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Lawrence Livermore National Laboratory

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Paper 79F

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Paper 79B

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Introduction

Experimental work with organic solvents at Lawrence Livermore National Laboratory has suggested that in situ thermal oxidation of these compounds via hydrous pyrolysis forms the basis for a whole new remediation method, called hydrous pyrolysis/oxidation. Preliminary results of hydrothermal oxidation using both dissolved O_2 gas and mineral oxidants present naturally in soils (e.g., MnO_2) demonstrate that TCE, TCA, and even PCE can be rapidly and completely degraded to benign products at moderate conditions, easily achieved in thermal remediation. Polycyclic aromatic hydrocarbons (PAHs) have an even larger thermodynamic driving force favoring oxidation, and they are also amenable to in situ destruction.

Today, the principal treatment methods for chlorinated solvent- and PAH-contaminated soil are to remove it to landfills, or incinerate it on site. The most effective method for treating ground water, Dynamic Underground Stripping (Newmark et al., 1995), still involves removing the contaminant for destruction elsewhere. Hydrous pyrolysis/oxidation would eliminate the need for long-term use of expensive treatment facilities by converting all remaining contaminant to benign products (e.g., carbon dioxide, water, and chloride ion). The technique is expected to be applicable to dense non-aqueous phase liquids (DNAPLs) and dissolved organic components. Soil and ground water would be polished without bringing them to the surface. This would dramatically decrease the cost of final site closure efforts. Large-scale cleanup using hydrous pyrolysis/oxidation may cost less than $10/yd. The end product of hydrous pyrolysis/oxidation is expected to be a clean site.

The delivery concept for hydrous pyrolysis/oxidation utilizes the established experience in heating large volumes of ground developed in the Dynamic Underground Stripping Demonstration (Newmark et al., 1995). Steam and possibly oxygen are injected together, building a heated, oxygenated zone in the subsurface. When injection is halted, the steam condenses and contaminated groundwater returns to the heated zone. It mixes with the condensate and oxygen, destroying any dissolved contaminants. This avoids many of the mixing problems encountered in other in situ oxidation schemes. In other oxidation schemes, an oxidizing reagent is injected into the subsurface resulting in the displacement of the contaminant. Without a return process such as the steam condensation, the contaminant and oxidant never mix. Using hydrous pyrolysis/oxidation, DNAPLs and dissolved contaminants may be destroyed in place, without surface treatment. This will improve the rate and efficiency of remediation by rendering the hazardous materials into benign ones via a completely *in situ* process. Because the subsurface is heated during this process, hydrous pyrolysis/oxidation also takes advantage of the large increase in mass transfer rates which make contaminant more available for destruction, such as increased

diffusion out of silty sediments. Many remediation processes are limited by the access of the reactants to the contaminant, making mass-transfer limitations the bane of remediation efforts in low-permeability media.

In preparation for testing this method at Lawrence Livermore National Laboratory (TCE in groundwater) and at a Southern California pole treating site (free product with PAH and pentachlorophenol), we are developing a concept for the implementation of hydrous pyrolysis/oxidation through co-injection of steam and possibly small amounts of oxygen, as well as evaluating the rate at which hydrous pyrolysis/oxidation occurs due to the natural presence of mineral oxidants such as manganese oxides when the water temperature is raised. We are also determining the thermodynamic properties (e.g., solubility, Henry's Law constants, etc.) of these hazardous compounds, as a function of T and P, in order to be able to predict effectiveness and required time for design purposes and to optimize clean-up through the use of process-oriented hydrologic transport and geochemistry models. In spite of recent advances in modeling capabilities, the thermodynamic data necessary to make design calculations for elevated temperatures are essentially nonexistent. Simple extrapolations from room-temperature data will not suffice.

Experimental Approach.

Over the last several years we have developed hydrothermal equipment and analytical capabilities ideally suited to investigating the reaction of solid, liquid and gaseous hydrocarbons and chlorinated hydrocarbons with water under conditions ranging from room temperature and pressure up to 450°C and 2 Kb. We have used this equipment to study the reaction of kerogen contained in oil shale with water to produce carboxylic acids and to study the interaction between the organic acids and reservoir minerals (Knauss et al., 1992, 1996; Knauss and Copenhaver, 1995a), to study the cracking of petroleum under both hydrous and anhydrous pyrolysis conditions (Jackson et al., 1995), to study the hydrous pyrolysis of organic solvents (including both chlorinated hydrocarbon and petroleum distillate based products) in the presence and absence of silicate minerals and, most recently, to make the measurements of the solubility of p-xylene as a function of temperature and pressure (Knauss and Copenhaver, 1995b). Because the reaction vessels are made of inert metals (gold and carefully passivated titanium) it is possible to work with the highly oxidizing fluids that are used in hydrous pyrolysis/oxidation.

The static autoclave experiments are run in Dickson-type, gold-bag rocking autoclaves. The reaction vessels use a flexible gold bag sealed with a high purity titanium head and are contained within a large steel pressure vessel (Figure 1). The vessel is loaded into a furnace capable of being continuously rocked through a 180° arc. Their design allows periodic sampling of the reaction cell under in situ conditions throughout the course of an experiment without disturbing the temperature

and pressure of the run. During the experiment, the solution contacts only Au and carefully passivated Ti so that unwanted surface catalytic effects are eliminated. We may, however, introduce any combination of solid, liquid or gaseous catalysts or oxidants into the reactors in order to study their effects on reaction mechanisms and rates. The sampled fluids and gases can be analyzed using a variety of analytical techniques including: ICP-ES, IC, GC and GC-MS (using either purge and trap or direct injection) and HPLC.

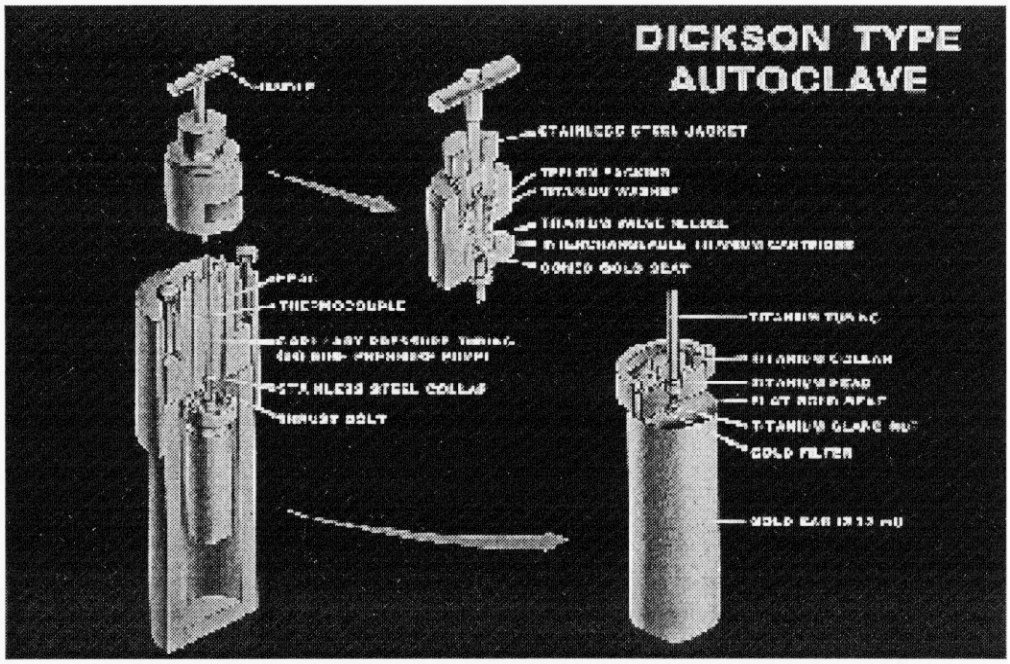

Figure 1. Schematic of the Dickson Autoclave system.

Because these runs are in closed systems, if desired we can load an excess of dissolved O_2 gas into the gold bag. This is accomplished by introducing a few ml of O_2 gas at 500 psi into the gold bag, letting it equilibrate at 500 psi overnight, and then removing the excess gas, yielding a single liquid phase containing dissolved oxygen. Experimental pressure is then held constant using a precise HPLC syringe pump at a total pressure just sufficient to keep the gas dissolved in the aqueous fluid at the desired run conditions. The runs with a soil mineral oxidant (e.g. MnO_2) only contain an amount of dissolved O_2 appropriate for air saturated water (i.e., approximately 8 ppm). In either case no headspace gas is present. All gases are dissolved in the liquid phase.

In order to conduct experiments which include a separate headspace gas, special pressure vessels that have pure Ti liners and heads machined of pure Ti are used. In these systems, the volume of the reactor is fixed, and the pressure changes as a consequence of sampling. If the initial pressure is sufficiently large and the sample size is small, the pressure change is minimal.

Initial Results for PAHs and Creosote Compounds

In our initial experiment, Visalia free product was equilibrated with water by stirring overnight. The water was decanted and placed in the bomb (no free product present). Oxygen gas was added to the system to establish an initial concentration of 18.5 umols/g. The pressure was maintained at 500 psi to keep the oxygen, and any product gas, in solution. This low pressure has no effect on the chemical reactions being measured. The temperature is increased as shown in Figure 2, until the reaction rate as measured by the production of carbon dioxide gas became rapid at 100°C After completion of the run, none of the starting contaminant chemicals were present (see

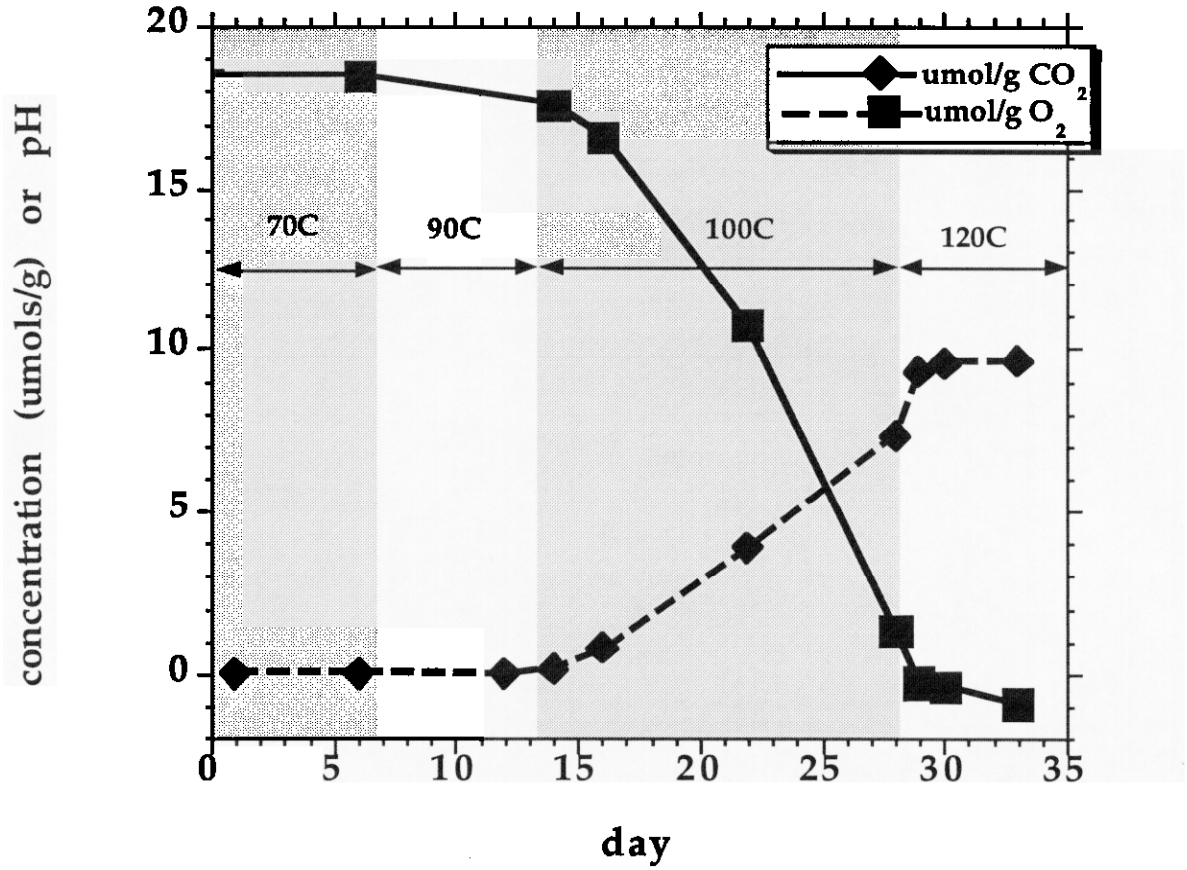

Figure 2. Oxidation of pole tar (Polycyclic Aromatic Hydrocarbons) dissolved in water, conducted in Dickson autoclave. The production of CO_2 is due to the oxidation of the dissolved pole treating chemicals by the oxygen introduced into the system. Free phase pole tar was present in this experiment.

Table 1 - "dissolved product").

In a second experiment (see Figure 2), free product pole tar was added to the Dickson autoclave in an amount exceeding the oxygen content of the water. This ensured that the oxidation

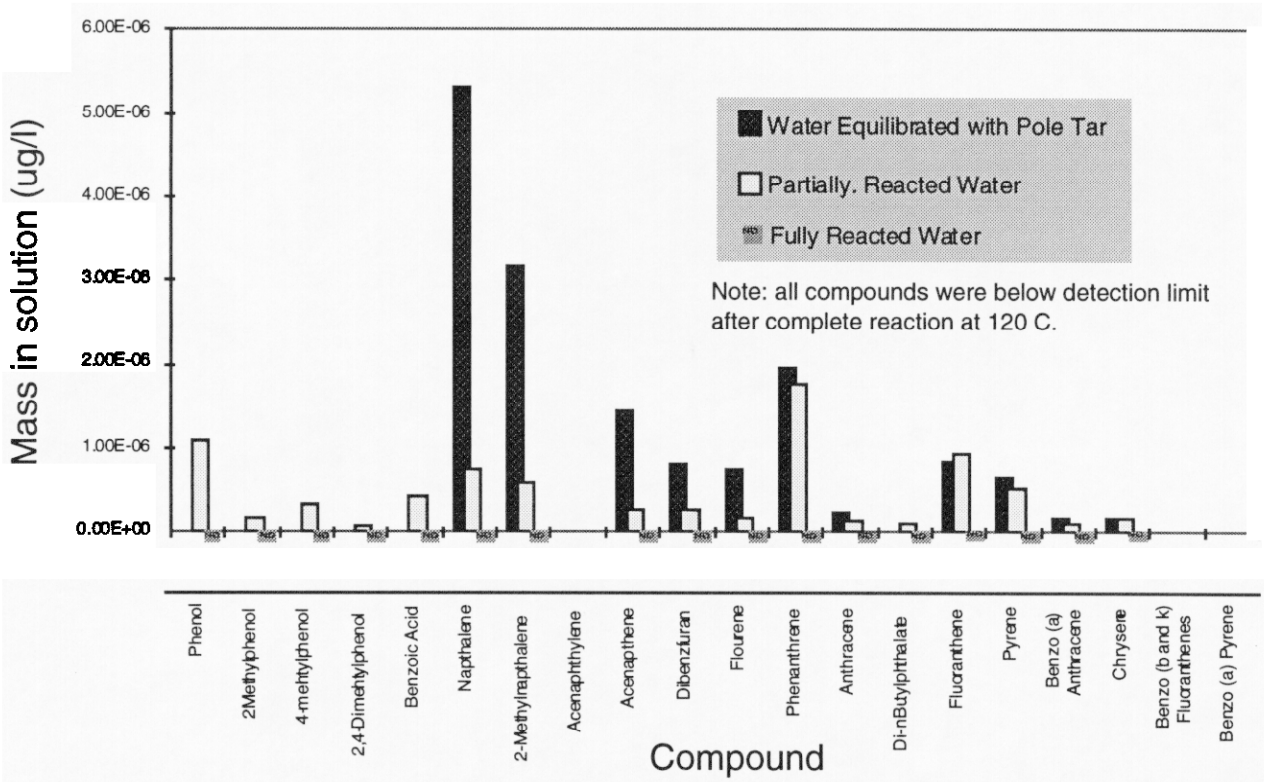

Figure 3. PAH compounds in pole tar tests, measured by EPA method 8270A.

reaction stopped before going to completion, allowing examination of intermediate products of the reaction. The results of this experiment are shown in Figure 2 and 3, and Table 1 "Free Product". All chemicals measured by EPA 8270 were reduced by the hydrous pyrolysis/oxidation reaction. The only new products formed, other than CO_2, were oxygenated phenols and carboxylic acids, which are innocuous compounds.

A series of experiments is underway to study the rates of HPO of two model compounds: naphthalene and pentachlorophenol (PCP). These are the two most abundant compounds in the main classes of compounds that comprise Visalia free product DNAPL. The initial emphasis was on determining the rate dependency on dissolved O_2 at temperatures easily achieved in thermal remediation (100° and 125°C). We found that, at dissolved O_2 concentrations as high or higher than the stoichiometric amount required to oxidize the dissolved naphthalene or PCP, the rates were independent of O_2 concentration.. We are continuing experiments to determine the rates and reaction order of naphthalene and PCP oxidation.

We are also measuring the aqueous solubility of fluorene, as a model compound for the PAHs found in Visalia pole tar. These measurements are being made up to 100°C.

Chemical	Equilibrated Water g/L	% Observed	Free Product Present Partially Reacted Water g/L	% Observed	Reportable Limit g/l	Dissolved Product Completely Reacted Water g/L
Phenol		0.0%	1.09E-06	14.35%	*<3.2E-08*	non-detect
2-Methylphenol		0.0%	1.35E-07	1.78%	*<3.2E-08*	non-detect
4-Methylphenol		0.0%	3.01E-07	3.96%	*<3.2E-08*	non-detect
2,4-Dimethylphenol		0.0%	5.20E-08	0.68%	*<3.2E-08*	non-detect
Benzoic Acid		0.0%	4.16E-07	5.48%	*<3.23E-07*	non-detect
Napthalene	5.29E-06	34.5%	7.39E-07	9.73%	*<3.2E-08*	non-detect
2-Methylnapthalene	3.14E-06	20.5%	5.62E-07	7.40%	*<3.2E-08*	non-detect
Acenapthene	1.44E-06	9.4%	2.48E-07	3.26%	*<3.2E-08*	non-detect
Dibenzfuran	7.95E-07	5.2%	2.62E-07	3.45%	*<3.2E-08*	non-detect
Flourene	7.22E-07	4.7%	1.76E-07	2.32%	*<3.2E-08*	non-detect
Phenanthrene	1.94E-06	12.7%	1.74E-06	22.91%	*<3.2E-08*	non-detect
Anthracene	2.26E-07	1.5%	1.25E-07	1.65%	*<3.2E-08*	non-detect
Di-nButylphthalate		0.0%	8.70E-08	1.15%	*<3.2E-08*	non-detect
Fluoranthene	8.36E-07	5.5%	9.11E-07	11.99%	*<3.2E-08*	non-detect
Pyrene	6.10E-07	4.0%	4.91E-07	6.46%	*<3.2E-08*	non-detect
Benzo (a) Anthracene	1.48E-07	1.0%	9.70E-08	1.28%	*<3.2E-08*	non-detect
Chrysene	1.78E-07	1.2%	1.64E-07	2.16%	*<3.2E-08*	non-detect
Benzo (b and k) Fluoranthenes					*<1.61E-07*	non-detect
Benzo (a) Pyrene					*<1.61E-07*	non-detect
Total Detected	1.53E-05	100%	7.60E-06	100%	*1.189E-06*	
Destruction			50%		>92%	

EPA Method 8270A, Calsience Environmental Laboratories, Inc, 2/1/96.

Table 1. Results of hydrous pyrolysis/oxidation testing of water saturated with pole-treating chemicals. "Equilibrated Water" was stirred with an excess of free-product (from a Southern California pole-treating site) for three days. "Partially Reacted Water" is the result of reacting the free-product/water mix at up to 120°C until all oxygen was consumed, stopping the reaction. "Completely Reacted" used the decanted, equilibrated water (no free product) with an excess of oxygen. The results of this experiment are also shown in Figure 13.

Chemical Hydrous Pyrolysis/Oxidation Process for TCE.

In the absence of measured values, group contribution estimation techniques may be used to calculate the free energies of formation of the aqueous and gas phase aliphatic chlorinated hydrocarbons, e.g., TCE. The estimated free energies may then be used to calculate the thermodynamic properties of hydrolysis and oxidation (HPO) reactions involving degradation of

those compounds, and thus estimate their thermodynamic driving force. For example, in a reaction written in the form:

Reactants = Products, the following equation is valid:

ΔG reaction = $\Sigma\Delta G$ products - $\Sigma\Delta G$ reactants

where: DG reaction = free energy of reaction

$\Sigma\Delta G$ products = sum of the free energy of formation of products

$\Sigma\Delta G$ reactants = sum of the free energy of formation of reactants

Calculations of this type can be made for aqueous and gas phase reactions (at 25°C) involving TCE as follows:

$$2C_2Cl_3H(aq) + 3O_2(aq) + 2H_2O = 4CO_2(aq) + 6H^+ + 6Cl^- \quad (1)$$

$$\Delta G = -467.9 \text{ kcal/mol}$$

$$2C_2Cl_3H(g) + 3O_2(g) + 2H_20(g) = 4CO_2(g) + 6HCl(g) \quad (2)$$

$$\Delta G = -414.1 \text{ kcal/mol}$$

$$C_2Cl_3H(aq) + 3MnO_2(s) + 3H^+ = 2CO_2(aq) + 3Mn^{+2} + 2H_2O + 3Cl^- \quad (3)$$

$$\Delta G = -228.1 \text{ kcal/mol}$$

$$C_2Cl_3H(aq) + 3Fe_2O_3(s) + 9H^+ = 2CO_2(aq) + 6Fe^{+2} + 5H_2O + 3Cl^- \quad (4)$$

$$\Delta G = -164.9 \text{ kcal/mol}$$

where: (aq) means aqueous.

(g) means gas.

(s) means solid.

Under the conditions of temperature, pressure and activity/fugacity implied in the above calculations, all these reactions have a significantly negative free energy of reaction, i.e., they are energetically favored. Although lacking the requisite calculated thermodynamic data, it is safe to assume that they would also be thermodynamically favored at higher temperature. We have shown experimentally that this is true. Furthermore, increased temperature greatly increases the kinetics of these reactions, which we have also shown experimentally. At 25°C these reactions are observed to proceed very slowly.

As an example, consider the results presented in Figure 4. It is clear that essentially complete mineralization of TCE has occurred within 2 weeks in air saturated water at 100°C. The reaction

products are in essentially the stoichiometric proportions appropriate for reaction (1) above. The TCE concentration has been reduced nearly 10,000-fold to a level below MCL.

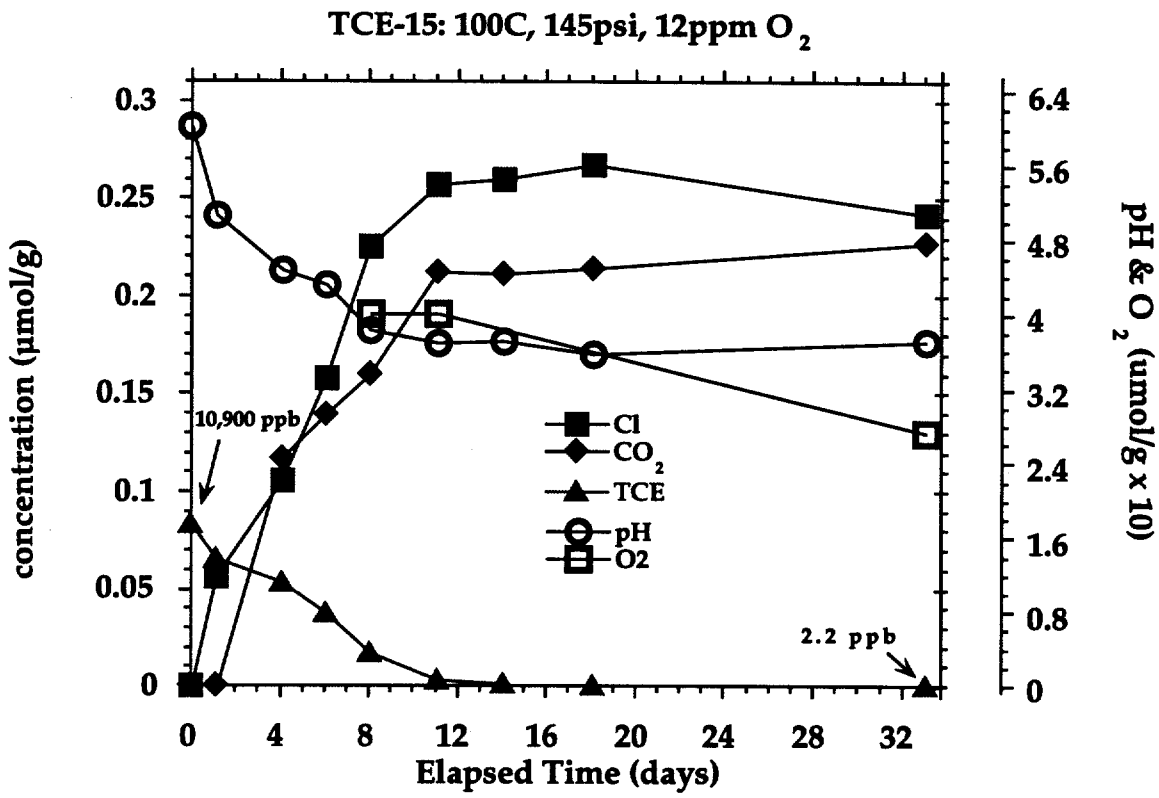

Figure 4 TCE Destruction via Hydrous pyrolysis/oxidation. Result of continuous sampling of a single run maintained a constant pressure and temperature using a Dickson autoclave system

Note that we have written reactions for both homogeneous gas and aqueous phase reactions, as well as heterogeneous reactions involving both an aqueous phase and the surface of a solid (oxide minerals commonly present in soils/aquifers). In an oxygenated environment, i.e., one in which the dissolved oxygen is present in more than the stoichiometric amount required to completely consume all the dissolved TCE, and one in which oxide minerals are present, both of these types of reactions would be occurring simultaneously. The surface chemical reactions would occur even at low dissolved oxygen levels, as long as the oxygen fugacity was sufficiently high to maintain the oxides as the thermodynamically stable form for Mn and Fe, i.e., as long as they were present. We also note that the dissolved oxygen concentration may be artificially increased, as appropriate, by injection of air, O_2, etc.

Use Of Hydrous Pyrolysis/Oxidation To Remediate TCE In Ground Water.

Initial assessment of the usefulness of hydrous pyrolysis/oxidation as a remediation method raised several critical issues which were addressed in the initial experimental program. These questions dealt with:

Oxygen Dependency. Because, generally speaking, homogeneous chemical reactions under a given set of temperature and pressure conditions tend to be more rapid than uncatalyzed heterogeneous ones, we focus our attention on reaction (1). We note that under conditions where the activity of water is one, because this is an aqueous reaction the concentration of water is never limiting and the reaction rate may safely be assumed to be independent of water activity, i.e., the reaction is zero order with respect to water. Similarly, at very high O_2(aq) activity measured rates may safely be assumed to be essentially independent of dissolved oxygen. The reaction rate may, however, depend upon the activity of O_2(aq) at lower concentrations. This can be determined by running a series of experiments at constant TCE(aq) in which O_2(aq) is varied over ~2 orders of magnitude.

Oxygen dependency becomes a critical engineering parameter if the oxygen existing in groundwater must be supplemented during steam injection. This requires more robust injection materials, and careful consideration to avoid the formation of a separate gas phase that can sparge contaminant. Similarly, if the reaction rate depends on oxygen content, treatment time could be affected by varying oxygen supplementation.

We have completed a series of experiments at 100°C in which TCE (aq) was fixed (~10 ppm) and O_2(aq) was varied by nearly two orders of magnitude (135 ppm - 3 ppm). In all these runs O_2(aq) was present in supra-stoichiometric amounts, relative to TCE (aq). The rate of TCE(aq) destruction is observed to be essentially independent of O_2(aq), in solutions that are sufficiently oxygenated to consume all the TCE initially present at 100°C. Since there is no benefit to using high oxygen concentrations, water saturated with air will suffice to destroy TCE in many cases. If large amounts of TCE need to be destroyed, such as from DNAPL, or if soil consumes oxygen, air can be added to the system to supplement the oxygen

Temperature Dependency. Because this reaction involves the breaking of C-C bonds, the activation energy is relatively high and the change in reaction rate with temperature is likely to be quite steep. By measuring the rate of reaction at fixed initial TCE(aq) and O_2(aq) at several temperatures, we can determine the Arrhenius activation energy for the reaction and extrapolate the reaction rate to conditions of lower temperature, where it is inconvenient to experimentally determine the rate.

A reasonable implementation of hydrous pyrolysis/oxidation involves a rapid destruction phase while steam is actively injected, and a residual destruction phase in which the remaining heat is

relied upon to more slowly destroy residual contaminant over a longer period of time. This will be important as a cost-savings measure. It will also be a critical parameter for the treatment of silty (impermeable) layers which are not readily penetrated by steam, but heat conductively.

We have made very preliminary measurements of the activation energy (E_a) by using runs that were conducted with very high TCE(aq) and O_2(aq) concentrations. The purpose of these runs was to determine the preferred pathways and the most common reaction products under the anticipated temperature and pressure conditions and to allow detection of deleterious reaction products that might result from reaction pathways with low yield, and so they were not optimized for the purpose of activation energy determination. Figure 5 shows the results of these studies. The observed activation energy of 81 KJ/mol is consistent with our expectations for this type of reaction. This corresponds to an increase in rate of approximately 2.2x for every 10°C rise in temperature.

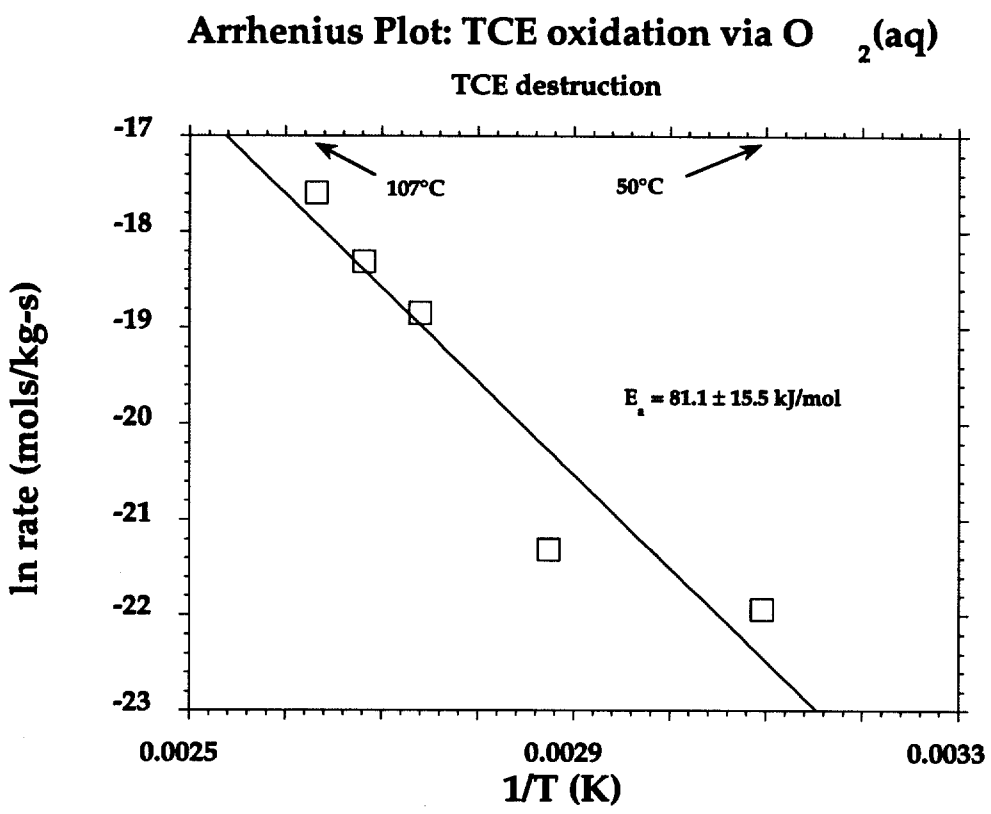

Figure 5. Dependence of the oxidation reaction on temperature.

Effects of 2-Phase Systems. The reaction of primary interest is that occurring in liquid water (reaction (1)). However, especially at higher temperatures in shallow systems (low hydrostatic pressure), two phases can exist upon heating and the thermodynamic and kinetic effects of partitioning of the reactants and products need to be determined. If oxygen supplementation is required, the effects of the separate gas phase on the reaction rate and on contaminant transport must be considered. For example, an important question is: will this reaction run in the vadose zone, or is it restricted to below-the-water-table application?

Initial results of these studies indicate that, as expected, the effect of partitioning TCE and possibly reaction intermediates into the vapor phase is to slow down the overall rate of TCE oxidation, relative to an equivalent single liquid phase experiment. We are continuing our investigations of the impact of mass transfer dynamics on the rate of TCE oxidation.

Soil and Ground Water Effects. Soil in the treatment zone can affect the process rate, as well as potentially releasing metal cations of regulatory concern. Affects on the reaction rate can be positive, through catalysis of the reaction or providing additional oxide surface reaction sites. One

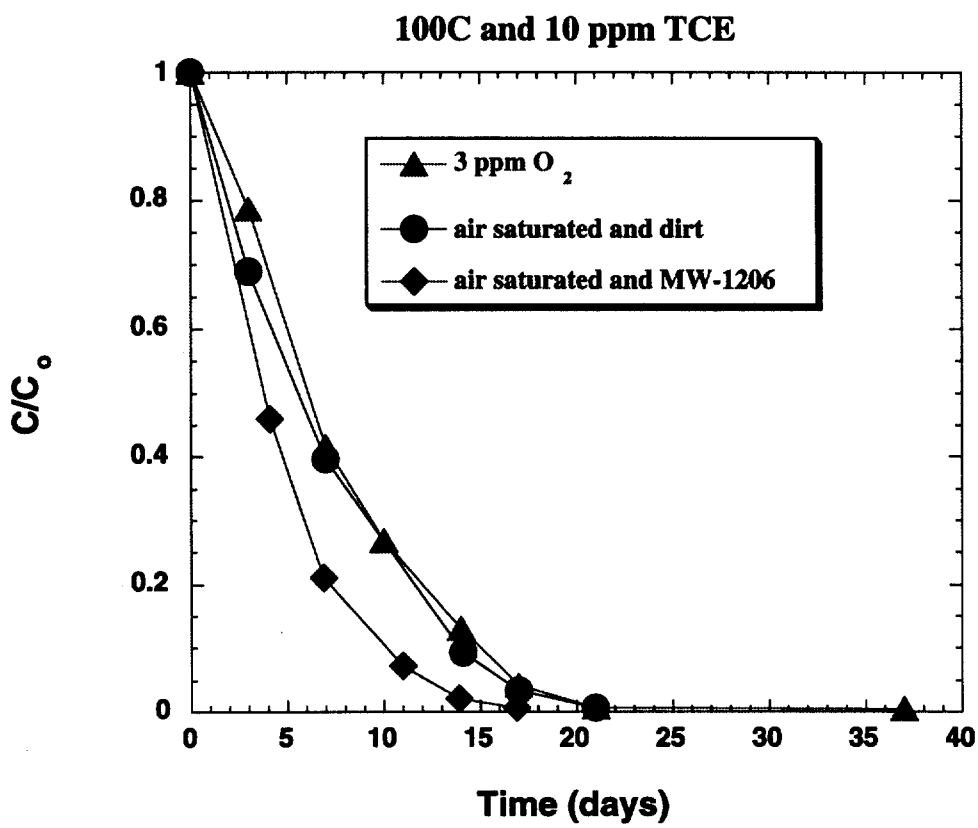

Figure 6. Oxidation rate experiments in with comparable oxygen and TCE content, showing the effects of the addition of site groundwater and site soil.

potential negative soil effect would be excess consumption of oxygen, through oxidation of metals or soil organic material (humates).

Figure 6 shows that there are no adverse effects from the presence of soil or groundwater recovered from a proposed test site at the Lawrence Livermore National Laboratory.

We have initiated runs to investigate the impact of high soil/water ratio on oxidation kinetics in both single liquid phase (+ soil) and two phase (vapor + liquid) experiments. We also plan to conduct runs specifically designed to investigate the oxidation of TCE coupled to the reductive dissolution of MnO_2.

Other Solution Effects. All of the reactions may have indirect dependency upon other solution parameters. For example, because the exact reaction mechanism is unknown, the reaction may actually be acid or base catalyzed and, hence, depend upon solution pH. The reaction may also depend upon solution ionic strength and, most certainly, this parameter affects the surface complex reactions involved in the coupled redox reactions that couple oxide mineral reductive dissolution to TCE oxidation. Knowledge of these effects is important for predicting the effectiveness of the reaction at a given site, as well as understanding whether the products of the reaction themselves may affect the rate (such as through build up of chloride ion derived from a substantial DNAPL source).We have run many experiments in low ionic strength solutions (see Fig. 1&2), where the pH was allowed to drift, because they contained Milli-Q deionized water with no buffer. In these runs the solution became progressively more acidic starting at pH 6 and dropping to between pH 4 and pH 3. We also ran two experiments in which the pH was buffered, either by the minerals present in the run or by the anions present in the groundwater. In these runs the pH was between 7 and 8. We are now conducting oxidation runs in which the solution pH is buffered using inorganic salts as buffers, in order to investigate the impact of solution pH on oxidation rate.

Field Implementation Concept for Hydrous pyrolysis/oxidation.

The oxidation of contaminants at steam temperatures is extremely rapid (several days to a week or so) if sufficient oxygen is present (Figures 2 and 4). This rapid destruction may presumably be utilized to eliminate contaminant *in situ.* This result can permit huge cost savings, because the operation of treatment facilities is the most expensive part of environmental restoration. Hydrous pyrolysis/oxidation may also permit treatment of radioactively-contaminated sites where groundwater cannot be extracted. Because the treatment is simple, it can be applied to large volumes of earth. The observed energy cost for heating soil of $1.50/cubic yard (heated to the boiling point by steam)(Siegel, in Newmark, ed., 1994) makes it feasible to consider hydrous pyrolysis/oxidation as a large-volume cleaning technique. An initial test of this method as a

source-area cleanup technique is currently in design at LLNL (Lawrence Livermore National Laboratory, 1996).

For the purposes of this feasibility assessment, we considered huff-and-puff treatment as the prime treatment method (Charles Carrigan et al., LLNL internal report, 1995). The feasibility assessment used the following additional assumptions:

1- Steam mixed with a small amount of oxygen or air (at most 100 ppm total oxygen in the steam/air mixture) is injected into a permeable zone to build a small steam zone. Approximately 400 lb. of steam are required for each cubic yard of soil. The soil itself serves as the inert containment (analogous to our gold vessels in the laboratory) since soil is already highly oxidized and has been shown in our tests to be unaffected by these conditions.

2- Steam injection is halted, and groundwater returns to the heated zone. About 1/15th of the water in the heated zone is condensed from the steam. Oxygen present in the steam dissolves in the water as the steam condenses.

3- Heat retained by the soil heats the returning groundwater (and entrained contaminant) to nearly the steam-water equilibrium temperature at the injection pressure. This will usually be considerably higher than 100°C, since steam is injected under several (2 to 7) bars pressure. Contaminant is oxidized by the oxygen contained in the water.

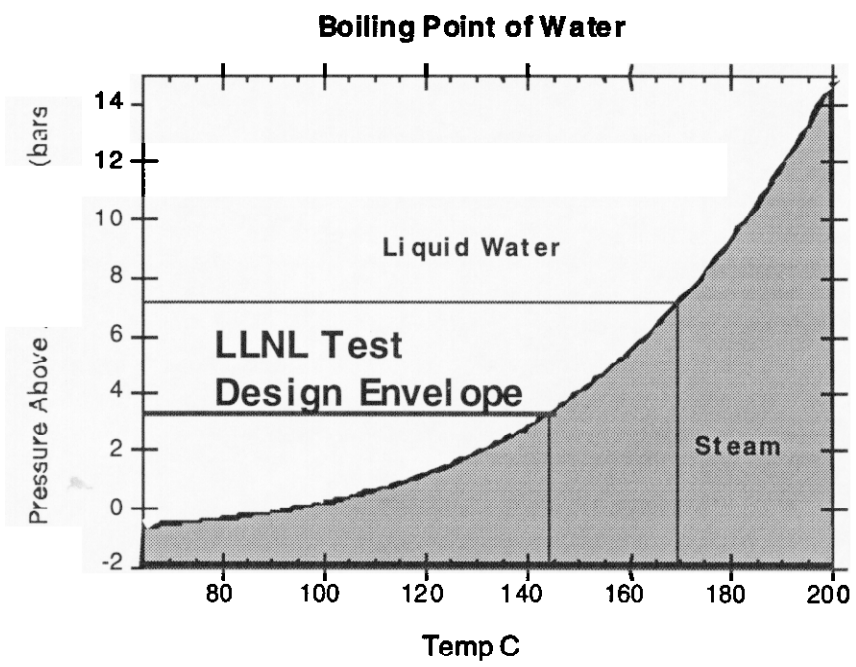

Figure 7. Boiling curve of water as a function of temperature and pressure. Superimposed is the range of expected temperatures and pressures for the LLNL test.

4- Steam is reinjected, building a larger heated zone and repeating the oxidation process. The process is repeated until the steam zone growth is limited by heat loss to the edges.

Injection Pressure:

Maximize injection pressure to keep steam zone displacement front vertical, evenly heat lower section of permeable zone.

The cyclic steaming ensures that any water displaced by the steam injection only moves a few meters before being pulled back through the hot zone and cleaned. The basic process is also conceived to benefit from the following conditions:

1- Current oxygen levels in many ground waters are greater than the stoichiometric amount of oxygen required to destroy existing contaminant. Contaminant can be expected to oxidize in heated areas even if no oxygen is added.

2- Manganese oxide minerals ubiquitously present in the subsurface, particularly in the western United Sates, have also been shown to oxidize contaminant.

3- Heating increases diffusion, dissolution, and transport, speeding the removal of contaminant from less permeable sediments.

After the heating system is shut off, residual heat will continue remediating the low-concentration areas around the source for many years. As the warm water migrates, contaminant will slowly degrade. Very little oxygen is required, particularly for chlorinated solvents. On a weight-for-weight basis, each gram of oxygen in water will destroy three grams of TCE. As heat diffuses into the impermeable zones, it will destroy the contaminant trapped in those layers utilizing the pre-existing oxygen in the formation. In this respect the heating methods are extremely robust; steam forces its way into the lowest permeable zones, and diffuses into the rest. If steam cannot get into part of the formation, then contaminant could not either. Since the contaminant is destroyed in place and does not have to be transported back out of the formation, the overall process is more robust than dynamic underground stripping as implemented at the LLNL gasoline spill area (Newmark et al., 1995).

Hydrous pyrolysis/oxidation has been tested on several other organic contaminant types, and has been effective in destroying all of them. These include TCA, which oxidizes more readily than TCE, and PCE, which oxidizes slightly less readily. PCE requires about a 20°C increase in temperature to maintain the same rate of oxidation as TCE. Other organics tested and oxidized include ethylbenzene, methyl tert-butyl ether, napthalene, pentachlorophenol, and a variety of polynuclear aromatic hydrocarbons. The most significant difference among these contaminants is

in their oxygen demand, the amount of oxygen required to completely destroy them. The chlorinated compounds are already highly oxidized, and require relatively little oxygen while aliphatic hydrocarbons can require a factor of ten more oxygen (Figure 8). At steam temperatures (100°C) approximately 25 ppm of air, and hence 5 ppm of oxygen, will dissolve in water. Dividing 5 ppm by the number shown for each contaminant in Figure 8 yields the maximum amount of contaminant that can be destroyed in solution in one steam/oxygen injection cycle. Thus for pentachlorophenol, 5/.34 = 15 ppm pentachlorophenol that can potentially be destroyed in solution by dissolved oxygen. Higher concentrations, or free product accumulations, would have to be destroyed by repeated injection and collapse of steam/air mixture.

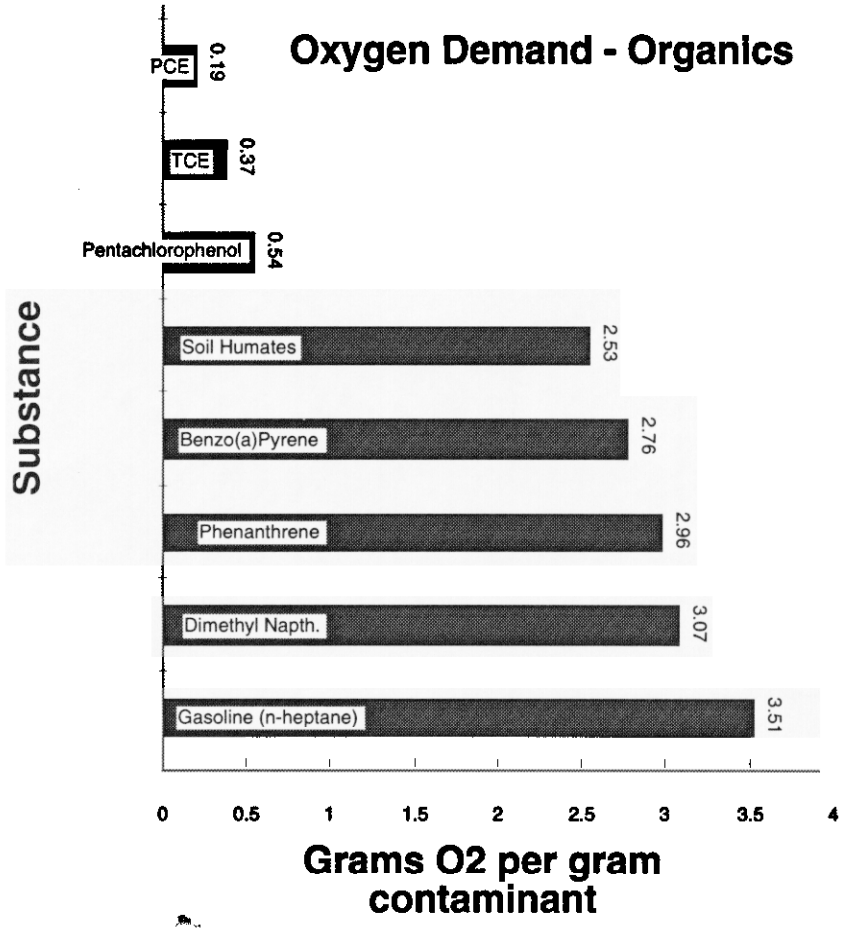

Figure 8. Oxygen required to completely destroy several organic contaminants and soil constituents via hydrous pyrolysis/oxidation.

Conclusions

Oxidation of organic chemicals dissolved in ground water appears to be routinely achievable at temperatures near 100°-120°C. At these temperatures TCE, PAH compounds, pentachlorophenol, PCE, TCA, ethylbenzene, methyl tert-butyl ether, and napthalene, have all been shown in laboratory studies to degrade to carbon dioxide, water, hydrogen ion, and chloride ion when stoichiometrically sufficient oxygen is present. The reaction is called hydrous pyrolysis/oxidation to reflect the similarities to the reactions noted in the higher-temperature cracking of crude oils in the presence of water, with the addition of an oxidative completion step.

The required temperatures can be achieved *in situ* through steam injection (Newmark et al., 1996.) It is envisioned that injection of steam in a cyclic fashion to promote mixing between the existing liquid, and injected gas phases will be sufficient in many cases to destroy contaminants *in situ*. Although some displacement of the contaminated water will occur during the initial injection of steam, that water will return to the steam-heated zone between injection pulses. It will be drawn back into the hot reaction zone by the condensation of the injected steam. The reaction zone will stay hot due to the large heat capacity of soil and the comparatively small volume of water contained within it. When large volumes of contaminant are present, such as in the case of DNAPL contaminant, injection of air or oxygen with the steam may be used to supplement existing oxygen and ensure complete mixing of the injected gases with the ground water. We believe that many contaminants can be completely destroyed *in situ* by this method.

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