itself react directly with organic compounds rather than going through the intermediate hydroxyl radical. Reactions of sulfate radical anion are discussed more fully in the next section.

In summary, the most suitable means of in situ hydroxyl radical generation appears to be Fenton's reagent. It would be difficult, however, to control and predict the behavior of this complex system. In addition, relatively large quantities of reagents would be required, due to the low yield of usable hydroxyl radicals, and precipitation of the iron could decrease the permeability of the aquifer and interfere with treatment.

**Sulfate Radical Anion (SRA).** This oxy-radical is almost as reactive as hydroxyl radical, and slightly more selective between substrates. Although its reaction mechanisms are different in some cases from those of hydroxyl radical (Walling et al., 1978), the products are frequently the same (Maruthamuthu, 1985).

SRA reacts by hydrogen abstraction (equation 18), electron transfer (equation 19), and addition to unsaturation (equation 20):
Further reactions of the radical species formed in equations 18-20 are shown in equations 21 (Rabani et al., 1974), 22 (Gilbert et al., 1974), and 23 (Walling et al., 1978).

\[
\cdot\text{CH}_2\text{O} + \text{O}_2 \rightarrow (\cdot\text{O}_2 + \cdot\text{CH}_2\text{O}) + \text{H}^+ + \text{CH}_2\text{O}
\]

\[
\cdot\text{CH}_2\text{OH} + S_2O_8^{2-} \rightarrow (\cdot\text{CH}_2\text{OH} + S_4\text{O}_6^{2-} + \cdot\text{SO}_4^-)
\]

The final product in equation 23, phenol, can further be polymerized by oxidative coupling (Chrostowski et al., 1983) to form dark-colored humic-like materials which may precipitate from solution as their molecular size increases.

Sulfate radical anion is the easiest to generate of the oxy-radicals considered in this project. It is conveniently produced from commercially available potassium peroxodisulfate (commonly called persulfate) either thermally (equation 24) or by metal (M) catalysis (equation 25).

\[
S_2O_8^{2-} \rightarrow 2 \cdot\text{SO}_4^-.
\]

\[
M^{2+} + S_2O_8^{2-} \rightarrow M^{3+} + \cdot\text{SO}_4^- + \text{SO}_4^-.
\]

The thermal reaction has two components, one of which is acid-catalyzed:

\[
k_{11} = k_a[S_2O_8^{2-}] + k_b[S_2O_8^{2-}][\text{H}^+] = (k_a + k_b[\text{H}^+])[S_2O_8^{2-}]
\]

where, for example, \(k_a = 0.112\) sec\(^{-1}\), and \(k_b = 1.18\) M\(^{-1}\)sec\(^{-1}\), at 100°C (Kolthoff and Miller, 1951; Goulden and Anthony, 1978). Substitution of \(\text{H}^+ = 10^{-\text{pH}}\) into equation 26 shows that the pH of the solution must be 4 or lower for the acid-catalyzed component to be important. Both Kolthoff and Miller (1951) and Goulden and Anthony (1978) reported that
the reaction proceeded anomalously fast in the presence of phosphate buffer, but they offered no explanation. The explanation for this phenomenon is that phosphate ion itself can serve as a proton source for the acid-catalyzed reaction, so that phosphate at 10^{-2} M swamps the effect of H_3O+ at 10^{-4} M (i.e., at pH 4). The implication is that if during the course of oxidation of organic compounds, hydrogen ions or strongly protic compounds are produced, the reaction may be autocatalyzed, i.e., it may pick up speed. Similarly, if electron-donating compounds are produced they can function similarly to the metal ion in equation 25.

As discussed in a previous section for hydrogen peroxide, "metal catalysis" may not actually be catalysis if the reduced form of the metal is not regenerated. The same problems apply to metal-catalyzed peroxodisulfate reactions which were raised with respect to hydrogen peroxide. One notable exception is the well-known catalysis by silver ion. The literature (e.g., House, 1962) indicates that silver is oxidized to either Ag(II) or Ag(III) by a reaction analogous to that in equation 12. Since those higher oxidation states of silver are not very stable in aqueous solution, Ag(I) is regenerated and can thus be considered catalytic. Silver is, of course, too expensive and too toxic to be used in the present application.

The rate of thermal decomposition of persulfate to produce SRA at ambient temperatures was estimated by extrapolation of the plot of log k vs 1/T, given in Figure 2 of Goulden and Anthony (1978). The resultant value of k_a was about 10^8.2 s^{-1} at 20^\circ C, which, as calculated from equation 10, gives an estimated half-life of 1270 days. It was anticipated that catalytic effects of other species present would decrease this half life to a value more suitable for in situ radical generation.

In summary, sulfate radical anion, generated by thermal or catalytic decomposition of peroxodisulfate salts, was chosen as the most suitable oxy-radical for chemical in situ aquifer reclamation. Though slightly less reactive than hydroxyl radical, it is more easily generated, and easier to control because of a simpler reaction mechanism. In addition, its by-products were judged to be less detrimental to a typical aquifer than those of other candidate reagents.

**Selection of Model Organic Substrate**

Some criteria for the model organic substrate were that it:

1) be representative of the type of compound which would be of concern if detected in an aquifer,

2) have intermediate water solubility/hydrophobicity, so that it can move at a reasonable rate in flow experiments but can still be retarded by sorption interactions with the solid phase,
3) not be too easily oxidized, so as to be stable in the laboratory and provide a reasonable test of in situ techniques,

4) not be sorbed so strongly to the solid material that recovery for analysis is difficult,

5) be easily analyzed by a simple extraction/chromatography procedure, using either flame ionization (FID) or electron capture detection (ECD), to allow maximum sample throughput and thus maximum experimental replication,

6) generate by-products which cause a minimum of complication by their own chemistry,

7) be nontoxic enough to be safely handled without access to a high-hazard laboratory.

Item 1 would indicate organic solvents; halogenated compounds such as pesticides, PCB's, DCD's, etc.; and aromatic hydrocarbons including polynuclear aromatic hydrocarbons (PNAs). Aliphatic hydrocarbons were eliminated on the basis of their lower toxicity and water solubility. Items 2 and 4 eliminate PCB's, many pesticides, and the higher PNAs. Item 3 essentially eliminates PNAs larger than naphthalene. Item 5 eliminates many other pesticides. Chlorinated solvents were eliminated on the basis of item 6, since the oxy-radical chemistry of organo-halogen compounds is much less understood than that of compounds composed of carbon, hydrogen, and oxygen. This chemistry can be complicated by the production of halogen radicals, as was seen in early studies of photolytic ozonation (Glaze et al., 1980). Halogenated dibenzodioxins and dibenzofurans are, of course, eliminated by item 7.

Benzene is an organic compound which meets all of the above criteria. It occurs in gasoline and as a solvent, and is frequently found in cases of ground-water contamination. It has an intermediate retardation factor (Jackson et al., 1985) with an octanol-water coefficient of $\log K_{ow} = 2.04$. It is not easily oxidized, nor is it very reactive with carbonate radical anion (Ross and Neta, 1979). Benzene is relatively easy to analyze, using gas chromatography, and can be safely handled using normal laboratory precautions. Finally, its free-radical chemistry is well understood. Therefore, despite some practical problems with volatility, benzene was chosen as the model substrate.
SECTION 2

EXPERIMENTAL PROCEDURES

SUMMARY OF EXPERIMENTS PERFORMED

Due to the exploratory nature of this work, the results in the next section are described chronologically by experiment. Despite the drawbacks to that format, in this case it is appropriate, since each experiment builds on the results of the previous ones. It is therefore helpful at this point to summarize the experiments performed.

The first seven experiments were kinetic runs at elevated temperatures in order to have reasonable experiment durations while the details were being worked out. It was discovered that a suitable analytical method for persulfate under the desired conditions had still not been found. Although some interesting information was obtained from experiments 1-6, it was not until experiment 7 that the analytical method was worked out.

Beginning with experiment 8, experiments were run at lower temperatures in order to extend our knowledge of the reaction rate constants already reported by Goulden and Anthony (1978) and Kolthoff and Miller (1951), toward temperatures which would exist under ground-water reclamation conditions. At the same time, other variables were introduced, such as the presence of sand and oxygen (experiment 8); sand, buffer, and alkalinity (experiment 9); and natural sand from a location adjacent to a Superfund site, compared to factory (Ottawa) sand (experiment 10). At this point two experiments (11 and 12) were run to determine where benzene losses were occurring and to further delineate the effects of alkalinity. Experiment 13 was an ill-fated attempt to simulate a flow experiment while adding influent batch-wise. Experiment 14 was a long-term batch experiment at near-ambient temperatures, using natural sand and alkalinity close to a reasonable value for water from a sandy aquifer.

MATERIALS

Sand

Ottawa sand was used in some of the batch and column experiments. This sand was obtained from the Ottawa Industrial Sand Company at Ottawa, Illinois and was in the size range of 50 to 70 mesh. It originates from a St. Peter sandstone deposit with a rounded-shape grain and is composed of 99% quartz. After being hydraulically mined, it is syphoned in a slurry to the surface where it is washed to remove the
clays (primarily kaolinite), dried, and sized. Water used in the mining process is recycled after being pumped into an old mine for precipitation of solids, with the clear water then being drawn up to a surface settling pond for reintroduction later in the mining cycle.

Natural sand material was obtained from the surface of a field in an area adjacent to a federal Superfund site in Illinois. This site, designated Site P, has been contaminated with solvents and paint pigments and was of interest because of its potential suitability as a demonstration site for the application of the present research to a real-world situation. Upon return to the laboratory the sand was sieved by means of a large mesh screen (plastic window screen) in order to remove large particles, rootlets, insects, etc., and was then air dried.

Reagents

Both the potassium persulfate, $K_2S_2O_8$, and benzene used in the course of the experiments were Fisher Scientific ACS certified grade. Sodium bicarbonate was Baker reagent grade, and phenanthroline monohydrate was from J. T. Baker Chemical Company. Tap water, obtained from in-house deionized (DI) water lines, was further purified by passing it through a DI polishing unit in early experiments, and a Barnstead Nano-pure(R) system containing carbon adsorption, high-capacity DI, and polishing DI cartridges.

Apparatus

Glassware. Eight-milliliter clear disposable mini-vials (Research Products International, Mt. Prospect, Illinois), clear 16.5-mL vials (Supelco, Inc., Bellefonte, Pennsylvania), and Amber 40-mL vials (Pierce Chemical Company, Rockford, Illinois) were used as reaction vessels and for sampling. In batch experiments with sand, 250 mL capacity Boston round amber bottles (American Scientific Products, McGaw Park, Illinois) were used. All vials and bottles were fitted with one-hole screw caps which had Teflon-faced silicone septa.

Two sizes of chromatographic columns, 450 mm in length x 25 mm i.d. and 1200 mm in length x 50 mm i.d. (Ace Glass, Inc., Louisville, Kentucky) were used. The body of the column was borosilicate glass and was fitted with internal threading at the ends which accommodated the externally threaded Teflon end fitting. Each end fitting came equipped with an FETFE o-ring and a filter disc. The disc, composed of polyethylene, had 100 micrometer pores for support of the column bed. The adapter had a 1/4 - 28 UNF 2B internal thread which would accept the Teflon tubing secured by the flange-free fittings (Alltech Associates, Inc., Applied Science Labs, Deerfield, Illinois).
For mobile phase introduction, each 1200-mm column was connected to a model RHS YOCKC Lab Pump Jr. (Fluid Metering, Inc., Oyster Bay, New York). A Rainen Type 50 4-way Teflon rotary valve fitted with a sample loop, which allowed syringe loading of various chemicals (i.e., KCl or benzene), was located between the pump and the column.

Water Bath. Experiments run at temperatures greater than 50°C utilized a Polytherm constant temperature Water Bath (Science/Electronics, Inc., Dayton, Ohio). During such tests the water surface was covered with Styrofoam spheres to reduce evaporation.

Constant-Temperature Box. In order to accommodate large columns during the tests requiring elevated temperatures (30°C - 50°C), a constant-temperature box was constructed. It consisted of a 4' x 6' plywood box divided vertically into two compartments. All doors, sidewalls, ceiling, and floor were covered by 3/4" Corning fiberglass insulation. Each of the two compartments was fitted with a Y.S.I. Model 63RC Temperature Controller (Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio) which controlled an infrared heat lamp. Constant air movement was assured by use of a Dayton recirculating blower (Stock #4C442, W. W. Grainger, Inc., Decatur, Illinois). Because of the dual control systems, each compartment could be adjusted independently of the other. Temperature records were kept manually by reading a calibrated thermometer and occasionally by insertion of an automatic temperature recorder (Science Associates, Inc., Princeton, New Jersey).

METHODS

Analytical Procedures

Persulfate Analysis. Several methods were tried for persulfate analysis before a suitable method was developed. Problems encountered were apparently due to interferences resulting from the presence of organic material in the sample. The method finally devised to determine persulfate concentrations consisted of a combination of several other analytical procedures.

If organic material was present, the original sample obtained from vials, bottles, or column experiments was passed through Alltech Maxi-Clean Cartridges containing 300 mg of bonded-phase C18 packing, in order to remove organic substances and/or particulates originating from humic material or reaction by-products of the substrate. The persulfate in solution was then reacted with ferrous iron, according to the method of Kolthoff et al. (1941). An aliquot of the remaining solution was then analyzed colorimetrically for ferrous ion, according to the method of Parker (1953). Blanks were run, using deionized water in place of sample. The initial concentration of ferrous ion (blank value), minus the final concentration of Fe²⁺ in the sample, gave the
amount of Fe(II) consumed by persulfate. This value was used to determine persulfate concentrations on the basis of the fact that ferrous iron reduces persulfate to sulfate on a 2:1 molar ratio:

$$\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2 \text{SO}_4^{2-} + 2 \text{Fe}^{3+}$$  \hspace{1cm} (27)

**Benzene Determinations.** A Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector (F.I.D.), coupled to a Hewlett Packard 3390A reporting integrator, was used for benzene determinations. An SP-2100 column was used with chromatographic conditions being determined by the extraction procedure. When methylene chloride was used as the extraction solvent, and octane as the internal standard, temperatures were set at 200°C for both injector and detector with the column at 40°C. When using decane as the extraction solvent with octane as the internal standard, temperature programming was necessary. The initial temperature was 100°C for 2 minutes, during which time both analyte and internal standard were eluted from the column. This was followed by programming at 40°C/min to the final temperature of 160°C, and holding for three minutes, in order to drive off the higher boiling extraction solvent. Injector and detector temperatures were 190°C. Carrier gas flow in both cases was 20 mL/min.

**Preparation**

**Sand Preparation.** Ottawa sand was washed three times with deionized water prior to use. It was dried overnight in a 105°C oven and allowed to cool to room temperature prior to dry packing in bottles or columns. Sand prepared in this manner was used in experiments 8, 9, and 10.

Native sand removed from an area adjacent to Site P was subjected to an upflow washing process (elutriation) to remove fines, after being sieved and dried. Removal of these fines helped to reduce analytical problems due to interferences. During a previous experiment, the fines were found to suspend in the liquid and cause handling and plugging difficulties as well. This washing was not expected to seriously bias the experiments for the purpose of the feasibility study, but rather to render the sand more like the actual aquifer material. Sand to be washed was placed in a 3-foot-long, cylindrical glass column with a 6-inch inner diameter and a solid metal closure for the bottom. A second metal plate with two openings was mounted on the top of the column. A 1/4-inch stainless steel tube inserted to within 4 to 6 inches of the bottom served as the water inlet. The second opening in the stainless steel plate served as the outlet for water and soil fines. Sand was washed with tap water for 1-1/2 hours with the inlet tube in one position. The plate was then rotated 180° and flow was resumed for an additional 1-1/2 hours. During this time, considerable amounts of dark-colored fine material was washed from the sand. The
4-foot (1200-mm) columns utilizing this sand were packed wet and were used in experiments 11, 12, 13, and 14. This sand is referred to as "rinsed" Site P sand.

In only one instance, experiment 10, was the Site P sand handled differently. After being sieved and dried, the sample was heated in 0.1 M K$_2$S$_2$O$_8$ for 30 minutes at 70°C to destroy the organic material which was present. The sand was then rinsed a minimum of twenty times with deionized water and dried overnight at 180°C. A summary of the sand preparation methods and the experiments is included in Table 3.

Preparation of Apparatus

The vials which were used included 8-mL clear disposable, 15-mL clear screw cap, and 40-mL amber screw cap varieties. These were washed with Alconox soap and rinsed three times in tap water, followed by three rinses in deionized (DI) water. Glassware was then allowed to air dry.

Amber bottles with a 250-mL capacity were presoaked in 0.1 M K$_2$S$_2$O$_8$ at an elevated temperature of 70°C for a 30-minute period. This procedure was followed by a minimum of twenty rinses with DI water. Bottles were then inverted, allowed to air dry, and capped with foil until needed. During experiments all vials and bottles were capped with one-hole screw caps fitted with Teflon(R)-lined silicone septa in order to prevent outgassing of volatiles or airborne contamination and yet provide for sample removal by syringe.

Chromatographic columns with dimensions of either 450 mm x 25 mm diameter or 1200 mm x 50 mm diameter were used for the sand experiments. They were washed with Alconox, rinsed with tap water, finally rinsed repeatedly with DI water, and allowed to air dry. The smaller columns were dry-packed with the appropriate sand. These columns were used in experiments 9 and 10. The larger columns were partially filled with water, then packed by adding portions of a sand slurry which was allowed to settle. A small layer of the slower-settling dark fines could be seen at the top of each sand portion, throughout the length of the column. After packing the columns they were conditioned for periods in which 5 to 20 pore volumes (approximately 1000 mL each) of water were eluted through each column in upflow, prior to commencement of experiments, to aid in air bubble removal. The 1200-mm columns were utilized in experiments 11, 13 and 14. All columns were equipped with PTFE end fittings which incorporated a porous polyethylene frit for bed support.
Table 3. Methods of Sand Preparation

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Temp, °C</th>
<th>Location</th>
<th>Sand type</th>
<th>Process</th>
<th>Container</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>50°</td>
<td>Box</td>
<td>Ottawa</td>
<td>Washed 3x with D.I. H₂O; dried at 105°C overnight</td>
<td>250 mL bottles</td>
</tr>
<tr>
<td>9</td>
<td>30°</td>
<td>Box</td>
<td>Ottawa</td>
<td>Washed 3x with D.I. H₂O; dried at 105°C overnight</td>
<td>450 mm columns</td>
</tr>
<tr>
<td>10</td>
<td>30°</td>
<td>Box</td>
<td>Ottawa</td>
<td>Washed 3x with D.I. H₂O; dried at 105°C overnight</td>
<td>450 mm columns</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Site P</td>
<td>Cooked with 0.1 M S₂O₆ for 30 min at 70°C; rinsed 20x with D.I. H₂O;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>dried at 180°C overnight</td>
<td></td>
</tr>
<tr>
<td>11,13, 14</td>
<td>Room Lab</td>
<td>Site P</td>
<td>Sieved through screen; washed in 3' columns with upward flow for 1-1/2</td>
<td>1200 mm columns</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>temp.</td>
<td></td>
<td>hrs.; inlet rotated 180° and washed for 1-1/2 hrs.; packed wet</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Room Lab</td>
<td>Site P</td>
<td>As for Experiment 11</td>
<td>250-mL bottles and</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>temp.</td>
<td></td>
<td>450-mm columns</td>
<td></td>
</tr>
</tbody>
</table>
Experimental Procedures

**Vials.** A series of experiments (experiments 1 through 7) were done in vials. The primary difference among these was temperature, with five experiments conducted at 70°C and two experiments at 90°C. During this period of experiments, various methods of persulfate analysis were tried before the most applicable one was selected. This method has been outlined in detail in the "Analytical Procedures" section.

All vials were filled with a solution which was 5.0 mM in K_2S_2O_8 and were then spiked with a volume of benzene-saturated water which gave a final concentration of 1 mM in benzene. Vials were immediately capped and placed in a water bath of appropriate temperature. They were removed at appropriate time intervals and quenched thermally. After returning to room temperature, a 3-mL sample was removed from the reaction vessel by syringe for use in the persulfate analysis and the remainder of the reaction solution underwent liquid-liquid extraction by the addition of 2 mL of extraction solvent which had been spiked with an internal standard. A 1.0-μL aliquot of the organic layer was removed by syringe and used in the benzene determinations.

**Bottles.** The original series of vial experiments helped determine methods of analyses, as well as temperature, buffering and the effects of oxygen. The sand was then introduced as a variable. Amber bottles with 250-mL capacity were used initially in the batch experiments. Into these were placed 90 mL of the solution of interest prior to the addition of 350 g of sand. The remaining atmosphere was sparged with nitrogen if this was required in the experimental protocol. Sample retrieval was achieved by insertion of a 6-inch needle attached to a 10-μL Hamilton gas-tight syringe. In the case of Site P sand (used in experiment 10), fines continually clogged the needle, so the samples were decanted.

**Column (450-mm).** Experiments 9 and 10 utilized the small (450-mm) columns. The procedure in these cases was to add to the column a specified volume of the solution of interest, which then was spiked with the model organic contaminant benzene at a final concentration of 1 mM after which sand was added to fill the column. The volume of solution was determined by prior measurement with the sand in order to know the correct amounts of each to fill the column with both phases, leaving no headspace. The system was closed by connecting the inlet and outlet Teflon adapters with Teflon tubing. Aliquots of the pore solution were removed periodically by disconnecting the Teflon tubing from the inlet (top) adapter and allowing the solution to drain into the sample container. Columns were housed in the insulated, temperature-controlled box described in detail previously. Experiments were conducted at an average temperature of 32.3°C ± 1.1°C for experiment 9 and 32.9°C ± 0.6°C for experiment 10.
Column (1200-mm length). The large (1200-mm) columns were packed with sand obtained from Site P and prepared in the manner detailed previously in this section. The porosity of each column was determined by injecting a known volume of an electrolyte, KCl, onto a column and determining its elution curve by means of a specific conductance meter (Amber Science) equipped with a flow cell. Porosity was calculated from the volume corresponding to the peak maximum, divided by the total volume of the column. Total porosity was found to be about 1 liter for the 1200-mm columns.

A retardation factor for benzene was also experimentally determined. The experiment was conducted with a flow rate of 19.5 mL per minute and an injection of 35 μL of benzene. The retention volume was determined to be 1229 mL yielding a retardation factor, $R_f$, of 1.18. When experiments were run at a much slower flow rate, sorption was much greater than is indicated by this value.

Three major experiments (11, 13, and 14) were conducted with the large (1200-mm) columns. Protocol for experiment 11 called for introduction of the organic contaminant by injection of 70 μL of pure benzene with a subsequent flush of the injection loop with 100 mL of the carrier solution designated for that column. Considering the solubility of benzene in water (1 mg/1.48 mL water; Merck Index, 1976), this corresponded to a slug of benzene-saturated water with a total volume of 80.8 mL and at a final concentration of 0.8 mM (62 mg/L), after the benzene dissolved. One hundred milliliter solvent aliquots -- or multiples thereof -- were added periodically over the next twelve days. The displaced eluate was analyzed for both analytes, C₆H₆ and S₂O₈²⁻. By the end of the experiment, a total of 1900 mL or about 1.9 pore volumes had been put through each column.

In experiment 13, both the method of benzene introduction and the frequency of sampling were changed. In preparation for the experiment each column was washed with 3 L (~3 pore volumes) of its respective carrier solution, which was already spiked with ~1 mM (~78 mg/L) benzene. Both inlet and outlet concentrations of each analyte were monitored in order to achieve equivalency in concentrations, which would serve as an indicator of saturation of adsorption sites in the column material. Aliquots were removed periodically by displacement with fresh solution, and their residence time on the column was calculated. Analyses were done after three days on the column, again at four days on the column (with five replicates for this period), and finally with a five-day residence time. Daily additions of 250-mL increments (or multiples thereof) were carefully tracked in order to determine residence times. Benzene was continually introduced at 1 mM concentration; therefore, there was no "chromatographic peak" as in experiment 11. Disappearance of benzene was monitored and related to its residence time upon the column.
The final experiment (14) of the project was a batch experiment, using the large columns. Before the experiment, on day zero, all columns were flushed with 5000 mL of their respective carrier solution and spiked with 1.0 mM benzene. Later, samples were withdrawn on sampling days by gravitational flow. The liquid which was removed in sampling was not replaced. Eluate samples were analyzed for benzene and persulfate concentrations.
SECTION 3

EXPERIMENTAL RESULTS

Several things were learned during this investigation which altered its original objectives. Since the results of one experiment invariably influenced the design of the next, it is logical to describe the results and conclusions by experiment.

A major difficulty encountered in this project was finding a suitable method of determining persulfate in the presence of organic material. So although the series of major (numbered) experiments began in early February 1986, a totally satisfactory analytical method was not found until June, just before experiment 7. Over twenty-one different variations of analytical methods were tried before a suitable method of analysis was found. More than 800 persulfate and 1000 benzene determinations were performed in the course of these experiments.

NOTATION

In the following sections, experiments are described which were designed to determine the effect of various parameters, such as buffering and presence of sand on the destruction of benzene by persulfate. The following notation is used in these sections to denote the various parameters:

- \( P \) = persulfate
- \( B \) = buffer
- \( O \) = presence of organic substrate (benzene)
- \( A \) = alkalinity, added to the solution as bicarbonate
- \( S \) = sand from Site P
- \( S^* \) = sand, cleaned of organic matter as described in the "Experimental Procedures" Section
- \( S_f \) = Ottawa (factory) sand

Thus, in a data plot, a curve bearing the label POAS would be from a kinetic experiment in which the reaction mixture contained persulfate and was unbuffered (no B), and in which benzene, alkalinity, and sand were present.
These experiments were batch kinetic runs on solutions containing only benzene and persulfate (PO), at two elevated temperatures, 70°C and 90°C. The purpose of operating at elevated temperatures was to speed up the reaction so that some factors might be eliminated as experimental parameters. In this way, the reliability of analytical methods might be checked before experiments taking weeks or months were begun. The persulfate analytical method and that for benzene did give erratic results in these two experiments. Both methods had worked previously on "clean" solutions. After both methods were modified, the 90°C experiment was repeated as experiment 3.

During the course of these experiments it was noticed that the reaction mixtures containing both benzene and persulfate became cloudy, and then on longer heating formed a precipitate. This precipitate appeared reddish- to yellowish-brown on the filter, and did not form in solutions which lacked either benzene or persulfate.

This was a batch kinetic experiment (PO), run at 90°C. The objectives of this experiment were to determine the rate constants for benzene and persulfate disappearance, to identify any stoichiometric relationships between those rates, and to test the modified analytical procedures. Solutions containing 1 mM benzene and 5 mM persulfate were made up in vials and placed in a constant-temperature water bath. Other vials containing only benzene or persulfate served as controls to indicate possible benzene loss due to volatilization and to furnish the persulfate decomposition rate in the absence of organic material, for comparison with literature values. Vials were removed as a function of time and analyzed for benzene and persulfate.

The results of experiment 3 are shown in Figure 1. Benzene disappeared almost exponentially in the presence of persulfate. There was almost no loss in the benzene control. Persulfate decomposition appeared to be of variable order (between zero- and first-order) in the presence of benzene, but the decomposition was faster and of higher than first-order in the absence of benzene. Linear regression of the first-order plots (equation 10) for those data showed that first-order kinetics fit the data within experimental error, producing first-order rate constants of $5.5 \times 10^{-2}$ min$^{-1}$ and $1.33 \times 10^{-2}$ min$^{-1}$, respectively, for benzene and persulfate disappearance. Multiplying these rate constants by initial concentrations provided initial reaction rates of $5.8 \times 10^{-5}$ and $6.0 \times 10^{-5}$ mol/L•min for benzene and persulfate removal. The virtually identical reaction rates implied a reaction stoichiometry of 1:1, i.e., decomposition of one persulfate ion results in the removal of one benzene molecule. In order to check on the validity of this experiment, this rate constant was superimposed on the plot of the
Figure 1. Benzene (squares) and persulfate (circles) disappearance at 90°C.
logarithm of the reaction rate constant versus reciprocal temperature for the data of Kolthoff and Miller (1951) and Goulden and Anthony (1978). The agreement in Figure 2 (point 3) was excellent, indicating that the persulfate analytical method performed adequately.

EXPERIMENT 4

A similar experiment was tried at 70°C to determine the kinetic behavior of the system at lower temperatures. The results are plotted in Figure 3. The benzene disappearance reaction was not first-order. This was confirmed by a first-order plot which showed a large initial decrease followed by a slight sinusoidal noise pattern superimposed on a slowly decreasing benzene concentration. Persulfate appeared to increase in both the experiment and control (Figure 3). This unreasonable result indicated that the persulfate analytical results were not correct. It is not known why these problems were not seen at 90°C. It was speculated that organic peroxy species were produced which interfered positively with the persulfate analytical method. The analytical methods were modified in an attempt to correct the problems and the experiment was repeated.

EXPERIMENT 5

Experiment 4 was repeated with two modifications. First, a phosphate-buffered experiment (5b) was run simultaneously, and second, oxygen was sparged from solution, using nitrogen, as the reaction mixtures were prepared, in order to avoid the possibility of production of organic peroxy compounds (Rabani et al., 1974; Downes and Sutton, 1973) by reactions of the type shown in equation 28:

\[
\begin{align*}
\text{R}^* + \text{O}_2 & \rightarrow \text{RO}_2^* \\
\text{RO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{organic products}
\end{align*}
\]

The results are shown in Figures 4 and 5. Benzene behaved similarly in the presence and absence of buffer, but the persulfate data in the presence of benzene were quite erratic during the first half of the experiment. Determination of the rate constant for persulfate decomposition in the persulfate control gave excellent agreement with that of previous investigators, as shown in Figure 2 (point 5). The fact that the persulfate concentrations during the last half of the runs are similar to those predicted by the persulfate control indicated that the interference is most significant during the first part of the reaction. The benzene disappearance rate constant was found to be \(6.17 \times 10^{-3}\) min\(^{-1}\) in unbuffered solution and \(5.49 \times 10^{-3}\) min\(^{-1}\) in buffered solution. The stoichiometric ratios of the initial rate of benzene
Figure 2. Comparison of determined rate constants with literature values. Data adapted from Goulden and Anthony (1978) includes that from Kolthoff and Miller (1951). Experiment numbers are shown near data points.
Figure 3. Disappearance curves, experiment 4 (70°C).
Figure 4. Effect of phosphate buffer on benzene disappearance at 70°C.
Figure 5. Effect of phosphate buffer on persulfate disappearance at 70°C.
disappearance to that of persulfate decomposition were calculated from the initial concentrations and the determined rate constants. These ratios were found to be 0.78 ± 0.12 and 0.67 ± 0.13 in unbuffered and buffered solution, respectively. Rate constants and stoichiometric ratios are tabulated in Table 4. Persulfate disappeared in unbuffered solution slightly faster in the presence of benzene than in its absence, contrary to the observation in experiment 3.

The precipitate which had formed in the high temperature (90° and 70°) experiments was collected on filters and subjected to limited solubility testing in an attempt to characterize it. The precipitate was insoluble in base, acid, and methylene chloride. Since 15-mL vials were used for the experiments and the initial concentration of benzene was about 1 mM, there was only about 1 mg of organic material per vial. Production of a filterable precipitate implied that conversion of benzene to precipitate must have been fairly efficient.

EXPERIMENT 6

An electrochemical method for persulfate analysis was attempted to overcome the difficulties encountered in the early part of experiment 5. The unbuffered part of that experiment was repeated using the new method. Although the method looked promising in pure water, it failed in the presence of benzene under reaction conditions. The data are shown in Figure 6. The benzene data were well-behaved, and a rate constant value of 7.09 ± 0.25 x 10⁻³ min⁻¹ was determined for the disappearance of benzene. Unlike previous results, the persulfate control was also erratic judging from this method.

EXPERIMENT 7

Once the final analytical method was found to be suitable for the analysis of persulfate in these samples the 70° experiment was repeated. This analytical method was used in all subsequent experiments. The data are shown in Figure 7. First-order plots yielded rate constants of 7.0 x 10⁻³ and 8.0 x 10⁻⁴ min⁻¹ for benzene and persulfate disappearance, respectively. The high value of R is consistent with an error in sample/standard preparation for the benzene samples, which should be 1 mM initially, rather than 1.4 mM. This apparent error did not change the value of the first-order reaction rate constant tabulated in Table 4. It was in good agreement with the previous value.
Table 4. Rate Constants and Stoichiometric Ratios for Kinetic Experiments

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Conditions (a)</th>
<th>Temperature, °C</th>
<th>Disappearance rate constant, (k), sec(^{-1})</th>
<th>Stoichiometric ratio (b) R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>P</td>
<td>90º</td>
<td>2.22 x 10(^{-4})</td>
<td>1.53 x 10(^{-5})</td>
</tr>
<tr>
<td>5</td>
<td>PO</td>
<td>70º</td>
<td>1.83 ± 0.12 x 10(^{-5})</td>
<td>1.71 ± 0.09 x 10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td></td>
<td>1.54 x 10(^{-5})</td>
<td>(c)</td>
</tr>
<tr>
<td></td>
<td>POB</td>
<td></td>
<td>1.51 ± 0.13 x 10(^{-6})</td>
<td>1.53 ± 0.15 x 10(^{-6})</td>
</tr>
<tr>
<td>6</td>
<td>PO</td>
<td>70º</td>
<td>(c)</td>
<td>1.97 ± 0.07 x 10(^{-6})</td>
</tr>
<tr>
<td>7</td>
<td>PO</td>
<td>70º</td>
<td>1.33 x 10(^{-5})</td>
<td>1.94 ± 0.19 x 10(^{-6})</td>
</tr>
<tr>
<td>8</td>
<td>POB</td>
<td>44 ± 2º</td>
<td>8.51 x 10(^{-7})</td>
<td>5.67 x 10(^{-6})</td>
</tr>
<tr>
<td>9</td>
<td>PB</td>
<td>32 ± 1º</td>
<td>3.8 x 10(^{-7})</td>
<td>4.08 x 10(^{-6})</td>
</tr>
<tr>
<td>10</td>
<td>PS</td>
<td>33.0 ± 0.6º</td>
<td>2.11 x 10(^{-7})</td>
<td>(c)</td>
</tr>
<tr>
<td></td>
<td>PSB</td>
<td></td>
<td>2.79 x 10(^{-6})</td>
<td>(c)</td>
</tr>
<tr>
<td>14</td>
<td>POS (d)</td>
<td>23.7 ± 0.3</td>
<td>3.56 x 10(^{-7})</td>
<td>5.52 x 10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>POS (e)</td>
<td></td>
<td>1.76 x 10(^{-7})</td>
<td>5.03 x 10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>POSA (e)</td>
<td></td>
<td>1.71 x 10(^{-7})</td>
<td>4.11 x 10(^{-6})</td>
</tr>
</tbody>
</table>

(a) P = persulfate, B = buffer, A = alkalinity, S = Site P sand, O = organic substrate (benzene) present
(b) Defined as \(R = \frac{k_{benzene}C_{benzene}}{k_{persulfate}C_{persulfate}}\) at \(t = 0\)
(c) Data scatter does not allow calculation
(d) Freshly prepared sand column
(e) Old sand column
(f) Computed from \(\Delta\) benzene/\(\Delta\) persulfate at \(t = 20\) days
Figure 6. Benzene and persulfate disappearance curves for experiment 6, 70°C.
Figure 7. Disappearance curves, experiment 7.
EXPERIMENT 8

The previous experiments were run at elevated temperatures to confirm agreement of kinetic data with the literature and to eliminate experimental problems before attempting longer runs at lower temperatures. This experiment was performed at $44 \pm 2^\circ$ in a thermostatted constant-temperature box. In addition to obtaining rate data at a lower temperature, the objectives of this batch experiment were to investigate the effects of the presence of sand and dissolved oxygen on the reaction rates of benzene and persulfate.

Sand was expected to alter the reaction rate, perhaps by a number of different mechanisms. Sorption of organic compounds to solids may drastically alter their reaction rates and pathways, and is the basis for most present-day catalysis. Voudrias et al. (1985) noted different reaction products when organic compounds were chlorinated while adsorbed to activated carbon, compared to those obtained in solution. Inorganic solids or the natural organic material attached to those solids may compete with the target compound for free radicals, reducing the efficiency of destruction.

The participation of oxygen in free-radical reactions, as represented by equation 28, was discussed above. In some systems the formation of the $R_2O_2^-$ radical may help guarantee that $R^+$ cannot "heal itself" by abstraction of a hydrogen atom from another source. Therefore, the effect of oxygen was also investigated in this experiment.

The experimental matrix is shown in Table 5. Ottawa sand was used after being washed with tap water in an attempt to have as clean a sand as possible, i.e., minimum organic content and water-soluble salts. Figure 8 shows the time-dependence of the disappearance of persulfate in these samples. The presence of sand caused a dramatic increase in the decomposition rate of persulfate in these experiments. What appeared to be small effects of oxygen and buffer are within experimental error of the sparged and unbuffered systems. Figure 9 shows that benzene removal followed somewhat the same trend. The removal in the sand-containing samples occurred much faster than in the others. In these plots, the slightly faster disappearance rate of benzene in nitrogen-sparged versus unsparged and in unbuffered versus buffered samples may be significant.

The unexpected catalytic effect of sand could be a severe detriment to in situ reclamation if it occurs in real systems. This is because it would allow less time for the persulfate to travel through the aquifer material to reach the substrate even though it speeds up the destruction of the substrate. This would require a high-permeability aquifer, high pumping rates, and/or many wells. The latter would of course increase the cost of cleanup.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Designation(a)</th>
<th>Oxygen removed(b)</th>
<th>Buffer added(c)</th>
<th>Sand present(d)</th>
<th>Initial reaction rates(e)</th>
<th>Reaction rate ratio, ( R_b/R_p )(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PO</td>
<td>X</td>
<td>--</td>
<td>--</td>
<td>9.15 x 10^{-3} 2.15 x 10^{-2}</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>POSf</td>
<td>X</td>
<td>--</td>
<td>X</td>
<td>1.72 x 10^{-1} 2.88 x 10^{-2}</td>
<td>(&gt;0.2)(g)</td>
</tr>
<tr>
<td>3</td>
<td>POB</td>
<td>X</td>
<td>X</td>
<td>--</td>
<td>1.08 x 10^{-2} 1.65 x 10^{-2}</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>PO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>8.75 x 10^{-3} 2.55 x 10^{-2}</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>POSf</td>
<td>--</td>
<td>--</td>
<td>X</td>
<td>1.46 x 10^{-1} &gt;3.95 x 10^{-2}</td>
<td>(&gt;0.3)(g)</td>
</tr>
<tr>
<td>6</td>
<td>POB</td>
<td>--</td>
<td>X</td>
<td>--</td>
<td>1.14 x 10^{-2} 1.35 x 10^{-2}</td>
<td>1.2</td>
</tr>
</tbody>
</table>

(a) \( P = \) persulfate present, \( O = \) organic substrate present, \( S_f = \) factory (Ottawa) sand, \( B = \) buffered
(b) By sparging with nitrogen
(c) 0.05 M phosphate at pH 8.11
(d) Ottawa sand from the factory, rinsed with tap water
(e) Calculated from \( (C(t=0) - C(t))/t \)
(f) Calculated from initial reaction rates (This stoichiometric ratio is only valid at the beginning of an experiment, before products have had time to accumulate.)
(g) Lower bound
Figure 8. Disappearance of persulfate at 50°C (experiment 8). Experimental conditions are listed in Table 5. See text for explanation of symbols.
Figure 9. Benzene removal by persulfate at 50°C (experiment 8). Experimental conditions are listed in Table 5. See text for explanation of symbols.
The first-order rate constants for persulfate disappearance in the buffered runs were calculated in order to compare our kinetic data with literature values. All literature values were obtained in phosphate-buffered solutions. The value found for the rate constant was $k = 3.10 \times 10^{-3} \text{ hr}^{-1} = 8.51 \times 10^{-7} \text{ sec}^{-1}$. This value was plotted (point 8) on the graph of the data of Kolthoff and Miller (1951) and Goulden and Anthony (1978), taken from the paper by the latter authors. This plot is shown in Figure 2. The point fell slightly above the line which represents the extrapolation of the data obtained at higher temperatures.

Initial rates calculated for the six sets of experimental conditions (called configurations), revealed some interesting results, which are given in Table 5. The benzene reaction rates given for configurations 2 and 5 are only upper bounds, since no benzene was found in the first samples taken. Thus, the corresponding entries in the last column of Table 5 are probably very different from the true values which are shown in parentheses. The values in the last column, which are the ratio of initial benzene disappearance to initial persulfate disappearance rates, show that the unbuffered system, whether oxygen is removed or not, was more efficient for benzene removal, based on the amount of persulfate decomposed. The reason for $R_b/R_p > 2$ is presently unknown.

One part of the original project plan was to coat "clean" sand with various loadings of organic material, either natural humic material or some synthetic polymer, to determine the effect of organic content of the sand on the reaction kinetics. It was intended to use commercial sand (Ottawa sand) for this purpose; however, the unexpected catalytic effect described above would make interpretation of those experiments difficult or impossible. It was therefore important to determine:

a) whether the effect was real (i.e., repeatable),

b) how other reaction conditions affected the catalysis, and

c) whether the effect was peculiar to this sand.

**EXPERIMENT 9**

It was clear that the effect of the sand was the dominant factor in the previous experiment. It was very important to find out if that effect was reproducible and how it interacted with other factors. The next major experiment was run at 32°C in order to further slow the reactions. The experiment utilized sand columns in the batch mode and was designed to separate out the effects of sand, buffer, and bicarbonate. Bicarbonate ion is a free-radical scavenger which is naturally present in ground water as a major component of alkalinity. It has the
potential to significantly affect free-radical reaction rates with organic compounds. The results obtained for benzene destruction in this experiment could not be quantitatively interpreted because of high benzene loss in the blanks, presumably due to volatilization and/or sorption on Teflon(R) fittings. However, some points were qualitatively significant:

1) With sand present, loss of benzene was faster in unbuffered than in buffered solution, i.e., the catalytic effect of Ottawa sand noted in the last experiment was lessened by a factor of two by the addition of buffer.

2) In the absence of Ottawa sand, benzene loss (in the presence of persulfate) was very close to that of the blank, i.e., no catalytic effect and a very slow reaction rate.

3) In unbuffered solutions, benzene loss was slower in the presence of bicarbonate than in its absence but was still faster than in any buffered run.

The persulfate disappearance curves for experiment 9 were much better behaved than the benzene curves. These data are shown in Figure 10. Each point is the average of a filtered and nonfiltered sample, with the range given by the error bars. Buffered experiments with Ottawa sand present, with and without added alkalinity (PBOASf and PBOSf, respectively) were within experimental error of each other and the blank (PB). Of the unbuffered runs, that with added alkalinity (POASf) was slower than the experiment without alkalinity (POSf), but both were considerably faster than all the buffered runs.

The initial solution pH values of PBOSf, PBOASf, POSf, and POASf were 8.0, 8.0, 3.3 and 7.6, respectively. Although pH 3.3 was low enough to allow participation of the acid-catalyzed persulfate decomposition (see equation 26), pH 7.6 was not. Greatly enhanced persulfate decomposition rates were observed in column POASf. By t = 70 hours the pH values of POSf and POASf were 2.4 and 2.2, respectively, yet the persulfate disappearance rate in POSf was greater than in POASf. Therefore, the enhancement cannot be merely a pH effect, but must involve some catalytic property of the sand. The rate constant for the buffered system (no sand) is plotted in Figure 2 (point 9).

This set of results led to the following observations:

1) The presence of buffer counteracts the catalytic effect of the Ottawa sand which was observed in the previous experiment. This effect was also seen qualitatively in the benzene disappearance as a consequence of the decreased persulfate decomposition rate.
Figure 10. Persulfate disappearance at 32°C (experiment 9). P = persulfate, B = buffer, O = organic substance, $S_f$ = factory (Ottawa) sand, A = alkalinity. See text for discussion of symbols.
2) The presence of bicarbonate actually slows the rate of persulfate decomposition, rather than merely competing with benzene for the active free radicals.

It might be reasoned from these results that the major effect on a natural system (where 0.05 M phosphate buffer is not present) would be the catalytic effect of the sand. It is reasonable that an effect of this type might be highly variable from one sand or soil to another, and that the presence of organic material would counteract that effect by acting as a competing radical scavenger. It was important to proceed directly to experiments which use sand/soil from an actual site, rather than attempting to coat varying amounts of organic material onto Ottawa sand.

EXPERIMENT 10

Surficial sand was collected just at an upgradient location from a Superfund site (hereinafter called "Site P") in Kankakee County, Illinois. Ground water at the site is contaminated with benzene, toluene, xylene, and other organic compounds. The sand deposit in this area extends downward from the surface for 40 to 60 feet. The sand taken was light grey-brown in color, indicating the presence of organic-containing "fines." This was confirmed in a later cleanup step performed on the sand. The area from which the sand was taken had been cultivated in previous years.

This experiment used Site P sand which had been sifted through plastic window screen to remove insects, rootlets, etc. and then had been air-dried. The premeasured reaction mixtures were added to the empty 1" i.d. x 45 cm chromatography columns and were then spiked with benzene concentrate. Sand was then added to the top of the column, and the column was quickly sealed and placed in the constant-temperature box at 33.0 ± 0.6°C.

The experimental matrix is shown in Table 6. The experiment was designed to separate the effects of buffer, bicarbonate, factory (Ottawa) sand vs. Site P sand, and Site P sand with and without organic material. The latter was obtained by digesting Site P sand in 0.1 M potassium persulfate for 30 minutes at 70°C in order to destroy any organic material which was present (see "Experimental Procedures" section). Because of the length of preparation time for the experiment, the columns were stored overnight (16 hours) at 8°C before "beginning" the run by bringing the columns up to 33°C.

The results, shown in Figure 11, indicated that the least amount of persulfate decomposition took place in the column with cleaned Site P sand (POS*), both during the overnight storage at 8°C and after warming to 33°C. The persulfate in the column which contained Ottawa sand, POSf, decomposed much more rapidly than any other, again
Table 6. Experimental Matrix for Site P Sand Column, Experiment 10

<table>
<thead>
<tr>
<th>Sample</th>
<th>Persulfate 5 mM</th>
<th>Site P sand</th>
<th>Phosphate buffer 0.05 M</th>
<th>HCO$_3^-$ 1 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td>X</td>
<td></td>
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<tr>
<td>3</td>
<td>X</td>
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</tr>
<tr>
<td>5</td>
<td>X</td>
<td>(a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>X</td>
<td>FS(c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7(b)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

(a) Pembroke sand cleaned with 0.1 M S$_2$O$_8^-$ at 70°C for 30 minutes to remove organic material
(b) Blank (prepared in 250-mL headspace-free bottle, rather than in 45-cm column)
(c) FS = Ottawa sand from factory, as used in previous experiments
Figure 11. Persulfate decomposition in 33°C small-column experiments (experiment 10) using Site P sand. Experimental conditions are listed in Table 6.
indicating a catalytic effect which was apparently absent from even cleaned Site P sand (POS*). Between samples PBOS, POS, and POAS, the sample which was buffered at pH 8 (PBOS) showed slower persulfate decomposition than those (POS and POAS) in which acidity increased, in agreement with previous results. Comparison of the latter two curves disclosed that the presence of bicarbonate did not affect the persulfate decomposition rate.

Figure 12 shows that all benzene samples analyzed had considerably less benzene than the blank. The least disappearance was observed overnight in POS*, the cleaned Pembroke sand. Fortunately, the blank was prepared in a 250-mL headspace-free bottle, rather than a column, like the samples. Otherwise, the full extent of benzene loss in the column samples would not have been determined so easily. The cause of the losses could not be determined from this information. Benzene disappearance may be attributable to sorption losses since the loss was too great to be due to the persulfate reaction overnight at 8°C (see the discussion of experiment 12, below). From Figure 12 it seemed as though more benzene disappeared from the columns containing only Pembroke sand or cleaned Pembroke sand and persulfate (POS and POS*) than from the columns which contained either buffer, bicarbonate, or no persulfate (PBOS, POAS, and OS, respectively). However, because of the sample volume required for analysis, the first two samples (at t = 0 and 24 hrs) were taken from a different column than were the last two (47 and 120 hrs). This accounts for the apparent discontinuities observed in curves POS and POS* (Figure 12) between 24 and 47 hours. In addition to this problem, the benzene determinations were complicated by the presence of murky brown or orange materials in the water, which presumably were the decomposition products of the humic material present in the sandy soil.

Although the inaccuracy of the benzene data makes quantitative conclusions difficult, the following observations may be offered:

1) Factory Ottawa sand catalyzed persulfate decomposition and benzene disappearance relative to natural or cleaned sand from Site P.

2) Alkalinity did not affect the persulfate decomposition rate in the presence of Site P sand.

3) Buffering with phosphate slowed persulfate decomposition relative to unbuffered solutions.

4) Persulfate decomposition in the presence of cleaned Site P sand was five times slower than with untreated Site P sand. This implied that some material present in the sandy soil before cleaning promoted persulfate decomposition. Benzene affected persulfate decomposition similarly in earlier experiments.
Figure 12. Benzene removal in 30°C small-column experiments (experiment 10) using Site P sand. Experimental conditions are listed in Table 6. Asterisk denotes sand cleaned with persulfate to remove organic matter.
5) Benzene losses of 40-70% were noted in all sand columns during the 15-hour holding period at 8°C prior to warming to room temperature. After warming only minor losses occurred during the following 120-hour period at 33°C. The losses were suspected to be due to physical (sorption, volatilization, etc.) rather than chemical causes.

6) Benzene destruction was very fast in the presence of Ottawa sand. In all of the other sand columns, benzene destruction (after $t = 0$) was probably equal, within experimental error.

These results indicated large losses of benzene, perhaps due to sorption on the sand or to the apparatus itself (PTFE parts). These losses were sufficient to obscure the effect which was under study.

**EXPERIMENT 11**

This experiment was designed to determine 1) to what extent adsorption accounts for the initial disappearance of benzene ($t<0$, Figure 12), and 2) whether a realistic concentration of bicarbonate essentially stops benzene disappearance or merely slows it. The latter point may be crucial in some in situ reclamation situations, and the general question of solute effects on oxy-radical reactions is currently under investigation (Peyton, 1986). For the purposes of the present feasibility study, it was important to estimate to what extent the natural bicarbonate concentration in ground water may diminish the efficiency of aquifer reclamation based on oxy-radical reactions. It was also desirable at this point to change from batch to flow experiments, in order to more closely simulate reaction in a slowly flowing aquifer.

This experiment used 1220 mm x 51 mm i.d. columns full of "rinsed" Site P sand. The sand was rinsed by placing it to a depth of about 2 feet in a 914 mm x 152 mm i.d. Pyrex(R) pipe with the bottom end closed, and then running tap water through a 3/8" tube which extended to the bottom of the pipe. Upward flow of tap water was continued for several hours, during which time much of the dark organic-containing fines were rinsed out of the sand. Nearly one-third of the sandy soil material was removed in this manner. The large columns were then packed by filling them with water, adding spoonfuls of wet rinsed sand, and allowing it to settle to the bottom of the column. The residual dark slower-settling fines were allowed to collect in layers on top of the coarser material, this method of column packing minimized the formation of unsaturated regions or voids due to trapped air bubbles.
As noted in the "Experimental Procedures" section, Site P sand had been collected from the surface, in a field adjacent to Superfund Site P. The field had been cultivated recently, and the sandy soil contained considerably more dark fine material than did the actual aquifer material. This latter material was observed in the sides of excavation trenches during the same site visit, but could not be legally removed from the site. Mixing the unrienced sand with water resulted in a dark grey, stable suspension of the fines, which interfered in several ways with the execution of the above experiments. The decision to rinse out these fines and use rinsed sand in subsequent experiments was based on the appearance of the actual aquifer material and on experimental expediency. It was decided that this feasibility study would benefit more from straightforward interpretation of the results than it would lose by not using the surficial sand exactly as it had been collected.

Tracer experiments using potassium chloride with conductivity detection were run to determine porosity and dispersion parameters of the column. The pore volumes of the columns used for the POS, POAS, and OS experiments were found to be $1016 \pm 7$, $950 \pm 15$, and $1039 \pm 11$ mL, respectively. These pore volumes corresponded to porosities of $42.3 \pm 0.3$, $39.6 \pm 0.6$, and $43.3 \pm 0.6\%$, respectively. A pulse injection tracer experiment was run using benzene as the tracer. Fractions were collected and analyzed for benzene by liquid-liquid extraction gas chromatography (LLE/GC), using a flame ionization detector (FID). The benzene elution curve determined by this technique yielded a retardation factor of approximately 1.2 compared with the factor obtained with potassium chloride. The flow rate during this 1-hour 45-minute experiment was 19.5 mL/minute. Benzene recovery was found to be 117%. During and after the benzene experiment, however, voids developed in the sand columns, probably due to the fairly rapid upward flow. Voids soon developed in the other columns as well. The idea of modeling the system using the one-dimensional transport model was abandoned because of the constantly changing voids.

Experiment 11 was an attempt to simulate a flow experiment with a pulse injection of benzene. The required flow rate for constant flow and the desired retention time on the column would have been in the range of 70 µL per minute (4.2 mL per hour), but no suitable means of maintaining that low flow rate was available. Therefore, flow was simulated by pumping 100 mL of persulfate solution onto the column each day and sampling the column effluent incrementally. Since dilution of the benzene by two or three orders of magnitude took place between injection and elution, the concentration of the injected slug should have been correspondingly higher than the effluent concentration. However, the limited water solubility of benzene made it necessary to inject pure benzene, which then dissolved in water while on the head of the column. A 70-µL portion of neat benzene was injected onto the head of the column and washed into the sand, using 100 mL of 5 mM potassium persulfate solution. The solubility of benzene is such that about
80 mL of water was required to dissolve the 70 μL injection. This provided an initial concentration of about 8.8 mM or about 700 mg/L. Temperature during this nine-day experiment was 24.8 ± 1.2°C.

Eighteen 6-mL effluent samples were collected each day and analyzed for persulfate and benzene. No benzene eluted from the columns during the first five days. The results of the benzene determinations during days 6 through 9 are shown in Figure 13. The peaks assumed the characteristic tailing gaussian shape. Even without the problem of column voids, referred to above, analysis by the one-dimensional transport model would not have been appropriate since the dispersion due to advection would be characteristic of the linear velocity of the mobile phase (water) added in 100-mL increments, while the diffusional dispersion was more representative of a nine-day experiment. The concentration discontinuities between sampling days can be seen, e.g., between the last sample of day 6 and the first sample of day 7 in the "persulfate only" curve on the left side of Figure 13. Since only alternate samples were analyzed, values for the intervening samples were interpolated so that the total amount of benzene which eluted from the column could be calculated by summing the concentrations multiplied by the sample volumes. When these recovered amounts were compared to the amounts of benzene which were injected, it was found that during the nine-day experiment, 74% was lost in the column containing persulfate and bicarbonate, 72% was lost in the column containing only persulfate, and 63% was lost in the control, through which only tap water was pumped. While the first two values were equal within experimental error, the loss of 63% of the benzene in the control column was still commensurate with the losses experienced in experiment 10, even though rinsed sand was used in experiment 11. This magnitude of loss was unexpected, particularly in view of the excellent benzene recovery obtained during the porosity and dispersion tests.

Persulfate concentrations in the effluents of the three columns are shown in Figure 14 for days 6 through 9. The observed concentrations of persulfate were quite low, particularly while benzene was eluting. The persulfate concentration appeared to increase slightly in the column containing only persulfate after the benzene had eluted. This effect was more obvious in the data from the column containing both persulfate and bicarbonate. It appears as though benzene or one of its breakdown products catalyzed the decomposition of persulfate. A similar effect was observed in previous experiments and may be represented by equation 22. All breakdown products would be expected to be more polar and more water-soluble than benzene, and so should move at the velocity of the water itself, i.e., with the "injection front". Benzene should have been the last organic compound to elute from the column. It appeared that persulfate, which trailed the benzene in the column, was destroyed to a lesser extent, since no organics were present to catalyze its decomposition.
Figure 13. Benzene elution curves, experiment 11.
Each line or space represents an individual 16-mL fraction.
Figure 14. Persulfate concentrations eluting from columns, experiment 11. Each line or space represents an individual 16-mL fraction.
Observations

1) It appeared that about 10% more benzene was destroyed in the columns containing persulfate than in the control.

2) The presence of bicarbonate was not detrimental to benzene removal.

3) More quantitative interpretation of these results cannot be made without knowledge of the reasons for apparent benzene loss in the control experiment.

4) Persulfate decomposition on the column may have been catalyzed by benzene and its breakdown products.

EXPERIMENT 12

This experiment was conducted to determine the cause of the benzene losses experienced in experiment 11. Causes considered included:

1) Sand -- sorption losses, catalyzed decomposition, biodegradation losses

2) PTFE frits, end fittings, and tubing on columns -- i.e., adsorption/absorption losses

3) Method of sample collection -- volatilization losses

Bottles containing 1 mM solutions of benzene were stored at room temperature for up to five days, with individual sample bottles withdrawn on days 1, 4, and 5 for analysis. Some bottles contained sand from the same batch used in experiment 11. Columns with PTFE end fittings were also used to test for sorption losses. Smaller columns were used, so that the ratio of PTFE surface to liquid volume was larger than in the 4-foot columns which would slightly exaggerate the sorption effects. To test for volatilization losses, samples were collected as in experiment 11, i.e., by allowing effluent to drip into vials. The control values were obtained by displacing sample from the bottle under nitrogen pressure, through tubing which dipped below the surface of the extraction solvent in the analysis vial. This would minimize volatilization losses.

The data are shown in Figure 15. Values of the benzene concentrations in the different sample types are shown normalized to the concentration found in the control samples analyzed with each data set. Volatilization losses were 10-20%, while sorption losses to the PTFE were in the range of 20-30%. Benzene losses of 55-60% were experienced in the sand tests, as seen in Figure 15. It was possible that losses
to the sand account for the major portion of benzene removal (63%) experienced in the control in experiment 11. The zero-time sample in the sand test was mishandled, and the data are believed not to be reliable. This data point has been placed in parentheses in Figure 15.

The shape of the sand experiment curve in Figure 15 indicated that the losses were due to sorption to the solids, rather than to catalytic decomposition or biodegradation. The loss was abrupt, within the first 24 hours, rather than gradual or continuing as would be expected with catalytic decomposition or biodegradation. It is impossible to tell whether the very slight decrease in benzene after 24 hours was significant. The scatter in the other two curves would seem to indicate that it was not. It was not known whether the benzene sorbed to the sand in experiment 11 was attacked by persulfate.

Conclusions

1) 50-60% removal of the benzene was experienced for batch contacting of 1 mM aqueous benzene and Site P sand.

2) Benzene removal may have been due primarily to sorption of the benzene to the solid material, with sorption to PTFE and volatilization during sample collection contributing considerably less.

3) Future experimental designs must avoid these problems, in order to detect chemical destruction above the scatter in the experimental results.

EXPERIMENT 13

This experiment was designed to simulate a flow experiment but to overcome the difficulties outlined above. The same 1220 mm columns were used that were prepared for experiment 11. These columns had a pore volume of about 1000 mL, which would require a pump with a flow rate of 0.17 mL-min⁻¹ for a four-day retention time. Metering pumps were purchased which should have been capable of 0.1 mL-min⁻¹ flow, but after a few hours of continuous operation these pumps were found to become erratic in their output or to cease entirely. Earlier experiments had indicated that much longer retention times than four days would be required if most of the benzene was to be destroyed. It was then decided to use the batch-elution approach, similar to that used in experiment 11.

Instead of a pulse injection of benzene, the columns were flushed with a solution which was 1 mM in benzene, in an attempt to saturate possible sorption sites. Portions of the solution were then added
Figure 15. Benzene losses due to different factors present in column experiments.
batchwise on a daily basis. The benzene solution in one of the three columns contained persulfate, that in another column contained persulfate and 0.5 M sodium bicarbonate, and that in the third column contained water only, as a control. These correspond to POS, POAS, and OS conditions, respectively. No attempt was made to sterilize the columns. Samples were taken from the middle of the effluent portion, in order to minimize mixing with other "slugs" on the column. Each work day, influent batches were made up and analyzed, to avoid analyte loss from feed solution upon standing. It was anticipated that removals from solution would be large at first, as sorption sites became saturated, but that removals would eventually level out to steady-state values. In observing these steady-state values, however, it was only meaningful to compare removals after equal times of retention on the column. The five-day workweek caused serious complications in the collection of these data for a given retention time, however, and only two or three sample sets could be collected each week for a selected retention time.

Differences between effluent and the corresponding influent concentrations were calculated for benzene and persulfate. These differences were plotted vs. number of days into the experiment. Only points which represent four days' retention time are plotted in Figure 16. As expected, removal started out relatively high, presumably as sorption sites were saturated. As the experiment proceeded, removals dropped, but removal from the control decreased faster than from the persulfate-containing solutions. The negative removal values on day 14 reflect both experimental difficulties and the inaccuracies that resulted from subtracting effluent concentrations from influent concentrations measured four days prior. Nonetheless, comparison of the three plots in Figure 16 led to the following conclusions:

1) Benzene removal in the persulfate columns was greater than in the control.

2) Apparent removal was greater at first than after day 10.

3) Much greater than four days of reaction time would be required to destroy a major portion of the benzene under these conditions.

4) The "simulated flow" technique was unsatisfactory. The experimental difficulties would be compounded in any attempt to extend this method to longer retention times.

Despite the advantages of stability to be gained by steady-state operation of a flow system, we were unable to construct a suitable flow or pulsed-flow (periodic addition of solution) system within the time and resource constraints of this project. It was decided that a batch experiment was necessary to simplify the experimental conditions so
Figure 16. Benzene (○) and persulfate (●) removal during experiment 13.
that the time-dependence of benzene disappearance could be determined. Further attempts to carry out a flow experiment were therefore abandoned.

**EXPERIMENT 14**

This was a batch experiment designed to determine the long-term time dependence of benzene destruction by persulfate in the presence of Site P sand. Four 1220 mm x 51 mm columns were set up: three with the same Site P sand used in experiment 13, and one new column with fresh Site P sand. The three established columns were filled with solutions of 1 mM benzene in 5 mM persulfate, 5 mM persulfate plus 0.5 M sodium bicarbonate, and deionized water, respectively. The same solution (i.e., POS, POAS, and OS) was used on each column as in previous experiments. The new column was used for a duplicate persulfate column, to compare the effect of fresh Site P sand with that which had been exposed to persulfate for a few weeks in prior experiments.

Four to five pore volumes of solution were pumped through each column. Then the columns were allowed to stand overnight to allow sorption equilibrium. Another two liters of solution were put through each column the next day, and the experiment begun. Samples were taken every few days and analyzed for both benzene and persulfate, to determine their disappearance.

Figure 17 shows the persulfate disappearance curves for experiment 14. The three columns which contained persulfate all yielded data which could be fit by first-order disappearance kinetics for the first 10-20 days but were linear after that period. The disappearance curves are virtually identical for the old column with persulfate (POS) and the column with persulfate plus alkalinity (POAS). From previous experiments, it was expected that with the new column (POS), faster persulfate degradation rates would have been observed. This would presumably be due to the increased amount of organic material and/or complexed metals which were thought to be present and which should promote persulfate decomposition.

First-order rate constants for the initial portion of the disappearance of persulfate in the new persulfate column, old persulfate column, and old persulfate plus alkalinity column were 3.56 x 10^{-7}, 1.76 x 10^{-7}, and 1.71 x 10^{-7} sec^{-1}, respectively. These values are plotted in Figure 2 and were somewhat above the extrapolation of the data of Kolthoff and Miller (1951) and Goulden and Anthony (1978). The pH values of samples were in the range of 6.0-7.6, so the possibility of contribution to the rate constant by acid-catalyzed persulfate decomposition (equation 26) could be discounted.
Figure 17. Persulfate disappearance, experiment 14. See text for details.
Figure 18 shows the disappearance curves of benzene in each of the four columns. The reason for the sharp dip in the curve on the first sampling date (day 4) is unknown. The same effect appeared to a lesser extent in the data from all columns for day 7. After that point, the data appeared to smooth out into more normal disappearance curves.

Benzene disappearance in the new column (POS') was slower than in the older columns, POS and POAS. This was opposite the outcome of the persulfate behavior shown in Figure 17. Benzene may have decreased slightly in the control.

Total organic carbon (TOC) determinations, run on sand taken from the column after the experiments, did not show an obvious correlation with disappearance data. As shown below, TOC was higher in the new column than in the older columns, even though the sand in the (old) control had never been exposed to persulfate. TOC values were found to be:

<table>
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<th>Description</th>
<th>TOC</th>
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<tr>
<td>New Persulfate (POS')</td>
<td>661 ± 30 ppm</td>
</tr>
<tr>
<td>Old Persulfate (POS)</td>
<td>527 ± 64 ppm</td>
</tr>
<tr>
<td>Old Persulfate + Alkalinity (POAS)</td>
<td>553 ± 35 ppm</td>
</tr>
<tr>
<td>Control (OS)</td>
<td>546 ± 38 ppm</td>
</tr>
</tbody>
</table>
Figure 18. Benzene disappearance, experiment 14. See text for details.
SECTION 4
DISCUSSION

PROJECT OBJECTIVES

The stated objectives of the project were:

1) To identify candidate reagents for the controlled in situ generation of hydroxyl radical.

2) To determine the batch kinetics of hydroxyl radical generation by those reagents as a function of temperature, pH, and presence of organic compounds and aquifer solids.

3) To determine the batch kinetics of model organic pollutant destruction by hydroxyl radical generated from these reagents.

4) to test the adequacy of batch kinetic data in predicting model pollutant destruction in flowing soil/sand column systems.

5) To evaluate the feasibility of oxidative in situ degradation of organic pollutants from laboratory sand/soil column studies.

The following sections discuss the extent to which each of these objectives were met.

Candidate Reagents

When the project was begun, it was expected that hydroxyl radical would be the active species which would be generated in situ to effect destruction of the organic pollutant molecule. It was determined from information gathered during the literature survey that persulfate was the most suitable reagent for in situ radical generation. It subsequently was determined from kinetic calculations that although some hydroxyl radical would be formed in the decomposition of persulfate, the primary active species in the system was sulfate radical anion, another free radical which is almost as reactive as and somewhat more selective than hydroxyl radical. Thus, the scope of objective 1 was broadened somewhat by information gained early in the project; and throughout the remainder of the above objectives, "hydroxyl radical"
should be read as "sulfate radical anion," abbreviated as SRA below. The details of the rationale for selection of persulfate as the candidate reagent were discussed in Section 1.

Batch Kinetics of SRA

The kinetics of SRA production is closely linked to that of persulfate since the former is generated directly from the latter by two pathways:

\[
\text{thermal: } \text{S}_2\text{O}_8^{2-} \rightarrow 2\cdot\text{SO}_4^{-} \quad (24')
\]

\[
\text{catalyzed: } M^+n + \text{S}_2\text{O}_8^{-2} \rightarrow M^+(n + 1) + \text{SO}_4^{-2} + \cdot\text{SO}_4^{-} \quad (25')
\]

The relative stoichiometry of SRA generation to persulfate decomposition depends on the relative extents to which reactions 24' and 25' occur in a given system.

Initial batch kinetic studies (experiments 1-7) were intended to determine the kinetics of thermal persulfate decomposition and to verify that our methods gave values in agreement with those of previous investigators. The two left-most points in Figure 2 verify that agreement. The rate constant determined in experiment 8 (see Table 4) was for reaction at 44 ± 2°C, a temperature lower than that studied by previous investigators. In Figure 3 this point (point 8, at 3.16 on the x-axis) is seen to be above the extrapolation of the data for higher temperatures, indicating a faster reaction than predicted. However, benzene was present in the reaction mixture during that experiment. Also shown in Figure 2 is the point from experiment 10, in which "cleaned" sand (i.e., sand which has had the organic material oxidized off of the surface) was used. This point fell lower than that for the benzene-containing solution. Finally, the point for the POS column in experiment 14 (\(10^3/T = 3.37\)) plotted even further (in log units) above the extrapolated line. This column had both sand and benzene present.

The lower right-hand corner of Figure 2 shows that as the temperature decreased, the experimental values of the rate constant \(k\) for experiments using sand and/or benzene deviated further from the extrapolated value of \(k\). This may be interpreted to mean that the catalyzed reaction (equation 25') becomes more important than the thermal reaction (equation 24'). The implication of this hypothesis is that in an actual aquifer reclamation situation, the persulfate decomposition kinetics (and thus those of SRA generation) would be dominated by the catalytic effect of the soil organic matter and perhaps the pollutant by-products as well. Under these conditions, the extrapolated value of the rate constants determined in the absence of solid and organic solute can be considered only a lower bound, and not even a particularly informative one.
Kinetics of Organic Compound Destruction

In almost all experiments (3, 5-9, 14) where the experimental design and precision of data allowed determination of the reaction order, initial benzene disappearance was found to be first-order. Entries in the last column of Table 4 indicate that the relationship between initial persulfate decomposition and initial benzene disappearance rates, called the stoichiometric ratio, varied from 0.67 to 4.79. This ratio did not, however, hold throughout the destruction process, and values higher than 1.5 - 2 may indicate that some slow adsorption is also included in that disappearance rate.

Stoichiometric ratios can actually be defined in two ways:

1) The instantaneous ratio, or the ratio of the reaction rates at a given time, \( R(t) \), and
2) The cumulative ratio, \( R_0(t) \), which may be defined as total benzene removal from \( t = 0 \) to time \( t \), divided by total persulfate removal during that time period.

For the regions where both benzene and persulfate reactions appear to be first-order, the instantaneous ratio may be given by

\[
R(t) = \frac{\text{rate of benzene disappearance at time } t}{\text{rate of persulfate disappearance at time } t}
\]

\[
= \frac{k_B B}{k_P P} = \frac{k_B B_0 e^{-k_B t}}{k_P P_0 e^{-k_P t}} = \frac{-(k_P - k_B) t}{R(t=0)e^{-k_P t}}
\]

where

\( B \) = benzene concentration
\( P \) = persulfate concentration
\( k's \) = first-order disappearance rate constants

\[
R(t=0) = \frac{k_B B_0}{k_P P_0}
\]

since \( e^{-k_B t} = 1 \) when \( t = 0 \).
Equation 29 predicts that the instantaneous ratio should decrease throughout the reaction.

The cumulative ratio is given by

\[
R_c = \frac{\Delta B}{\Delta P} = \frac{B_0 (1 - e^{-k_B t})}{P_0 (1 - e^{-k_P t})}
\]  

(31)

It can be shown that the integral of \( R(t) \) is not equal to \( R_c \). The values of stoichiometric ratios tabulated in Table 4 are instantaneous ratios calculated for \( t = 0 \), unless otherwise noted. Values in excess of 2 probably reflect a sorptive process which may be active in the early part of the curve.

For prediction of process performance in aquifer cleanup, where near-complete removal of benzene would be required, the (empirical) cumulative ratio, \( R_c \), is more informative. This ratio is plotted as a function of time in Figure 19 for the data from experiment 14. Since \( \Delta B \) and \( \Delta P \) are small compared to \( B \) and \( P \) in the early stages of the experiment, the experimental uncertainties are larger than the property being calculated in that region. In the later stages, \( \Delta B \) and \( \Delta P \) are much larger and the relative experimental uncertainties much smaller. Error bars corresponding to points at \( t = 7, 46, \) and 67 days have been included in Figure 19 for comparison. By this time, the ratio has decreased to about 0.15 in the old columns and 0.06-0.08 in the new column. This ratio can be interpreted directly as the average number of benzene molecules destroyed for each persulfate ion decomposed throughout the reaction. The low value of this efficiency was due in part to the fact that a significant fraction of sulfate radicals probably reacted with oxidation products of benzene. This reaction is, of course, desirable from the point of view of aquifer cleanup, but without a knowledge of products it is impossible to calculate an efficiency which is representative of destruction of all organic pollutants which are present.

The only reaction product which was detected was the precipitate which was formed at higher temperatures. This precipitate is thought to be a material of high molecular weight, resembling a polymer, which results from oxidative coupling of phenols, etc., formed as by-products of the reaction of sulfate radical anion. This precipitate was not seen at temperatures below 70°C, but the quantity formed at higher temperatures makes it seem likely that fragments of lower molecular weight were formed at lower temperatures. These fragments would have water solubilities that are intermediate between parent compound and
Figure 19. Cumulative stoichiometric ratio for experiment 14.
"polymer," and apparently did not exceed their solubility limit. If it were formed in the sand experiments, the polymer would be difficult to detect.

Prediction of Sand Column Results from Kinetic Data

As was indicated above, the rate of persulfate decomposition at temperatures below 40°C, in the presence of either sand or organic substrate, was an order of magnitude or more higher than that predicted by the thermal decomposition alone, i.e., the extrapolated line in Figure 2. Results (e.g., experiments 10 and 14) have also indicated that the rate will be related to the amount of catalytic material present in the soil or sand. This, in turn, may change with the length of time the sand is exposed to persulfate (compare curves POS and POS' in Figure 17). This implies that:

1) The kinetics may be system-specific, in which case they must be determined for the soil/sand and pollutant of interest.

2) The kinetics will change as the treatment proceeds, due to oxidation of pollutant, natural organic material, and/or complexed metals.

At this point a suitable model for this complex system has not been developed, and, particularly in view of 2) above, there has probably not been sufficient data collected to verify the generality of a model if developed.

However, it appears that the model should include at least the following features:

1) It must take into consideration both the "catalytic" and competitive effects of the soil material.

2) It should include both catalysis and competition from the reaction products of the organic pollutant.

The following model explicitly includes those points. It has been included only for completeness, as it is anticipated that this work will continue beyond the termination of this project. In the equations which follow,

\[ B = \text{benzene} \]
\[ P = \text{persulfate} \]
\[ X = \text{competitor substance on soil} \]
\[ X_p = \text{promoter substance in soil} \]
\[ Y = \text{competitor products from benzene destruction} \]
\[ Y_p = \text{promoter substances from benzene destruction} \]
\[ S = \text{sulfate radical anion} \]
The following reactions are considered.

**Radical production, promoter destruction**

\[
P + X_p \rightarrow S \quad (32)
\]

\[
P + Y_p \rightarrow S \quad (33)
\]

**Promoter production, competitor production/destruction, substrate destruction**

\[
S + B \rightarrow Y_p + Y \quad (34)
\]

\[
S + X \rightarrow f_x X_p + \frac{n_x - 1}{n_x} X \quad (35)
\]

\[
S + Y \rightarrow f_y Y_p + \frac{n_y - 1}{n_y} Y \quad (36)
\]

The parameters \(n_x\) and \(n_y\) are the number of times \(x\) or \(y\) must be "hit" by \(S\) before it is "destroyed," i.e., converted to noncompetitor. The fraction \(f_x\) is the fraction of \(X\) which are promoter sites, assumed constant throughout the reaction, i.e., \(x_p = f_x X\). The above model leads to the following rate equations:

\[
\frac{dP}{dt} = -k_{32}PX_p - k_{33}PY_p = -(k_{32}X_p + k_{33}Y_p)P \quad (37)
\]

\[
\frac{dS}{dt} = k_{32}PX_p + k_{33}PY_p - k_{34}SB - k_{35}SX - k_{36}SY \quad (38)
\]

\[
\frac{dB}{dt} = k_{34}SB \quad (39)
\]

\[
\frac{dx}{dt} = -k_{35}SX + \frac{n_x - 1}{n_x} k_{35}SX
\]

\[
= -\frac{1}{n_x} k_{35}SX \quad (40)
\]

\[
\frac{dY}{dt} = -\frac{1}{n_y} k_{36}SY \quad (41)
\]

\[
\frac{dX_p}{dt} = -k_{32}PX_p + k_{35}f_x X_p = (k_{35}f_x - k_{32}P)X_p \quad (42)
\]
\[ \frac{dy_p}{dt} = -k_{33}Y_p + k_{36}f_Yp = (k_{36}f_Y - k_{33}P)y_p \quad (43) \]

Sulfate radical anion (S) is reactive enough that the steady-state assumption (Moore and Pearson, 1981, p. 313), \( dS/dt = 0 \), may be invoked, giving

\[ S = \frac{(k_{32}X_p + k_{33}Y_p)P}{(k_{34}B + k_{35}X + k_{36}Y)} \quad (44) \]

so that

\[ \frac{dB}{dt} = \frac{-k_{34}(k_{32}X_p + k_{33}Y_p)}{(k_{34}B + k_{35}X + k_{36}Y)} PB = k'B \quad (45) \]

One simplifying first assumption is that the rate constants for SRA reaction with benzene and competitors are approximately equal, i.e., \( k_{34} \approx k_{36} \), where \( k_{34} \) is known (Ross and Neta, 1979). Similarly, for a first approximation we assume \( k_{32} = k_{33} \), leading to

\[ \frac{dB}{dt} = \frac{-k_{32}(X_p + Y_p)PB}{(B + X + Y)} = k'B \quad (46) \]

and

\[ \frac{dP}{dt} = -k_{32}(X_p + Y_p)P = -k''P \quad (47) \]

The first-order rate constant of the persulfate decomposition, \( k'' \), can thus be used to evaluate \( k' \), by

\[ k' = k'' (B + X + Y)^{-1} \quad (48) \]

but at \( t = 0, Y = 0 \), so

\[ X = \frac{k''}{k'} - B \quad (49) \]

If \( k_{32} \) can be evaluated from the literature, e.g., for Fe(II) or electron-donating organic compounds, then \( f_x \) can be determined from \( f_x = x_p/x \).
Thus, the system is entirely determined, except for the parameters \( n_x, n_y, f_x, \) and \( f_y \). By making further assumptions, such as that there is only one promoter amongst the benzene degradation products (e.g., the quinone/hydroquinone couple), the system can be further simplified. At that point, unsuitable assumptions must be culled by comparing the predicted kinetic behavior with the experimental data. This must be done by computer modeling, and although the program is presently being developed, more extensive data will probably be required before the utility of such a model can be determined.

**Feasibility of Oxidative In Situ Degradation**

The experiments described in this report have demonstrated that benzene can be destroyed by sulfate radical anion, generated from persulfate, in the presence of natural sandy soil. Even \( 0.5 \text{ M sodium bicarbonate, the equivalent of 50 ppm of alkalinity, does not seem to have an adverse effect on benzene removal rate or efficiency. These conclusions are illustrated most clearly in the results of experiment 14 (Figures 17-19). These results also seem to indicate that pollutant destruction may be quite dependent on the duration of exposure of the soil material to the persulfate reagent, although it was seen in experiment 14 that no logical relationship to TOC could be deduced. It thus seems likely that as treatment progresses, changes take place in the organic material which reduce its effectiveness as a promoter. The increased rate of persulfate disappearance in the new column (POS) in Figure 17 seems consistent with this explanation.**

Judging by the decreasing cumulative stoichiometric efficiency \( R_\text{C} \) (Figure 19) and the disappearance curves in Figures 17 and 18, it is likely that complete benzene removal would not be achieved, even if the experiment were carried out to essentially 100% persulfate disappearance. However, these conditions (1 mM benzene, 5 mM persulfate) were selected (more or less arbitrarily) at the beginning of this sequence of experiments. Furthermore, experiment 14 was a batch experiment and thus had a fixed persulfate:benzene ratio. In an actual contaminated aquifer, the organic compound would be retarded in its movement relative to persulfate, and the latter could be replenished. It should be recalled that if the organic compound were not retarded in its movement, that would indicate that it was not being sorbed to the aquifer material, and therefore in situ treatment would offer little or no advantage over a destructive pump-and-treat technology. Indeed, abiotic in situ treatment may find use as a means of mobilizing hydrophobic pollutants to be completely destroyed at the surface by another process.

Thus, although there are undoubtedly limiting conditions beyond which the process is not feasible, the results reported here support the conclusion that oxidative in situ degradation of organic compounds could be successful under some contaminated aquifer conditions.
There are, of course, many unanswered questions. This study has not, in general, identified conditions which are detrimental to the process, or even estimated limits of organic carbon, alkalinity, complexed metals, etc., which could be tolerated without severe detriment to the efficiency of the process. The nature of the dependence of the kinetics on natural materials present, the origin and role of the promoter substances, and many other questions need further study. The kinetic model needs development and verification, and thus more data must be collected. Questions such as on the role of coupled hydraulic and kinetic control, and the effect of grain size (i.e., soluble vs. sorbed reaction) have not even been addressed in this study. Nonetheless, results such as those from experiment 14 indicate that this innovative technology shows promise of feasibility.
SECTION 5

CONCLUSIONS

1) Abiotic oxidative in situ degradation of organic pollutants using sulfate radical anion generated from persulfate appears to be feasible in some cases.

2) Below about 50°C the kinetics of the radical-generating reaction appear to be dominated by the nature of the promoters present in, or generated from, the natural organic material and/or degradation products. This promoted reaction was at least an order of magnitude faster than the thermal reaction. Since it is probably system-specific, it must presently be determined by experiment until it is understood well enough to be modeled.

3) Persulfate decomposition, and thus radical generation, is in general faster in the presence of natural sand than in the presence of the same sand with the organic matter removed.

4) The equivalent of 50 mg/L of alkalinity had no detrimental effect on the process, even though bicarbonate is a known free-radical scavenger.
SECTION 6
RECOMMENDATIONS

Because of the indicated feasibility in some cases, this process should be further investigated. In particular:

1) More needs to be known concerning the nature of the promoters, both those present in the natural organic material and those formed as organic substrate reacts.

2) Further testing is needed, using actual soil/sands and ground water rather than synthetic ground water.

3) The role of sorbed versus dissolved substrate should be carefully considered.

4) Development and verification of a kinetic model of the process is needed, in order to better understand and optimize conditions for the process.

5) To the extent possible, the products of the reaction should be investigated, in order to better understand their competitive and catalytic function. This may be better done by HPLC methods than by GC/MS, because the products are probably not particularly volatile or stable.
REFERENCES


