



# Analysis of the steam injection at the Visalia Superfund Project with fully compositional nonisothermal finite difference simulations

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## Abstract

By injecting steam, over 1.1 million pounds of creosote has been recovered at the Visalia, California Superfund Site from an aquifer 102 ft underground. In the first 6 weeks of injection 320,000 lb of creosote were recovered or destroyed versus <1 lb per day in a pump and treat. The finite difference simulator STARS<sup>1</sup>, which is widely used in the oil industry to model thermal recovery, has been used to simulate simplified models of the project, to analyze recovery mechanisms, and to demonstrate how the operation of similar projects can be improved.

The simulations indicate that vaporization of dense, nonaqueous, phase liquids (DNAPLs) is the most important recovery mechanism, that liquid production is enhanced because a gas phase is present, and that the project could have been completed more rapidly if an additional injector or producer had been added in the center of the site. In addition, the mineralization (conversion to carbon dioxide) of DNAPLs could result from reaction with water, injected air or, most likely, both. The mechanisms are likely to be similar to subcritical water oxidation.

While this analysis suggests methods to improve operation of future steam projects, Visalia has been a very successful demonstration of the potential of steam injection to clean up recalcitrant hydrocarbons and will be an inspiration for future projects. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Background of site and history of steam remediation

The Visalia site was used to soak power line poles in “pole oil” [1]. The oil was initially a mixture of diesel and creosote but later 5% pentachlorophenol (PCP) was dissolved in

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<sup>1</sup>Developed, maintained and marketed by Computer Modeling Group Ltd., Calgary, Alta., Canada.

diesel. The site was used for 57 years and was contaminated by pipeline and tank leaks that seeped into a 27 ft thick aquifer 102 ft underground.

The contaminated aquifer is one of several high permeability, 500–10,000 md (0.0005–0.02 cm/s) sand/gravel layers beneath the site. Active wood treating stopped at the site around 1980. Approximately 4 acres were contaminated, i.e. around 1,000,000 cubic yards. An underground barrier was installed to halt movement of the contamination in the aquifer, and a pump and treat operation began in 1976–1977. After 20 years of operation, <1 lb of contaminant was being recovered each day from several production wells, even though the contamination in a high permeability zone of the aquifer was as much as 4% of the pore volume. The average concentration in the aquifer zone must have been at least 1.5% if the contaminated zones contained over 1 million pounds of DNAPLs.

The Visalia, California site had the advantage for the use of steam to enhance remediation of being near some of the oldest and larger oil field steam injection projects in the world, Fig. 1. Steam has been injected in nearby oil fields for almost 50 years [2]. This means that the equipment and experienced personnel needed to organize a steam injection project were readily available.

Years before the Visalia project, research began at UC Berkeley into the use of steam to clean up contaminants [3]. In 1992, Lawrence Livermore National Laboratory (LLNL) remediated 1 acre of gasoline-contaminated aquifer and clay layers by injection of steam and limited use of electrical resistance heating. The site was cleaned in 6 weeks [4].

A few years later, Southern California Edison (Edison), the current owner of the Visalia site, selected steam to clean up the aquifer. Steam was chosen since the pump and treat could not clean up the site for thousands of years and enhanced bioremediation techniques were

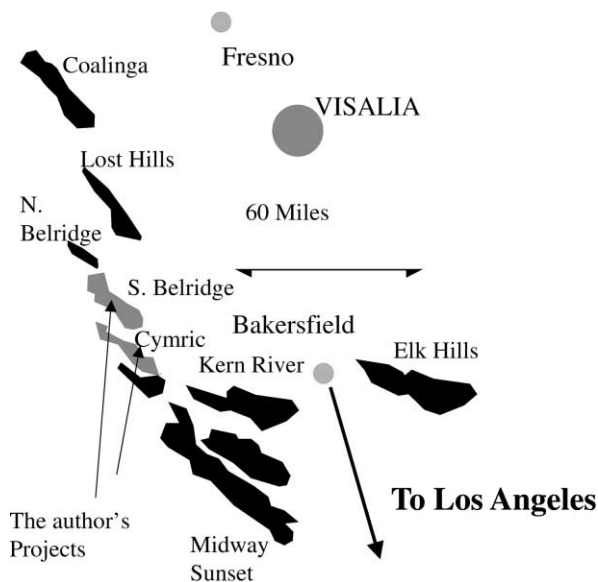


Fig. 1. Location of Visalia and major oil fields in the San Joaquin Valley.

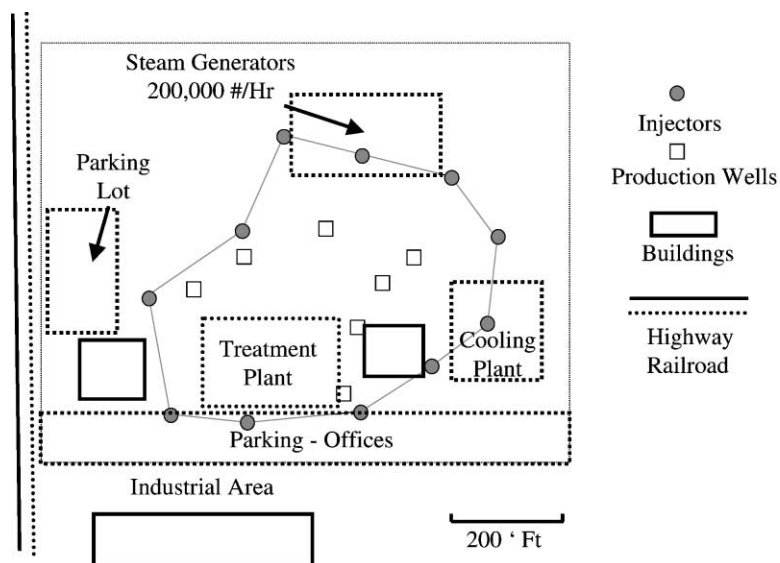


Fig. 2. Visalia site map.

also shown to be very slow. Edison's economic calculations indicated that steam injection would have a larger initial cost, however, it would have a present value savings of almost US\$ 100 million. Steam saved money because the site would be decontaminated in a few years and additional expenses would not accrue for hundreds of generations.

Steam injection began in 1997. The facilities depicted in Fig. 2 included seven producers arranged in two lines, surrounded by 11 steam injectors [5]. Steam was initially supplied by four 50,000 lb/h steam generators leased from and operated by a regional steam injection contractor. The original equipment could inject 13,500 barrels per day of steam (200,000 lb per day) or enough for several 100 acres of injection at a California heavy oil production project. The initial injection rate was high so that the steam temperature at 65 psig and 310 °F would rapidly heat the formation enough to increase vaporization and enhance decomposition reactions. After the initial period the injection rate was decreased so that only one steam generator was used later in the project. Steam injection ended in 1999 after recovery or destruction of 1.13 million pounds of DNAPLs. The site is now in the process of being delisted.

## 2. Recovery mechanisms with steam

A pump and treat cannot recover a large portion of a NAPL because it is trapped by water, but a gas phase reduces the trapping drastically. The mechanisms work this way [6]. When the NAPL first enters the aquifer and water is displaced, the NAPL is a continuous phase whose relative permeability (drainage curve in Fig. 3) is a few percent of water's relative permeability.

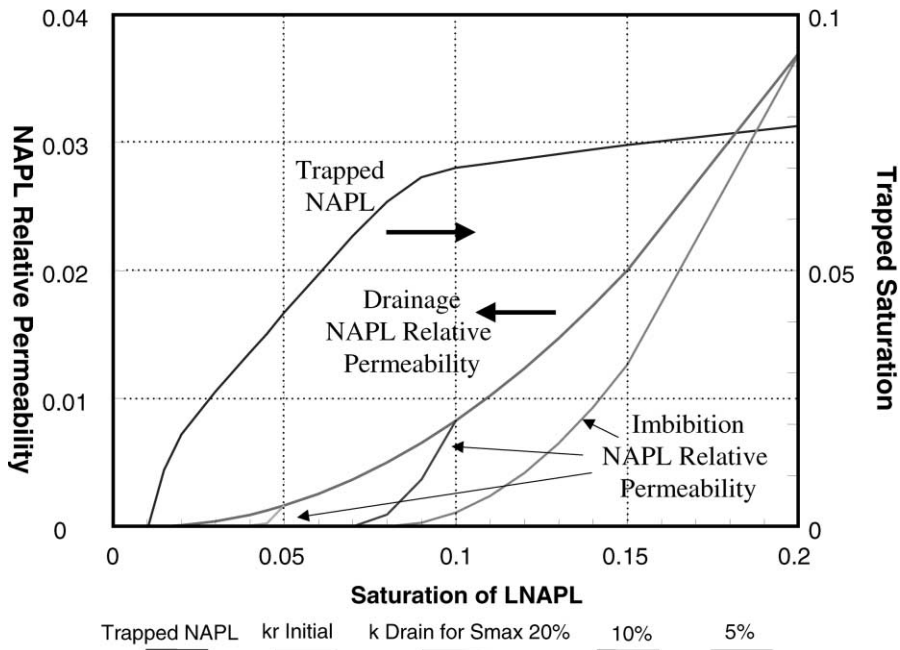


Fig. 3. Drainage and imbibition relative permeability for a spreading NAPL.

The NAPL saturation increases until it is in capillary equilibrium with the surrounding water. Thus, a 10 ft thick layer of free-product might have a maximum saturation of 10%. A thicker layer could have a higher initial saturation and relative permeability.

### 2.1. NAPL trapping

When the water imbibes and its saturation increases, the NAPL relative permeability decreases. As water flows in (imbibition-curve) the water first fills the pore throats between sand grains and breaks up the NAPL into elongated blobs. When the blobs become short enough, the pressure gradient in the aquifer cannot move them and they are trapped. The trapped saturation is determined by the maximum NAPL saturation at that depth. Thus, Fig. 3 contains a spectrum of imbibition curves and trapped saturations that are determined by the local maximum saturation. It may take many years for a pump and treat to reduce the NAPL saturation to the trapped saturation, but recovery of significant quantities of NAPL will decline rapidly as the relative permeability decreases and large volumes are left behind.

### 2.2. NAPLs with vapor

When an immiscible gas (steam or air for instance) is injected into the aquifer and the NAPL, e.g. gasoline or diesel, spreads between the gas and water the NAPL relative

permeability increases since gas now fills the center of the pores and water drains from the pore throats. This means that the NAPL surrounds the gas, is a continuous phase again, and is no longer trapped by water. Therefore, its relative permeability increases. There are many models of how the relative permeability changes in the presence of gas. The simplest is to interpolate linearly between the imbibition and the NAPL-gas curves as the gas saturation increases [7].

Since the NAPL is no longer trapped by water, there can be a 20:1 reduction in the residual volume of NAPL by injecting a gas. Thus, a soil-vapor-extraction project (SVE) can recover additional NAPL even without vaporizing the contaminant. Unfortunately, drainage of NAPL in the presence of a vapor can still take many years.

### 2.3. Vaporization

Fig. 4 is a plot of the boiling points (at one atmosphere and reduced pressure) of normal alkanes labeled with the boiling points of a few common contaminants [8].

The plot shows that small molecules, like benzene and chlorinated solvents, vaporize around the boiling point of water, while PCBs and mercury boil at high temperatures. Lowering the subsurface pressure to the contaminants vapor pressure reduces the boiling temperature of the NAPL. This is shown as the 100 mm (0.135 atm) vapor pressure curve in Fig. 4. The 100 mm curve also represents the temperature at which a contaminant could comprise 13.5% of the gas volume in a vadose zone at 1 atm and be produced by

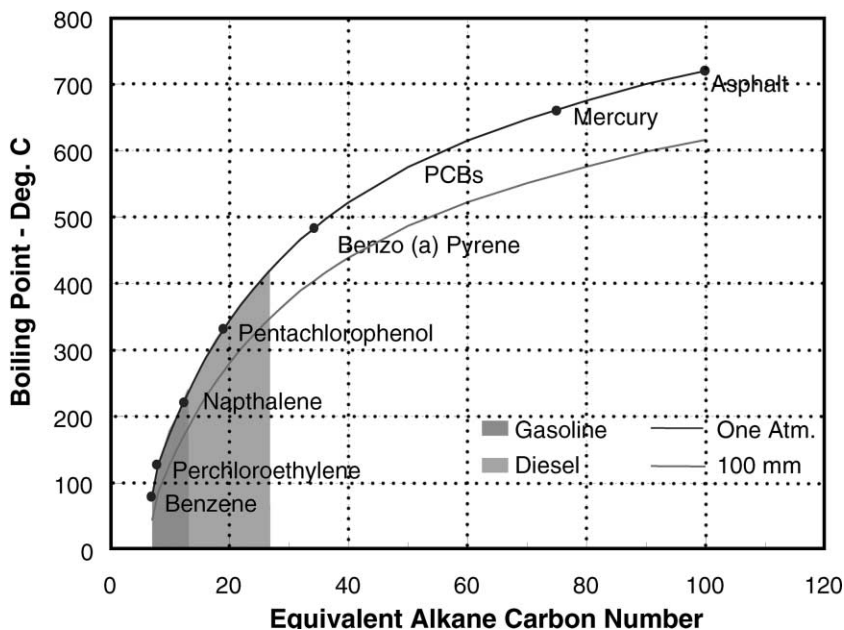


Fig. 4. Vapor pressures of normal alkanes and common contaminants.

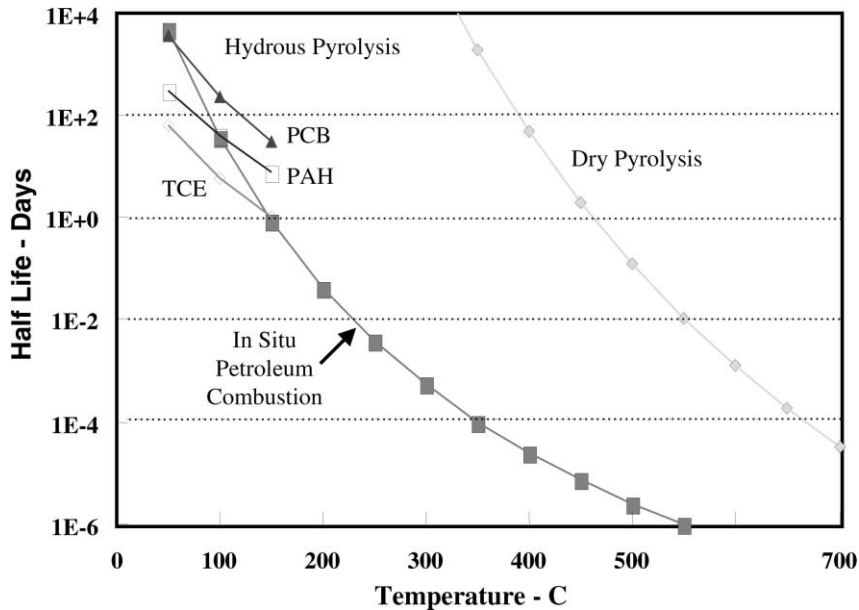


Fig. 5. Half Lives of DNAPLs in several oxidation and pyrolysis reactions.

steam stripping. The temperature of steam increases substantially with injection pressure. Thus, steam injected at 150 psig (200 °C) will slowly vaporize DNAPLs like pyrene (a large component of creosote) just as injected air will slowly vaporize gasoline in a SVE project [9].

#### 2.4. DNAPL decomposition

Fig. 5 shows how the half-lives of contaminants are affected by several reactions at elevated temperature. The figure shows that while contaminants oxidize in a few weeks at 150 °C, they pyrolyze or oxidize in a few milliseconds at 700 °C. Pyrolysis, for instance, is the preferred method to manufacture ethylene.

Hydrous pyrolysis is an oxidation reaction involving oxygen, water and hydrocarbon contaminants and may be similar to coal gasification reactions [10–12]. It is the low-temperature analog of “subcritical or supercritical water oxidation” [13]. The reaction is a useful method to decompose low-vapor-pressure compounds like pyrene that do not oxidize quickly at low concentrations in typical gas-phase, light oil air oxidation reactions [14]. In fact, it may be the first step of the in situ oxidation sequence that is ignored by petroleum engineers in the several in situ combustion projects currently underway in the San Joaquin valley [15]. Pyrolysis is high-temperature decomposition of a chemical via a free-radical mechanism. It can proceed after all water has evaporated at in situ, thermal (conduction) destruction heating projects [16].

### 2.5. Summary of mechanisms

Increasing temperature reduces the viscosity of a DNAPL, thus pole oil, which has a viscosity of 30 cP at 25 °C, would have a viscosity of 1.5 cP at 100 °C. So, viscosity reduction, relative permeability enhancement by gas injection, increased vaporization, and decomposition reactions are all mechanisms that contribute to thermal remediation projects.

## 3. Discussion of computer simulations of remediation with steam

STARS, the leading oil-field thermal simulator, was used to simulate steam injection at the Visalia Superfund Site. STARS has several dozen models of advanced, in situ processes built into its code. It is used for geomechanical, geochemical, and compositional modeling with both orthogonal and nonorthogonal grids. In addition, it has explicit models of fluid flow in wells and heat loss from wells. The model can be used with over 100,000 grid blocks, up to 22 reacting solid, liquid or gaseous components and dozens of wells. Phase behavior is modeled with  $K$  values input by the user or calculated by equation-of-state models. STARS is used by over a thousand engineers to model steam injection, in situ combustion, electrical resistance heating and surfactant flooding. The simulator is supported by Windows based model building and three-dimensional stereoscopic, visualization post-processing software and is user friendly. These simulations were conducted on 200 and 400 MHz PCs with 128 and 256 Mbyte of RAM.

The layers of the models used in this study consisted of 525 (15/35) 15 ft square cells. Both two- and three-dimensional models were used. All models had 18 vertical injection and production wells and a horizontal water injection model to mimic water influx into the “intermediate aquifer” at Visalia. A single layer, 27-ft thick, 500 md, 30% porosity model of the aquifer (model 1), containing 740,000 lbs of DNAPL, was used for most simulations. Three-dimensional simulations were conducted in an 11-layer model containing about 6,000 cells and 1,000,000 lbs of DNAPL (model 2). A horizontal injector allowed air influx into the vadose zone in this model, and the “intermediate aquifer” was subdivided into three layers. One of these layers was 2 ft thick, had a permeability of 10,000 md and 4% (pore volume) DNAPL saturation to mimic a “hot streak” in the aquifer.

Permeability randomly varied by 20% and both the porosity and permeability increased as the formation dilated during injection and decreased as it compacted during production. Lower permeability layers above the “intermediate aquifer” were not modeled explicitly, but vertical permeability was 20% of horizontal permeability

“Pole oil” was modeled as a four-component fluid consisting of  $C_{10}$ ,  $C_{20}$ ,  $C_{30}$  and  $C_{40}$  alkane equivalents. A  $C_{20}$  alkane, for instance, has approximately the same vapor pressure as PCP, while creosote has the vapor pressures of  $C_{10}$ – $C_{40}$  alkanes, and diesel contains  $C_{10}$ – $C_{24}$  alkanes and aromatics. The viscosity of the each component was adjusted to obtain the 30 cP pole oil viscosity reported by Udell and coworkers [3]. Both models were used to simulate 5 years of a pump and treat followed by up to 427 days of steam injection and contaminant production.

Mineralization of the DNAPL was simulated by allowing each component to react with water and/or oxygen using kinetic parameters derived from descriptions of “hydrous

pyrolysis”. The nature of these reactions will be discussed in more detail later. Steam was injected either continuously or for 7 days, followed by a 21-day production period. Air was injected either concurrently with the steam slugs or as a separate slug.

#### 4. Results of computer simulations

##### 4.1. Vaporization

Steam enhances recovery of a DNAPL by reducing DNAPL viscosity, increasing its relative permeability in the presence of gas, and vaporizing immobile DNAPLs. The resulting liquid and vapor production are reported for model 1 in Fig. 6. The steam was injected continuously for 6 weeks, followed by a 21-day depressurization cycle. Then steam was injected in 13, 7-day injection periods each followed by 21 days of depressurization. Fig. 6 illustrates the following: first, almost 80% of the production in the first 6 weeks results from vaporization. At 400 days over 90% of the DNAPL is produced in the vapor phase. Next, production is highest when steam is injected. There is less production during the depressurization cycle. Finally, the components produced in the liquid and vapor are reported by the simulator. The components with the highest vapor pressure are mostly produced in the vapor, but the fraction produced as vapor decreases with decreasing vapor pressure. This means that almost all of the low-boiling contaminant is produced as vapor, but the harder to distill components are left behind. Specifically, all DNAPLs with boiling points lower than eicosane ( $C_{20}$ ) were produced in the steam. Virtually all the diesel diluent is produced quickly as a vapor. The un-ionized PCP, which has the boiling point of a  $C_{20}$ , can be readily

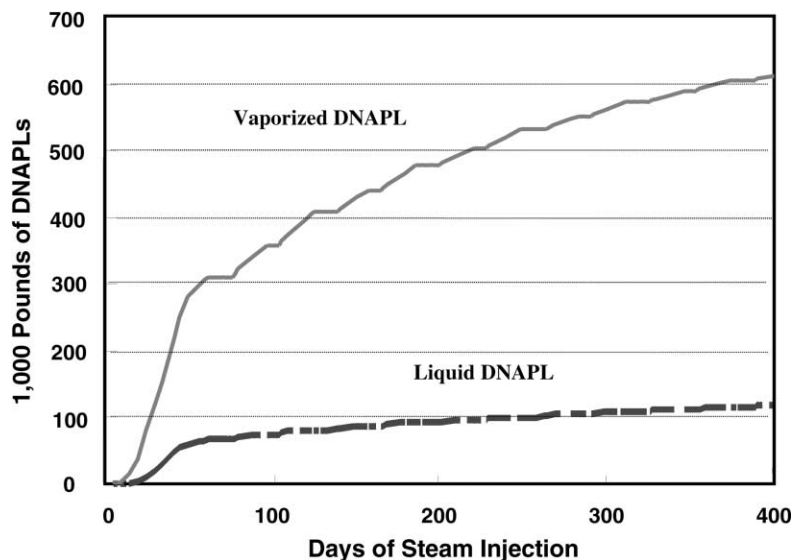


Fig. 6. Recovery of liquid and vaporized DNAPLs from model 1.



produced, and about half of the creosote components can be produced quickly as vapor. The rest of the contaminants are produced gradually as they are steam stripped from the DNAPL remaining in the model.

Since vaporization of DNAPLs is the primary recovery mechanism, the DNAPLs can move wherever the steam moves, and steam like all hot gases rises. When the steam rises out of the contaminated aquifer in a project like Visalia, it carries vaporized DNAPLs with it through the vadose zone that had been contaminated as the pole oil drained towards the aquifer. Thus, steam can move DNAPLs into the vadose zone. Fig. 7 depicts how steam could have redistributed DNAPLs at Visalia. Fig. 7a shows the initial conditions of a simulation. The intermediate aquifer (bottom three layers) is highly contaminated, and there is much less contamination in the vadose zone. After 10 months of steam injection the aquifer is almost clean. However, the DNAPL concentration has increased in the vadose zone, Fig. 7b. Fig. 7c reports the hydrocarbon concentration in the gas phase and shows that the DNAPLs in Fig. 7b condense from the gas phase in the cooler lower pressure zones closer to the producers.

#### 4.2. Well locations

The producers in Fig. 2 are arranged in two roughly parallel lines. This allows DNAPLs to collect between these wells. Fig. 8 shows how adding either a central injector or central producer to this pattern decreases the time required to clean model 1 with continuous steam injection. About 90% of the contaminant is removed after one year of steam injection with the wells shown in Fig. 2. However, if a central producer is included, 98% of the DNAPL is removed in one year. If a central injector is used, the site is cleaned in 250 days.

Fig. 9 contains maps of remaining contamination and shows why the removal was faster with alternative well configurations. Initially, the contamination is a constant 2% in the area between the injector wells. With no center well (Fig. 9a) the contamination increases between wells. When either a central injector or producer is added, that oil is removed (Fig. 9b and c). Alternatively, cycling the two rows of producers on and off (Fig. 9d) pushes the contaminant from the central area towards a bank of producers for removal.

#### 4.3. Mineralization reactions

Researchers at LLNL coined the term “Hydrous Pyrolysis” [10–12] to describe the oxidation of chlorinated and unchlorinated DNAPLs that occurs in hot water in the presence of excess oxygen. They observed that a DNAPL, like PAHs (polycyclic aromatic hydrocarbons) or TCE (trichloroethylene), would decompose in hot water to phenols and then be completely mineralized when excess oxygen was added. For naphthalene, they found an energy of activation of 22.9 kcal/mol. The preexponential factor (A) can be calculated for first order reactions (Appendix A) using literature values of hydrogen, oxygen [17] and naphthalene solubility [12]. These calculations yield A of  $6.1 \times 10^8$  and  $3.3 \times 10^{13}$ , respectively, for water and oxygen as reactants.

The reactions of petroleum and oxygen have been studied for decades [14,15]. The main type of reaction has an energy of activation of over 30 kcal/mole and occurs in the vapor phase or in the oil, at higher temperature and concentrations than “Hydrous Pyrolysis”. This “oil field” reaction is not significant at Visalia conditions because both oxygen and

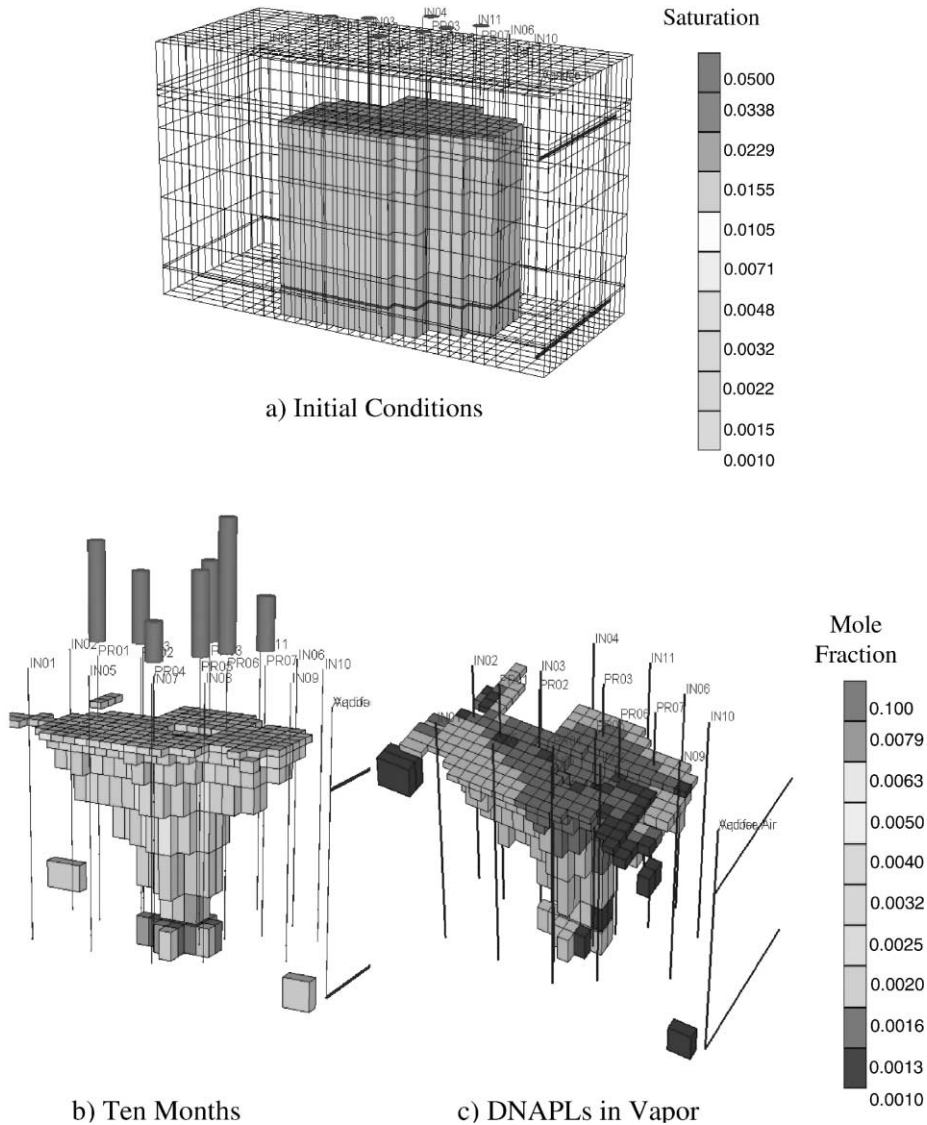


Fig. 7. Redistribuition of vaporized DNAPLs in model 2: (a) initial conditions; (b) 10 months; (c) DNAPLs in vapor.

fuel are too dilute in the vapor. Thus, the experience of the petroleum industry is consistent with LLNL's observation that "Hydrous Pyrolysis" occurs in water and is similar to the low temperature oil oxidation that has been ignored as an oil reservoir spontaneously heats to 300 °C [15]. The low temperature oil oxidation reaction produces water-soluble phenols and emulsions that have not been important to the oil recovery process.

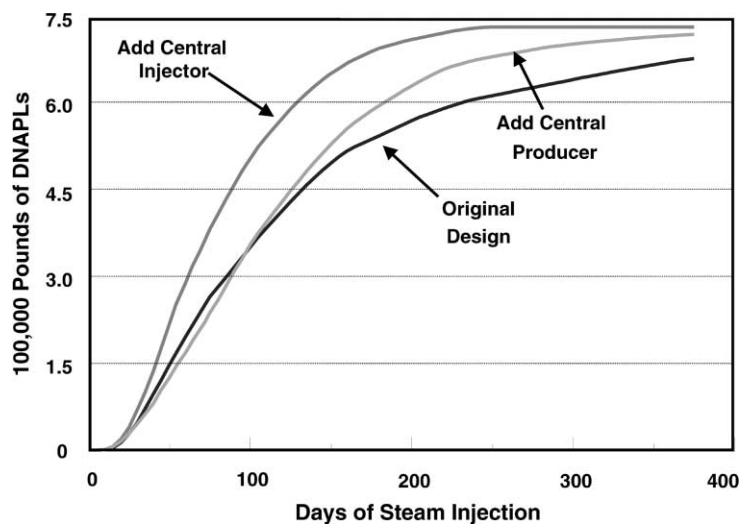


Fig. 8. Effect of well location on production from model 1.

Since hydrous pyrolysis occurs in water, and oxygen solubility in water is limited, the reactivity of PAHs with water must be considered. When water converts anthracene to carbon dioxide and hydrogen at 100 °C, the free energy of formation is 323 kcal/mole and  $K_{eq}$  is  $10^{-190}$ . This looks very unfavorable, but the calculations in Appendix B confirm that all soluble anthracene should be oxidized by liquid water when equilibrium is reached since the solubility of the product gases ( $CO_2$  and  $H_2$ ) in water are very low. Thus, kinetics, not equilibrium, controls the aqueous oxidation in water.

The powerful oxidizing activity of the hydroxyl-radical must be also considered. While the oxidation potentials for OH radical formation in the presence of oxygen [17] can be used to calculate an equilibrium concentration of  $10^{-20}$ , a free radical chain is an effective mechanism for maintaining a reaction, and a coupled oxygen–water reaction mechanism is likely.

A practical consideration must also be mentioned. The reaction rates used in simulations are several orders of magnitude higher at lower temperature than those measured in the laboratory. This is because laboratory experiments have a uniform temperature, but grid block the size of a room in a simulation does not. Thus, the average reaction rate in a grid block which has hot spots and high local rates is much higher than that calculated from laboratory rates because the average block temperature is lower than the temperature in the hot spots. Thus, it is necessary to increase A (pre-exponential factor of the reaction rate equation) of reactions by up to three orders of magnitude in order to predict what happens in situ.

Results of simulations in a two-dimensional model using  $6.1 \times 10^{11}$  as the pre-exponential factor for a water-DNAPL reaction and  $3.3 \times 10^{16}$  as for the  $O_2$ -DNAPL reactions are reported in Figs. 10 and 11. Steam and air were coinjected continuously in model 1 for 6 weeks followed by a 3 week blow down period. Then steam and air were coinjected for 13,

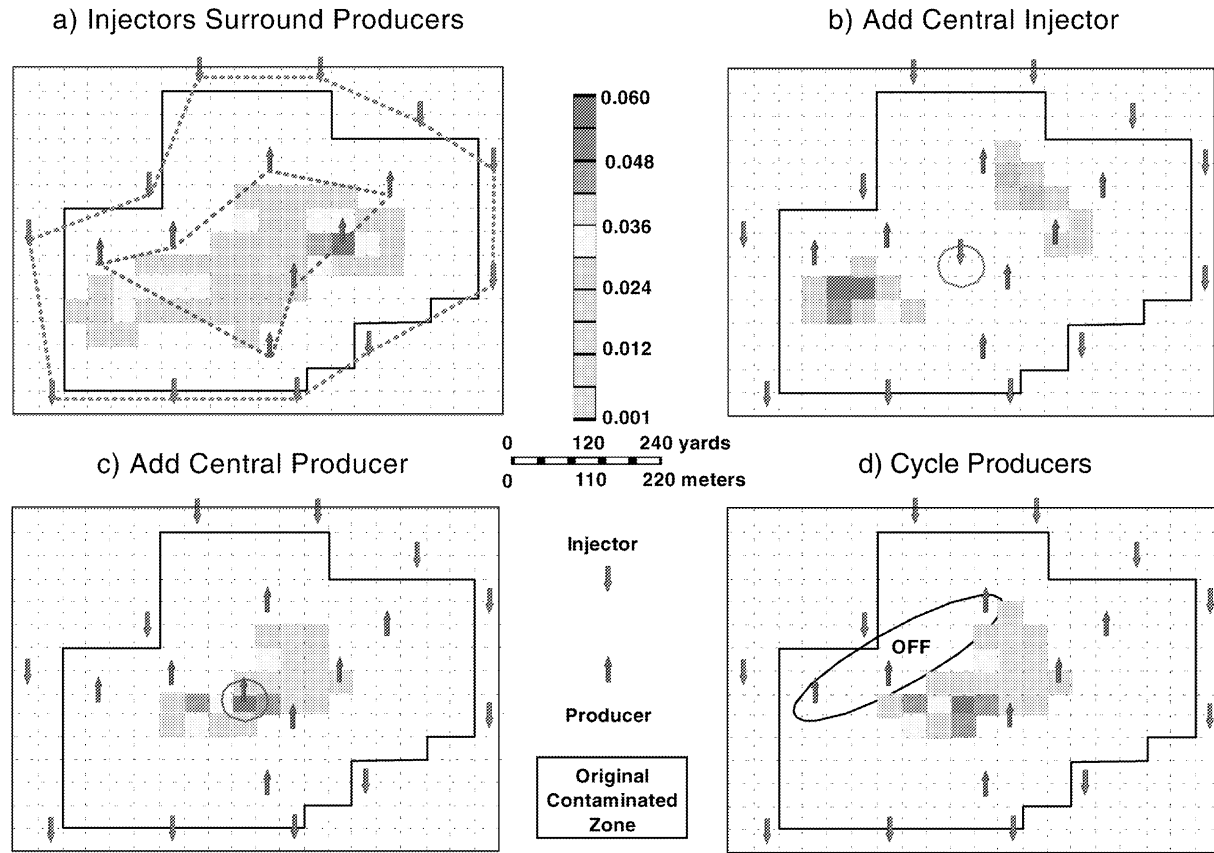


Fig. 9. Effect of well location on DNAPL distribution.

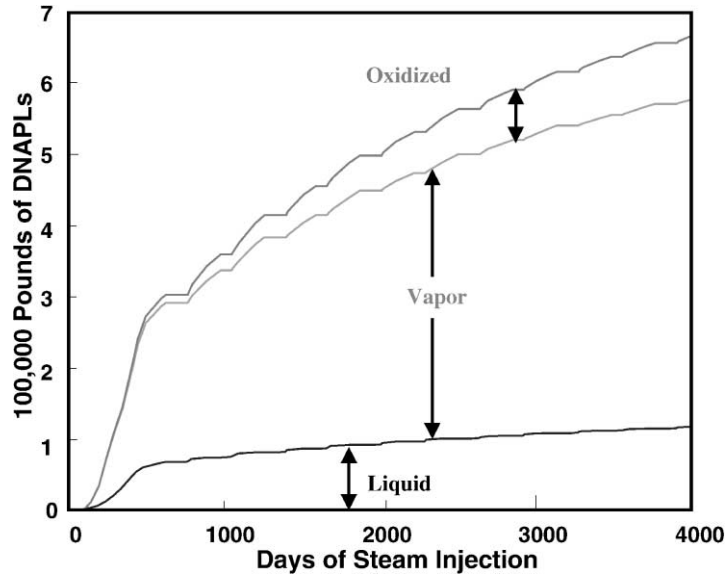


Fig. 10. Production with hydrous pyrolysis.

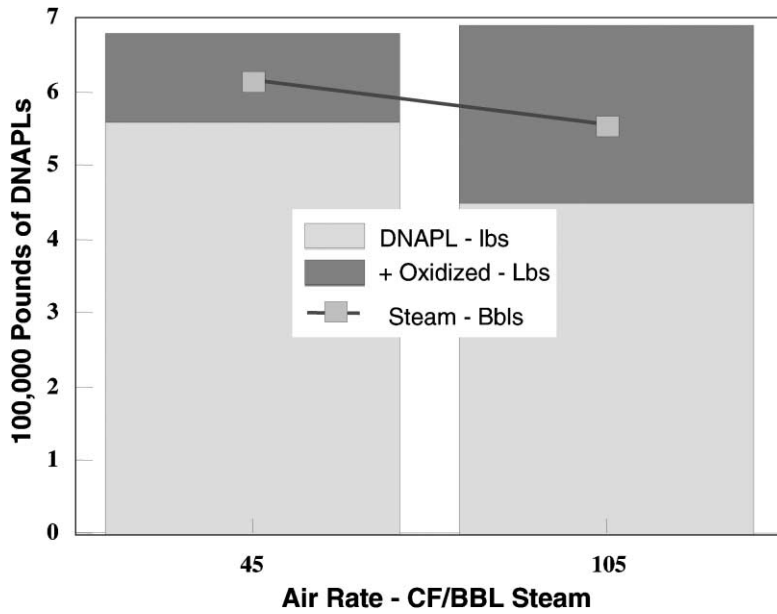


Fig. 11. Effect of increased air injection.

7 day injection and 3 week production cycles. Forty-five cubic feet of air was injected per barrel of water in the steam (0.13 ft<sup>3</sup>/lb). Fig. 10 presents the distribution of liquid, vapor and mineralized DNAPL production. Fig. 11 compares mineralized DNAPL with liquid and vapor production.

Fig. 10 shows that the ratio of oxidized DNAPL production increases steadily as liquid and vapor production decrease. However, the total mass of DNAPL removed is only 6% larger than in Fig. 6 (no oxidation) even though almost 15% of the DNAPL was mineralized. This is because “Hydrous Pyrolysis” mineralizes some DNAPLs that would have been produced. Fig. 11 shows that doubling the volume of air being coinjected and oxidizing twice as much DNAPL only increases total production by around 1%. However, the volume of steam injected decreases by 10%. While the lack of increased production might seem disappointing injecting less steam saves money thereby justifying increased air injection.

The relative effectiveness of water and oxygen as oxidants are shown in Fig. 12a and b. Fig. 12a presents the effect of increasing the oxygen reaction pre-exponential factor by five orders of magnitude. Total production only increases by 4% even though about 20% of the produced DNAPL is mineralized. Fig. 12b shows that the DNAPL-water reaction causes 5% of the DNAPL production to be mineralized. A total of 10% of the production is mineralized when the DNAPL-oxygen rate constant is raised to  $3.3 \times 10^{16}$ . However, there is little increase in total production. An oxygen reaction frequency factor of the order of  $10^{16}$  is about as large as can be supported by the laboratory rate data. This suggests that 50–60% of the mineralization results from oxygen addition, while the rest results from reaction with water similar to coal-gasification or sub-critical water oxidation.

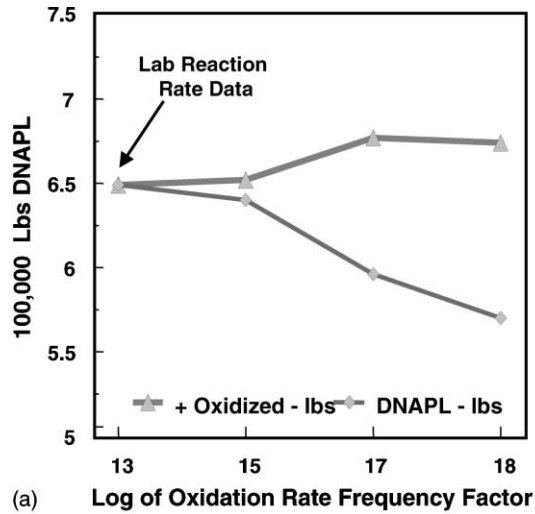
Steam and air must be coinjected for the “Hydrous Pyrolysis” reactions to occur. If the fluids are injected separately, the air evaporates water and cools the formation, thereby stopping the reaction. Thus, if air is injected separately, only the water-DNAPL reaction occurs.

#### 4.4. Mineralization versus production

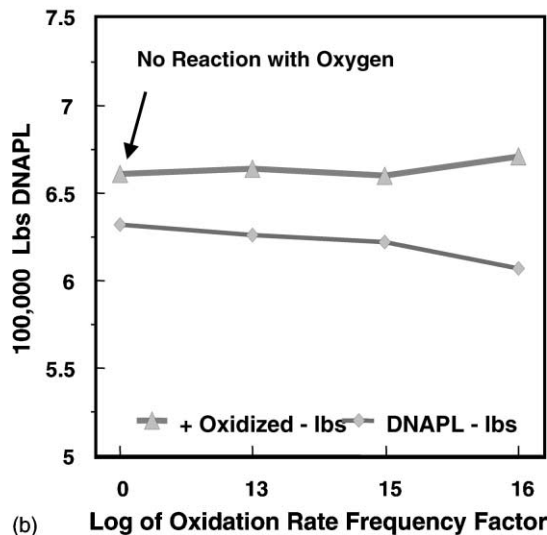
Vaporization is clearly the dominant recovery method. However, it is much less effective for less volatile DNAPLs like the C<sub>40</sub> component. Results reported in Table 1 illustrate this point. The table presents the fraction of each component produced and mineralized for the simulation reported in Fig. 10.

Table 1  
Comparison of total and mineralized production

	Total	Mineralized/total
C <sub>10</sub> Equivalent	96.45%	10.26%
C <sub>20</sub> Equivalent	88.40%	13.27%
C <sub>30</sub> Equivalent	87.72%	39.20%
C <sub>40</sub> Equivalent	89.04%	45.00%
Total recovery	92.37%	N.A.
Fraction reacted	9.90%	15.88%



(a) Log of Oxidation Rate Frequency Factor



(b) Log of Oxidation Rate Frequency Factor

Fig. 12. Effect of reaction with oxygen with and without concurrent water reaction: (a) oxygen reaction alone; (b) reaction with oxygen and water.

The data show that over 96% of the  $C_{10}$  (naphthalene-low diesel) component is produced in 427 days of continuous and cyclic production. A lower fraction of the  $C_{20}$  (PCP, diesel) and  $C_{30}$  (diesel, 3–4 ring PAH) components are produced. However, more of the  $C_{40}$  (pyrene) component is removed because it is left behind in the hot zone near the injectors and is therefore available for reaction. Mineralization is the dominant recovery mechanism for less volatile contaminants.

## 5. Discussion of results

The purpose of this paper has been to use simple models of an aquifer and vadose zone to show how DNAPLs are recovered or destroyed by coinjection of steam and air. This model appears to capture the major results of the process, such as mass of DNAPL produced, mass of DNAPL destroyed, movement of steam and DNAPL upwards from the intermediate aquifer and location of the DNAPL not recovered in phase I of the project. A secondary purpose was to evaluate how hydrous pyrolysis performed, how it related to light-oil-air-injection reactions, and how it could best be implemented.

These goals appear to have been satisfied even without building a detailed model of the site that included the layering and heterogeneity that are known to exist at Visalia. This is a demonstration that most of the processes that determine DNAPL recovery at the Visalia project are phenomena that have been modeled for years at petroleum recovery projects throughout the world. This should instill confidence in the use of steam for aquifer remediation.

The new information from Visalia includes (a) the ability of hydrous pyrolysis to mineralize contaminants, and (b) how to operate production wells in a leaking aquifer. As pointed out above, hydrous pyrolysis appears to be the first stage of light-oil-air-injection reactions that have been studied extensively in the petroleum business. Hydrous pyrolysis is ignored in the petroleum industry because their purpose is to oxidize enough oil to convert air to flue gas, a more efficient improved oil recovery fluid. The oxidized oil becomes a sludge that is left behind the oxidation front.

These simulations support the idea that hydrous pyrolysis is an abiotic reaction (i.e. not high temperature bioremediation) and that it requires both oxygen and water to proceed. However, they do not address the issue of what role reservoir minerals play in the hydrous pyrolysis reaction.

Any oxidation reaction must produce oxidized water-soluble hydrocarbons such as phenols. These have been identified in LLNLs laboratory experiments [10–12]. Phenols are likely to reduce the oil-water interfacial tension and stabilize emulsions either at the surface [18] or in situ. Their effect has not been included in these simulations since quantitative data is not available and because the experience of the petroleum industry is that generating emulsions in situ is more likely to decrease liquid production than to increase it.

Finally, these simulations did not address the issue of bottom water influx because quantitative data had not been published when these simulations were started [19]. Now, an influx of 3-gal/ft<sup>2</sup> per day has been reported. This water influx occurred under the production wells which were being produced with as much as 10 psi vacuum. That much water would have certainly delayed heating at the wells and slowed production of DNAPLs. The operators of the project chose to inject steam into the deeper aquifer in phase II of the project to displace the bottom water and finish cleaning the site [19]. Other methods of limiting bottom water influx can be evaluated in future simulations and gleaned from the experience of oil producers. For instance, completing the central injector considered above in the deeper aquifer would have displaced the cool water in the aquifer and rapidly completed the project.



## 6. Conclusions

STARS, the most popular oil-field simulator for modeling thermal projects, has been used to study how steam removes DNAPLs from a 102 ft deep aquifer at the Visalia, California Superfund site. The results of the computer simulations show that:

- Vaporization of DNAPLs appears to be the dominant recovery mechanism, although recovery of liquid DNAPLs is enhanced through the presence of the gas phase and DNAPL viscosity reduction.
- Because steam rises and travels throughout the formation, vaporization can redistribute DNAPLs into the vadose zone.
- Adding a central injector or producer well will reduce the time to complete similar steam injection projects substantially.
- The simulations suggest that the “Hydrous Pyrolysis” reaction observed at the site appears to involve water as well as oxygen. Thus, it is similar to “Coal Gasification” or “Sub-critical Water Oxidation”, but appears to be enhanced by additional oxygen injection.
- The results of the simulations show that air must be coinjected with steam to effectively oxidize DNAPLs; this reduces the volume of steam injection and costs.
- The results also show that mineralization is most effective for the less volatile components and becomes more important in the later stages of the project.

## Acknowledgements

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## Appendix A. Apparent frequency factor for reactions of water and oxygen with naphthalene

Frequency factor reported for naphthalene hydrous pyrolysis in [12]	2.0724 mol/kg/s.
Converted to units used in the simulation	42,974 lb mol/cubic ft per day.
Solubility of naphthalene in water at 100 °C <sup>12</sup> —1,000 ppm	7.8125 mmol/kg = 0.0000703 mol fraction.
Solubility of oxygen in water at 100 °C <sup>17</sup>	2.3 cc/100 cc = 0.0000018 mol fraction.
The frequency factor for a reaction with oxygen	$3.07 \times 10^{13}$ lb mol/ft <sup>3</sup> per day.
The frequency factor for a reaction with water	$6.11 \times 10^8$ lb mol/ft <sup>3</sup> per day.

## Appendix B. Equilibrium constant and equilibrium concentrations in an aqueous water gas shift reaction

For anthracene,



Therefore,  $K_{\text{eq}} = 10^{-190}$  (This looks very unfavorable);

But,

$$K_{\text{eq}} = \left[ \frac{(\text{H}_2)^{33}(\text{CO}_2)^{14}}{(\text{C}_{14}\text{H}_{10})(\text{H}_2\text{O})^{28}} \right]$$

where  $\text{H}_2\text{O} \sim 0.999$ ,  $\text{H}_2 = 0.0000068$ , and  $\text{CO}_2 = 0.00072$ , since the pressure is low.

Thus, at equilibrium:

$$\text{C}_{14}\text{H}_{10} = \frac{2.97 \times 10^{-204} \times 10^{-57}}{[10^{-190} \times 0.973]} = 3.05 \times 10^{-71}$$

So, virtually all anthracene will be consumed, and PAH consumption in water is controlled by kinetics not equilibrium.

A similar calculation can be used to show that PAHs will not be converted to  $\text{CO}_2$  and  $\text{H}_2$  if the PAHs have been vaporized, unless the hydrogen is oxidized to water.

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