

Field Aspects of Oxidation and Enhanced Biodegradation: Understanding and Controlling Chemical Reactions during the Injection of Hydrogen Peroxide for *In Situ* Remediation of Petroleum Hydrocarbons

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Abstract

Oxidation and enhanced biodegradation (OEB) is an *in situ* remediation technology that couples the reaction between a strong oxidant (hydrogen peroxide) and organic carbon with slower aerobic biodegradation to mineralize petroleum hydrocarbon (PHC) compounds. Hydrogen peroxide (15% - 35%) is a strong oxidant that participates in several chemical reactions to degrade organic compounds when introduced into the subsurface, yielding heat, water and gases (carbon dioxide and oxygen) as final products. The oxygen produced from the decomposition of hydrogen peroxide will additionally support the subsequent biodegradation of residual PHCs. OEB differs from *in situ* chemical oxidation using Fenton's reagent (ISCO) in that an iron catalyst is not added. The reaction intensity of the injected hydrogen peroxide solution is therefore in part limited by the iron concentrations occurring in the native soil. As a result, OEB reactions are more subdued than the reactions generated by the injection of catalyst and oxidant solutions typically used for ISCO. The production of gases and heat in the subsurface during the oxidization of organic compounds using OEB will be more manageable, although the time required to achieve remedial objectives may be longer.

Field experience shows that many of the health and safety concerns as well as physical disruption issues associated with ISCO can be minimized and managed effectively using OEB, especially in urban developed areas. To apply OEB in the field, the authors constructed a special wellhead adapter that created a closed injection system with which moderate well pressurization was used to enhance the injection of hydrogen peroxide. The progress of oxidation (foaming), monitoring of pressure build-up and safe venting of the system can also occur through the wellhead adapter, providing better process management and control in the field. In this paper, field data collected during several injection programs are presented and discussed in order to develop a conceptual model to help understand the nature of and control the chemical reactions involved.

Introduction

The application of chemical oxidants for the *in situ* remediation of PHC impacted soil and groundwater may be a viable treatment alternative where more commonly practiced technologies (e.g. excavation, pump and treat, vapor extraction, bioremediation) are either impractical or require augmentation due to site conditions. Reduced time for site remediation, the capability of selected oxidants to degrade recalcitrant chemical

compounds and, in some cases, a lower relative cost are some benefits cited by proponents of chemical treatment technologies in comparison to other treatment options.

Considerable experimental research literature and case studies involving compounds such as hydrogen peroxide, persulfates and permanganates have been produced from the increasing use of chemicals for *in situ* remediation. Often, bench scale testing has been utilized to both demonstrate the proof of concept and determine the optimum chemical “dose” for the site. Estimations of oxidant mass for a project are based on the oxidant required to oxidize both the target PHCs and the natural “soil oxidant demand” that will compete with the PHC compounds for the oxidant (Haselow *et al*, 2003). To deliver chemical oxidants into the subsurface during field piloting and full-scale applications, a high pressure jetting technique with injection pressures up to 2000 psi may be used (Jacobs and Testa, 2003).

Consequently the general proof of concept that chemical remediation of PHCs can be successful in certain situations has been demonstrated. However, the safe, practical and effective physical delivery of the treatment chemical into the subsurface to contact the target contaminant remains to be a significant technical challenge and source of uncertainty for any remediation professional considering a chemical remediation strategy (Nyer, 1999).

Hydrogen peroxide is a highly reactive oxidant that participates in several chemical and biological oxidation-reduction and acid-base reactions summarized in Figure 1. The decomposition of hydrogen peroxide [A] produces water, oxygen and heat, whereas the complete oxidation of an organic compound by hydrogen peroxide [B] results in carbon dioxide, water and heat as end products.

Although hydrogen peroxide itself is a reasonably strong oxidizer, it is the capacity of the hydroxyl radical ($\cdot\text{OH}$) produced by reactions between peroxide and iron (Fe) catalyst (Fenton’s Reagent) to mineralize organic compounds that often makes hydrogen peroxide a desirable remediation compound [C]. The relative oxidizing power of various common oxidants are summarized in Table 1.

Additionally, hydrogen peroxide molecules will also donate protons in acid-base reactions, interact with other metal species such as manganese or copper, and react with radical species produced from Fenton’s Reagent [D]. Therefore, a generalized conceptual chemical equation for reactions of hydrogen peroxide in subsurface environments would include petroleum hydrocarbons, natural organic

Table 1 – Relative Oxidation Power of Common Oxidants

Oxidant	Relative Oxidizing Power (Cl ₂ = 1.0)
Fluorine	2.23
Hydroxyl radical	2.06
Atomic oxygen (singlet)	1.78
Ozone	1.50
Hydrogen peroxide	1.31
Perhydroxyl radical	1.25
Potassium Permanganate	1.24
Chlorine Dioxide	1.15
Bromine	0.80
Iodine	0.54

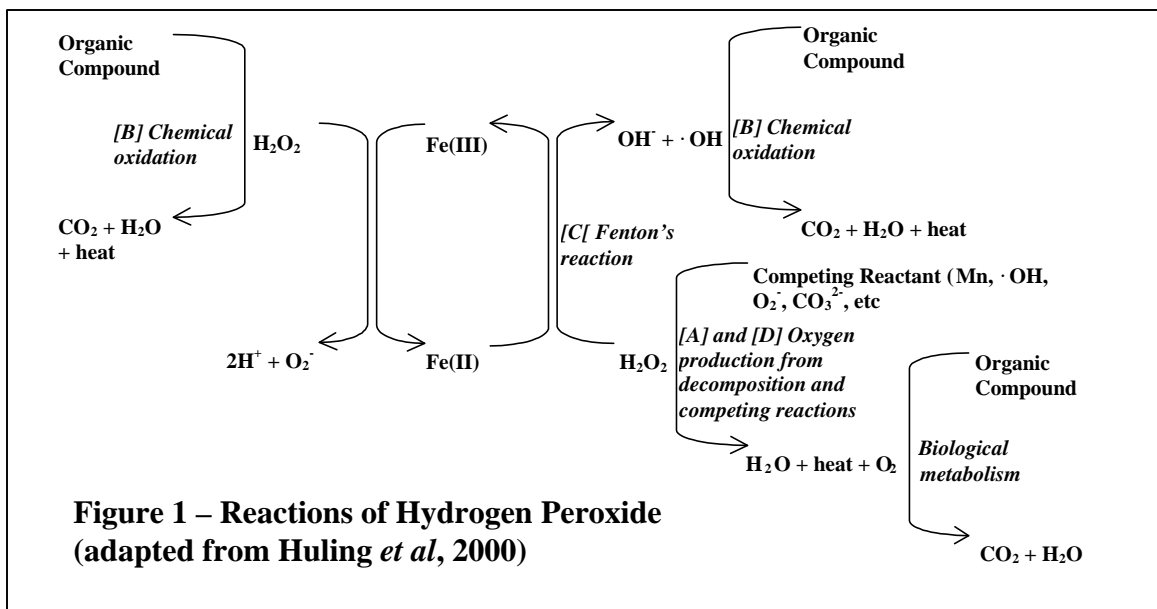
(adapted from Nyer, 1999)

carbon, reduced metals, proton acceptors (e.g. OH^- , CO_3^{2-}) as reactants and carbon dioxide, oxygen, water, oxidized metals and heat as end products.

On a laboratory scale and in the absence of significant organic compounds, reactions between hydrogen peroxide and iron solutions containing 200 mg/L of soluble iron are known to occur rapidly (within 20 minutes), vigorously off-gassing and producing temperatures up to 100°C (Peters *et al*, 2001). Reactions of hydrogen peroxide in soil slurries may produce similar reaction profiles without the addition of catalysts when sufficient peroxide concentrations are used. Optimization of hydroxyl radical production in Fenton's Reagent requires that the peroxide and iron catalyst solutions come into contact on a molecular level within an acidic (pH 2-5) and warm ($30 - 50^\circ\text{C}$) environment. Consequently, PHC remediation in alkaline soils using Fenton's Reagent will generally require the separate injection of oxidant, catalyst and an acid buffering solution.

When considering the nature of the reaction involving hydrogen peroxide, it is apparent that the injection of hydrogen peroxide has the potential for a rapid build-up of pressure and temperature in the subsurface and at the injection wellhead. The use of high pressure jetting to inject solutions combined with the injection of oxidant, catalyst and acid solutions in a full scale Fenton's Reagent application may magnify the potential for uncontrolled reactions that could compromise safety of personnel implementing the technology.

In developed urban areas (e.g. commercial sites adjacent to residential properties, operating facilities) where *in situ* remediation may be desirable for various reasons, it is possible that an optimized Fenton Reagent process may not be feasible or appropriate due to health and safety issues. In addition to the need for the control of reactions in the injection well, the on site management and storage of multiple chemicals and materials for the injection program in a manner that satisfies the health and safety requirements of project stakeholders and regulatory agencies may not be practical.



The OEB Process

Oxidation and enhanced biodegradation (OEB) is an alternative approach that provides the benefits of hydrogen peroxide injection on sites where oxidation reactions are required, but high pressure injection of Fenton's Reagent is not practical or desired. The OEB approach utilizes the injection of hydrogen peroxide solutions without the addition of iron catalyst or acid buffering solutions. The approach capitalizes on the oxidative capacity of concentrated hydrogen peroxide solutions and the presence of naturally occurring iron in the subsurface to promote chemical oxidation. Residual oxygen levels remaining from the decomposition of peroxide solutions after the initial oxidation reactions promotes the redevelopment of microbial populations and stimulates biodegradation of the remaining contaminant compounds.

The OEB process involves the injection of hydrogen peroxide under gravity feed that reduces the health and safety concerns related to high-pressure injection processes. To promote the transport of the peroxide solutions into the subsurface and enhance the radius of influence of oxidation reactions, a closed wellhead is used to capture gases (O₂ and CO₂) produced by the chemical reactions to generate a slight wellhead pressure (10 to 20 psi). Additional pressure to further the distribution of peroxide into the subsurface can be created by head-loading the injection well with water or by confining the reaction using borehole packers. After characterizing each injection well for solution capacity, a systematic injection benchmarking process of repeated chemical injections using progressively higher peroxide concentration and volume allows for optimization in the field. Real-time monitoring of temperature in the well and pressure at the wellhead provide indicators of the reaction progress and can be used to help regulate the intensity of the reaction.

OEB Injection and Monitoring Equipment

Equipment and materials used for OEB field applications were selected considering chemical compatibility with concentrated hydrogen peroxide solutions as well as performance under expected maximum pressures of 30 psi and the target operational temperature range of 30°C to 50°C. Based on these criteria, polyvinyl chloride (PVC) and high-density polyethylene (HDPE) were determined to be most suitable based on availability and cost.

Gravity fed injection of peroxide solutions augmented by low-pressurization of the injection well was selected over high-pressure injection techniques for the OEB applications. A manual polyethylene siphon pump was used for the transfer of peroxide and water into the well. In order to create low-pressures in the injection well to promote entry of the peroxide solutions into the subsurface, both the capture of gas produced from the reaction and the head-loading of the injected peroxide solutions by injecting water were utilized. To facilitate these processes, an injection well and a wellhead adapter were constructed specifically for the OEB applications.



Photo 1 - Injection Well Screen and Riser



Photo 2 – A Wellhead Adaptor

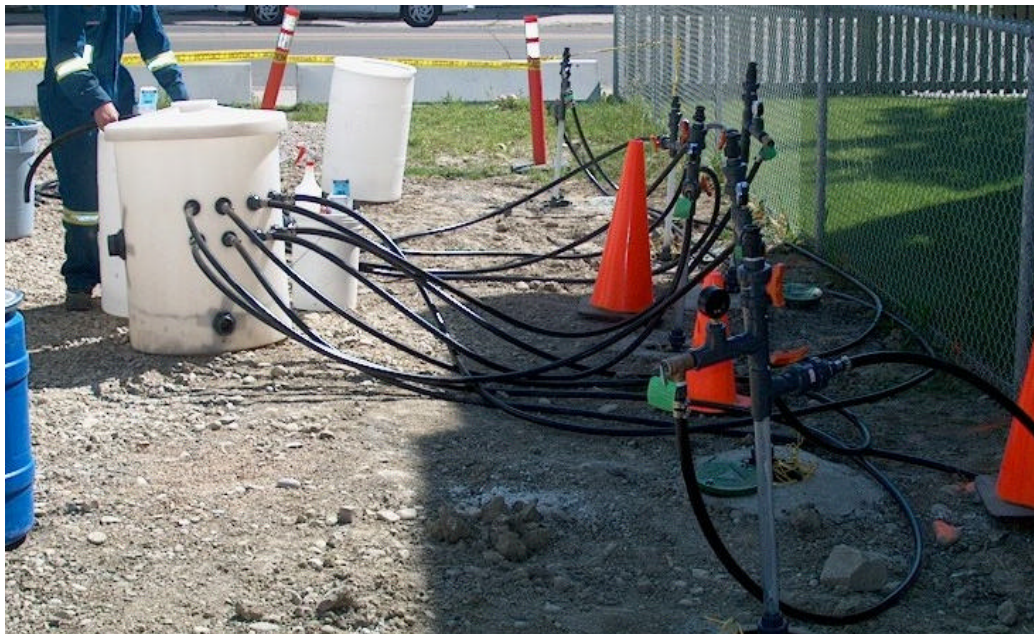


Photo 3 - Wellhead Adaptors Connected to a Collection Tank

New well installations were designed to maximize the well volume in the screened section of the well allowing for peroxide solutions to initially accumulate adjacent to the screen where infiltration into the formation would occur. The large relative volume within the screened section was created by constructing a 3" ID by 5.5" OD PVC pre-packed screen 3' in length. Above the screen, the well volume was reduced by connecting the pre-pack screen to a 1" ID PVC riser 15' to 20' in length (Photo 1). The length of the riser is designed to coincide with the impacted zone. As a result, less gas production or volumes of water would be required to generate a 10 psi to 15 psi pressure at the well screen to promote peroxide entry and dispersion away from the injection screen. To collect temperature data at the well screen, epoxy coated thermocouples were inserted into the pre-pack and wired to the surface during well installation.

Specialized wellhead adapters (Photo 2) were built and fitted to the top of the injection wells to close the injection system allowing for the safe capture of reaction gases. Constructed by fitting a 1" clear PVC riser with two valves and a pressure relief valve (PRV) in a cross configuration, the wellhead adapters were designed to accomplish five primary functions. The wellhead adapters were designed to:

1. Serve as an injection port for peroxide and water solutions;
2. Provide a visual indicator of liquid levels and reaction activity (e.g. foaming) in the standpipe;
3. Allow for pressure and temperature monitoring at the wellhead by either electronic or analog gauges;
4. Provide a safe manual mechanism to vent gas, foam or solutions from volatile reactions in the injection well, and;
5. Provide an automatic mechanism to vent the system through a PRV should pressure build up too rapidly in the well for manual venting to be effective.

Once fitted to each well, the wellhead adapters were collectively connected to a 300 L HDPE collection tank (Photo 3) into which off-gases, foam or reacting solutions could be safely vented and captured.

OEB Field Applications

In two OEB applications conducted during 2004, injection wells were constructed and installed as previously described. After installation, the ability of each well to accept fluid was characterized by repeatedly injecting known volumes of water to estimate the maximum liquid capacity of each well. Peroxide injections were initially conducted using 10L 3.5% and 8% hydrogen peroxide. Each injection was immediately followed by a 10L injection of water to headload the well, with the total volume of liquid injected was intentionally limited to 40% to 60% of the each well's liquid capacity. Wellhead adapters were closed to capture reaction gases and pressure changes monitored. An operational wellhead pressure limit of 9 psi was set as a conservative level at which the well could be safely managed and vented. Temperature measurements at the well screen and the seal

above the screen were collected throughout the reactions. Following the initial low concentration applications, injection concentrations were increased to 17.5% hydrogen peroxide while volume was reduced to 5L per well. Concentration and volume were then increased to 20L of 35% hydrogen peroxide over nine injection cycles.

Field Observations from OEB Applications

Observations near the Well Screen

A single injection of 10L of hydrogen peroxide (35%) without a subsequent water injection was monitored at the well screen by suspending a Levellogger™ in the well. During the reaction, the pressure at the well screen peaked immediately after the injection and subsided with time (Figure 2). In contrast, well screen temperatures were observed to peak later than pressure peaks occurred. Additionally the elevated temperature in the well was sustained for a longer time period. During repeated injection cycles, temperatures were observed to increase to the optimum well screen temperature wellhead pressure ranges as hydrogen peroxide concentration were increased from 3.5% to 35% (Figure 3). During the injection program, each well was observed to exhibit a unique temperature and wellhead pressure profile during the reaction for each combination of peroxide concentration and volume applied. Temperatures after injection were observed to range from 20°C to 80°C in the well, with peak temperatures occurring between 0.5 to 6.0 hours from the time of injection. In general, peak temperature after each injection cycle increased with increasing injection volumes using 35% hydrogen peroxide (Figure 4). However, during the repeated injection of 35% peroxide at the same volume, peak reaction temperatures were observed to occur later and decrease with an increasing number of injection cycles, apparently due to depletion of organic carbon in the vicinity of the injection well.

Observations at the Well Head

Pressures observed at the wellhead during injections were observed to range from less than 1 psi to greater than 9 psi. Pressures greater than 9 psi were vented manually to maintain operational safety. Maximum pressures were observed to occur within 0.5 hour of the injection. Similar to well screen temperature, each well exhibited a unique wellhead pressure profile during injection programs. In some wells, measurable pressures were sustained in the well for greater

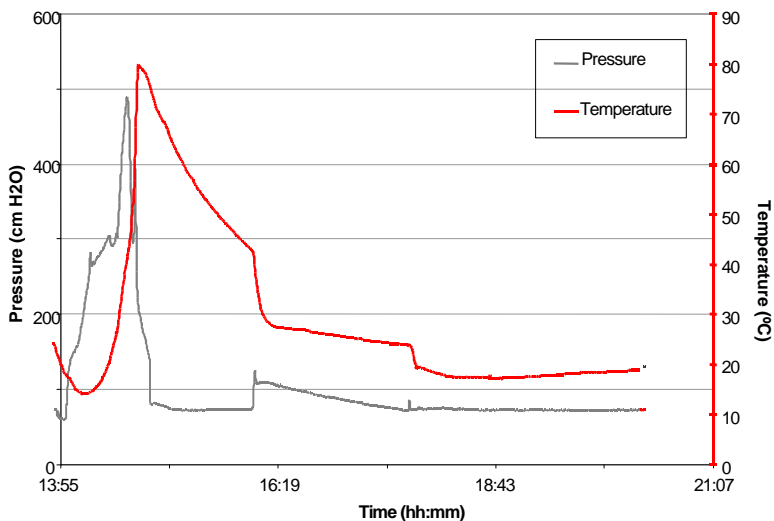


Figure 2 – Pressure and Temperature Observations at the Well Screen during the Injection of 10L 35% Hydrogen Peroxide

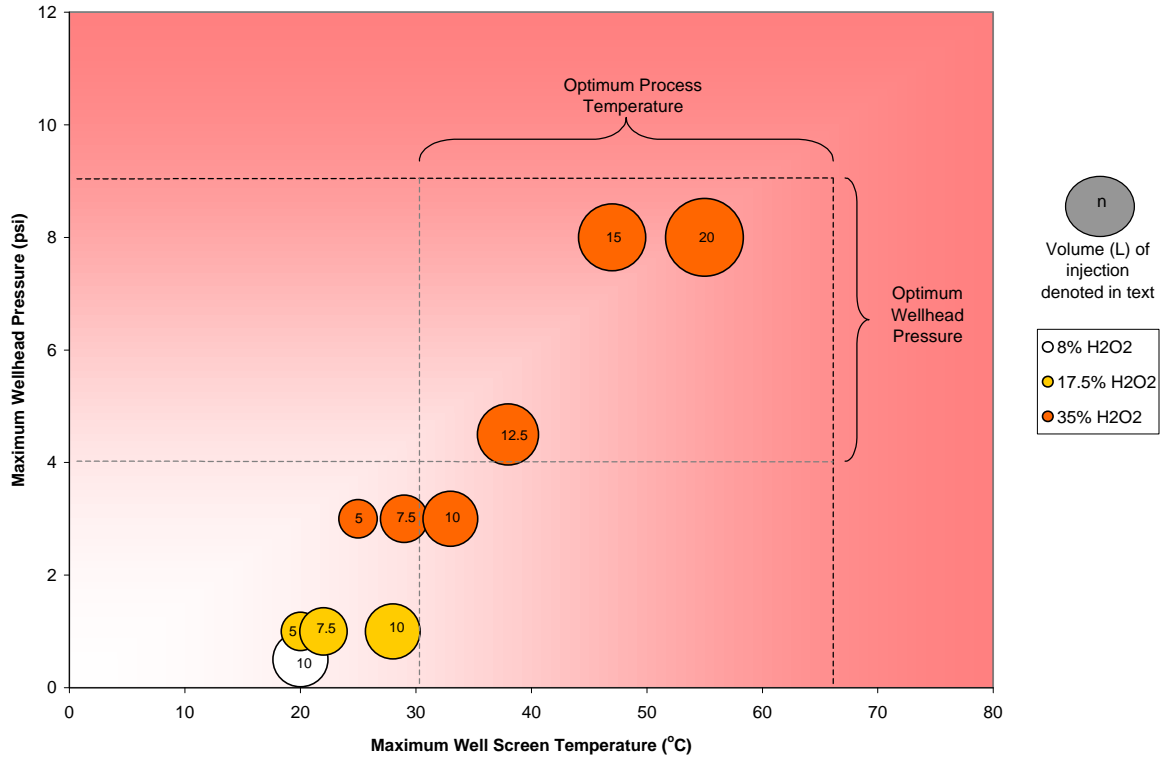


Figure 3 – Maximum Well Screen Temperatures and Wellhead Pressures Observed During Systematic Increases of Concentration and Volume During Hydrogen Peroxide Injection

than one hour after the initial injection, while in others, pressure increases were periodic or undetectable (Figure 5). In general, pressure at the wellhead was observed to peak before temperatures at the well screen.

Baseline and post injection concentrations of carbon dioxide and oxygen gas in the headspace of the injection well were collected through the wellhead adapter. Measurements of CO₂ gas in selected wells were observed to increase from approximately 350 ppm before injections to greater than 5000 ppm after injections. Similarly, oxygen gas levels were observed to increase from approximately 20.9% prior to injection to greater than 30% after an injection.

Discussion

Observations made during the monitoring of the OEB applications provide some insight into the nature of the chemical reaction occurring in the injection well. In general, the increase of O₂ and CO₂ gas concentrations in the well, combined with increases in pressure and temperature observed provide evidence that the reaction of peroxide solutions is occurring readily within and likely adjacent to the well. Increases of O₂ gas and CO₂ gas indicate that the decomposition of peroxide and the oxidation of organic compounds occurred. Temperature profiles at the well

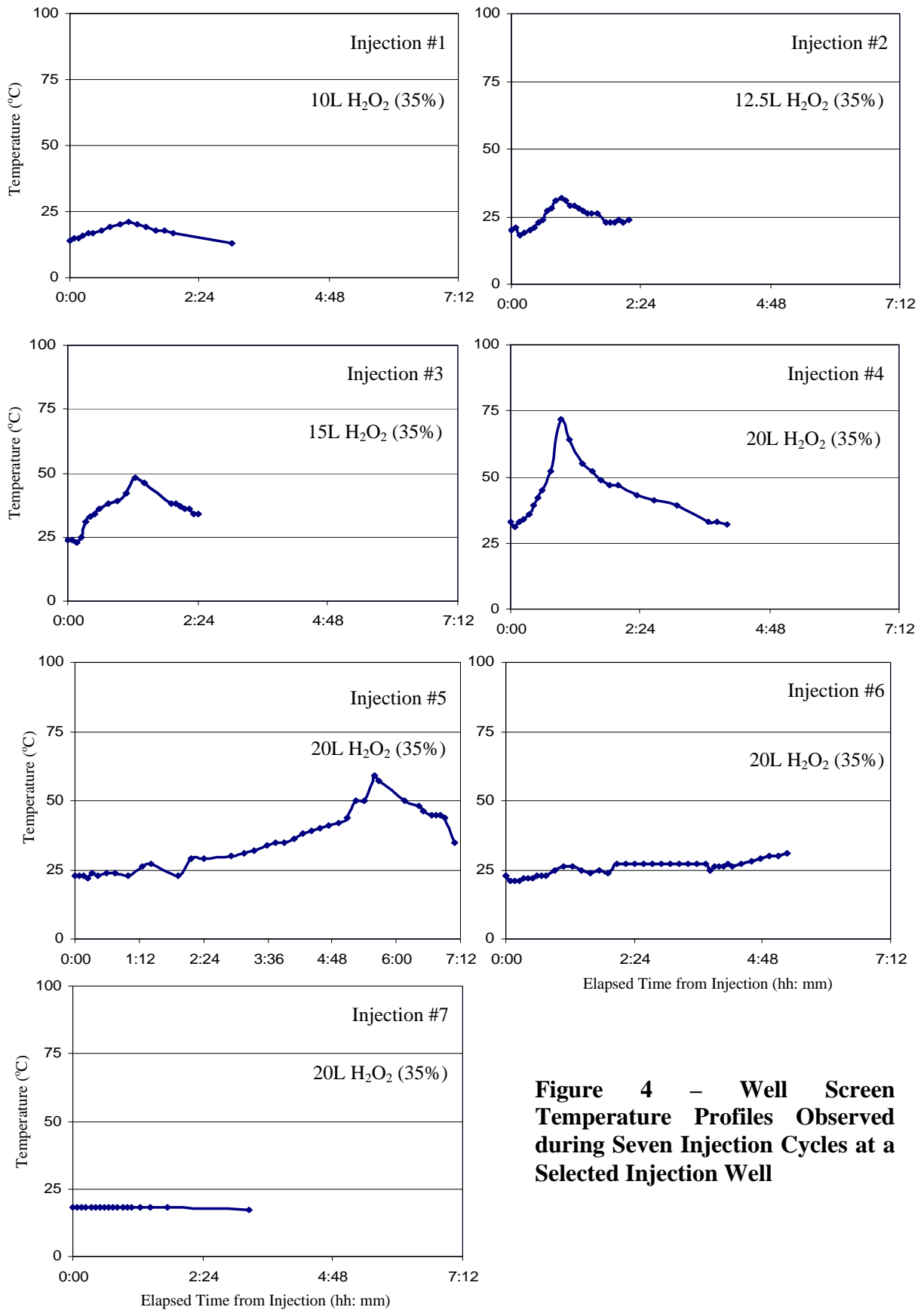


Figure 4 – Well Screen Temperature Profiles Observed during Seven Injection Cycles at a Selected Injection Well

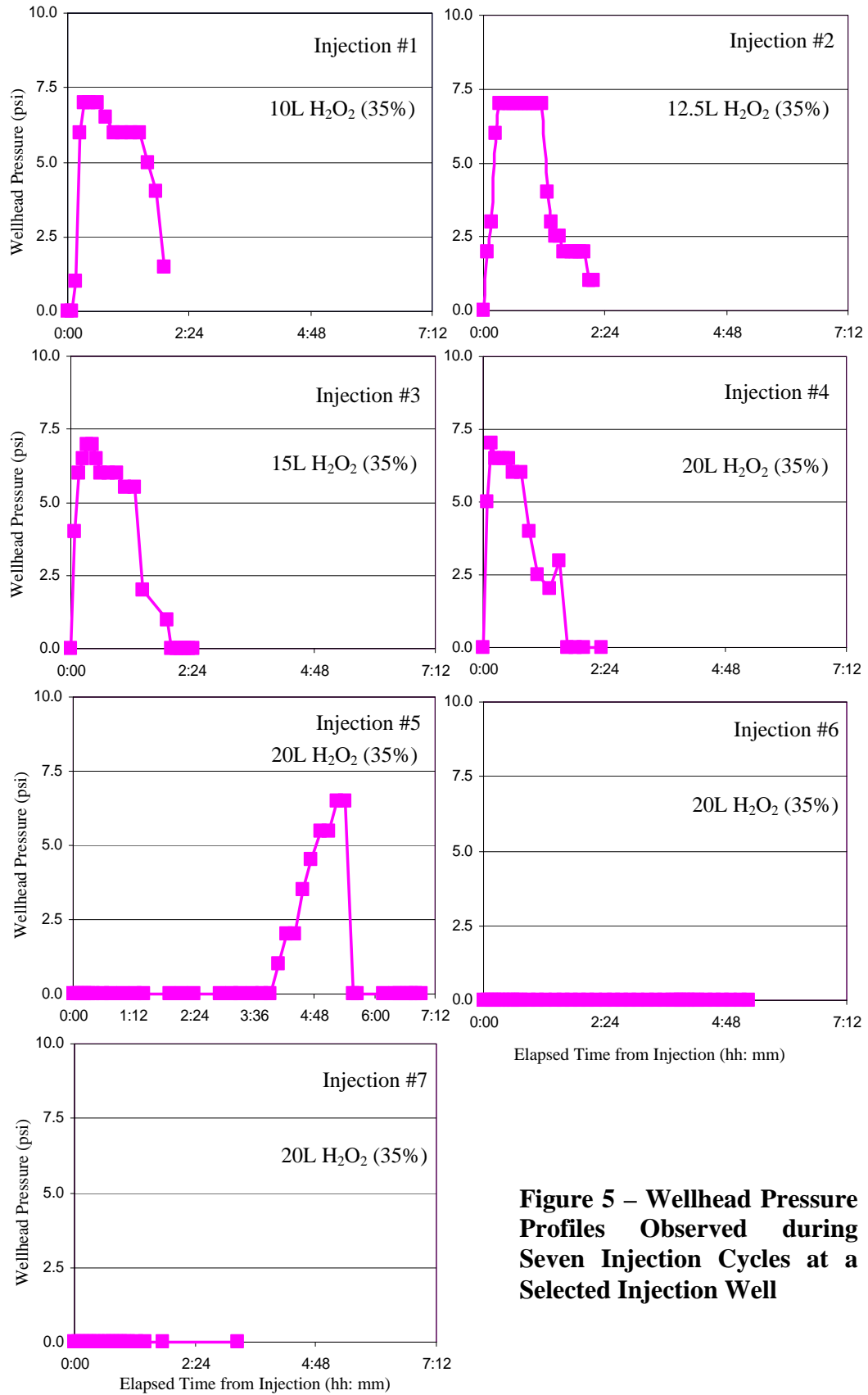


Figure 5 – Wellhead Pressure Profiles Observed during Seven Injection Cycles at a Selected Injection Well

screen exhibit similar characteristics to Fenton's Reagent reactions as observed in previous laboratory experimental trials with aqueous solutions and soil slurries (Peters *et al.*, 2001). This observation suggests that some interaction between naturally occurring iron in the soil and the injected peroxide is likely occurring to a limited extent, providing an increase in oxidizing power to the injected solution.

During repeated injections, the reaction pressure and temperature profiles become more subdued, delayed or both. This change over time, despite the injection of greater volumes of hydrogen peroxide, suggests that the initial intensity of the reaction in the well may be a result of mineralization of organic compounds (both PHCs and other organic matters) immediately adjacent to the well. As these reactants near the well are consumed, the peroxide solution has opportunity to travel farther into the subsurface prior to complete decomposition or reaction.

Even without applying an iron catalyst, temperatures in some wells were observed to periodically (less than 15 minutes) exceed the optimal temperatures for the reaction and the well installation materials. This indicates that when new installations are required, use of materials (e.g. CPVC pipe) with a higher temperature rating but equal chemical resistance may be appropriate. However, the ability to manipulate the injection solution concentration and or volume through process monitoring to maintain optimal temperatures indicates that using existing PVC installations as injection points is feasible, if required.

Experience shows that each well demonstrates a unique reaction characteristic that cannot be predicted with the level of information generally available prior to the injection program. Consequently, repeated injections using the OEB process requires careful monitoring to characterize each well and provide the greatest level of process control possible in the field. Real-time process monitoring at the wellhead and in the subsurface allowed for incremental chemical dosing during repeated injection events. As a result, some optimization was realized during the field application. Although the information collected proves valuable in terms of operation and process control, the radius of influence of both the initial oxidation reaction and the residual oxygen available for enhanced bioremediation as a result of hydrogen peroxide injection point has not been completely determined. An increased density of monitoring points for temperature and pressure around the injection well screen should yield useful information in this respect. Consequently, further study to examine the radius of influence is ongoing.

Further Development of the OEB Process

Initial applications of the OEB process indicate that the desired reactions (oxygen generation and organic carbon oxidation) occur readily during hydrogen peroxide injection. Furthermore, process monitoring in the field provides evidence that the technology can be safely implemented by characterizing the reaction at each injection point. To further develop and refine the OEB process, the following work has been identified:

1. Determining the radius of influence of the oxidation reactions of the injected solution by a applying combination of controlled laboratory experimentation, modeling and field ground truthing.
2. Determining the influence of the oxidation reactions and residual oxygen on ability of the native bacterial populations to re-colonize the chemical oxidation zone.
3. Determining the radius of influence of residual oxygen available for enhanced bioremediation outside the oxidative zone.
4. Improving peroxide entry into the subsurface through well design and optimizing the use of moderate wellhead pressurization.

Conclusions

In conclusion, the OEB process capitalizes on the oxidation reactions and enhanced aerobic conditions that occur during and after the injection of concentrated hydrogen peroxide solutions. The combined use of a specialized injection well, a wellhead adapter and real-time process monitoring was used to implement the technology in a safe, practical and effective manner. Data collected from the field applications of OEB indicate that the desired oxidation and decomposition reactions occur during the injection. However, during the field applications it was determined that each injection well exhibits a unique response in terms of wellhead pressure and well screen temperature to the peroxide solutions injected. To further refine the OEB process, the authors propose future work in determining the radius of influence of the injected solution and further refinement of moderate well pressurization to enhance peroxide entry into the subsurface.

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