

Sodium Citrate (Hydrogen Peroxide Stabilizer)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Product is the conjugate base of citric acid, a carboxylic acid. In a water solution, sodium citrate dissociates into sodium ions and citric acid.
3. MSDS - See attached file
4. Number of Field Applications: 15 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Sodium citrate is used to stabilize hydrogen peroxide. Conventional use of hydrogen peroxide involves the catalyzation of peroxide by the addition of a ferrous iron catalyst, resulting in a vigorous Fenton's type reaction. The Fenton's reaction gives off excess heat and large quantities of oxygen gas. One of the biggest weaknesses of Catalyzed Hydrogen Peroxide (CHP) is that the peroxide is completely consumed within hours, often times before the peroxide can fully disperse into the aquifer.

A new innovative and patent-pending process has been developed called Stabilized Hydrogen Peroxide (SHP) that involves the addition of a carboxylate stabilizer, such as sodium citrate, sodium malonate, or sodium phytate, that slows the normal rapid decomposition of peroxide. SHP extends the life of the peroxide from less than one day to up to 10 to 14 days. The slowed decomposition of peroxide lessens the buildup of subsurface pressure and dampens the rapid increase in temperature. By controlling the concentration of the stabilizer, the peroxide reaction can be muted sufficiently to minimize the adverse side effects which result in chemical daylighting.

Sodium citrate is a naturally occurring chemical which is present in many common food products (fruits, vegetables, and grains) and promotes key functions within the human body. Citric acid acts as an anti-oxidant, buffering agent, antacid, and anticoagulant in the body

Minimal impact would be expected on water quality due to the extremely low quantities of stabilizer added (less than 1 percent compared to peroxide). Stabilizers have been used in the market place for 7 years.

Sodium Phytate (Hydrogen Peroxide Stabilizer)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Product is the conjugate base of phytic acid, a carboxylic acid. In a water solution, sodium phytate dissociates into sodium ions and phytic acid.
3. MSDS - See attached file
4. Number of Field Applications: 15 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Sodium phytate is used to stabilize hydrogen peroxide. Conventional use of hydrogen peroxide involves the catalyzation of peroxide by the addition of a ferrous iron catalyst, resulting in a vigorous Fenton's type reaction. The Fenton's reaction gives off excess heat and large quantities of oxygen gas. One of the biggest weaknesses of Catalyzed Hydrogen Peroxide (CHP) is that the peroxide is completely consumed within hours, often times before the peroxide can fully disperse into the aquifer.

A new innovative and patent-pending process has been developed called Stabilized Hydrogen Peroxide (SHP) that involves the addition of a carboxylate stabilizer, such as sodium citrate, sodium malonate, or sodium phytate, that slows the normal rapid decomposition of peroxide. SHP extends the life of the peroxide from less than one day to up to 10 to 14 days. The slowed decomposition of peroxide lessens the buildup of subsurface pressure and dampens the rapid increase in temperature. By controlling the concentration of the stabilizer, the peroxide reaction can be muted sufficiently to minimize the adverse side effects which result in chemical daylighting.

Sodium phytate is a naturally occurring chemical which is present in many common food products (fruits, vegetables, and grains) and promotes key functions within the human body. Phytic acid acts as an anti-oxidant and as a cancer fighting agent.

Minimal impact would be expected on water quality due to the extremely low quantities of stabilizer added (less than 1 percent compared to peroxide). Stabilizers have been used in the market place for 7 years.

Sodium Malonate (Hydrogen Peroxide Stabilizer)

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Product is the conjugate base of malonic acid, a carboxylic acid. In a water solution, sodium malonate dissociates into sodium ions and malonic acid.
3. MSDS - See attached file
4. Number of Field Applications: 15 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Sodium malonate is used to stabilize hydrogen peroxide. Conventional use of hydrogen peroxide involves the catalyzation of peroxide by the addition of a ferrous iron catalyst, resulting in a vigorous Fenton's type reaction. The Fenton's reaction gives off excess heat and large quantities of oxygen gas. One of the biggest weaknesses of Catalyzed Hydrogen Peroxide (CHP) is that the peroxide is completely consumed within hours, often times before the peroxide can fully disperse into the aquifer. A new innovative and patent-pending process has been developed called Stabilized Hydrogen Peroxide (SHP) that involves the addition of a carboxylate stabilizer, such as sodium citrate, sodium malonate, or sodium phytate, that slows the normal rapid decomposition of peroxide. SHP extends the life of the peroxide from less than one day to up to 10 to 14 days. The slowed decomposition of peroxide lessens the buildup of subsurface pressure and dampens the rapid increase in temperature. By controlling the concentration of the stabilizer, the peroxide reaction can be muted sufficiently to minimize the adverse side effects which result in chemical daylighting.

Sodium malonate is a naturally occurring chemical which is present in many common food products (fruits, vegetables, and grains) and promotes key functions within the human body. Malonic acid is an important intermediate in the formation vitamin B1 and B6 and acts as an anti-inflammatory agent.

Minimal impact would be expected on water quality due to the extremely low quantities of stabilizer added (less than 1 percent compared to peroxide). Stabilizers have been used in the market place for 7 years.

Evaluation of Stabilizers of Hydrogen Peroxide for Inclusion in the General WDR Permit

**By: Gary Cronk, P.E.
JAG Consulting Group, Inc.**

December 12, 2013

Physical Description of Peroxide Stabilizers

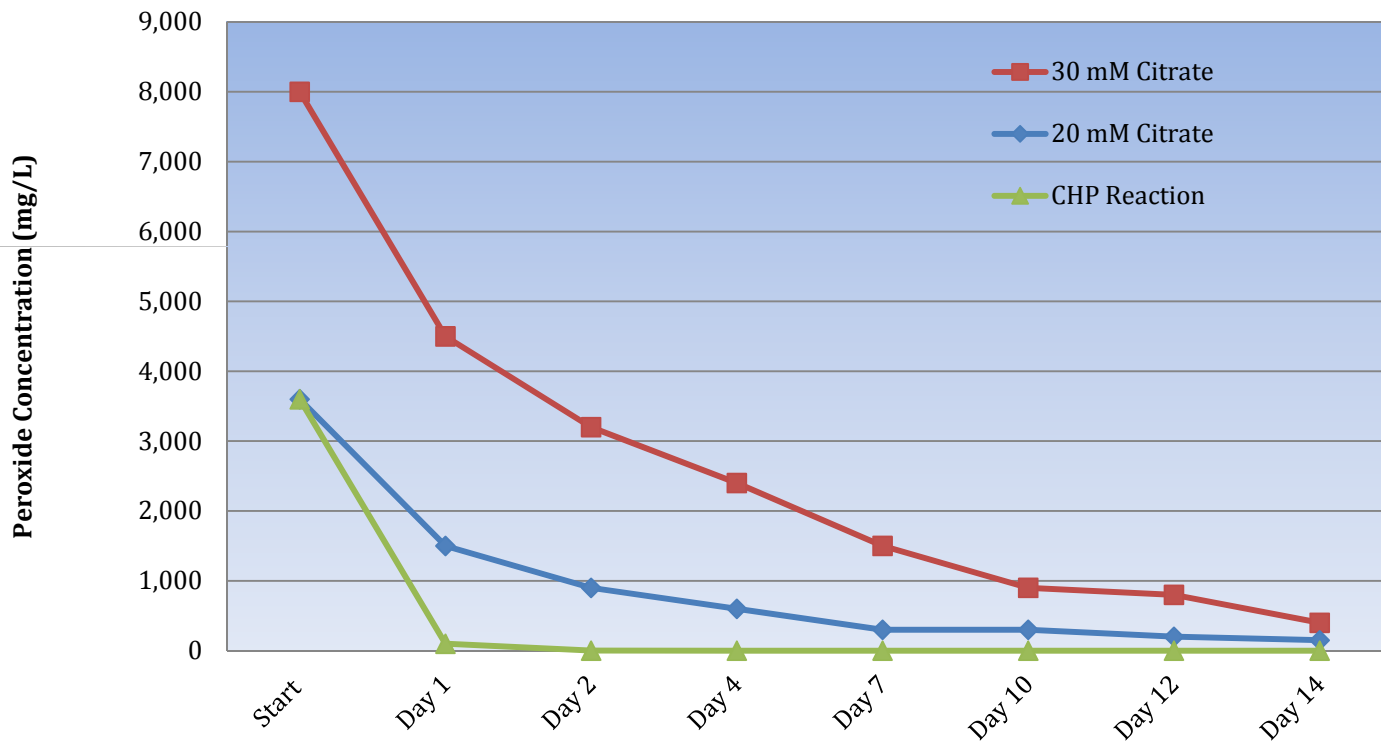
- Stabilizers are used to stabilize the catalytic effect of naturally occurring iron on hydrogen peroxide (acts as a chelating agent).
- Stabilizers include three carboxylate chemicals:
 - Sodium Citrate: $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$
 - Sodium Malonate: $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4$
 - Sodium Phytate $\text{Na}_{12}\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6$
- Carboxylic stabilizers easily dissociate into a carboxylate anion C-O-O and a positively charged hydrogen ion (H^+)
- Three percent rule applies: very low quantities of stabilizers applied (10-20 milli-moles per mole of peroxide). Approx. 100 lbs per 25,000 lbs of peroxide (0.4%)



Bench Testing to Ensure Peroxide Effectiveness

- Dose of Stabilizer should be evaluated by peroxide persistence testing in laboratory
- Life of peroxide can be extended from less than 24 hrs to 10-14 days by using a stabilizer
- A Treatability Test should also evaluate VOC destruction using various doses of peroxide
- Stabilized Hydrogen Peroxide can also be effectively used with Sodium Persulfate

Figure 1. Hydrogen Peroxide Persistence Testing



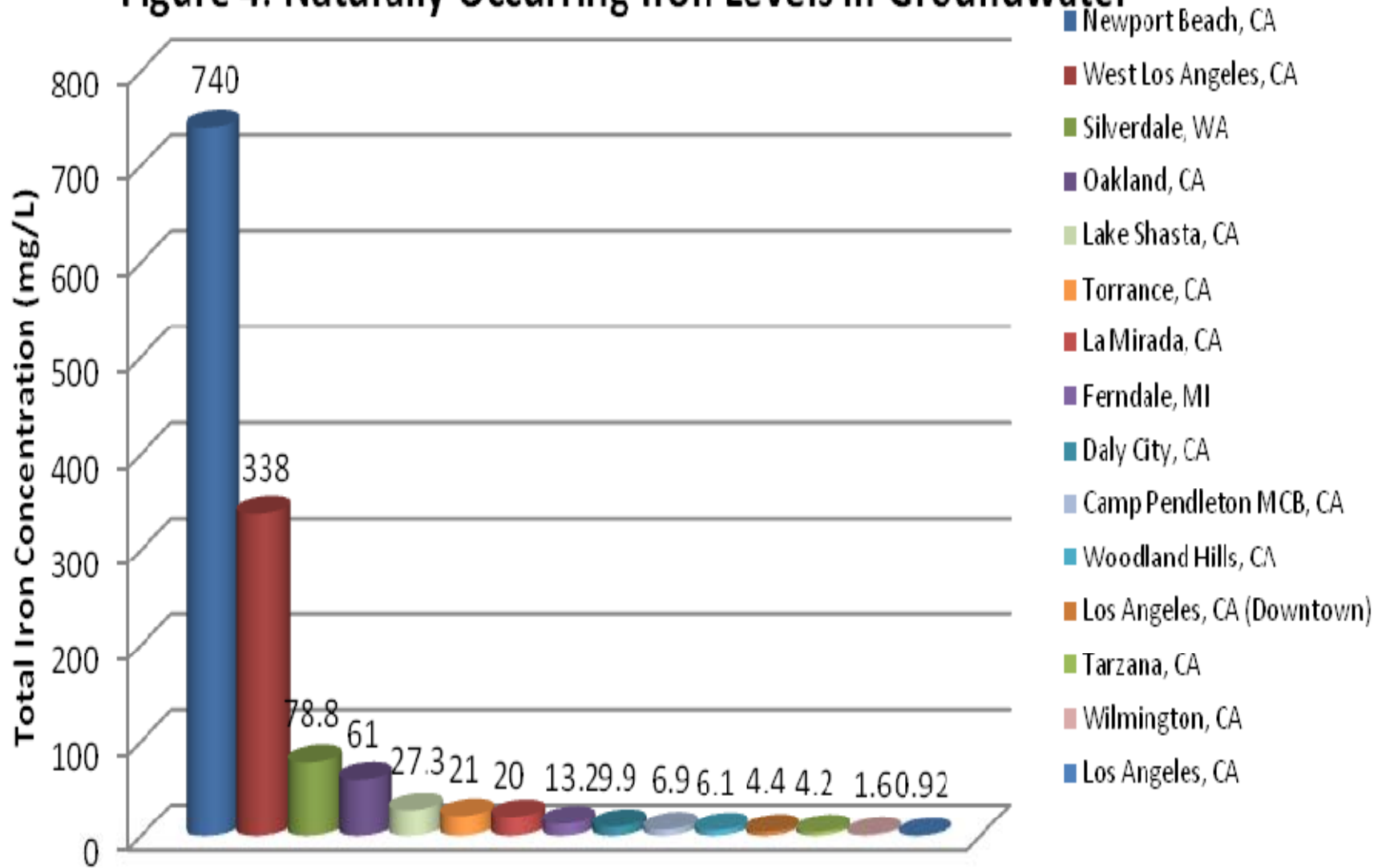
Impact on Health and Water Quality

- Stabilizers are naturally occurring chemicals in common food products (fruits, vegetables, and grains) and promote key functions within the human body
- Citric acid acts as an anti-oxidant, buffering agent, antacid, and anticoagulant in the body
- Malonic acid is an important intermediate in the formation vitamin B1 and B6 and acts as an anti-inflammatory agent
- Phytic acid acts an anti-oxidant and as a cancer fighting agent
- Minimal impact on water quality. Sodium level increase will be very low, due to limited quantity of stabilizer added.
- Stabilizers have been used in the market place for 7 years

Stabilized Hydrogen Peroxide: A Patent Pending Process of JAG Consulting Group

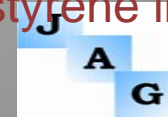
- SHP involves the physio-chemical control of the catalyzation of hydrogen peroxide
- The dose of Stabilizer is adjusted to site conditions to control the exothermic Fenton's reaction (dependent on iron levels)
- Excess pressure buildup is controlled
- Excess temperature buildup is controlled
- Chemical daylighting is controlled

Figure 4. Naturally Occurring Iron Levels in Groundwater

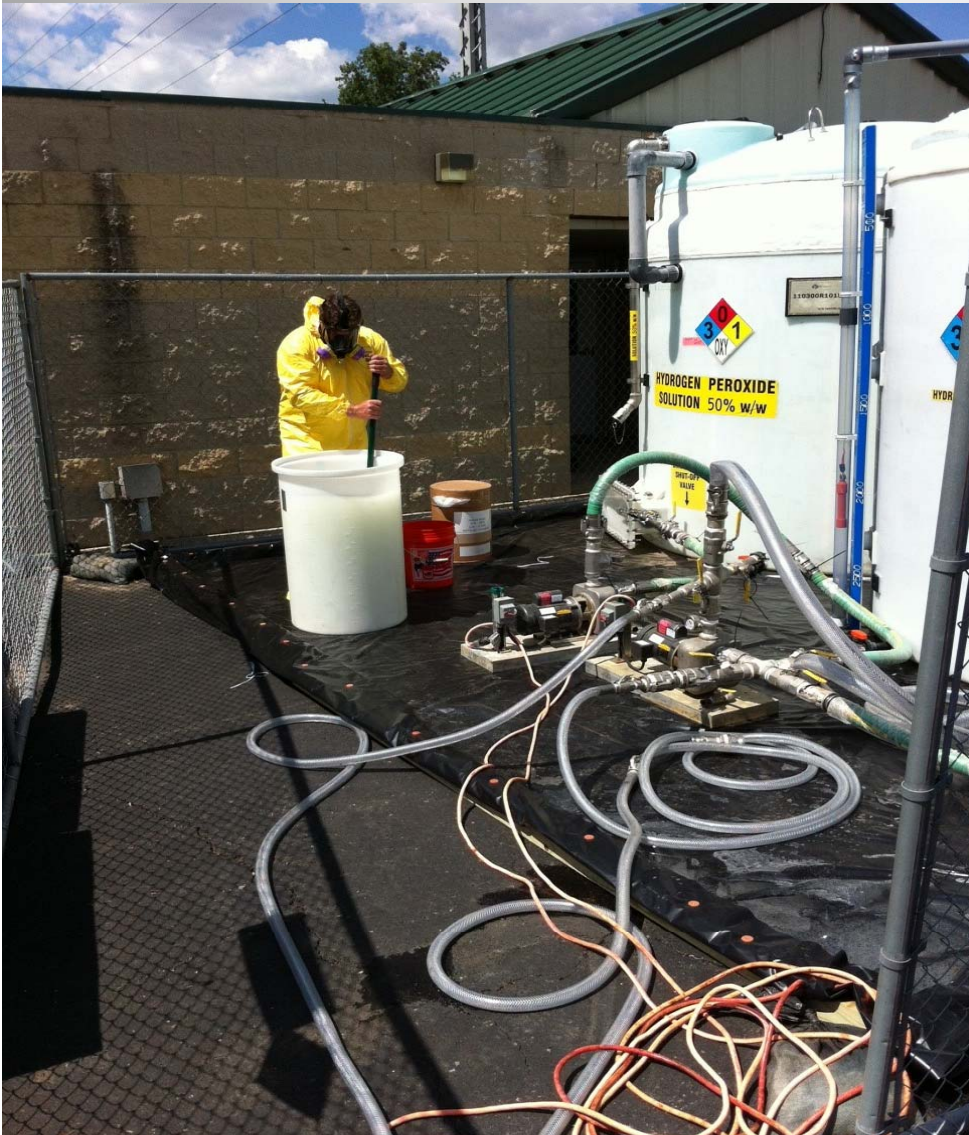


Case Study No. 1 – SHP Injections at Former Chemical Plant, Ferndale, Michigan

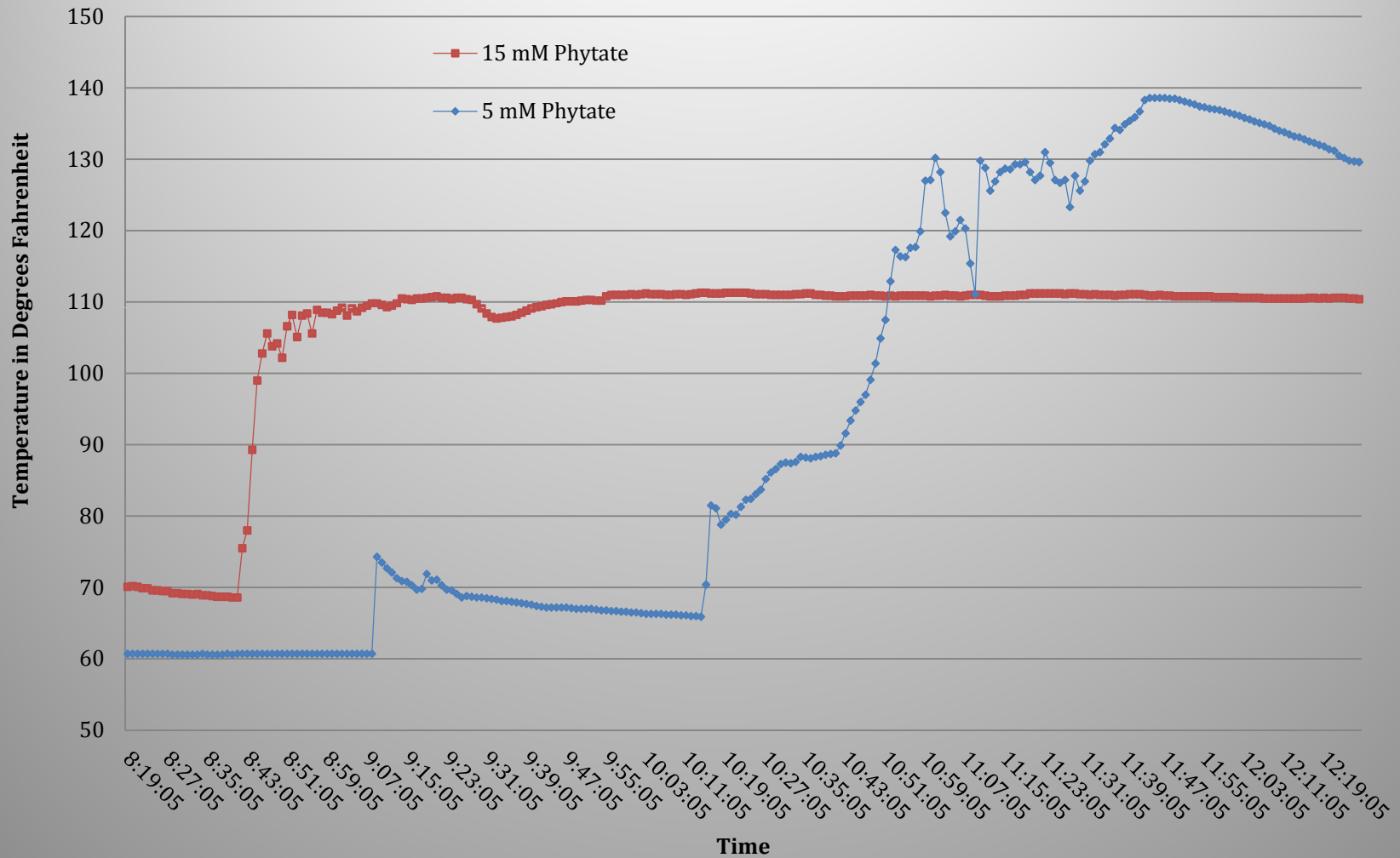
- Extremely elevated levels of chlorinated and petroleum VOCs (TCE, styrene, toluene, and ethylbenzene) were present at the site (NAPL levels)
- Site has been re-developed as a mini-storage facility
- Injected 8,100 gallons of 8% hydrogen peroxide into 13 extraction wells (used as injection wells). Sodium phytate (5 mM) used as the peroxide stabilizer
- In-situ temperature and pressure were controlled by increasing the dose of sodium phytate (from 5 mM to 15 mM). Maximum temperature was reduced from 139 degrees F to 111 degrees F by increasing dose of Phytate.
- Failure of the well seals in multiple wells (prior to increasing Phytate dose) caused chemical daylighting
- SHP injections attained over 96% destruction of TCE and styrene in four monitoring wells.



Case Study No. 1 – Former Chemical Plant, Ferndale, Michigan



Temperatures in Well E1-12G Using Varying Doses of Phytate



Case Study No. 2 – SHP Injections at Gas Station Site, Silverdale Washington

- Active gas station site. Performed injections under a federal UIC permit.
- Injections performed into 8 direct push borings at 2 ft depth intervals from 20 feet to 10 feet (bottom up).
- Injected 2,900 gallons of 10% peroxide and 1,200 gallons of persulfate
- Temperature and pressure controlled by use of 30 mM of citrate. Maximum temperature recorded during injections was 114 degrees F.
- No significant daylighting occurred.
- Attained 97% destruction of TPH gas and 99% destruction of toluene and xylenes after 58 days.

Case Study No. 2. Gas Station, Silverdale, WA



TPH gas Levels Following ISCO Injections

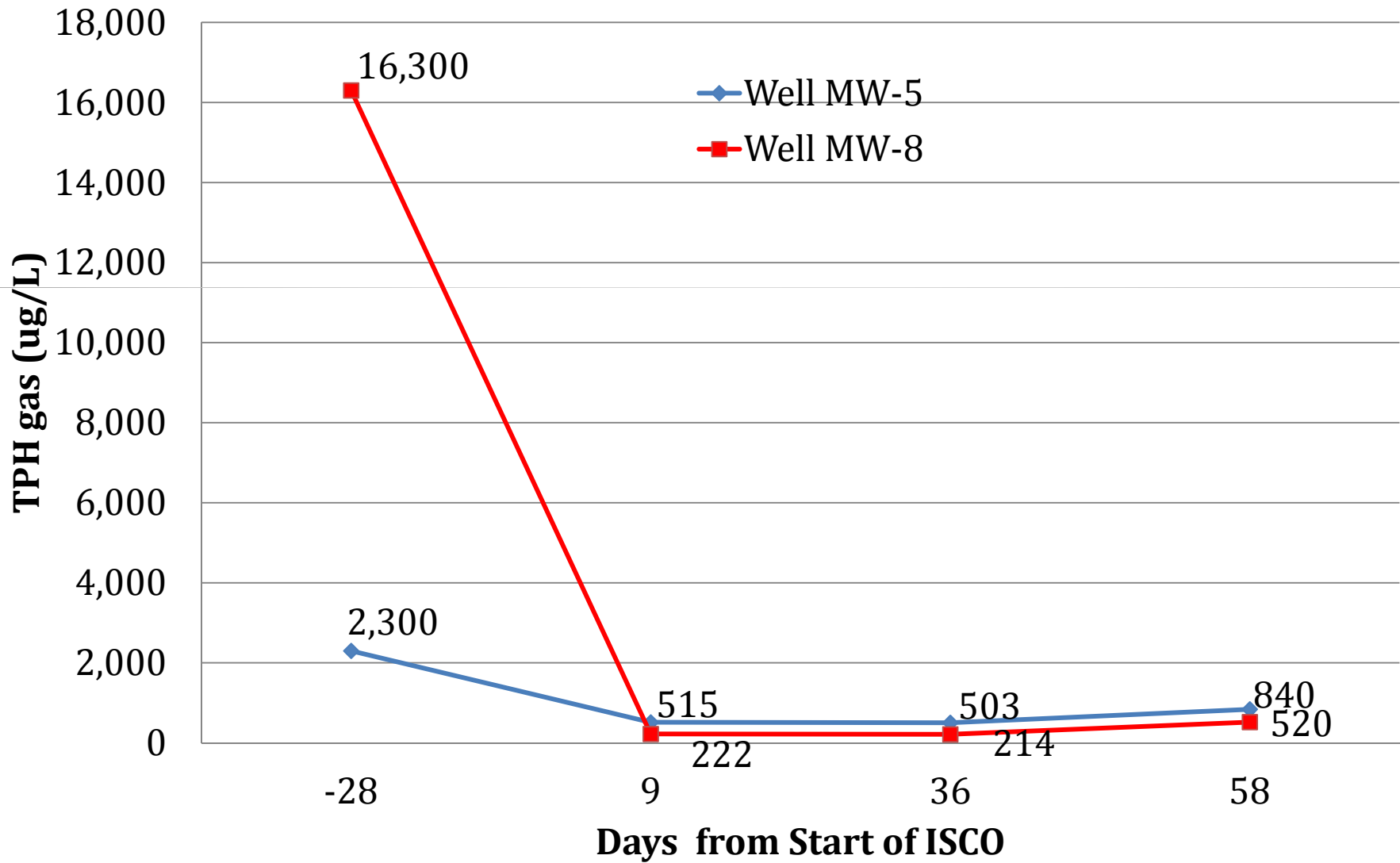
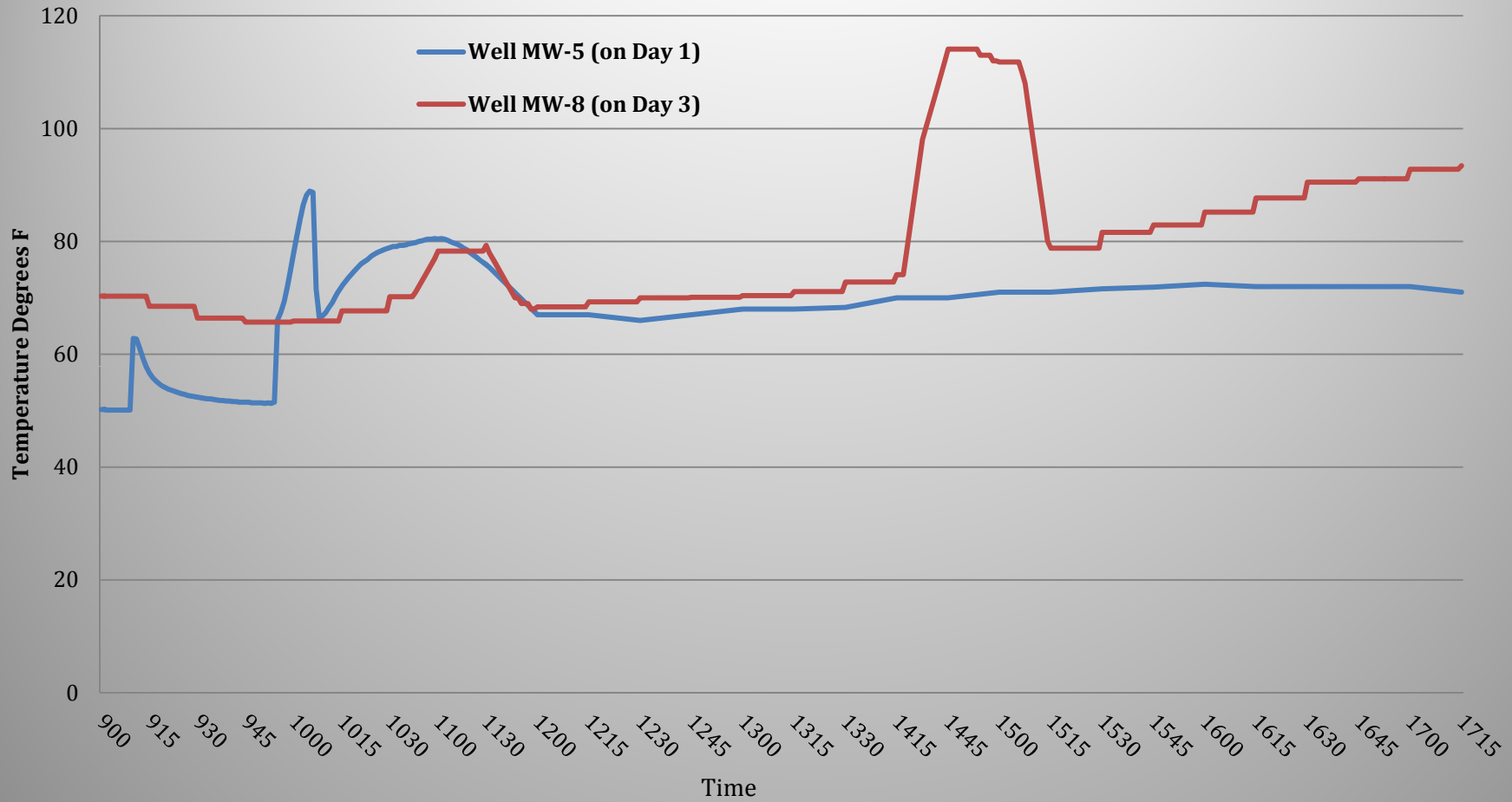
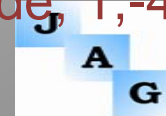


Figure 10. Continuous Temperature Measurements in Monitoring Wells

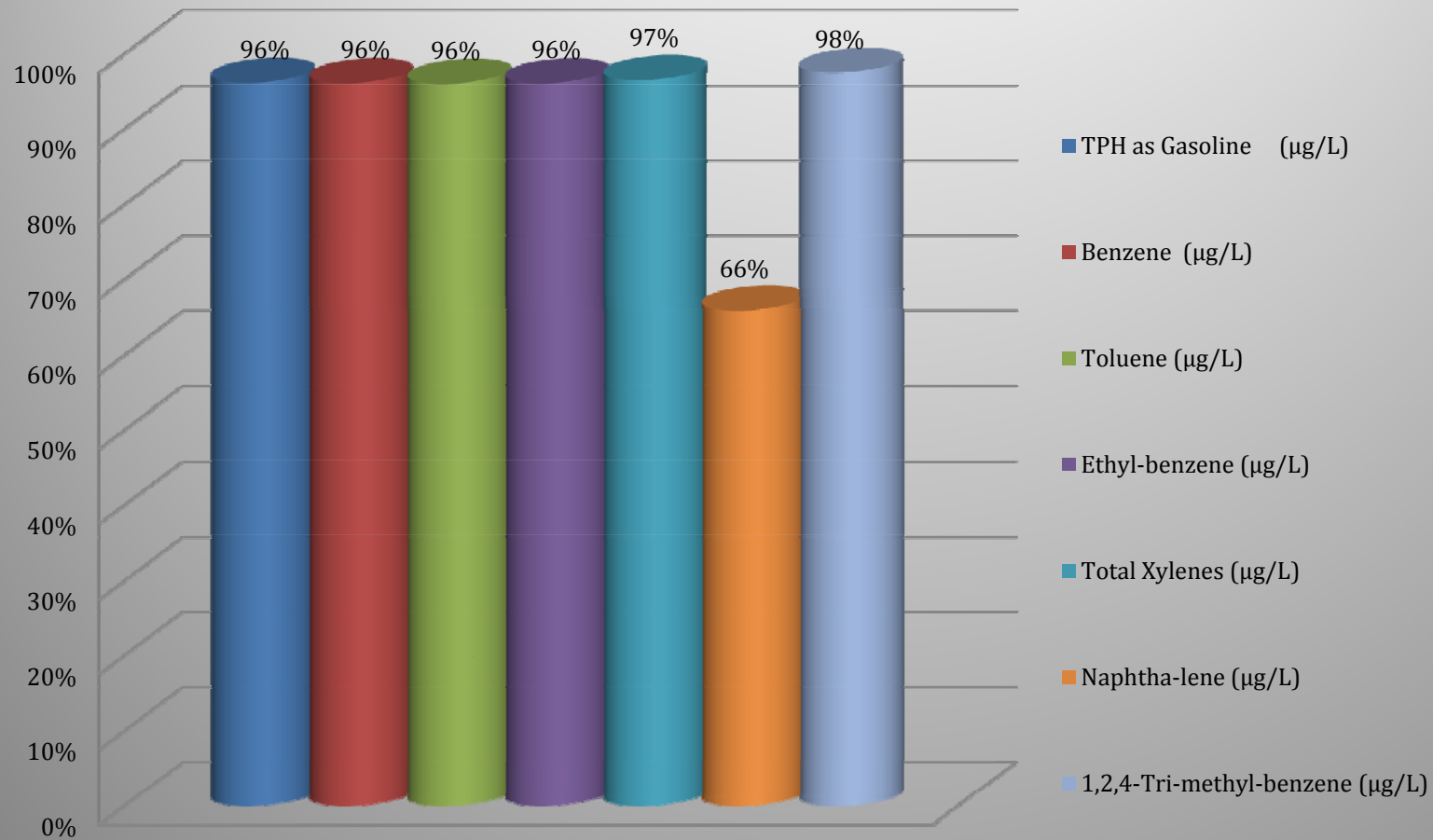


Additional Case Studies: Treatability Testing

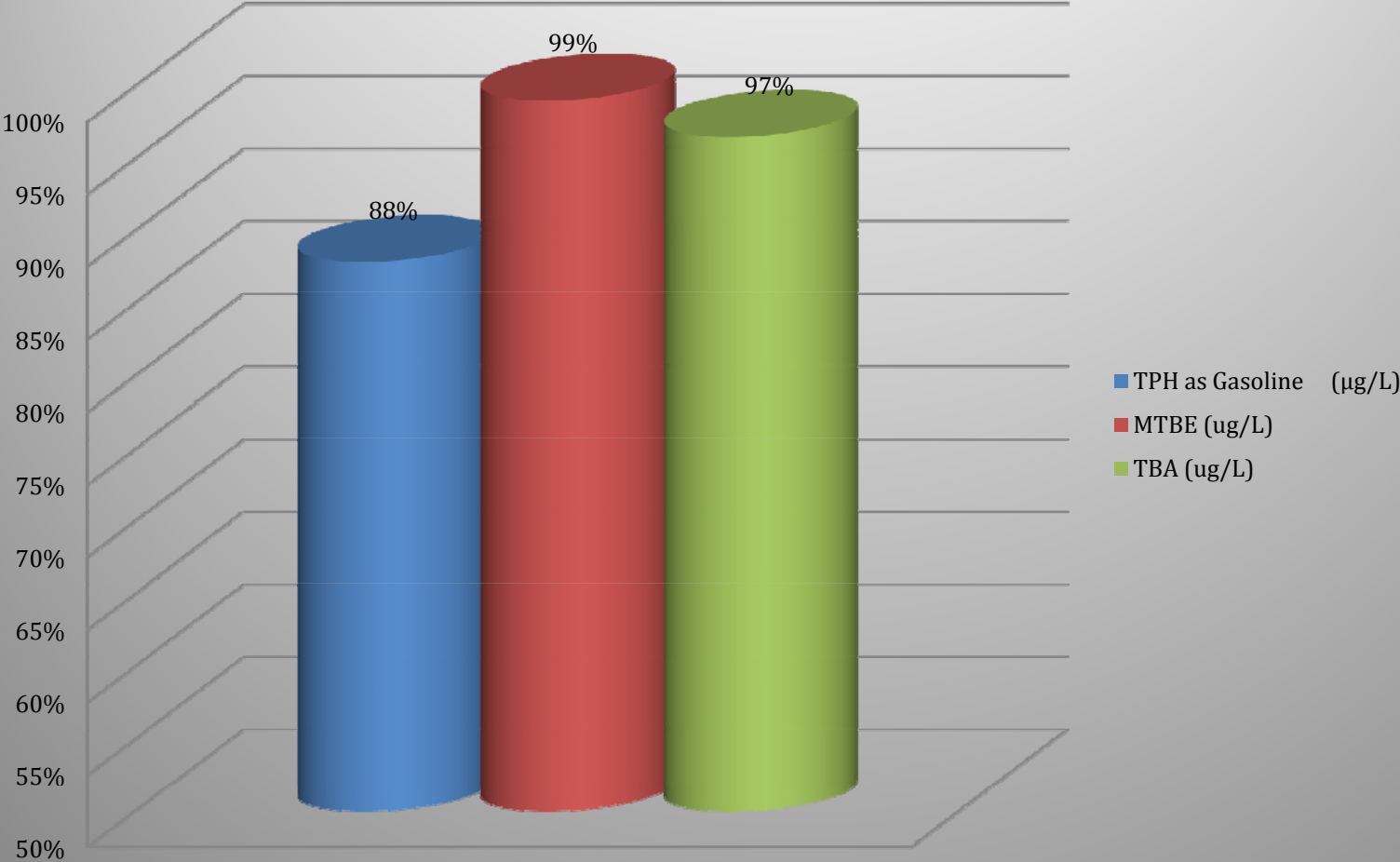
- Treatability Tests performed by JAG Consulting on soil and groundwater samples collected from the following sites:
 - Irvine
 - Los Angeles
 - Santa Barbara
 - Oakland
 - Daly City
- Tests have shown peroxide persistence can be extended up to 10 days using all three carboxylate stabilizers, sodium citrate, sodium phytate, and sodium malonate
- Over 95% destruction of TPH gas, BTEX, MTBE, and TBA have been consistently shown in these tests
- Over 95% destruction of TCE, 1,2-DCA, vinyl chloride, 1,4-dioxane, and other chlorinated compounds



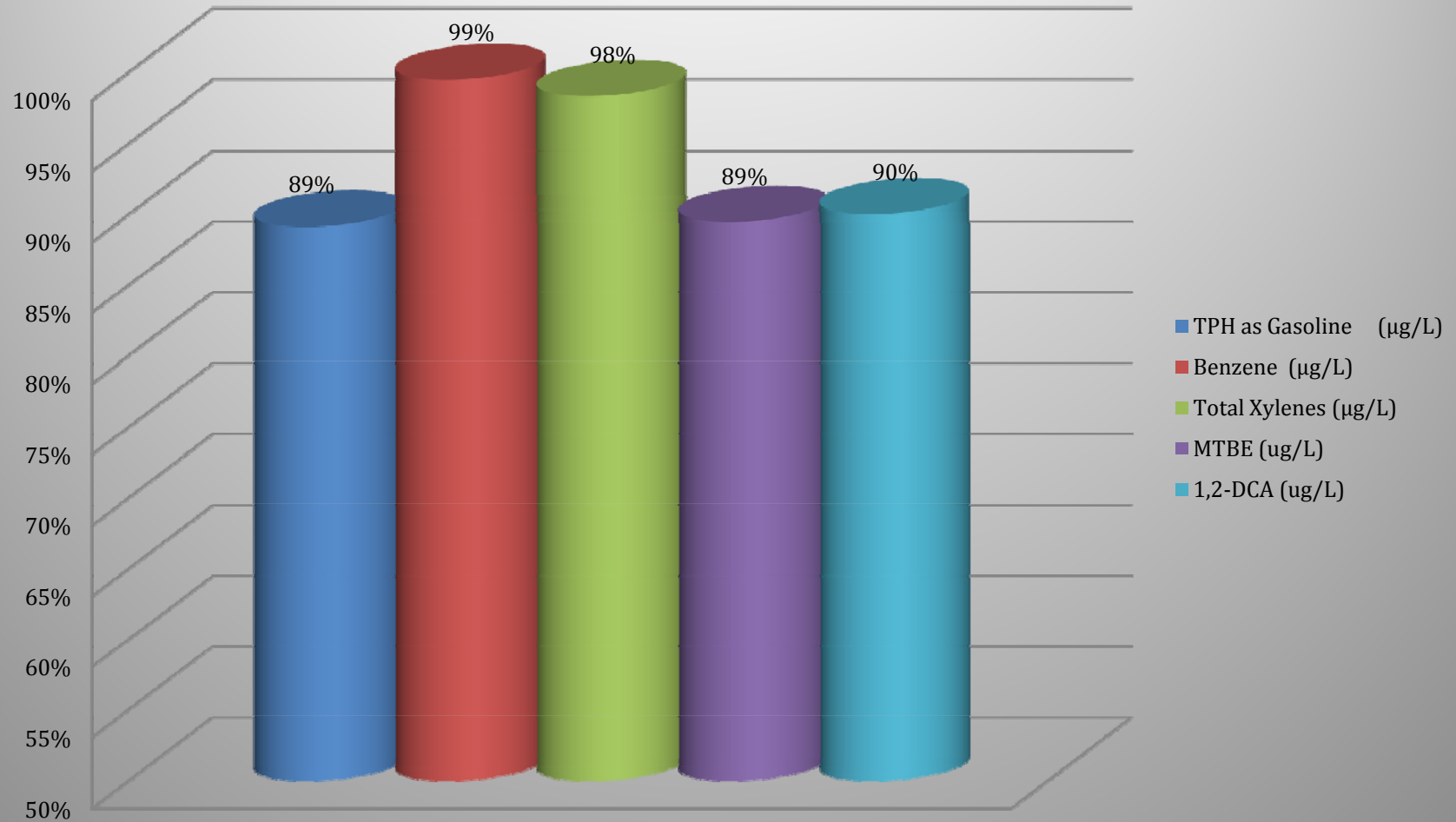
Reduction of VOCs by SHP at Irvine UST Site



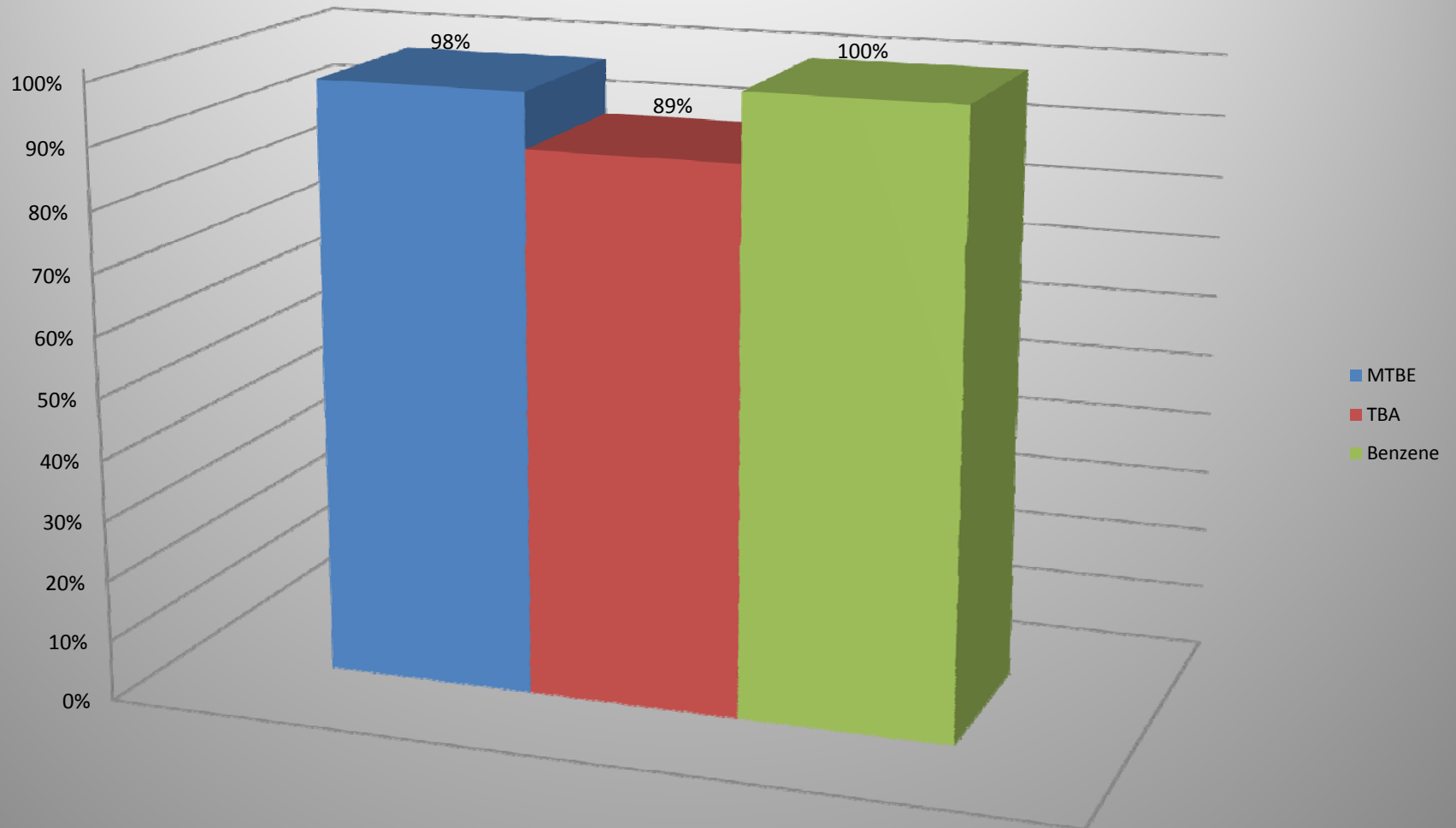
Reduction of VOCs by SHP at Los Angeles UST Site



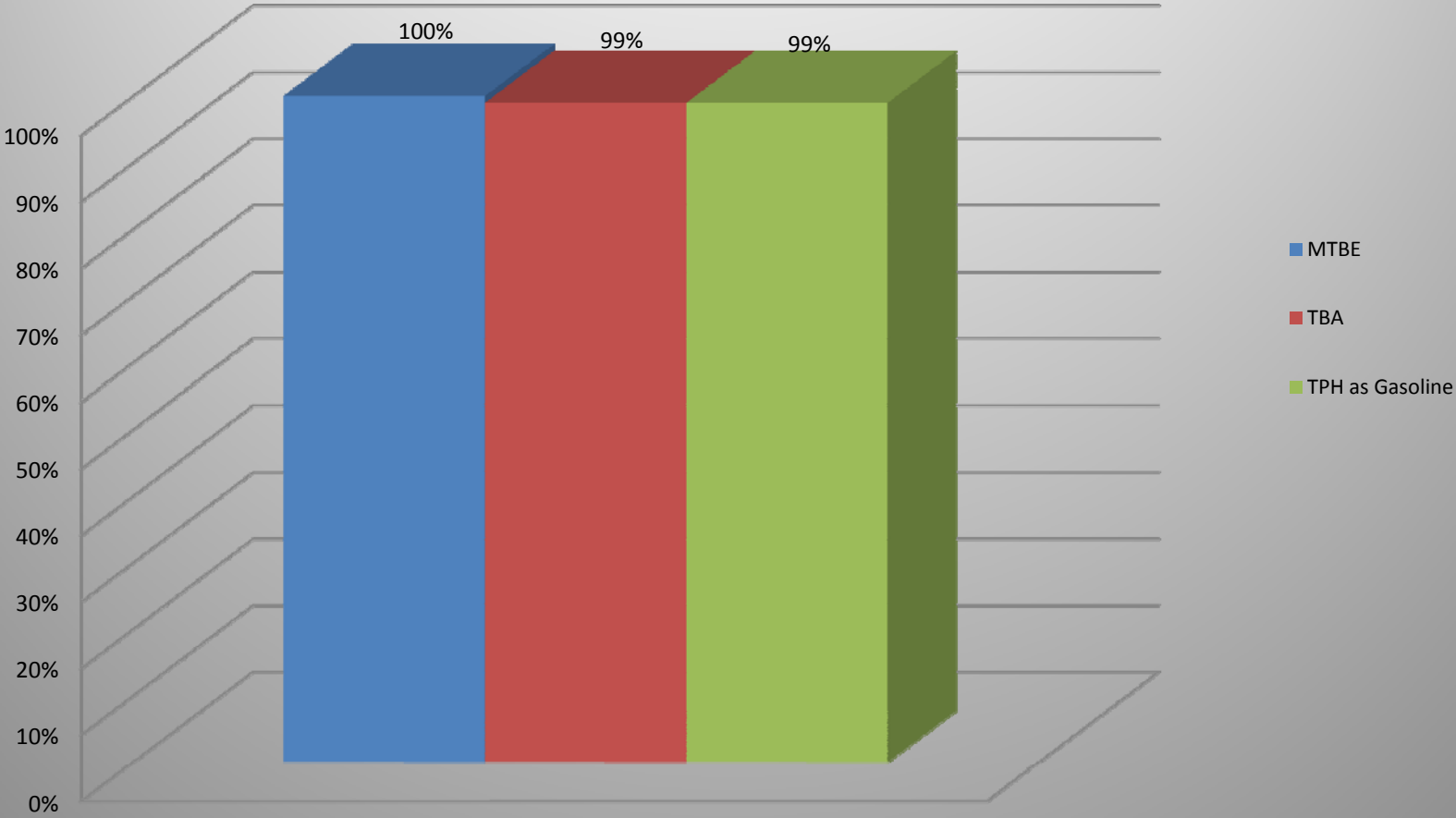
Reduction of VOCs by SHP at Santa Barbara UST Site



Contaminant Destruction Using SHP, Oakland, CA



Contaminant Destruction Using SHP, Daly City, CA



Use of a Carboxylate Stabilizer to Control the Exothermic Temperature of the Catalyzed Fenton's Reaction

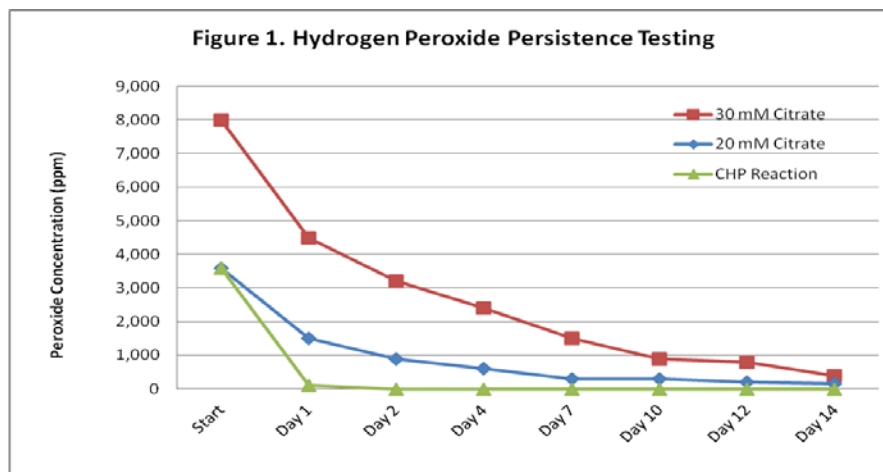
Gary Cronk, P.E., JAG Consulting Group, Inc.

Abstract

Use of carboxylate stabilizers have been shown to significantly dampen the rapid decomposition of peroxide which normally occurs during a catalyzed Fenton's reaction. The stabilized hydrogen peroxide (SHP) is characterized by a significantly lower temperature increase compared to the highly exothermic catalyzed hydrogen peroxide (CHP) reaction. Groundwater temperatures monitored during peroxide injections have demonstrated that SHP can reduce subsurface temperatures by 40 to 70 degrees Fahrenheit compared to CHP reactions. The temperature increase is dampened as a direct result of extending the life of the peroxide from less than one day to up to 14 days by the use of a stabilizer. The use of SHP has also been shown to minimize the occurrence and severity of chemical daylighting.

Introduction

A new innovative process called Stabilized Hydrogen Peroxide (SHP) has been developed that involves the addition of a carboxylate stabilizer, such as sodium citrate, sodium phytate, or sodium malonate, that slows the normal rapid decomposition of hydrogen peroxide. SHP extends the life of the peroxide from less than one day to up to 10-14 days. Figure 1 below compares the persistence of peroxide using increasing doses of sodium citrate against a CHP reaction. Similar persistence is achieved using other carboxylate stabilizers, including sodium phytate and sodium malonate.

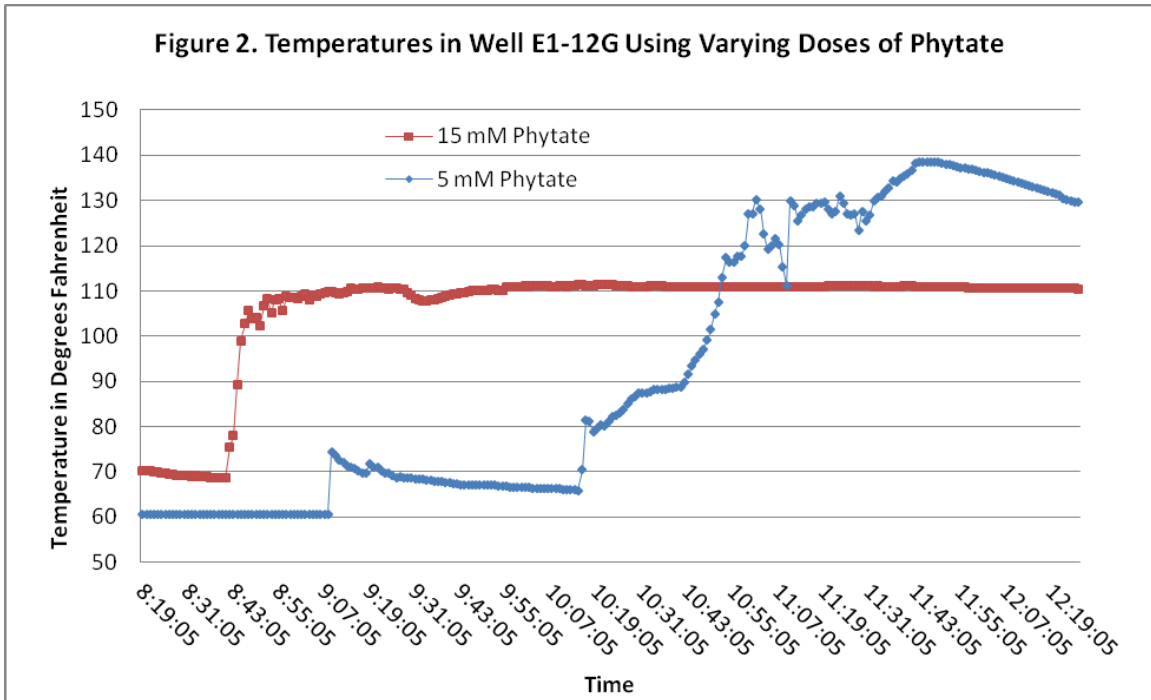


Project Background

The project Site is a former chemical plant located in Ferndale, Michigan. The site has been redeveloped as a mini-storage facility. Extremely elevated levels of TCE, vinyl chloride, styrene, toluene, and ethylbenzene were present at the site (NAPL levels). The treatment area measured approximately 9,660 square feet in size. Depth to groundwater beneath the site was approximately 5 to 7 feet below ground surface (bgs). The shallow groundwater zone is comprised primarily of silty sands and sandy silts to a depth of 14 feet. Below 14 feet lies a substantial clay unit. NAPL is known to exist in the source area.

Control of Temperatures

A total of 8,100 gallons of 8% hydrogen peroxide was injected into 13 existing extraction wells, which were used as injection wells. An initial sodium phytate dose of 5 milli-moles (mM) was used as the peroxide stabilizer. Within the first 4 hours of injections, groundwater temperatures in the injection wells rapidly increased to 130 to 139 degrees F and caused chemical daylighting in three wells due to the failure of the well seal. As a means of controlling the rapid temperature increases, the dose of sodium phytate was increased from 5 mM to 15 mM. As a result, the maximum temperatures were reduced from 139 degrees F to 111 degrees F. A graph showing the comparison of the temperature increases in well E1-12G using the two doses of phytate is provided in Figure 2.



Control of Chemical Daylighting

Failure of the well seals occurred in several wells (prior to increasing phytate dose) and caused chemical daylighting. The photograph below shows the typical impact of chemical daylighting.



After increasing the phytate dose, daylighting was controlled.

This project has shown that by increasing the concentration of the stabilizer, the peroxide reaction can be controlled to both minimize the temperature increase and minimize (or eliminate) the occurrence of chemical daylighting.

References

Cronk, Gary and Richard Cartwright, 2006. "Optimization of a Chemical Oxidation Treatment Process for Groundwater Remediation". Proceedings from the *Battelle 5th International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, May 2006.

Use of Stabilized Hydrogen Peroxide to Control the Temperature and Pressure Side Effects of the Catalyzed Fenton's Reaction

Gary Cronk, P.E., JAG Consulting Group, Inc.

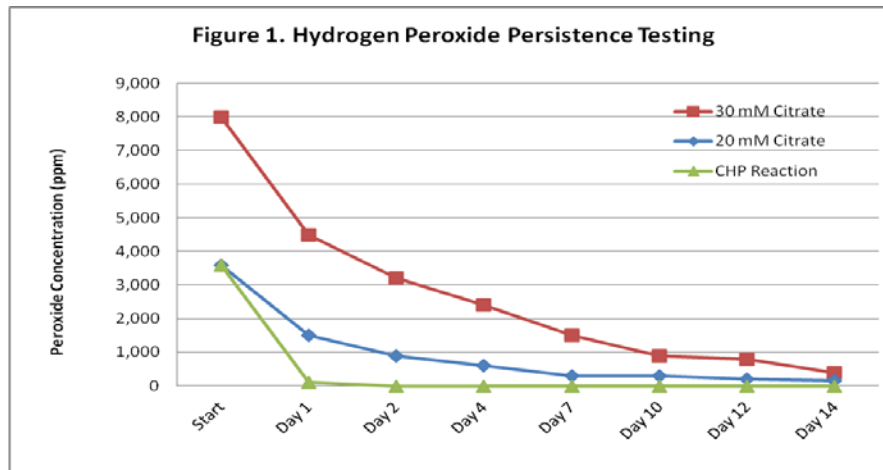
Abstract

Use of stabilized hydrogen peroxide has been shown to significantly dampen the rapid decomposition of peroxide which normally occurs during a catalyzed Fenton's reaction. One of the benefits of stabilized hydrogen peroxide (SHP) is a significantly lower temperature increase compared to the highly exothermic catalyzed hydrogen peroxide (CHP) reaction. Groundwater temperatures monitored during peroxide injections have demonstrated that SHP can reduce subsurface temperatures by up to 70 degrees Fahrenheit compared to CHP reactions. Laboratory studies have shown that the life of the peroxide can be extended from less than one day to up to 14 days by the use of a stabilizer. By controlling the temperature increase and the pressure increase (due to rapid oxygen release), use of SHP has also been shown to minimize the occurrence and severity of chemical daylighting.

Introduction

Use of catalyzed hydrogen peroxide (CHP) has been used for many years for the rapid destruction of organic contaminants by injection into the subsurface via in-situ chemical oxidation. Catalyzed hydrogen peroxide involves the use of hydrogen peroxide with a ferrous iron catalyst, resulting in Fenton's type reaction. The Fenton's reaction gives off excess heat and large quantities of oxygen gas. One of the biggest weaknesses of the CHP reaction is that the peroxide is normally completely consumed within 24 to 48 hours, often times before the peroxide can fully disperse into the subsurface.

A new innovative process called Stabilized Hydrogen Peroxide (SHP) has been developed that involves the addition of a carboxylate stabilizer, such as sodium citrate or sodium malonate, that slows the normal rapid decomposition of hydrogen peroxide. SHP extends the life of the peroxide from less than one day to up to 10-14 days. Figure 1 below compares the persistence of peroxide using increasing doses of a stabilizer (sodium citrate) against a CHP reaction.



The slower decomposition of peroxide lessens the buildup of subsurface pressure and dampens the rapid increase in temperature. By controlling the concentration of the stabilizer, the peroxide reaction can be muted sufficiently to minimize the adverse side effects which result in chemical daylighting. The two photographs below shows the typical impact of chemical daylighting and the resulting cleanup that is required.

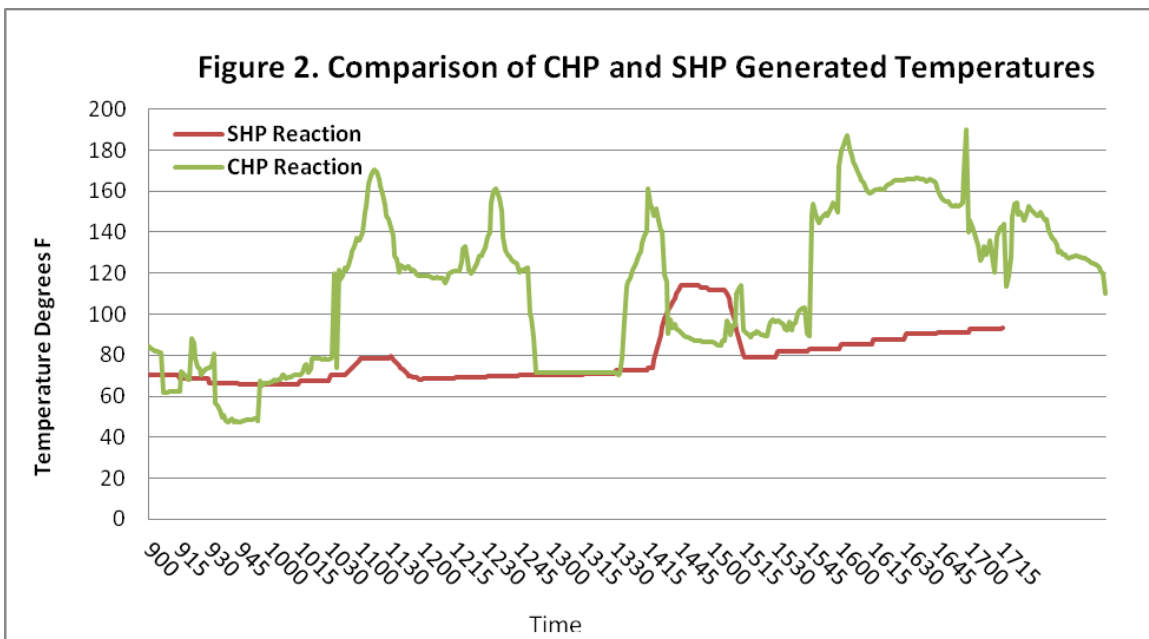


Controlling Subsurface Temperature Increases

Field measurements have confirmed that the temperature increases within an injection well casing during peroxide injections may rise to as high as 240 degrees F during CHP reactions. The temperatures reached during CHP injections are directly related to the concentration of peroxide used, with higher temperature attained during injection of higher peroxide concentrations. Peroxide concentrations of 17% were shown to reach a maximum subsurface temperature of 240 degrees F (consistent temperatures of around 180 degrees F) at a Site in La

Mirada, CA, while a maximum temperature of 218 degrees F (with consistent temperatures of 170 degrees) was measured at a site in Rancho Dominguez, CA. The author previously reported these CHP temperatures in a paper published in 2006 (Cronk and Cartwright, 2006).

At a 10% peroxide concentration, the maximum CHP temperatures reached 187 degrees at Lake Shasta, CA. SHP temperatures are much more depressed as the stabilizer acts as a chelating agent and slows down the iron catalyzed reaction with the peroxide. The maximum temperatures recorded during a SHP injection at a site in Silverdale, WA was 114 degrees F. A graph showing the comparison of the temperature increases during SHP versus CHP injections are provided in Figure 2.



The controlled injection of stabilized hydrogen peroxide, reduces the rapid decomposition of peroxide by extending the life of the peroxide from less than one day to over 10 days. The slower decomposition of peroxide lessens the buildup of subsurface pressure and dampens the normal increase in water temperature. By controlling the concentration of the stabilizer, the peroxide reaction is muted sufficiently to minimize the adverse side effects which result in chemical daylighting.

Bench Scale Test Simulation of Temperature Increases

Dr. Richard Watts previously performed several bench scale laboratory studies using stabilized hydrogen peroxide. In 2005, Dr. Richard Watts determined that use of sodium citrate or sodium malonate could be effectively used to extend the life of hydrogen peroxide and verified that use of

these stabilizers (along with sodium phytate) produced hydroxyl radicals and superoxide radicals in the same relative abundance as catalyzed peroxide reactions (Watts, et al, 2005). Watts reported little or no temperature increase during the SHP reactions.

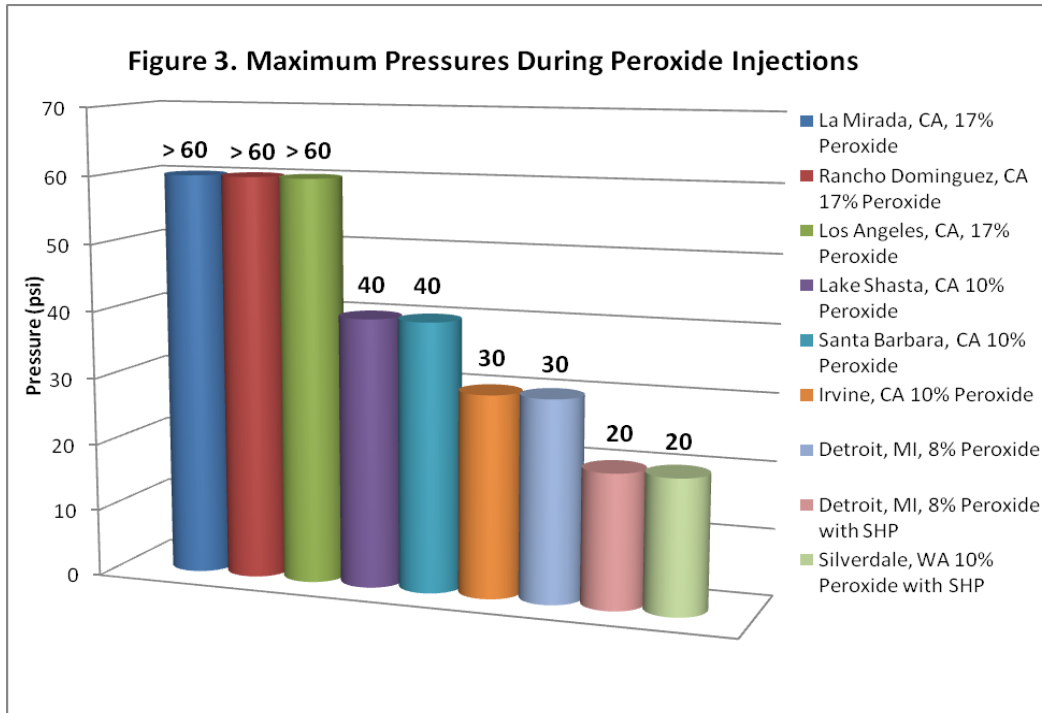
No significant temperature increase is detectable during normal Bench Testing of CHP or SHP reactions. It is probable that the typical small scale bench scale experiments (using small reactor vessels and low soil to water ratios) do not adequately simulate field conditions. Since it is well known that significant temperature increases of 80 degrees F or more are created during CHP peroxide injections in the field, a series of improved bench scale experiments were designed by the author to simulate the temperature increases during field injections. The improved bench scale experiments were designed using much larger reactor vessels (i.e., a 55-gallon drum), use of a 1-inch diameter well screen (with pre-packed sand pack) for injection of the peroxide, use of heterogeneous soils (alternating sands and clays) to simulate the semi-confined conditions in the field, and use of thermocouple and a datalogger to continuously record temperature changes within the well casing.

The improved Bench Tests were successful in replicating the temperature increases that normally occurs during the CHP Fenton's reaction in the field. The Bench Testing was able to replicate temperatures of 100 to 128 degrees F using 10% peroxide and ferrous iron (200 mg/L). The addition of 10 milli-moles (mM) of sodium citrate as a stabilizer lowered the temperatures by 30 to 35 degrees F.

Controlling Subsurface Pressure Increases

The conventional use of catalyzed hydrogen peroxide commonly results in an immediate buildup of subsurface back pressure (60 psi and greater) due to the rapid release of oxygen and a rapid temperature increase. The increasing pressure in the subsurface often causes the oxygen and peroxide to be forced upwards through fractures created in the soil towards the ground surface, creating a release of peroxide at the ground surface (referred to as chemical daylighting). This situation often becomes a continuing health and safety issue during the injection of catalyzed hydrogen peroxide at sites where people and buildings are nearby.

The use of SHP shows a reduction in subsurface pressure to less than 20 psi using sodium citrate. Figure 3 (below) shows the maximum pressure from use of CHP (30 psi to >60 psi) and the much lower pressures measured during the use of SHP (less than 20 psi).



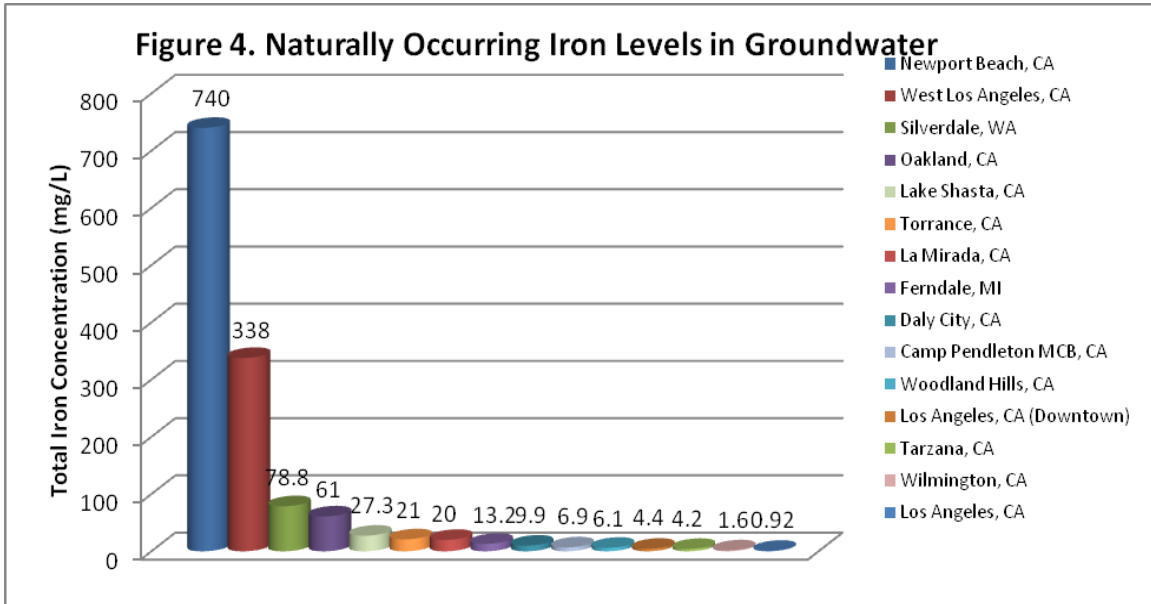
Peroxide Catalyzation by Naturally Occurring Iron

An interesting observation when using catalyzed hydrogen peroxide has been that no addition of ferrous iron or ferric iron is necessary to initiate the Fenton's reaction. Iron supplementation has commonly been a requirement of other peroxide based patents (i.e, Vigneri 1996 and Greenberg 2001). The author has determined that the naturally occurring iron levels in the groundwater and soil are almost always sufficient to initiate the catalyzation of peroxide. Further, it has been determined that the dissolved iron levels in the groundwater are more important than the iron contained within the soil structure for initiating the Fenton's reaction. This is due to the fact that the primary chemical reactions occur in the water phase (dissolved). Thus, the best confirmation for determining site suitability for using SHP is to determine the total iron level in the groundwater, since the Fenton's reaction can be initiated by either ferrous iron (Fe^{+2}) or ferric iron (Fe^{+3}).



In our survey of over 14 sites used for ISCO injections, we have determined that nearly all the sites have had a naturally occurring total iron level of at least 1 mg/L or more (which is sufficient for CHP). Several sites had iron levels over 100 mg/L or more. A summary of the naturally occurring iron levels (total iron) measured at 14 ISCO sites across the United States is provided

in Figure 4. Although iron is most commonly the metal in highest concentrations, other transition metals, such as manganese, can also contribute to the catalyzation of peroxide.



It has been determined from bench tests that the dissolved iron level increases after the addition of peroxide due to the lower pH of the peroxide which causes iron and other metals to become more soluble. This phenomenon helps to contribute more available iron to the Fenton's reaction.

Stabilizing Agents and Chelating Agents

SHP involves the addition of a simple carboxylate stabilizer, such as sodium citrate or sodium malonate, that stabilizes the hydrogen peroxide and can extend the life of the peroxide to 10-14 days. Without a stabilizer, the life of peroxide is usually less than one day due to rapid CHP reaction. The carboxylate stabilizer is a simple chelating agent (one ligand) and is significantly different from the more complex chelating agents used in other patented processes used in the remediation business, which are either EDTA based or phosphate based. EDTA is a polydentate chelating agent that forms six bonds with iron (and other transition metals) and creates a chelate complex that is very stable. The use of chelated iron (EDTA) has been used to control and extend the peroxide reaction, however its use extends the life of the peroxide for a longer period of time (21 days or more) than is desired for optimal treatment of groundwater.

The patent of Richard Watts and Richard Greenberg (1998) involves the combined use of iron EDTA, ferrous sulfate, sulfuric acid, phosphoric acid, and monopotassium phosphate to control the catalyzed peroxide reaction. This patent involves maintaining a low pH in the groundwater between 3 and 5 pH units. Additionally, EDTA is a chemical that causes health concerns

because it is a large complex molecule that breaks down into NTA (nitrilotriacetic acid,) a chemical that is a suspected human carcinogen. For this reason, use of EDTA is generally not acceptable to many state regulators responsible for approval of injection projects.

Phosphate based chelating agents include phosphonates, which have an amine group (NH₄) in the molecular structure that increases the iron binding ability. The patent of Richard Greenberg (2001) involves the combined use of phosphoric acid, monopotassium phosphate, iron salts, and iron chelates to control the catalyzed peroxide reaction. In addition, this patent involves maintaining the pH of the groundwater between 5 and 8 units. However, the drawback of this technology is that large quantities of phosphates and iron salts (both are considered secondary drinking water contaminants) are added to the aquifer to create the pH buffering effect.

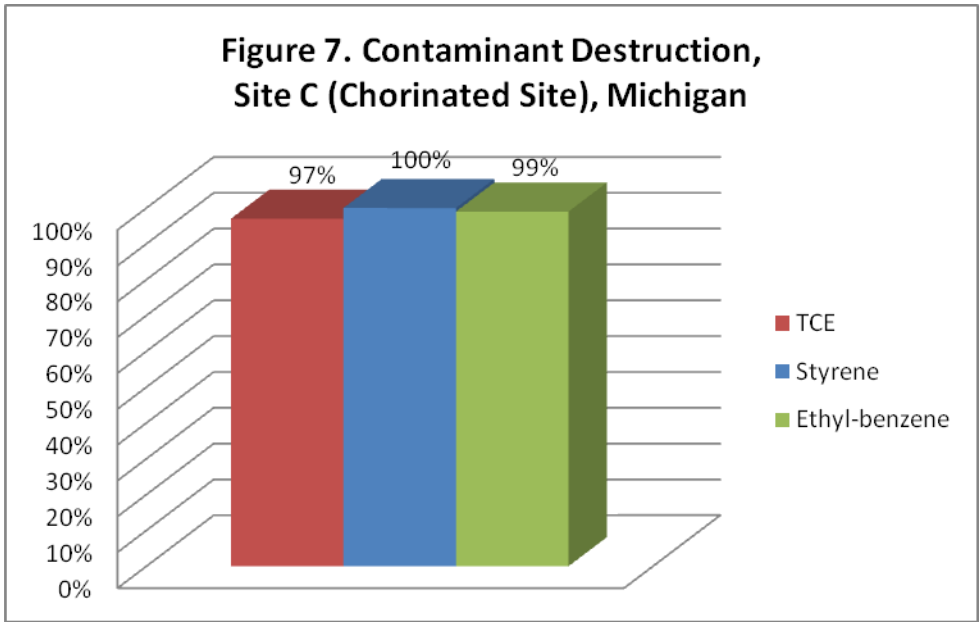
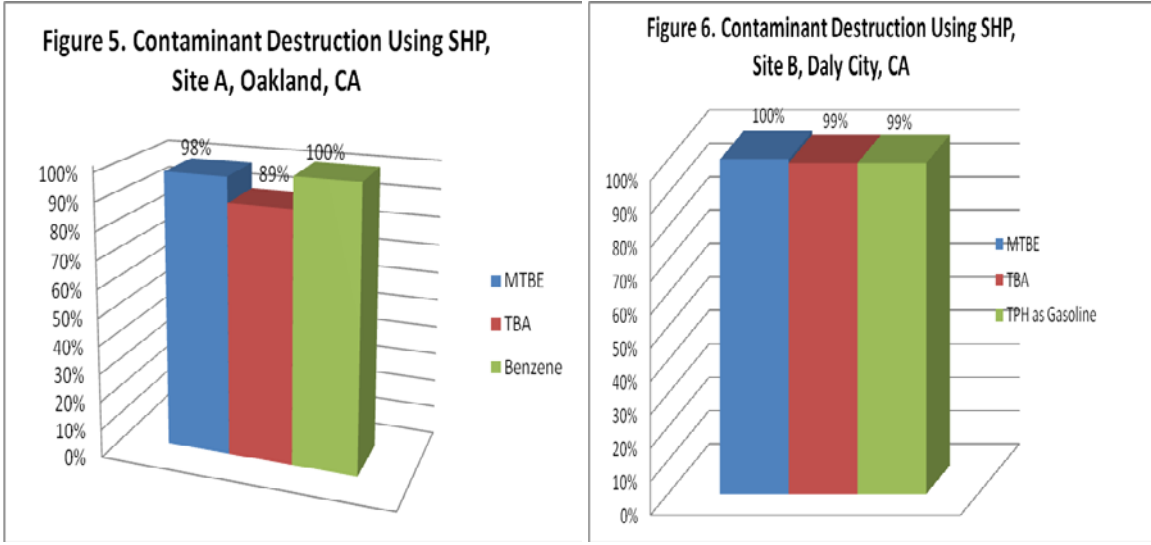
Benefits of Stabilized Hydrogen Peroxide

In the SHP process, the pressure and temperature is monitored continuously in the subsurface to allow for control of the pressure and temperature increase. By increasing the dose of the stabilizer used, the pressure and temperature increase can be controlled to minimize the severity and occurrence of chemical daylighting. The optimal temperature range is 100 to 120 degree F and the optimal pressure range is 20 to 30 psi. Generally those sites with elevated levels of naturally occurring iron in the groundwater (over 10 mg/L) create a more vigorous CHP reaction and require a slightly higher dose of stabilizer to control the reaction.

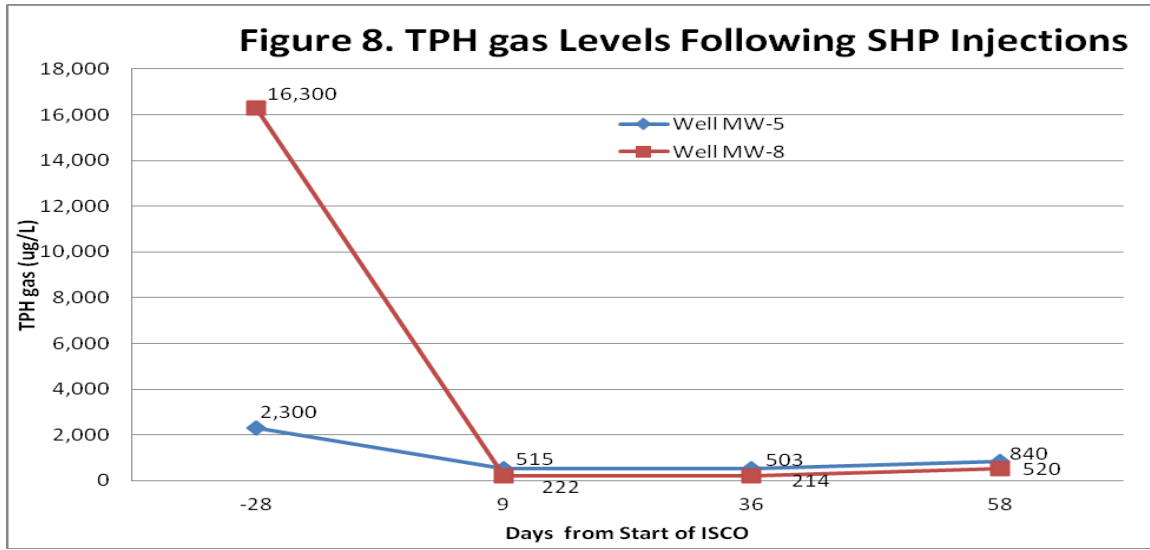
The SHP process does not include addition of iron solution (Fe⁺² or Fe⁺³) or an acid to lower the pH of the groundwater. The SHP process relies on naturally occurring iron in the groundwater and soil. The hydrogen peroxide itself is acidic and typically lowers the pH of the groundwater to a range of 3.5 to 6.5. However, this decrease in pH is temporary in nature and generally returns to a neutral pH within 30 to 45 days (depending on the buffering capacity of the soils).

VOC Destruction Efficiency

The use of SHP in the lab and field has also been shown to provide excellent VOC destruction efficiency. As shown in Figures 5, 6, and 7 below, the contaminant destruction rates using SHP in treatability tests have been measured at petroleum hydrocarbon sites as high as 100% for MTBE, 99% for TBA, and 100% for TPH as gasoline. At chlorinated sites, contaminant destruction rates as high 97% for TCE and 100% for styrene have been measured. These SHP contaminant destruction rates are equivalent to the destruction rates achieved by CHP.



A field pilot test injection was performed at a gasoline station in Silverdale, WA, using Stabilized Hydrogen Peroxide. Within 58 days of the completing the SHP injections, the TPH as gas levels in well MW-8 were reduced from 16,300 µg/L to 520 µg/L (97% reduction), toluene was reduced from 383 µg/L to 3.4 µg/L (99% reduction), and xylenes were reduced from 2,340 µg/L to 35 µg/L (99% reduction). The decline in TPH as gas levels in two wells (MW-8 and MW-5) following SHP injections are shown in Figure 8 (below).



Conclusions

The use of SHP is a safe alternative to CHP and is capable of achieving a similar high level of contaminant destruction without the adverse side effects. The life of hydrogen peroxide is extended to up to 10-14 days by use of SHP allowing it to disperse further into the groundwater for greater treatment potential. By controlling the temperature and pressure in a SHP reaction, the physical conditions causing chemical daylighting are greatly minimized.

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Enhanced stability of hydrogen peroxide in the presence of subsurface solids

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Abstract

The stabilization of hydrogen peroxide was investigated as a basis for enhancing its downgradient transport and contact with contaminants during catalyzed H_2O_2 propagations (CHP) in situ chemical oxidation (ISCO). Stabilization of hydrogen peroxide was investigated in slurries containing four characterized subsurface solids using phytate, citrate, and malonate as stabilizing agents after screening ten potential stabilizers. The extent of hydrogen peroxide stabilization and the most effective stabilizer were solid-specific; however, phytate was usually the most effective stabilizer, increasing the hydrogen peroxide half-life to as much as 50 times. The degree of stabilization was nearly as effective at 10 mM concentrations as at 250 mM or 1 M concentrations. The effect of stabilization on relative rates of hydroxyl radical activity varied between the subsurface solids, but citrate and malonate generally had a greater positive effect than phytate. The effect of phytate, citrate, and malonate on the relative rates of superoxide generation was minimal to somewhat negative, depending on the solid. The results of this research demonstrate that the stabilizers phytate, citrate, and malonate can significantly increase the half-life of hydrogen peroxide in the presence of subsurface solids during CHP reactions while maintaining a significant portion of the reactive oxygen species activity. Use of these stabilizers in the field will likely improve the delivery of hydrogen peroxide and downgradient treatment during CHP ISCO.

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Keywords: Hydrogen peroxide stabilization; Phytate; Malonate; Citrate; Fenton's reagent; Catalyzed H_2O_2 propagations (CHP); Superoxide; Hydroxyl radical

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1. Introduction

Contamination of the subsurface by persistent organic contaminants remains a significant problem, even after decades of research on remediation technologies. Over the past ten years, in situ chemical oxidation (ISCO) has been used increasingly for the treatment of contamination in the subsurface. Four oxidants have been employed for ISCO remediation: ozone, permanganate, activated persulfate, and catalyzed H_2O_2 propagations (CHP—modified Fenton's reagent). CHP is the most reactive of the ISCO processes, proceeding through two initiation reactions:



and a series of propagation reactions, which include:



The reactions shown in Eqs. (1)–(5) generate hydroxyl radical ($\text{OH}\cdot$), perhydroxyl radical ($\text{HO}_2\cdot$), superoxide radical anion ($\text{O}_2\cdot^-$), and hydroperoxide anion (HO_2^-) (Walling, 1975; De Laat and Gallard, 1999). Hydroxyl radical is a strong, nonspecific oxidant that reacts with >95% of contaminants of concern at near diffusion-controlled rates (i.e., $k_{\text{OH}\cdot} > 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Dorfman and Adams, 1973; Buxton et al., 1988; Haag and Yao, 1992). Hydroperoxide, the conjugate base of hydrogen peroxide ($\text{p}K_a = 11.75$), is a strong nucleophile (Edwards and Pearson, 1962; David and Seiber, 1999). Perhydroxyl radical is a weak oxidant that has minimal reactivity in aqueous systems (Afanas'ev, 1989). Superoxide is a nucleophile and a reductant that has been considered unreactive in aqueous systems, though it is highly reactive in aprotic solvents such as dimethyl sulfoxide and dimethyl formamide. The increased reactivity of superoxide in CHP systems relative to its negligible reactivity in deionized water is due to the presence of hydrogen peroxide, which is less polar than water and increases the reactivity of superoxide in the same manner as aprotic solvents (Smith et al., 2004).

The mix of reactive oxygen species generated by CHP provides near universal reactivity with contaminants found in the subsurface. For example, carbon tetrachloride, a contaminant not reactive with hydroxyl radical, is effectively destroyed by superoxide generated in CHP reactions (Smith et al., 2004). In addition, CHP destroys hydrophobic contaminants more rapidly than their corresponding rates of desorption (Watts et al., 1999, 2002), and DNAPLs are destroyed at rates greater than their rates of dissolution (Yeh et al., 2003; Watts et al., 2005; Smith et al., 2006). However, the use of CHP for ISCO has been limited by its rapid rate of decomposition in the subsurface. When hydrogen peroxide is injected into the subsurface, it is rapidly decomposed by soluble iron and iron and manganese oxides. In most cases, hydrogen peroxide travels no more than 3–4 m, and often decomposes within 1–2 m of the injection well (Watts and Teel, 2005). Some attempts have been made to stabilize hydrogen peroxide in the subsurface, primarily through the addition of phosphates to bind transition metals (Hinchee et al., 1991); however, hydrogen peroxide stabilization has not been effective to date.

Organic acids that chelate transition metals have been used to initiate CHP reactions. Sun and Pignatello (1992) screened over 30 organic acid–iron (III) complexes as CHP catalysts and found a wide range of activity. The low activity of some of the iron ligands is likely related to their high stability constants (Sheldon and Kochi, 1981); these ligands that strongly bind iron may also stabilize hydrogen peroxide in the presence of subsurface solids. The conceptual model for such stabilization is to add the sodium salt of the organic acid to the hydrogen peroxide. When the hydrogen peroxide–organic acid mixture is injected into the subsurface, the labile transition metals in the subsurface would bind to the organic acid, reducing their catalytic activity and lowering the rate of hydrogen peroxide decomposition. The purpose of this research was to investigate the potential for increased hydrogen peroxide stability in subsurface solids slurries using sodium salts of a number of low molecular weight organic acids, and to assess their effect on CHP reactivity.

2. Materials and methods

2.1. Materials

Diethylenetriamine pentaacetic acid (DTPA), sodium citrate, sodium gallate, sodium malate, sodium malonate, sodium oxalacetate, sodium oxalate, sodium phytate, sodium pyruvate, and sodium succinate were purchased from Sigma-Aldrich (Milwaukee, WI). Sodium hydroxide, sulfuric acid, and mixed hexanes were obtained from Fisher Scientific (Fair Lawn, NJ). Hydrogen peroxide was provided *gratis* by Solvay Interlox (Deer Park, TX). A Barnstead NANOpure II system was used to purify water used in all reactions to >18 M Ω -cm.

2.2. Subsurface solids

Four subsurface solids collected from different regions of the United States were used to evaluate the stabilization of solids-mediated hydrogen peroxide decomposition. Subsurface samples were collected from the Corinna Mills Superfund site in Maine; a leaking underground storage tank site in Marietta, Georgia; a contaminated groundwater system in Humboldt County, California; and the Palouse region of Washington State. The solids were characterized for particle size distribution by the pipette method (Gee and Bauder, 1986). Organic carbon was determined by combustion at 900 °C with evolved CO₂ trapped in KOH and measured by back-titration of unreacted KOH (Nelson and Sommers, 1982). Cation exchange capacity was established by saturation with sodium acetate at pH 8.2 (SCS, 1986). Crystalline and amorphous iron and manganese oxyhydroxides were determined by citrate-bicarbonate-dithionite extraction (Jackson et al., 1986). Surface areas were determined by BET analysis under liquid nitrogen on a Coulter SA 3100 (Carter et al., 1986). The characteristics of the four solids are listed in Table 1.

2.3. Screening of potential hydrogen peroxide stabilizers

Sun and Pignatello (1992) screened over 30 organic chelators of iron (III) for their potential to promote the CHP-mediated degradation of 2,4-dichlorophenoxyacetic acid (2,4-D). Ten of the ligands were found to be minimally effective in promoting the CHP treatment of 2,4-D, and therefore may have potential to lower hydrogen peroxide decomposition rates. Ligands that are ineffective CHP catalysts may strongly bind free and surface-labile transition metals, deactivating their ability to mediate hydrogen peroxide decomposition. These ten organic ligands, listed in

Table 1
Characteristics of the Georgia, Maine, California and Washington subsurface solids

	Subsurface solid			
	Georgia	Maine	California	Washington
Sand (%)	47.4	54.0	78.7	32.4
Silt (%)	14.3	33.5	8.0	15.6
Clay (%)	38.3	12.5	13.3	52.0
Crystalline iron oxides (mg/kg)	4300	7200	11,000	6900
Crystalline manganese oxides (mg/kg)	170	183	340	380
Amorphous iron oxides (mg/kg)	16	8	780	150
Amorphous manganese oxides (mg/kg)	160	250	330	360
Organic carbon (%)	0.062	0.51	0.08	1.08
Surface area (m ² /g)	5.5	2.5	1.5	6.3
Cation exchange capacity (cmol/kg)	7.9	3.6	22.0	25.0

Table 2, were screened for their ability to lower the activity of the four solids for catalyzing hydrogen peroxide decomposition. The potential stabilizers were screened by adding each stabilizer to 5 ml of a 2% solution of hydrogen peroxide and then adding the hydrogen peroxide-stabilizer solution to 1 g of each of the four solids. The pH of the slurries was not adjusted but was near neutral (pH 7 ± 0.4) for each of the four systems. Aliquots were collected and analyzed for hydrogen peroxide at time points that accounted for exponential decomposition of hydrogen peroxide. The rates of hydrogen peroxide decomposition were then compared to rates in parallel systems with no stabilizers. Results from the initial screening efforts showed that phytate, citrate, and malonate were the most effective stabilizers. The structures of the three compounds are shown in Fig. 1.

2.4. Evaluation of the most effective stabilizers

The most effective stabilizers—phytate, citrate, and malonate—were subsequently investigated in further detail. The potential for the compounds to stabilize hydrogen peroxide was investigated in slurries containing each of the four subsurface solids. Each of the stabilizers was added to 2% hydrogen peroxide at a concentration of 10 mM or 1 M (250 mM for phytate, due to its limited water solubility); 5 ml of the stabilized solution was then added to 1 g of each subsurface solids. Reactions were conducted in 20-ml borosilicate glass reactors. Aliquots of 0.1 ml were then collected at time points that accounted for the exponential hydrogen peroxide

Table 2
Organic ligands tested for hydrogen peroxide stabilization

Organic ligand
DTPA (Diethylenetriamine pentaacetic acid)
Citric acid
Gallic acid
Malic acid
Malonic acid
Oxalacetic acid
Oxalic acid
Phytic acid
Pyruvic acid
Succinic acid

decomposition and analyzed for hydrogen peroxide residuals. Control reactions were conducted in parallel with hydrogen peroxide but no stabilizer.

2.5. Probe compounds and measurement of relative hydroxyl radical and superoxide activity

The probe compounds were selected based on their ability to react solely through either oxidation or reduction. Hexachloroethane (HCA) was used as a superoxide probe because it is readily degraded by superoxide in CHP systems, in which hydrogen peroxide acts as a cosolvent (Afanas'ev, 1989; Watts et al., 1999; Smith et al., 2004), but is not oxidized by hydroxyl radicals ($k_{\text{OH}\cdot} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Watts et al., 1999; Hui, 2001). In contrast, 1-hexanol was used as an oxidant probe because it is readily oxidized by hydroxyl radicals ($k_{\text{OH}\cdot} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) but is not readily reduced ($k_{\text{e}^-} = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988). Based on the linear range of analysis, initial concentrations of HCA and 1-hexanol were 10 μM and 2 mM, respectively.

Each of the probes was added to stabilizer—2% hydrogen peroxide solutions. Using a volume of 5 ml, the solutions containing the probe, stabilizer, and hydrogen peroxide were added to 1 g of each of the subsurface solids. A set of triplicate 20-ml borosilicate glass reactors was established for each time point. The entire contents of each triplicate set of reactors were extracted with hexane and analyzed for residual probe compound concentration. Two sets of control reactions were conducted in parallel: one with hydrogen peroxide but no stabilizer, and one with stabilizer but no hydrogen peroxide.

2.6. Analysis

Residual probe compound concentrations were quantified using Hewlett-Packard 5890A gas chromatographs with electron capture detector (for HCA) and flame ionization detector (for 1-hexanol), each fit with 10 m \times 0.53 mm DB-1 capillary columns. Conditions for 1-hexanol analysis included injector temperature of 240 $^\circ\text{C}$, detector temperature of 260 $^\circ\text{C}$, initial oven

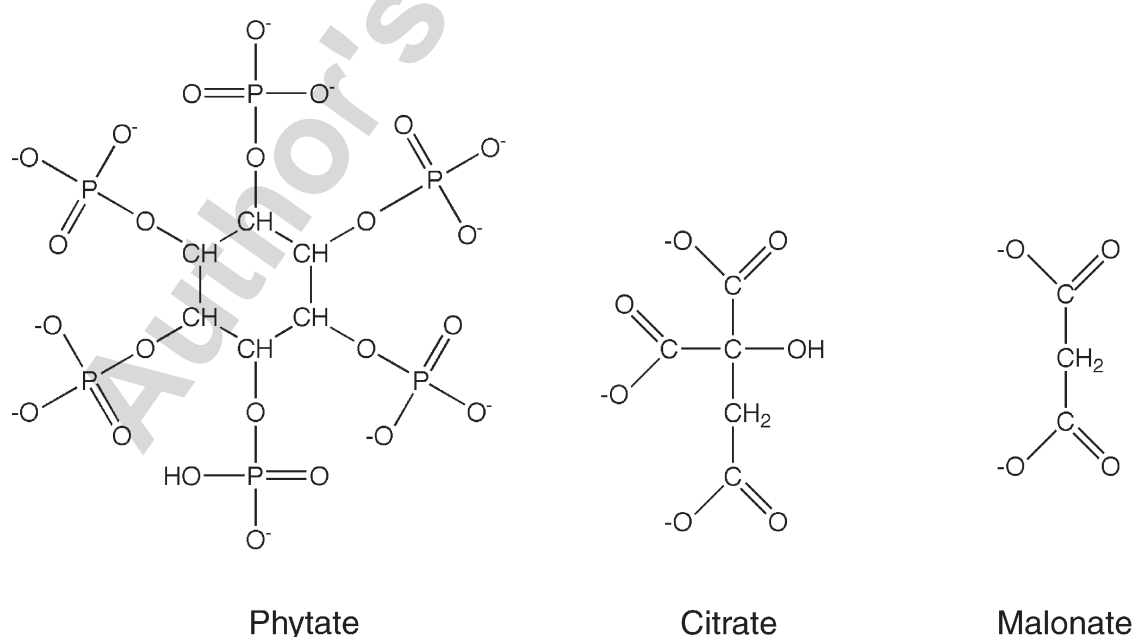


Fig. 1. Structures of the stabilizers phytate, citrate, and malonate.

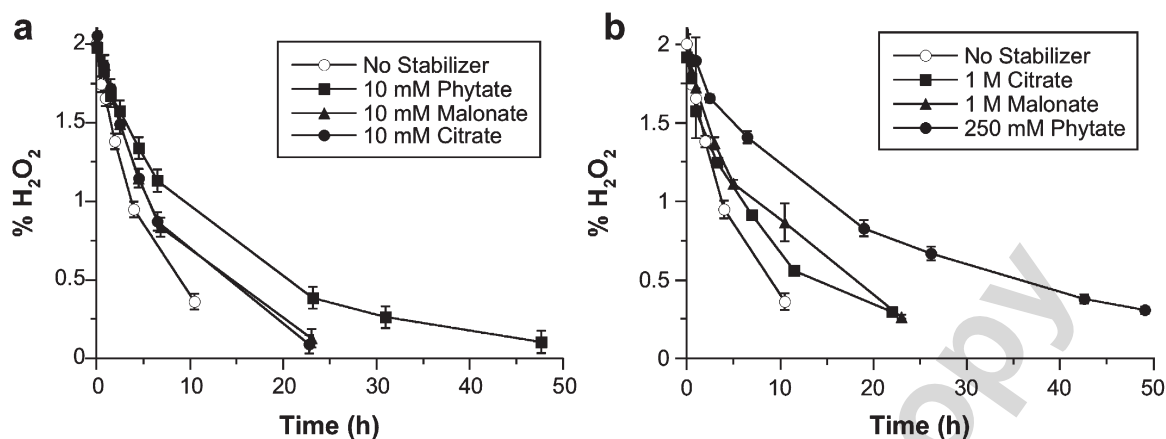


Fig. 2. Decomposition of hydrogen peroxide in the Georgia subsurface solids without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer.

temperature of 60 °C, program rate of 10 °C/min, and final temperature of 200 °C. Conditions for HCA analysis included injector temperature of 200 °C, detector temperature of 220 °C, initial oven temperature of 40 °C, program rate of 10 °C/min, and final temperature of 180 °C. Hydrogen peroxide concentrations were measured by iodometric titration using 0.1 N sodium thiosulfide as the titrant (Schumb et al., 1955).

3. Results and discussion

3.1. Hydrogen peroxide decomposition and stabilization in subsurface solids

Hydrogen peroxide decomposition in slurries containing the Georgia subsurface solids is shown in Fig. 2a–b. The hydrogen peroxide half-life in this slurry was approximately 4 h. Phytate addition at both 10 mM and 250 mM increased the hydrogen peroxide half-life; with 10 mM phytate addition, the hydrogen peroxide half-life increased to 9 h (Fig. 2a), and the addition of 250 mM phytate increased the half-life to 15 h (Fig. 2b). Malonate and citrate were also effective in increasing the hydrogen peroxide half-life; 10 mM malonate or citrate increased the half-life to 6 h, and 1 M citrate or malonate increased the half-life to 7 h.

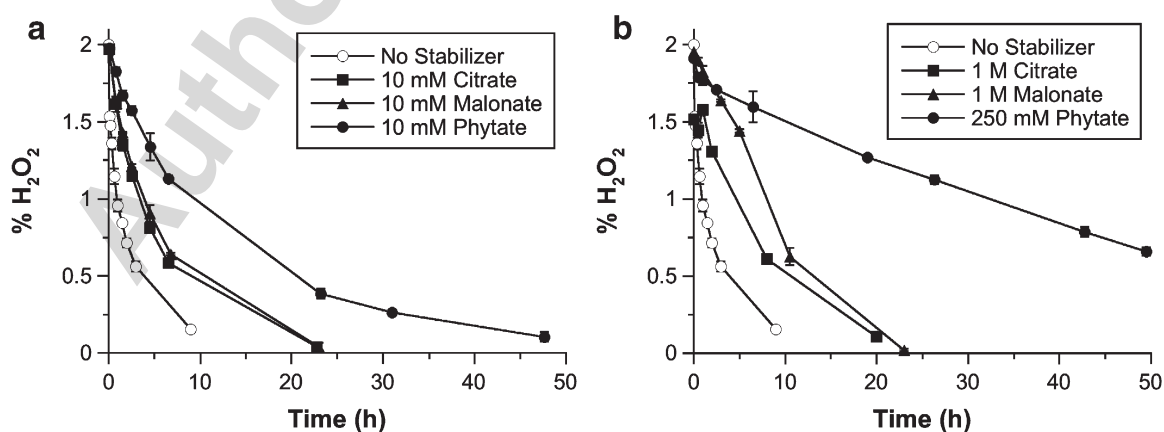


Fig. 3. Decomposition of hydrogen peroxide in the Maine subsurface solids without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer.

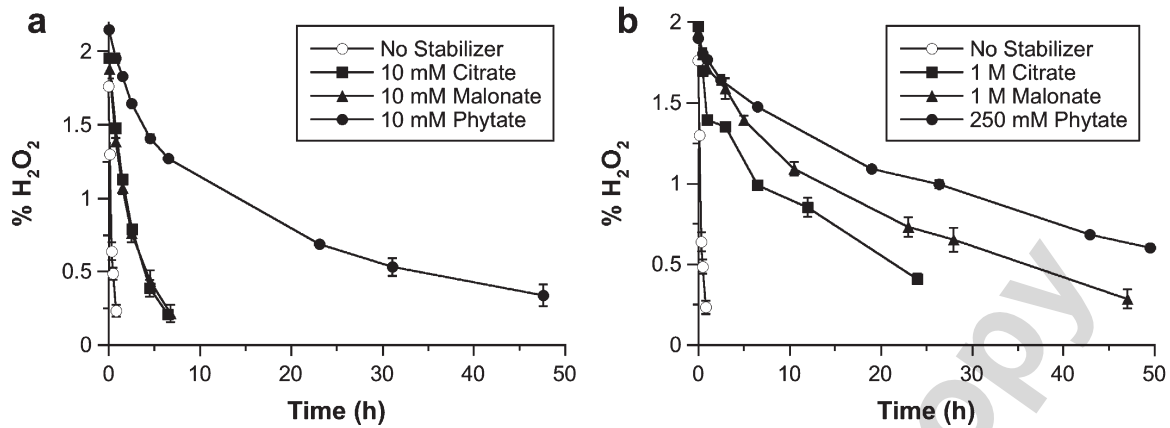


Fig. 4. Decomposition of hydrogen peroxide in the California subsurface solids without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer.

Hydrogen peroxide decomposition in the presence of the Maine subsurface solids is shown in Fig. 3a–b. With no added stabilizer, the hydrogen peroxide half-life was 1.5 h. Stabilization of the Maine subsurface solids with phytate was highly effective; 10 mM phytate increased the hydrogen peroxide half-life to 10 h, and 250 mM phytate increased the half-life to 32 h. As in the Georgia subsurface solids, the effectiveness of malonate and citrate was similar. Addition of 10 mM citrate or malonate increased the hydrogen peroxide half-life to 4 h. Using 1 M citrate or malonate, the hydrogen peroxide half-life increased to 5 h and 8 h, respectively.

The decomposition of hydrogen peroxide without stabilization in the California subsurface solids slurry was rapid with a half-life of <0.5 h (Fig. 4a–b). However, stabilization with phytate was highly effective, increasing the hydrogen peroxide half-life to 12 h with 10 mM phytate and 26 h with 250 mM phytate. Stabilization using citrate and malonate was strongly influenced by the stabilizer concentration. Using 10 mM citrate or malonate, the hydrogen peroxide half-life increased to 2 h; however, 1 M citrate increased the half-life to 6 h, and 1 M malonate increased the half-life to 12 h.

Hydrogen peroxide concentrations as a function of time in slurries containing the Washington subsurface solids are shown in Fig. 5a–b. The unstabilized hydrogen peroxide half-life in the Washington subsurface solids was 4 h. Hydrogen peroxide decomposition in the Washington

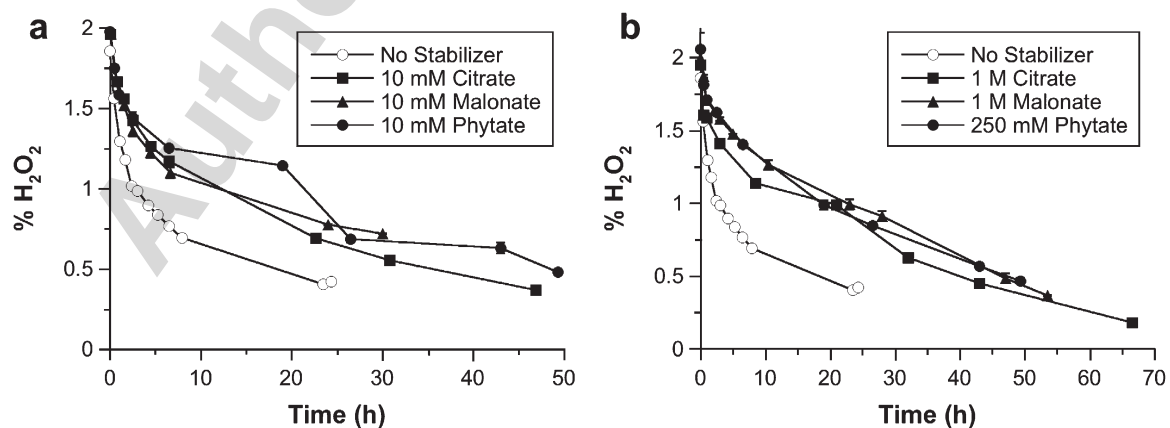


Fig. 5. Decomposition of hydrogen peroxide in the Washington subsurface solids without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer.

subsurface solids was unique among the four solids studied in that all three stabilizers were equally effective, and the stabilizer concentration had minimal effect on the rate of hydrogen peroxide decomposition. The hydrogen peroxide half-life for all three stabilizers at 10 mM concentrations was approximately 12 h, and at high (250 mM phytate or 1 M citrate or malonate) stabilizer concentrations the half-life was approximately 20–22 h.

The results shown in Figs. 2–5 demonstrate that stabilization of hydrogen peroxide was most effective with phytate in the three subsurface solids from Georgia, Maine, and California, while citrate, malonate, and phytate were equally effective in stabilizing hydrogen peroxide in the subsurface solids collected from Washington state. The two characteristics of the Washington solids that are notably different from the other solids are the high clay content and the high soil organic carbon (SOC) content. Both clays and SOC exchange metals, such as iron and manganese, and these exchanged transition metals have been shown to be active as CHP catalysts (Huling et al., 2001; Hui, 2001). Citrate, malonate, and phytate may be equally incapable of deactivating these exchanged transition metals, which would result in lesser, and near-equal, degrees of stabilization for the three ligands.

3.2. Effect of stabilizers on hydroxyl radical generation

Increased hydrogen peroxide stability beyond what is currently observed in the field is critical to the effective implementation of CHP ISCO; however, the activity of the reactive oxygen

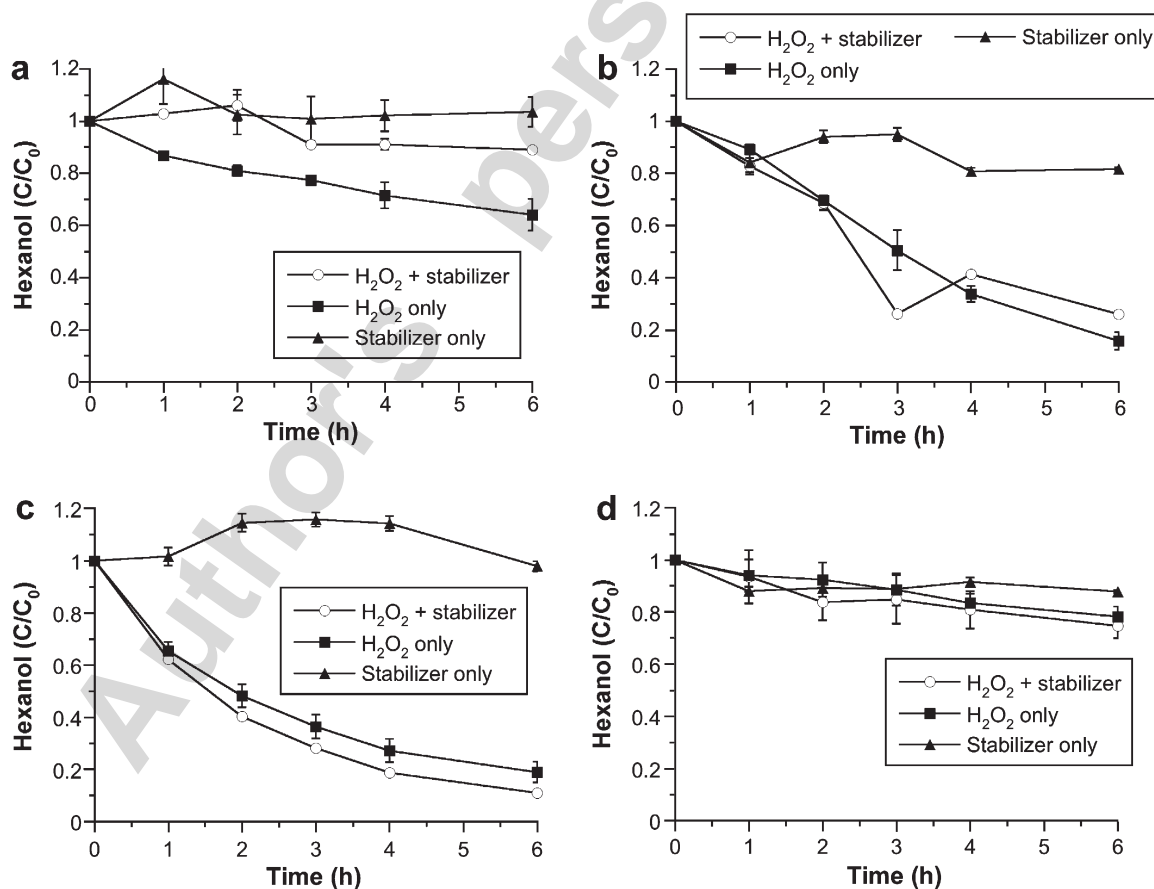


Fig. 6. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM phytate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

species generated in the CHP systems must be maintained when the hydrogen peroxide is stabilized. Therefore, the relative rates of oxidant and reductant generation were evaluated in stabilized and unstabilized hydrogen peroxide slurries. The relative production of hydroxyl radical in slurries of each of the four solids with and without stabilization by 10 mM phytate was measured by oxidation of the probe molecule hexanol (Fig. 6a–d). Relative rates of hydroxyl radical generation in the unstabilized systems were different for each of the four subsurface solids. Relative hydroxyl radical production in the Georgia subsurface solids was lower in the presence of phytate; 10% of the hexanol was oxidized in the phytate-stabilized system while 36% was oxidized without phytate relative to the control (Fig. 6a). There was less difference in relative hydroxyl radical generation rates between the unstabilized and stabilized slurries of the Maine and California subsurface solids; 68% and 80% of the hexanol was oxidized in the stabilized and unstabilized Maine solids, respectively, and 90% and 81% was oxidized in the stabilized and unstabilized California solids, respectively (Fig. 6b and c). The relative rate of hydroxyl radical production was low in the Washington subsurface solids, and there was little difference in hexanol oxidation rates between the systems with and without phytate, with 15% and 11% oxidation of the hexanol in the stabilized and unstabilized systems (Fig. 6d).

Relative rates of hydroxyl radical generation in CHP slurries containing each of the four solids with and without citrate stabilization are shown in Fig. 7a–d. In the Georgia subsurface solids

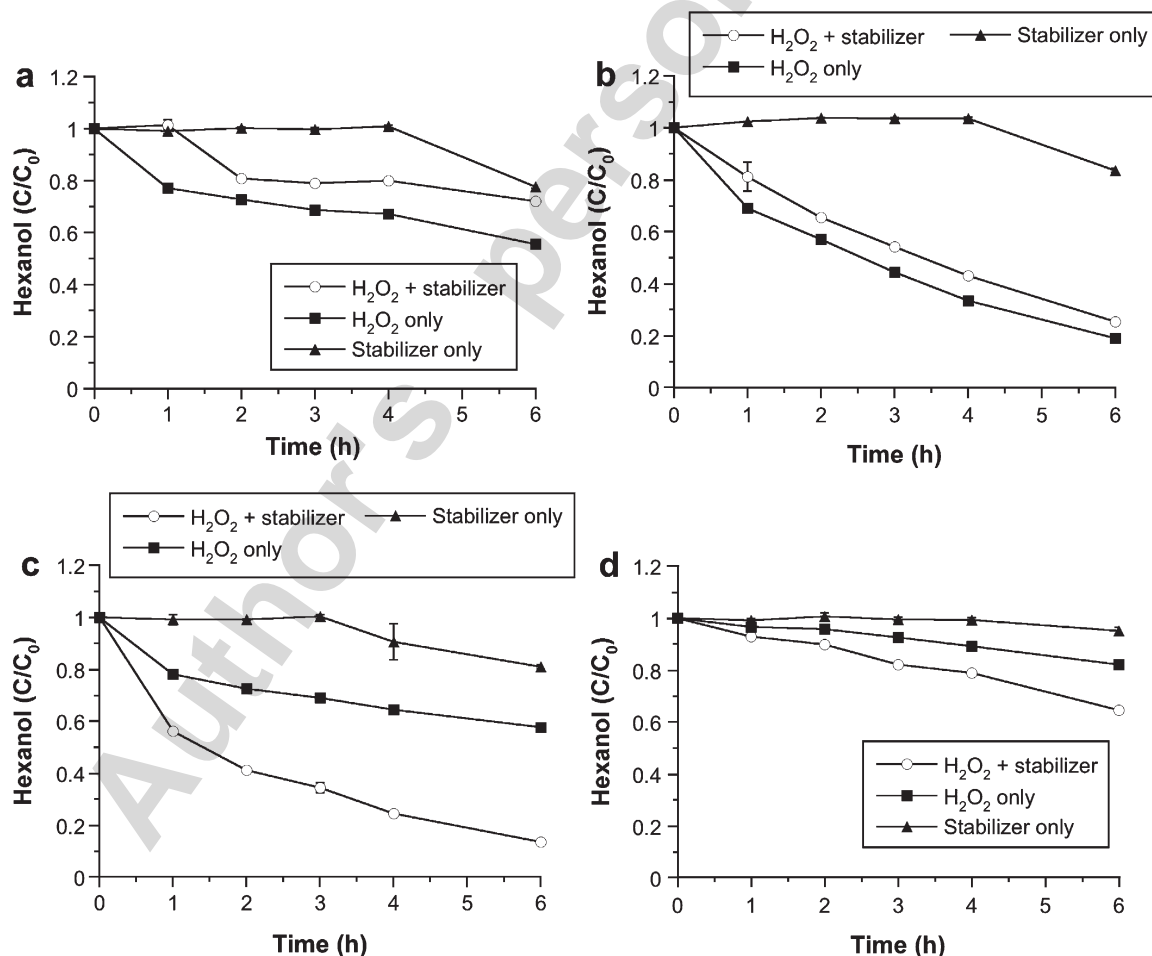


Fig. 7. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM citrate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

slurries, the hydroxyl radical generation rate was lower with citrate addition than without stabilization; nonetheless, oxidation of the hydroxyl radical probe was slow in both, with 30% hexanol oxidation in the unstabilized system and 8% oxidation in the citrate-stabilized system relative to the control (Fig. 7a). There was minimal difference in hydroxyl radical activity between the unstabilized and citrate-stabilized systems in slurries of the Maine subsurface solids, with 77% hexanol oxidation in the stabilized system and 70% in the unstabilized system (Fig. 7b). However, relative hydroxyl radical production in the California subsurface solids (Fig. 7c) was markedly different; it was significantly greater with citrate stabilization, with 84% hexanol oxidation in the citrate-stabilized system, and 28% oxidation in the unstabilized system. Similar results were observed in the CHP systems containing the Washington subsurface solids (Fig. 7d), with 32% and 14% hexanol oxidation in citrate-stabilized and unstabilized systems, respectively.

The relative rates of hydroxyl radical generation in solids slurries with and without malonate stabilization are shown in Fig. 8a–d. These data indicate that the presence of malonate has a significant effect on hydroxyl radical generation rates in some solids systems but not in others. Rates of hydroxyl radical generation in the unstabilized and malonate-stabilized Georgia subsurface solids were not significantly different, with approximately 43% of the hexanol oxidized in each relative to control systems (Fig. 8a). In the Maine subsurface solids, however, hydroxyl radical generation rates were greater in the stabilized system, with >99% of the hexanol oxidation in the system with malonate, compared to 80% in the unstabilized system (Fig. 8b). Relative hydroxyl radical generation rates were also greater with malonate stabilization in the California subsurface solids with >99% hexanol oxidation, compared to 44% in unstabilized systems

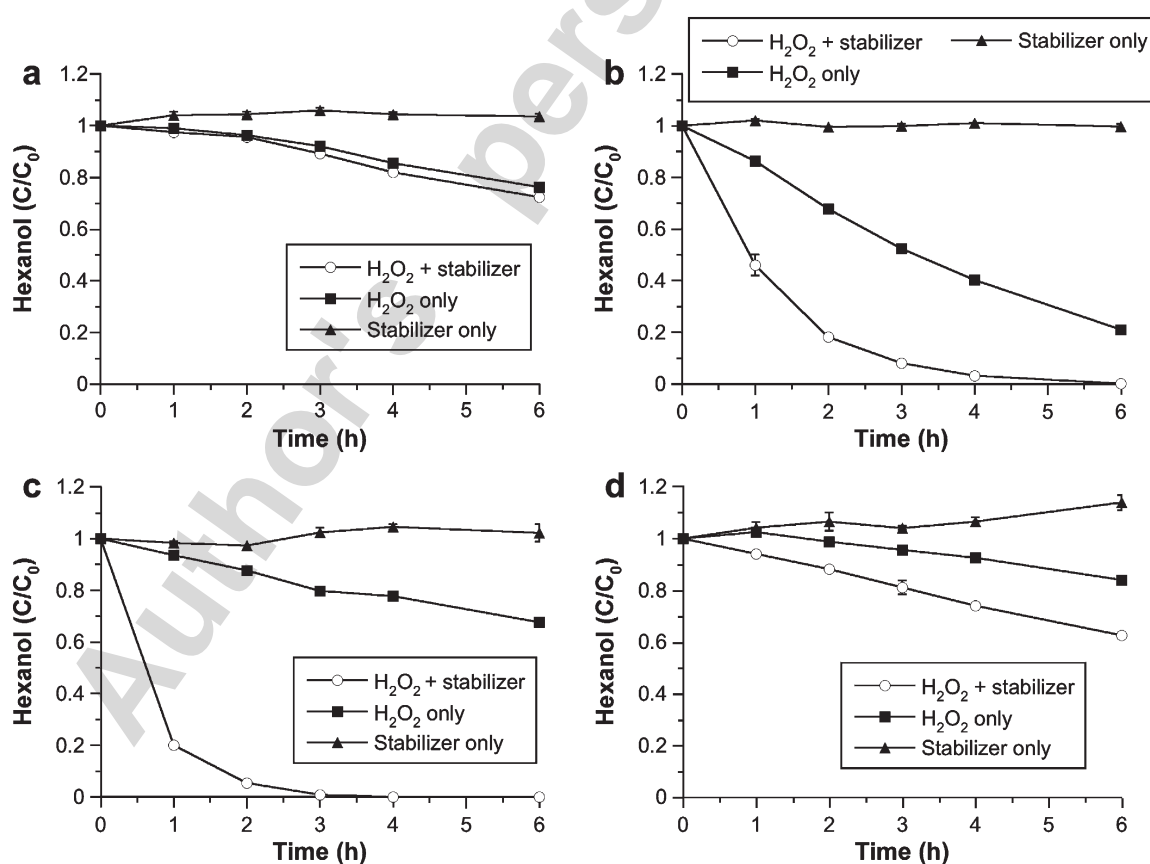


Fig. 8. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM malonate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

(Fig. 8c). A similar trend was observed in the Washington subsurface solids; hexanol oxidation in the malonate-stabilized system was 52% compared to 35% in the unstabilized system (Fig. 8d).

Based on the data presented in Figs. 6–8, the systems that showed increased relative hydroxyl radical generation in stabilized systems apparently did so because the oxidant source, hydrogen peroxide, was maintained in the slurries. The highest increase in stabilization occurred in the California subsurface solids system, and hydroxyl radical generation increased in this system with each of the stabilizers. Baciocchi et al. (2004) demonstrated that the residual hydrogen peroxide concentration is an important parameter in CHP contaminant oxidation. The results shown in Figs. 4a, 6c, 7c, and 8c strongly suggest the maintenance of the hydrogen peroxide residual aids in maintaining hydroxyl radical generation in the California subsurface solids system.

For each of the four solids systems, addition of phytate had the greatest negative effect on the relative rates of hydroxyl radical generation; it had minimal effect on hydroxyl radical generation rates in the California and Washington solids systems, and it decreased hydroxyl radical generation rates in the Georgia and Maine solids systems. In contrast, the addition of malonate had the greatest positive effect on relative hydroxyl radical generation rates in each of the four solids systems; it had minimal effect on hydroxyl radical generation rates in the Georgia solids slurries (compared to the decrease seen with phytate and malonate), and it increased hydroxyl radical generation rates in the other three systems. The positive effect of malonate on hydroxyl radical activity may be related to its low rate of reactivity with hydroxyl radicals ($k_{\text{OH}\cdot} = 2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), which would minimize its

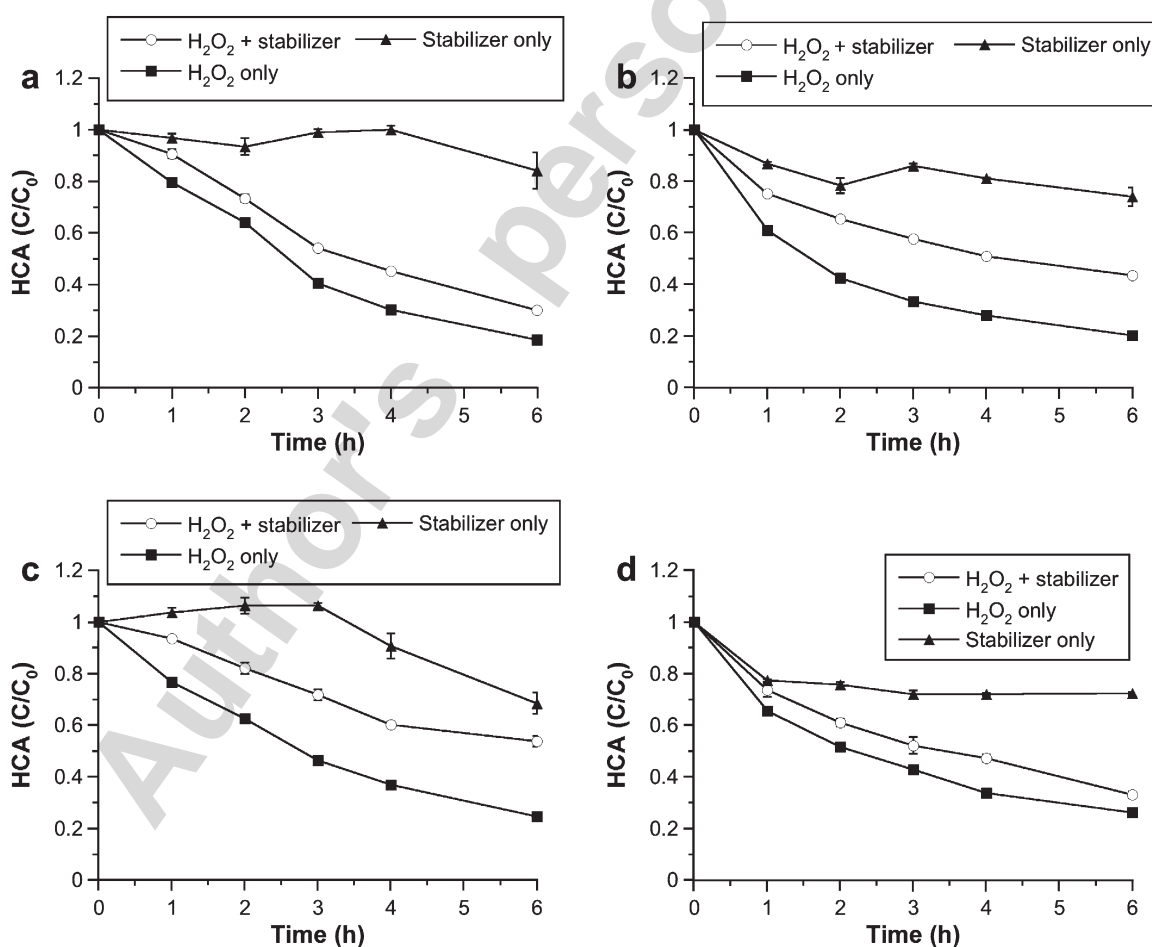


Fig. 9. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM phytate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

scavenging of hydroxyl radicals in the system. Citrate may have been less effective in maintaining hydroxyl radical generation because its reactivity with hydroxyl radical is slightly greater than that of malonate (citrate $k_{\text{OH}^\cdot} = 5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).

The results shown in Figs. 6–8 demonstrate that stabilization usually had minimal negative effect on the generation of hydroxyl radical. Relative hydroxyl radical generation rates increased in some stabilized systems and decreased in other stabilized systems relative to the corresponding rates in unstabilized systems; however, most of the differences between the relative rates of generation were minimal and should not negatively impact the efficacy of CHP treatment.

3.3. Effect of stabilizers on superoxide generation

The effect of phytate stabilization on superoxide generation in the four solids systems using the probe molecule hexachloroethane (HCA) is shown in Fig. 9a–d. The relative rates of superoxide generation were greater in all four of the unstabilized systems relative to the phytate-stabilized systems. The difference in relative superoxide generation was small in the Georgia subsurface solids slurries with 78% HCA degradation without phytate and 64% HCA degradation in the phytate-stabilized system relative to the control (Fig. 9a). Differences in relative superoxide generation were more pronounced in slurries of the Maine subsurface solids (Fig. 9b). With no stabilization, 73% of the HCA was degraded, while 40% of the HCA was degraded in the phytate-stabilized system. The differences in superoxide generation were even more pronounced in the

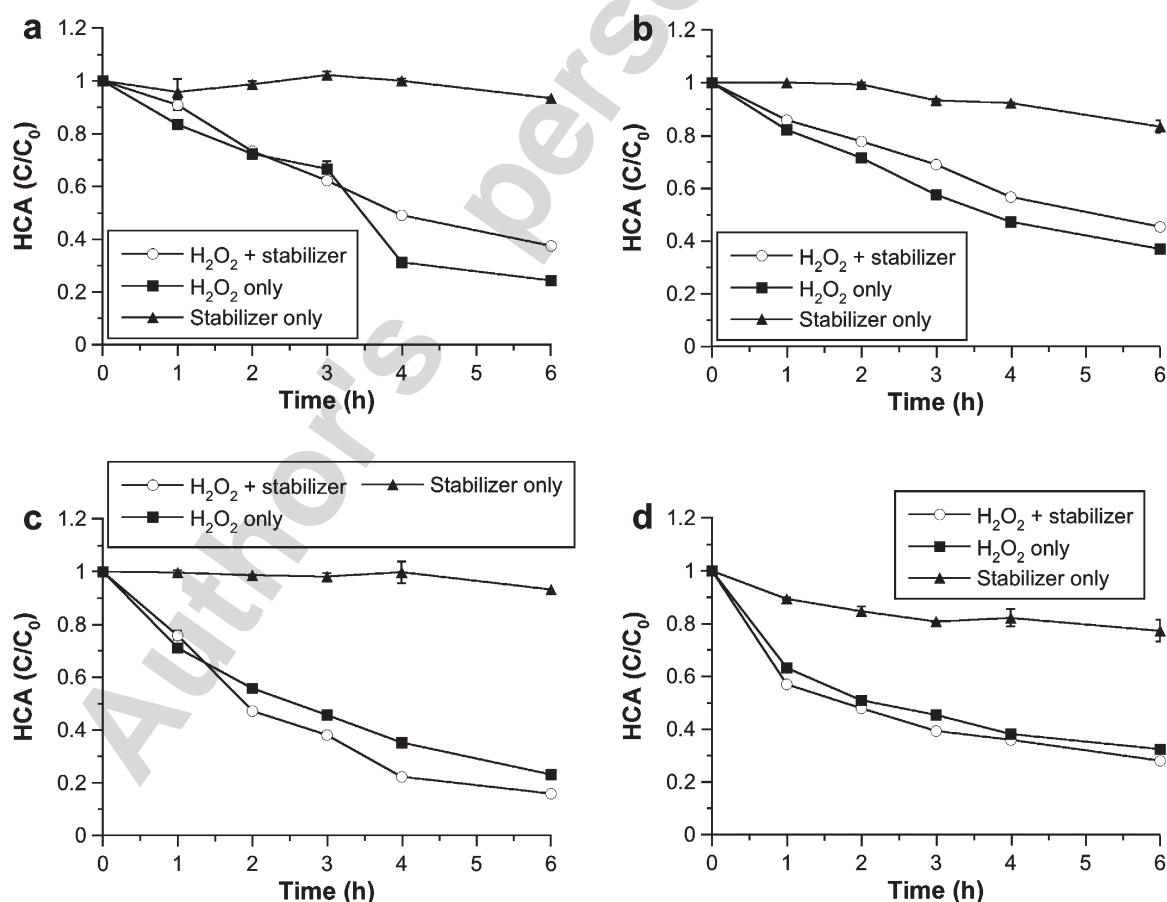


Fig. 10. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM citrate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

California subsurface solids system, with 70% of the HCA degraded in the unstabilized system and 22% degraded in the phytate-stabilized system (Fig. 9c). A difference similar to that of the Georgia subsurface solids system was observed in the Washington subsurface solids, with 63% HCA degradation in the unstabilized system and 53% degradation in the presence of phytate (Fig. 9d).

Relative rates of superoxide generation in unstabilized and citrate-stabilized subsurface solids are shown in Fig. 10a–d. Small differences in relative rates of superoxide generation were observed in the four solids slurries. There was a small difference in relative rates of superoxide generation between unstabilized and citrate-stabilized samples of the Georgia subsurface solids, with 73% HCA degradation in the unstabilized system and 60% HCA degradation in the presence of citrate relative to the control system (Fig. 10a). Similarly, in Maine subsurface solids slurries, unstabilized hydrogen peroxide provided slightly higher relative superoxide generation (Fig. 10b), with 54% and 45% HCA degradation in the unstabilized and stabilized systems, respectively. Differences in relative superoxide generation were minimal in slurries of the California subsurface solids (Fig. 10c) with 83% and 75% HCA degradation in the unstabilized and stabilized systems, and in the Washington subsurface solids (Fig. 10d), with 59% HCA degradation in the unstabilized system and 63% HCA degradation in the stabilized system.

Relative rates of superoxide generation in unstabilized and malonate-stabilized systems are shown in Fig. 11a–d. As with the other stabilizers, HCA degradation was generally lower in the

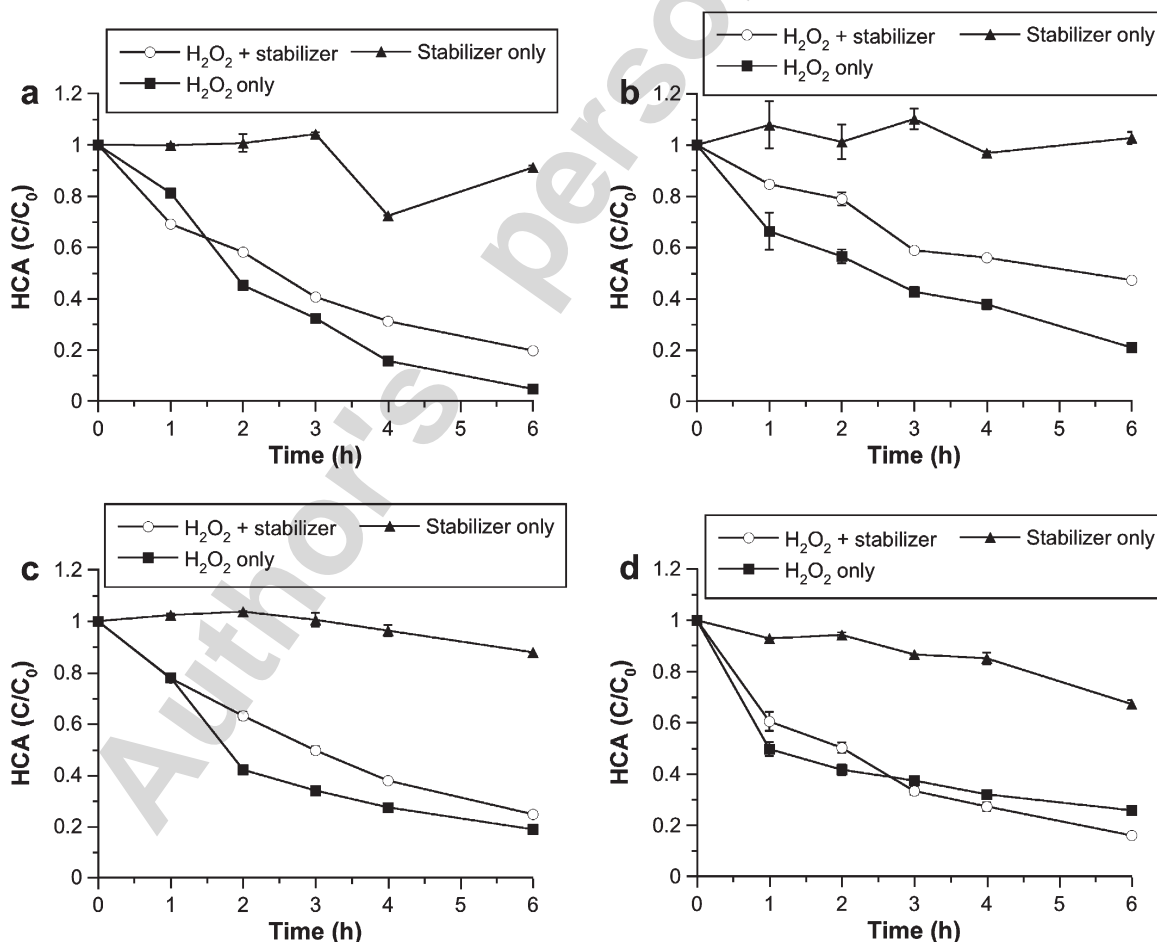


Fig. 11. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM malonate. (a) Georgia subsurface solids; (b) Maine subsurface solids; (c) California subsurface solids; (d) Washington subsurface solids.

stabilized systems, although the differences between unstabilized and stabilized systems were generally small. Addition of malonate decreased relative superoxide generation in Georgia subsurface solids slurries, with 95% and 78% HCA degradation in the unstabilized and stabilized systems, respectively (Fig. 10a). The greatest difference in relative superoxide generation was in the Maine subsurface solids, with 80% HCA degradation in unstabilized systems compared to 52% in slurries stabilized with malonate (Fig. 11b). Differences in relative superoxide generation rates between unstabilized and malonate-stabilized systems were minimal in slurries of the California and Washington subsurface solids (Fig. 11c–d). HCA degradation in unstabilized and stabilized systems was 78% and 73% for the California subsurface solids. In the Washington subsurface solids, the HCA degradation was 59% in the unstabilized system and 64% in the stabilized system.

The results of Figs. 9–11 demonstrate that superoxide was generated in all four solids systems. The relative rates of superoxide generation were usually somewhat lower in the stabilized systems relative to the unstabilized systems, but there was no consistent trend between stabilizers or between solids. The data suggest that in some systems, the stabilizer may scavenge superoxide. However, relative rates of superoxide generation in stabilized systems do not appear to be lowered sufficiently to negatively affect CHP remediation.

The rapid rate of hydrogen peroxide decomposition in the subsurface represents the greatest limitation in the use of CHP for subsurface remediation. The results of this research demonstrate that hydrogen peroxide in CHP reactions can be stabilized significantly using the stabilizers phytate, citrate, or malonate without affecting contaminant destruction. Although 10 mM–1 M concentrations of the stabilizers were used in this study, the most effective stabilizer and stabilizer concentration is likely to be site specific. A major advantage of the use of stabilizers is the potential ease of delivery; under current practice, acid, soluble iron, or iron chelates are first injected into the subsurface followed by a second delivery of hydrogen peroxide. Use of the stabilizers may provide the potential for treatment using a single injection; hydrogen peroxide and the stabilizer could be mixed in a supply tank and injected into the subsurface together. Use of the stabilizers developed through this research has the potential to improve hydrogen peroxide transport and its contact with contaminants, resulting in more effective CHP ISCO remediation of contaminated groundwater.

4. Conclusions

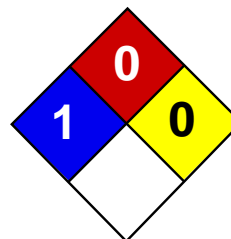
- Hydrogen peroxide decomposition rates in four subsurface solids were lowered by up to a factor of 50 using the stabilizers phytate, citrate, or malonate with minimal effect on the generation of reactive oxygen species.
- The most effective stabilizer for extending hydrogen peroxide half-life in most of the systems was phytate.
- Phytate, citrate, and malonate had minimal effect on superoxide generation in CHP reactions in the four subsurface solids relative to unstabilized reactions.
- Phytate had minimal effect on hydroxyl radical generation in CHP reactions compared to unstabilized systems. Citrate and malonate had minimal effect on hydroxyl radical generation in some of the solids and actually enhanced hydroxyl radical generation in other solids relative to unstabilized systems.

Acknowledgment

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Health	1
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet

Sodium citrate dihydrate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Sodium citrate dihydrate

Catalog Codes: SLS4237, SLS3442, SLS1225

CAS#: 6132-04-3

RTECS: GE8300000 (Sodium Citrate, anhydrous)

TSCA: TSCA 8(b) inventory: No products were found.

CI#: Not available.

Synonym: Citnatin, Citreme, Citrosoedine, Citrosodna, Natrocitral; Trisodium citrate dihydrate; 1,2,3-Propanetricarboxylic acid, 2-hydroxy-, trisodium salt, dihydrate

Chemical Name: Citric acid, trisodium salt, dihydrate

Chemical Formula: C₆H₅Na₃O₇·2H₂O

Contact Information:

Sciencelab.com, Inc.

14025 Smith Rd.

Houston, Texas 77396

US Sales: **1-800-901-7247**

International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:

1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Sodium citrate dihydrate	6132-04-3	100

Toxicological Data on Ingredients: Not applicable.

Section 3: Hazards Identification

Potential Acute Health Effects: Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:

CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. Repeated or prolonged exposure is not known to aggravate medical condition.

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

Skin Contact:

Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:

Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO₂). Some metallic oxides.

Fire Hazards in Presence of Various Substances:

Slightly flammable to flammable in presence of heat. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:

Slightly explosive in presence of open flames and sparks. Non-explosive in presence of shocks.

Fire Fighting Media and Instructions:

SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: As with most organic solids, fire is possible at elevated temperatures

Special Remarks on Explosion Hazards:

Fine dust dispersed in air in sufficient concentrations, and in the presences of an ignition source is a potential dust explosion hazard.

Section 6: Accidental Release Measures

Small Spill:

Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:

Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions:

Keep away from heat. Keep away from sources of ignition. Do not breathe dust. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection: Safety glasses. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Crystalline granules solid.)

Odor: Odorless.

Taste: Cool, Saline.

Molecular Weight: 294.1 g/mole

Color: White.

pH (1% soln/water):

8 [Basic.] The aqueous solution is slightly alkaline to litmus; pH about 8

Boiling Point: Not available.

Melting Point: Not available.

Critical Temperature: Not available.

Specific Gravity: Not available.

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility:

Easily soluble in hot water. Soluble in cold water. Insoluble in alcohol. Soluble in 1.3 parts water. Soluble in 0.6 parts boiling water.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, dust generation, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Decomposes at red heat. Becomes anhydrous at 150 deg. C

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.

Toxicity to Animals:

LD50: Not available. LC50: Not available.

Chronic Effects on Humans: Not available.

Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans:

Potential Health Effects: Skin: Possible irritation on prolonged contact with moist or sensitive areas of the skin. Eyes: No adverse effects expected, but dust may cause mechanical irritation. Inhalation: Inhalation of large amounts of dust may cause irritation to the respiratory tract. Low hazard for usual industrial handling. Ingestion: Ingestion of large amounts may cause gastrointestinal tract irritation/disturbances. May affect behavior (convulsions), respiration (cyanosis).

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations: No products were found.

Other Regulations: Not available.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):

This product is not classified according to the EU regulations. S24/25- Avoid contact with skin and eyes.

HMIS (U.S.A.):

Health Hazard: 1

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:

Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Safety glasses.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/10/2005 08:27 PM

Last Updated: 11/01/2010 12:00 PM

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2450 Reservoir Avenue • Trumbull, CT 06611

Tel: (203) 372-8811 • Fax: (203) 372-8816

e-mail: sales@fabricheminc.com

Safety Data Sheet

According to Regulation (EU) No. 1907/2006 (REACH), Annex II

Version: 1.0/EN

Product name: Sodium phytate

Revision date: 18/02/2011

Printing date: 18/02/2011

Section 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Product name: Sodium phytate; Phytic acid sodium salt; Phytic acid dodecasodium
Substance name: Myo-Inositol, hexakis(dihydrogen phosphate), sodium salt
REACH Reg. No.: No registration number is given yet for this phase-in substance.
Index No.: Not Listed.
CAS No.: 14306-25-3
EC No.: 238-242-6

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses: Used as antioxidant, chelating agent, whitening ingredients.
Uses advised against: No uses advised against.

1.3 Details of the supplier of the SDS

Manufacturer: FabriChem, Inc.
Address: 2450 Reservoir Avenue, Trumbull, Connecticut, 06611, USA
E-mail: sales@fabricheminc.com
Telephone: (203) 372-8811
Fax: (203) 372-8816

1.4 Emergency telephone number

(203) 372-8811

Section 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [CLP]

This product does not meet the criteria for classification in any hazard class according to Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures.

Classification according to Council Directive 67/548/EEC [DSD]

This product does not meet the criteria for classification in any hazard class according to Directive 67/548/EEC on classification, labelling and packaging of substances.

2.2 Label elements



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Labelling according to Regulation (EC) No 1272/2008 [CLP]

No labelling information (such as hazard pictogram, signal word, hazard statement, precautionary statement) available. This product does not meet the criteria for classification in any hazard class according to Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures.

2.3 Other hazards

No information available.

Section 3: Composition/information on ingredients

3.1 Substance information

Substance name	CAS No.	EC No.	Index No.	Molecular Formula	Classification	% (w/w)
Myo-Inositol, hexakis(dihydrogen phosphate), sodium salt	14306-25-3	238-242-6	Not listed.	C ₆ H ₁₈ O ₂₄ P ₆ xNa+yH ₂ O	Not classified.	96

Remark: The rest unspecified ingredients are impurities.

Section 4: First aid measures

4.1 Description of first aid measures

General notes: In all cases of doubt, or when symptoms persist, seek medical attention.

Following inhalation:

Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. If symptoms persist, seek medical advice.

Following skin contact:

Immediately flush skin with plenty of water while removing contaminated clothing and shoes. Seek medical advice if irritation persists.

Following eye contact:

Immediately flush eyes with plenty of water, occasionally lifting the upper and lower eyelids. Seek medical advice if irritation persists.

Following ingestion:

Never give anything by mouth to an unconscious person. Rinse mouth with water. Get medical aid.

Notes for the doctor:

Treat symptomatically and supportively.

4.2 Most important symptoms and effects, both acute and delayed

No relevant information available. To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

4.3 Indication of the immediate medical attention and special treatment needed

No information available.



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Section 5: Fire-fighting measures

5.1 Extinguishing media

Suitable extinguishing media:

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Unsuitable extinguishing media:

For this substance no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

May be combustible at high temperature.

Hazardous combustion products: Carbon oxides, oxides of phosphorus, sodium oxides.

5.3 Advice for fire-fighters

Do not stay in dangerous zone without self-contained breathing apparatus.

In order to avoid contact with skin, keep a safety distance and wear suitable protective clothing.

Prevent fire-fighting water from entering surface water or groundwater.

Section 6: Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures¹

Wear respiratory protection. Avoid breathing vapors, mist or gas. Ensure adequate ventilation.

Remove all sources of ignition. Evacuate personnel to safe areas.

6.2 Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

Discharge into the environment must be avoided.

6.3 Methods and material for containment and cleaning up

Sweep up and shovel. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

See Section 7 for information on safe handling.

See section 8 for information on personal protection equipment.

See Section 13 for information on disposal.

Section 7: Handling and storage

7.1 Precautions for safe handling

Provide appropriate exhaust ventilation at places where dust is formed.

Normal measures for preventive fire protection.



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7.2 Conditions for safe storage, including any incompatibilities

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated.

Section 8 : Exposure controls/personal protection

8.1 Control parameters

Occupational exposure limit values:

No occupational exposure limit values established.

DNEL(Derived No Effect Level) for workers and the general population:

No DNEL values available for workers and the general population.

PNEC(Predicted No Effect Concentration) values:

No PNEC values available for the substance.

8.2 Exposure controls

Appropriate engineering controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal protective equipment:

Eye and face protection: Wear appropriate protective eyeglasses or chemical safety goggles.

Skin protection: Wear appropriate protective clothing and gloves to prevent skin exposure.

Respiratory protection: In an emergency, respiratory protection must be worn.

Environmental exposure controls:

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

Discharge into the environment must be avoided.

Industrial hygiene:

Handle in accordance with good industrial hygiene and safety practice.

Avoid inhalation of vapour or mist.

Section 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

Appearance:	Solid, powder
Colour:	White
Odour:	Odourless
pH:	11.5 at 1% aqueous solution



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Melting point:	No data available.
Boiling point:	No data available.
Density:	No data available.
Vapour pressure:	No data available.
Partition coefficient (n -octanol/water):	No data available.
Solubility(ies):	Soluble in water.
Flash point:	No data available.
Auto-ignition temperature:	No data available.
Flammability:	Not flammable.
Explosive properties:	Not explosive.
Oxidising properties:	No oxidising properties.

9.2 Other information

No other information available.

Section 10: Stability and reactivity

10.1 Reactivity

Stable under recommended storage and handling conditions (see section 7, handling and storage).

10.2 Chemical stability

Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions

No hazardous reactions known.

10.4 Conditions to avoid

Incompatible materials. Strong heating. Moisture.

10.5 Incompatible materials

Strong oxidizing agents, strong oxidizing agents, strong acids.

10.6 Hazardous decomposition products

Carbon oxides, oxides of phosphorus, sodium oxides.

Section 11: Toxicological information

11.1 Toxicokinetics, metabolism and distribution

No relevant information available.

11.2 Information on toxicological effects

Acute toxicity:



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Quantitative data on the acute oral/inhalation/dermal toxicity of this product are not available.

Other toxicity data:

LD₅₀ = 195 mg/kg (rat, intraperitoneal); LD₅₀ = 83 mg/kg (mouse, intraperitoneal);

LDLo = 4000 mg/kg (guinea pig, subcutaneous); LDLo = 400 mg/kg (guinea pig, intraperitoneal);

LDLo = 23 mg/kg (rabbit, intravenous); LDLo = 1400 mg/kg (rabbit, subcutaneous);

Skin corrosion/irritation:

No information available.

Serious eye damage/irritation:

No information available.

Respiratory or skin sensitization:

No information available.

CMR effects (Carcinogenicity, Mutagenicity and Toxicity for Reproduction):

No information available.

STOT-single exposure and repeated exposure:

No information available.

Additional information:

RTECS No.: NM7535000.

Section 12: Ecological information

12.1 Toxicity

Quantitative data on the acute fish/daphnia/algae/bacteria toxicity of this product are not available.

12.2 Persistence and degradability

Based on best current information, there is no data known associated with this product.

12.3 Bioaccumulative potential

Based on best current information, there is no data known associated with this product.

12.4 Mobility in soil

Based on best current information, there is no data known associated with this product.

12.5 Results of PBT and vPvB assessment

PBT/vPvB assessment information is not available as chemical safety assessment not conducted.

12.6 Other adverse effects

No other adverse effects known.

Section 13: Disposal considerations

13.1 Waste treatment methods

Waste must be disposed of in accordance with state and local environmental control regulations.



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Section 14: Transport information

14.1 Land transport (ADR/RID/GGVSE)

This product is not regulated as a hazardous material or dangerous goods for transportation.

14.2 Sea transport (IMDG-Code/GGVSee)

This product is not regulated as a hazardous material or dangerous goods for transportation.

14.3 Air transport (ICAO-TI/IATA-DGR)

This product is not regulated as a hazardous material or dangerous goods for transportation.

14.4 Additional information

No other information available.

Section 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

EU regulation:

Authorisations:

No information available.

Restrictions on use:

No information available.

EINECS:

CAS# 14306-25-3 is listed in the inventory.

DSD (67/548/EEC):

CAS# 14306-25-3 is not listed in the Annex I.

Other chemical regulation:

USA - TSCA:

CAS# 14306-25-3 is listed in the inventory.

Canada - DSL/NDSL:

CAS# 14306-25-3 is not specified on any list.

Australia - AICS:

CAS# 14306-25-3 is listed in the inventory.

Korea - ECL:

CAS# 14306-25-3 is not listed in the inventory.

Japan - ENCS:

CAS# 14306-25-3 is not listed in the inventory.

China - IECSC:

CAS# 14306-25-3 is listed in the inventory.

15.2 Chemical Safety Assessment

No Chemical Safety Assessment has been carried out for this substance.

Section 16: Other information

16.1 Revision Information:

Date of the previous revision: Not applicable.

Date of this revision: 18/02/2011.

Revision summary: The first new SDS

16.2 Abbreviations and acronyms



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- CLP:** EU regulation (EC) No 1272/2008 on classification, labelling and packaging of chemical substances and mixtures.
- CAS:** Chemical Abstracts Service (division of the American Chemical Society).
- EINECS:** European Inventory of Existing Commercial Chemical Substances.
- RID:** European Rail Transport.
- IMDG:** International Maritime Code for Dangerous Goods.
- IATA:** International Air Transport Association.
- OSHA:** The United States Occupational Safety and Health Administration.
- TSCA:** Toxic Substances Control Act, The American chemical inventory.
- DSD:** Dangerous Substance Directive (67/548/EEC).
- IECSC:** Inventory of existing chemical substances in China.
- DSL:** Domestic Substances List, The Canadian chemical inventory.
- AICS:** The Australian Inventory of Chemical Substances.
- ECL:** Existing Chemicals List, the Korean chemical inventory.
- ENCS:** Japanese Existing and New Chemical Substances.

16.3 Key literature references and sources for data

ESIS Dataset: European chemical Substances Information System.

NLM: U.S. National Library of Medicine.

The Chemical Database: The Department of Chemistry of the University of Akron.

16.4 Relevant R-phrases and H-statements

Not applicable. This product does not meet the criteria for classification in any hazard class according to EU Classification Regulation.

16.5 Training advice

Provide adequate information, instruction and training for operators.

16.6 Declare to reader

The information in this Safety Data Sheet (SDS) was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use or disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of the product. This SDS was prepared and is to be used only for this product. If the product is used as a component in another product, this SDS information may not be applicable. According to REACH Article 31(5), the SDS shall be supplied in an official language of the Member State(s) where the substance or mixture is placed on the market, unless the recipient Member State(s) concerned provide otherwise. It should also be noted that this SDS is applicable to the countries with English as an official language.

----- End of the SDS -----

Your Position: [Chemical Search](#) > [Chemical Dictionary](#) > Sodium Malonate

Sodium Malonate

MSDS Name: Sodium Malonate Material Safety Data Sheet
 Synonym: Disodium Malonate; Propanedioic Acid, Disodium Sal

Section 2 - COMPOSITION, INFORMATION ON INGREDIENTS

name: Sodium Malonate
 CAS: 141-95-7
 content: ca 100
 EINECS: 205-514-0

Hazard Symbols: None Listed.
 Risk Phrases: None Listed.

Section 3 - HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

The toxicological properties of this material have not been fully investigated.

Potential Health Effects

Eye:

May cause eye irritation. The toxicological properties of this material have not been fully investigated.

Skin:

May cause skin irritation. The toxicological properties of this material have not been fully investigated.

Ingestion:

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May cause irritation of the digestive tract. May cause cardiac disturbances. The toxicological properties of this substance have not been fully investigated.

Inhalation:

May cause respiratory tract irritation. The toxicological properties of this substance have not been fully investigated.

Chronic:

May cause digestive tract and cardiac disturbances.

Section 4 - FIRST AID MEASURES

Eyes: Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid.

Skin:

Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid if irritation develops or persists. Wash clothing before reuse.

Ingestion:

Never give anything by mouth to an unconscious person. Get medical aid. Do NOT induce vomiting. If conscious and alert, rinse mouth and drink 2-4 cupfuls of milk or water. Wash mouth out with water.

Inhalation:

Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid if cough or other symptoms appear.

Notes to Physician:

Section 5 - FIRE FIGHTING MEASURES

General Information:

As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. During a fire, irritating and highly toxic gases may be generated by thermal decomposition or combustion.

Extinguishing Media:

Use agent most appropriate to extinguish fire. Use water spray, dry chemical, carbon dioxide, or appropriate foam.

Section 6 - ACCIDENTAL RELEASE MEASURES

General Information: Use proper personal protective equipment as indicated in Section 8.

Spills/Leaks:

Vacuum or sweep up material and place into a suitable disposal container. Clean up spills immediately, observing precautions in the Protective Equipment section. Avoid generating dusty conditions.

Provide ventilation.

☉ Section 7 - HANDLING and STORAGE**Handling:**

Wash thoroughly after handling. Use with adequate ventilation.

Minimize dust generation and accumulation. Avoid breathing dust, vapor, mist, or gas. Avoid contact with eyes, skin, and clothing.

Avoid contact with skin and eyes. Keep container tightly closed.

Avoid ingestion and inhalation. Use only in a chemical fume hood.

Storage:

Store in a tightly closed container. Store in a cool, dry, well-ventilated area away from incompatible substances.

☉ Section 8 - EXPOSURE CONTROLS, PERSONAL PROTECTION**Engineering Controls:**

Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate ventilation to keep airborne concentrations low.

Exposure Limits CAS# 141-95-7: Personal Protective Equipment Eyes: Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

Skin:

Wear appropriate protective gloves to prevent skin exposure.

Clothing:

Wear appropriate protective clothing to prevent skin exposure.

Respirators:

Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

☉ Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

Physical State: Powder
Color: white
Odor: Not available.
pH: Not available.
Vapor Pressure: Not available.
Viscosity: Not available.
Boiling Point: Not available.
Freezing/Melting Point: 966 deg C
Autoignition Temperature: Not applicable.
Flash Point: Not applicable.
Explosion Limits, lower: Not available.
Explosion Limits, upper: Not available.
Decomposition Temperature: Not available.
Solubility in water: soluble in water
Specific Gravity/Density: Not available.
Molecular Formula: CH₂(COONa)₂
Molecular Weight: 147.9912

Section 10 - STABILITY AND REACTIVITY

Chemical Stability:

Stable under normal temperatures and pressures.

Conditions to Avoid:

Incompatible materials, dust generation, excess heat.

Incompatibilities with Other Materials:

Oxidizing agents.

Hazardous Decomposition Products:

Carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, toxic fumes of sodium oxide.

Hazardous Polymerization: Has not been reported.

Section 11 - TOXICOLOGICAL INFORMATION

RTECS#:

CAS# 141-95-7: 001750000 LD50/LC50:

Not available.

Carcinogenicity:

Sodium Malonate - Not listed by ACGIH, IARC, or NTP.

Other:

See actual entry in RTECS for complete information.

⊙ **Section 12 - ECOLOGICAL INFORMATION**

⊙ **Section 13 - DISPOSAL CONSIDERATIONS**

Products which are considered hazardous for supply are classified as Special Waste and the disposal of such chemicals is covered by regulations which may vary according to location. Contact a specialist disposal company or the local waste regulator for advice. Empty containers must be decontaminated before returning for recycling.

⊙ **Section 14 - TRANSPORT INFORMATION**

IATA

No information available.

IMO

No information available.

RID/ADR

No information available.

⊙ **Section 15 - REGULATORY INFORMATION**

European/International Regulations

European Labeling in Accordance with EC Directives

Hazard Symbols: Not available.

Risk Phrases:

Safety Phrases:

S 28A After contact with skin, wash immediately with plenty of water.

S 37 Wear suitable gloves.

S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

WGK (Water Danger/Protection)

CAS# 141-95-7: No information available.

Canada

CAS# 141-95-7 is listed on Canada's DSL List.

CAS# 141-95-7 is not listed on Canada's Ingredient Disclosure List.

US FEDERAL

TSCA

CAS# 141-95-7 is listed on the TSCA inventory.

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