

## **Sodium Hydroxide (Activator of Sodium Persulfate)**

1. Submitted by Gary Cronk, JAG Consulting Group, Inc.
2. Sodium hydroxide is commonly called caustic or caustic soda. It is used to raise the pH of soil and water to act as an activator of sodium persulfate. In a water solution, sodium hydroxide dissociates into sodium ions and hydroxide ions.
3. MSDS - See attached file
4. Number of Field Applications: 500 (estimated)
5. Case Studies - See attached files
6. Technical Summary: Sodium hydroxide is used as a high pH activator of sodium persulfate. Sodium hydroxide is most commonly used in the field at a concentration of 25%. Hydroxide is normally delivered by Tanker Trucks (3,000 gal) or in totes (330 gal).

When added to groundwater, sodium hydroxide will cause the pH of the surrounding treatment area to increase to over 10.5 pH units. A bench scale soil buffering test should be performed in the laboratory to determine the quantity of caustic required to raise the pH to 10.5 units and to maintain that pH for up to 4 hours. A properly designed buffering test will determine the soil buffering capacity in units of grams of NaOH per kilogram of soil. Soil buffering capacity can vary greatly between sites (over 10 fold).

Immediately after injection, sodium levels will increase by approximately 20% over baseline levels within the radius of influence. Sodium ions are quickly diluted and dispersed by groundwater flow until the effects are no longer detectable.

Hydroxide ions will cause an immediate increase of pH that lasts about 30 days. At properly designed sites, the pH will typically return to normal within 30 to 60 days. The natural soil buffering capacity slowly neutralizes the high pH conditions and restores the groundwater to a neutral pH.

Sodium hydroxide is highly corrosive and must be handled with established safety precautions. Sodium hydroxide can cause serious burns to the skin, eyes, and lungs, so use of proper PPE is critical. A full face respirator and chemical resistant clothing and gloves are required when handling caustic.

# Evaluation of Sodium Hydroxide for Inclusion in the General WDR Permit

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JAG Consulting Group, Inc.

May 15, 2013

# Physical Description of Sodium Hydroxide

- Simple molecular structure: NaOH
- Liquid solution also known as Caustic Soda or Caustic
- Used to raise the pH of groundwater (to 10.5 units) for the effective activation of sodium persulfate
- Sodium hydroxide is most commonly used in the field at a concentration of 25%.

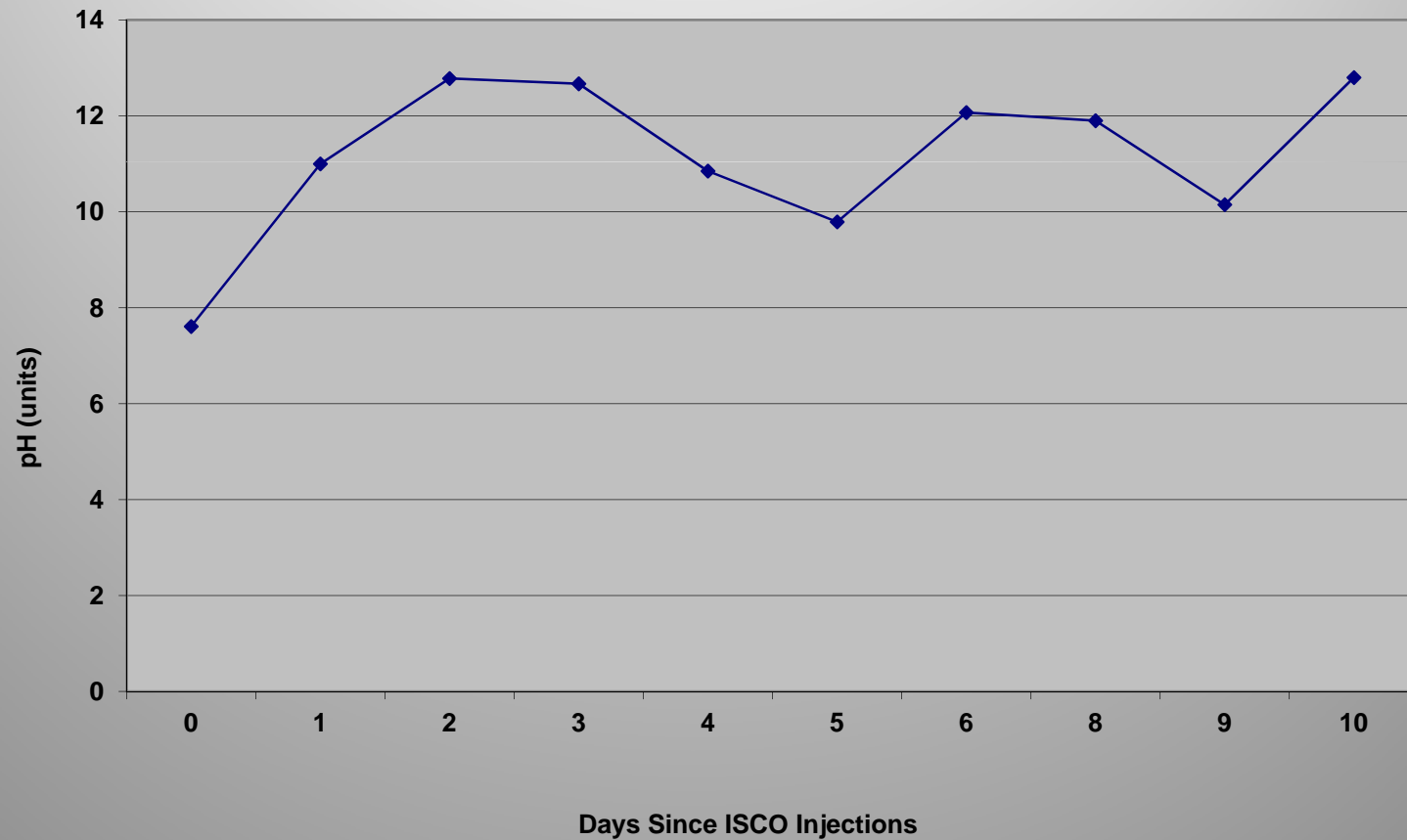
## ***Bench Testing to Ensure Effectiveness***

- Soil buffering test should be performed initially
- Determines the amount of hydroxide required to raise and maintain the pH over 10.5 units
- A properly designed test will determine the soil buffering capacity in units of grams NaOH per kilogram of soil
- Soil buffering capacity can vary greatly between sites.
- A Treatability Test should be performed to evaluate VOC destruction at various doses.

# *Impact on Water Quality*

- NaOH in water disassociates into sodium ions and hydroxide ions
- Sodium levels may increase by approximately 20% within the radius of influence
- Sodium ions are diluted and dispersed by groundwater flow until the effects are no longer detectable
- Hydroxide ions will cause an immediate increase of pH that lasts about 30 days
- At properly designed sites, the pH will typically return to normal within 30 to 60 days
- Soil buffering capacity slowly neutralizes the alkaline conditions and restores the site to a normal pH

### pH Levels in Monitoring Well MW-6



# *Minimize Health & Safety Issues*

- Safe handling of sodium hydroxide requires close adherence to established safety precautions.
- Sodium hydroxide can cause serious burns to skin and lungs so use of proper PPE is critical.
- Dermal and respiratory are the primary routes of exposure for caustic
- Chemical delivered by Tanker Trucks (3,000 gal) or by Totes (300 gal)

# *Additional Health & Safety*

- For safety reasons, never use 50% hydroxide.
- Do not mix sodium hydroxide with persulfate. Always keep hydroxide self contained within storage tank, pumps and hoses
- Secondary containment should be provided for the sodium hydroxide storage tank and the persulfate mixing tank by placement of a wood berm (6-inches high) surrounding the tanks and then covering the berm with plastic sheeting.
- A rubber mat should be used to cover the nearby storm drain inlets and sand bags can used to control flow direction.
- The local Fire Department (HazMat Unit) should be notified (as a courtesy) regarding the chemical storage and operations being performed at the facility in the event of an uncontrolled chemical release.
- For safety reasons, always use an experienced injection contractor



## Case Study No. 1 - Circuit Board Manufacturer Newport Beach, CA

- Injected 5,600 gallons of 25% hydroxide and 3,100 gallons of persulfate into 6 injection wells
- Caustic delivered via tanker truck and stored in a 3,000 gallon tank (double walled).
- Extremely elevated levels of chlorinated VOCs were present at the site.
- In one monitoring well in the source zone, attained 99% destruction of TCE, 96% destruction of 1,1-DCE, 78% reduction of cis-1,2-DCE, 83% reduction of toluene, and 68% reduction of 1,4-dioxane after 6 months of monitoring.
- However, another monitoring well showed nearly no change after 6 months.

# Case Study No. 1 - Circuit Board Manufacturer Newport Beach, CA



## Case Study No. 2. Sun City, CA (former gas station site)

- Injected 3,300 gallons of 25% hydroxide and 1,700 gallons of persulfate into 8 injection wells
- Worked at night to minimize impact on retail business (Walgreens store)
- Attained 90% to 95% destruction of TPH gas in three monitoring wells after 4 months
- Attained 60% to 99% destruction of benzene in three monitoring wells after 4 months.

## Case Study No. 2. Sun City, CA (former gas station site)





## Case Study No. 3 Chicago, IL (Automotive Chemicals site)

- Soil treatment project only (groundwater treatment not required)
- Injected 6,300 gallons of hydroxide and 7,800 gallons of persulfate into 12 vadose/GW zone injection wells and an infiltration gallery (including horizontal wells under building).
- Attained 99% destruction of PCE, 99% destruction of methylene chloride, and 73% to 99% destruction of TCE in soil samples.
- The ISCO injections attained the soil cleanup criteria established by the State of Illinois EPA and “No Further Action” was granted for Area #1 and Area #2 in 2009.

## Case Study No. 3 Chicago, IL (Automotive Chemicals site)





## Case Study No. 4. Huntington Harbor, CA (gas station site)

- Injected 2,900 gallons of hydroxide and 1,500 gallons of persulfate into 3 wells
- BTEX levels reduced by 82% to 100% and TPH gas reduced by 81%

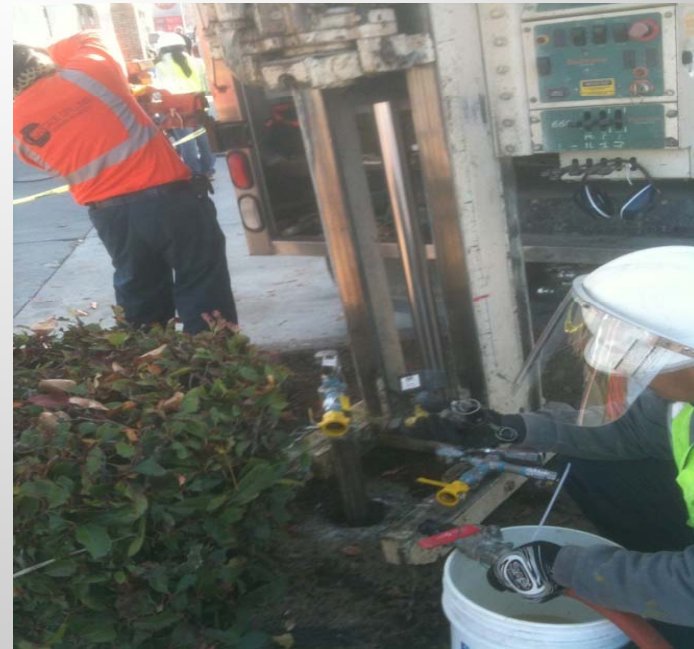


## Case Study No. 5. Milpitas, CA (gas station site)

- Injected 2,300 gallons of hydroxide and 4,500 gallons of persulfate into 16 direct push borings
- Attained moderate results, up to 74% destruction of TPH as gas, 85% reduction of Toluene, 89% reduction of xylenes, and 76% reduction of ethylbenzene, and 29% reduction of benzene in one monitoring well.
- pH levels did not increase to above 10 pH level and inhibited the activation of persulfate.
- After further Bench Scale Testing, it was determined this site had very high Soil Buffering Capacity (7.16 g NaOH/kg soil) which was causing problems with proper activation of persulfate.



# Case Study No. 5. Milpitas, CA



# CASE STUDY COMPARISON OF MULTIPLE ACTIVATION METHODS FOR SODIUM PERSULFATE ISCO TREATMENT

Gary Cronk, P.E. (JAG Consulting Group)

Presentation at the Battelle 6<sup>th</sup> International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 19-22, 2008

**ABSTRACT:** Several methods are available for activating sodium persulfate, including hydrogen peroxide, ferrous iron or chelated iron, alkaline conditions (high pH), and heat. This paper discusses in-situ chemical oxidation (ISCO) case studies (both full scale and pilot studies) which were designed and implemented using varying methods for activating persulfate. A total of six case studies are discussed with regards to selection of activator, reduction in contaminant levels, and site conditions affecting the ISCO treatments.

To obtain optimal contaminant destruction and efficiency, the proper activation method for persulfate must be selected. Selection of the activation method is dependent upon both the contaminant(s) of concern and the site conditions. As a general rule of thumb, FMC Corporation has stated the most aggressive means of persulfate activation is by use of high pH and/or hydrogen peroxide. However, there are certain site conditions where these activators might not be the best choice. For shallow groundwater UST sites, the high pH or peroxide might cause corrosion or damage to utilities and metal objects that may come into contact with the activator or the persulfate. In addition, hydrogen peroxide often reacts very aggressively in the subsurface and care must be taken to adequately vent off-gas production and control the reaction so that peroxide does not come to the surface. FMC does not recommend iron activation for destruction of gasoline range and diesel range organics, although it is effective on MTBE, TBA, BTEX, and other hydrocarbons. In addition, iron activation is not recommended for treatment of vinyl chloride, methylene chloride, carbon tetrachloride, TCA or DCA.

The six ISCO case studies were all sites located in California. The following is a breakdown of the activators used on the sites:

- Hydrogen peroxide activation – 2 sites
- High pH activation – 2 sites
- Iron activation - 2 sites

Good to excellent contaminant reductions (generally exceeding 85% reduction) were achieved in all these case studies, due in large part to the matching of site conditions to the best activation method.

## INTRODUCTION

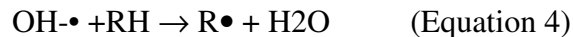
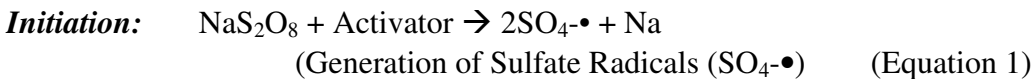
In recent years, sodium persulfate has become a commonly used oxidant for many contaminated groundwater sites. Persulfate is a strong and versatile oxidant capable of

treating a wide spectrum of organic contaminants. The activation of sodium persulfate can be achieved by any of the following methods:

- Hydrogen Peroxide
- Ferrous Iron or Chelated Iron
- High pH
- Heat

Once the persulfate is activated by one of the above methods, it results in the formation of sulfate free radicals ( $\text{SO}_4\text{-}\bullet$ ) as represented in Equations 1 through 4 below. The sulfate radicals can also produce hydroxyl radicals (see Equation 2). Free radicals are molecular fragments that have an unpaired electron causing them to be strong oxidizing agents and are known to rapidly oxidize many VOCs. In addition to its oxidizing strength, persulfate and sulfate radical oxidation has several advantages over other oxidants. First, it is kinetically fast. Second, the sulfate radical is more stable than the hydroxyl radical and thus able to transport (diffuse) greater distances and create a larger radius of treatment.

#### ***Sulfate Radical Generation and Reactions:***



Where: RH represents an organic compound;

R• represents oxidized organic compound

Soil oxidant demand and metals also contribute to oxidant consumption.

Note: Free radical chemistry is not necessarily stoichiometric or straightforward.

#### **SELECTION OF THE RIGHT ACTIVATOR**

To obtain optimal contaminant destruction and efficiency, the right activation method must be selected. Selection of the activation method is dependent upon both the contaminant of concern(s) and the site conditions. For example, for cleanup of gasoline or diesel contaminated UST sites, the best activator would be high pH or hydrogen peroxide. Heat could also be used, but generating or obtaining a source of heat is often costly (unless the site is already producing steam or another source of heat). FMC Corporation does not recommend iron activation for destruction of gasoline range and diesel range organics, although it is effective on MTBE, TBA, BTEX, and other hydrocarbons.

For mixed solvent plumes containing chlorinated ethenes, such as TCE, PCE, DCE, and vinyl chloride, any of the four activation methods would work well. However, if the site contains high levels of vinyl chloride, methylene chloride, carbon tetrachloride, TCA or DCA, activation by iron activation is not recommended. In this situation, high pH or hydrogen peroxide would be the activator of choice. 1,4-dioxane can be treated by activation by iron, high pH, or peroxide.

As a general rule of thumb, FMC has stated the most aggressive means of persulfate activation is by use of hydrogen peroxide and/or high pH. However, there are certain site conditions where these activators might not be the best choice. For shallow groundwater UST sites, the high pH or peroxide might cause accelerated corrosion of utilities and metal objects that it comes into contact with. In addition, hydrogen peroxide often reacts aggressively in the subsurface and care must be taken to adequately vent off-gas production and to minimize peroxide coming to the surface. Sensitive sites where the surfacing of hydrogen peroxide could cause issues for the owner's business operations would not be good candidates for peroxide.

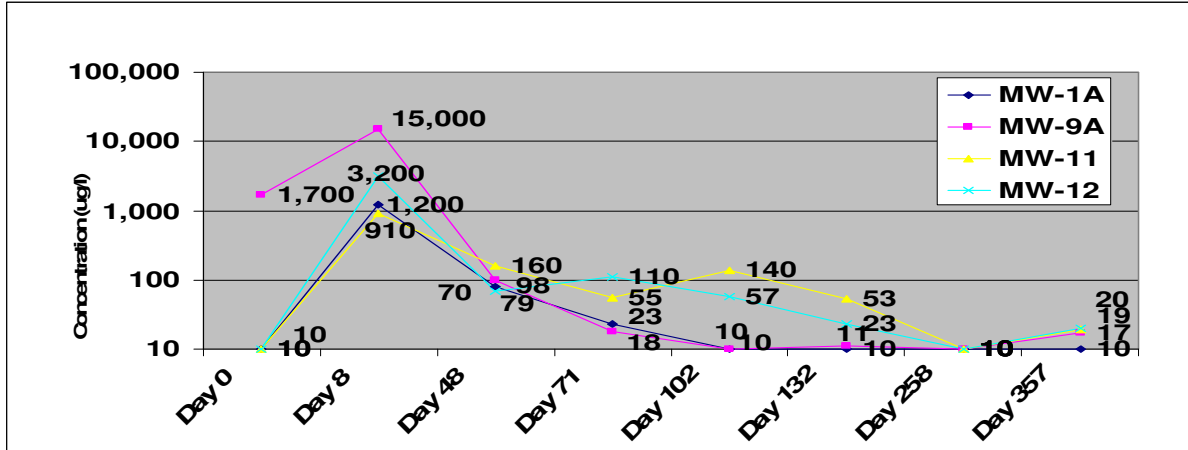
### **Site 1. Hydrogen Peroxide Activation**

Site 1 is an industrial site located in Ranch Dominguez, CA (Los Angeles County). Hydrogen peroxide activation was selected for treatment of this methylene chloride DNAPL site. This activation technique, which incorporates combined oxidizing power of peroxide and persulfate along with heat given off by the Fenton's reaction, was selected because of the recalcitrant nature of methylene chloride and the difficult site conditions. This project was extremely difficult because most of the contaminant plume was under an active industrial building and the contaminants were isolated within a clayey formation at a depth of 40 to 50 feet. A total of 16 of the 23 injection wells were located inside the building with several slant wells installed in sensitive areas where the owner's equipment could not be re-located.

### **Results – Site 1.**

Pre-treatment methylene chloride levels over 15,000 µg/l were reduced to levels less than 50 µg/l within 258 days. "Surfacing" of hydrogen peroxide occurred at this site and off-gas venting issues caused some minor damage to the asphalt pavement. Closure of this site has recently been granted by the Los Angeles Regional Water Quality Control Board.

**FIGURE 1. Reductions in methylene chloride following persulfate treatment**



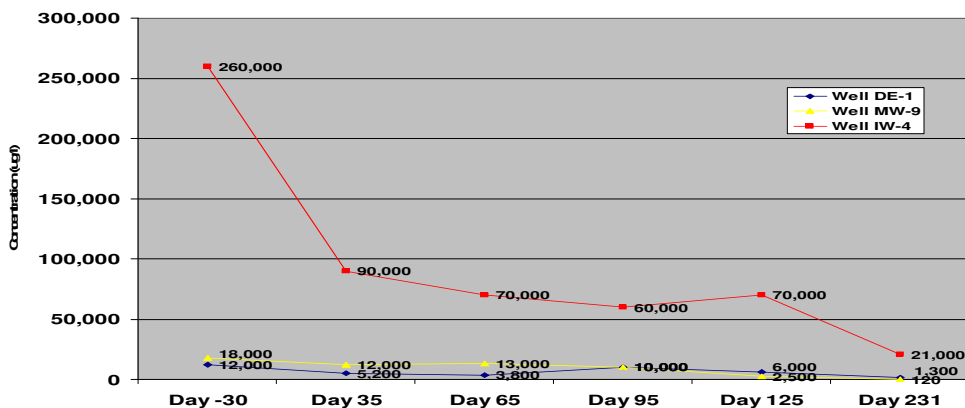
**Site 2. Hydrogen Peroxide Activation**

Site 2 is an industrial site located in Huntington Beach, CA (Orange County). Hydrogen peroxide activation was selected for the 8 well pilot scale treatment of 1,4-dioxane and chlorinated solvents, due to the extremely elevated levels of these recalcitrant contaminants. Depth to groundwater was approximately 12 feet.

**Results – Site 2.**

After 231 days, the 1,4-dioxane levels were reduced substantially, with levels as high as 260,000 µg/l being reduced to 21,000 µg/l (92% reduction). “Surfacing” of peroxide did occur at this site. As a result of the highly successful pilot test, further ISCO treatment of the site is being planned.

**FIGURE 2. Reductions in 1,4-dioxane following persulfate treatment**



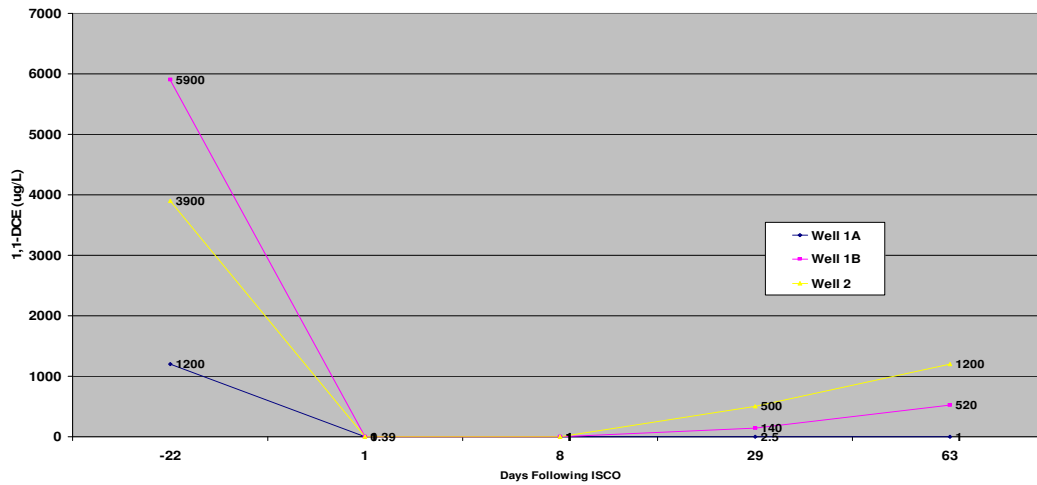
### **Site 3. High pH Activation**

Site 3 is an industrial site located in Santa Ana, CA. Alkaline activation of sodium persulfate using 25% sodium hydroxide was used for the pilot scale treatment of a mixed chlorinated solvent plume. Two injection wells were utilized. Depth to groundwater was approximately 25 feet.

### **Results – Site 3.**

Significant reductions were observed within 30 days for TCE (95%), 1,1-DCE (99%), and other contaminants, but a moderate rebound effect was observed after 45 days of the injection. The rebound effect was believed to be due to release of adsorbed contaminants from the soil. In addition, continued migration of contaminants from the source area likely masked the results in the treatment area, which was located downgradient of the source area.

**FIGURE 3. Reductions in 1,1-DCE Following Persulfate Treatment.**



### **Site 4. High pH Activation**

Site 4 is an active gas station site located in Huntington Harbor, CA. High pH activation of persulfate using 25% sodium hydroxide was selected for this site because of its treatment effectiveness on gasoline range hydrocarbons. Depth to groundwater was at 30 feet bgs, so no interference with shallow utilities was anticipated. Three existing monitoring wells surrounding the UST source area were used as injections wells for this treatment project.

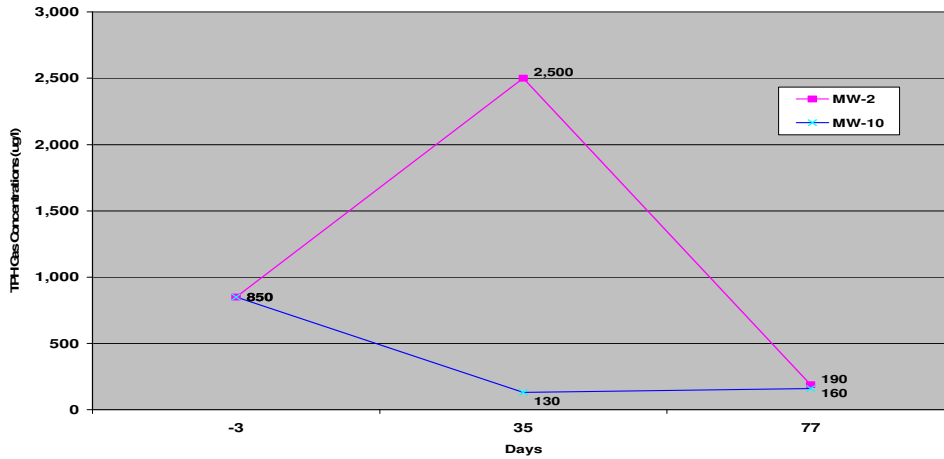
**FIGURE 4. Mixing of persulfate solution.**



**Results – Site 4.**

After 77 days, the TPH gas levels were reduced substantially, with levels as high as 860  $\mu\text{g/l}$  reduced to 160  $\mu\text{g/l}$  and BTEX levels reduced by 82% to 100%. This site is early in the monitoring phase and additional results over the next several months will likely continue to show reductions in contaminant levels.

**FIGURE 5. Reductions in TPH as gas following persulfate treatment.**



**SITE 5. Ferrous Sulfate Activation**

Site 5 is an industrial site located in La Mirada, CA (Los Angeles County). Ferrous iron was selected to activate sodium persulfate for treatment of a small but highly concentrated benzene plume. Three injection wells were utilized. Depth to groundwater was approximately 80 feet.



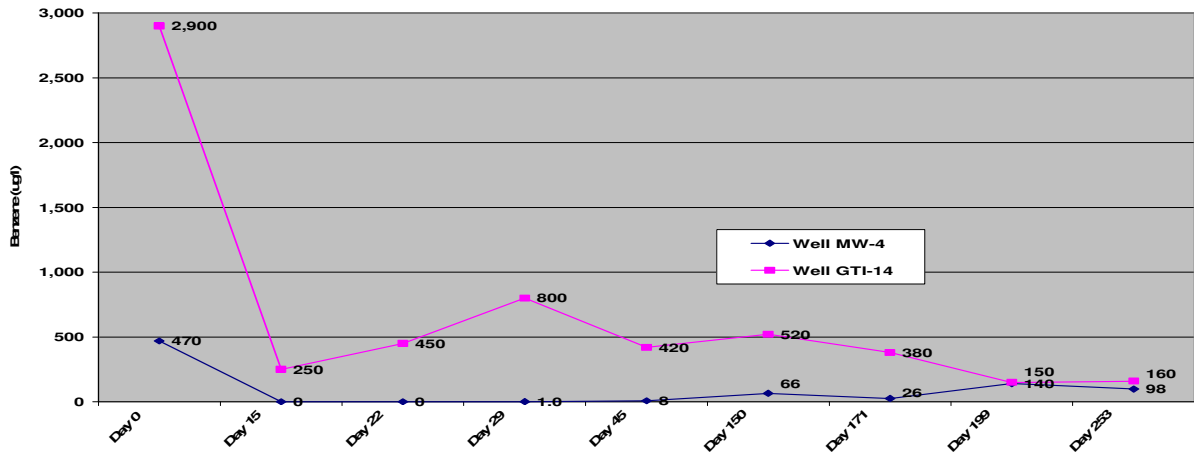
**FIGURE 6. Mixing of ferrous sulfate into solution.**



**Results – Site 5.**

Reduction of benzene levels from 2,900 µg/l to 160 µg/l was achieved after 253 days of the persulfate injection. A mild rebound effect occurred at this site after 30-60 days, due primarily to a rising water table and cross contamination from the deep vadose zone. Following removal of the deep vadose zone contamination using soil vapor extraction, the benzene levels did not rebound again and have remained below 160 µg/l. Closure of the benzene plume at this site is currently being pursued with the Los Angeles RWQCB.

**FIGURE 7. Benzene reductions following persulfate treatment (iron activation)**



**Site 6. Chelated Iron Activation**

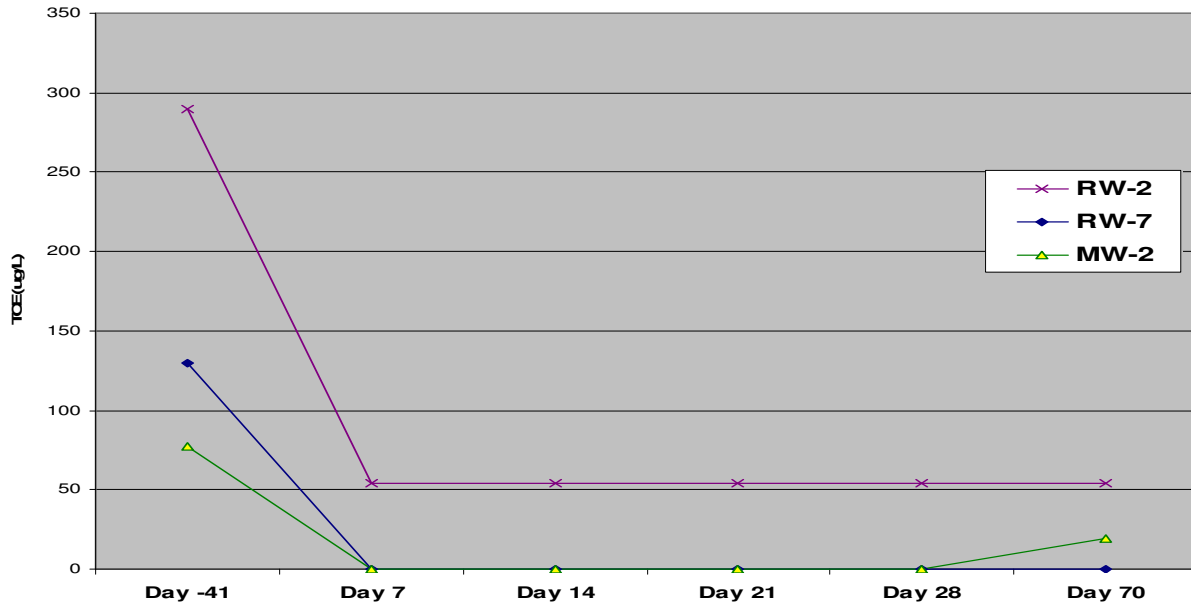
Site 6 is an industrial site located in La Mirada, CA (same site as Case Study 5). Chelated iron (EDTA) was selected to activate sodium persulfate for treatment of a TCE and 1,4-Dioxane plume. A three well injection was recently performed using existing monitoring wells. Depth to groundwater is approximately 80 feet.



### **Results – Site 6**

Reduction of TCE levels from 290 µg/l to 50 µg/l was achieved after 70 days of the iron-activated persulfate injection.

**FIGURE 8. TCE reductions following persulfate treatment (iron activation)**



### **REFERENCES**

FMC Corporation, 2008. “Activation Know How”, located on the FMC website.

FMC Corporation, 2008. Table of Klozur Activation Chemistries, located on the FMC Website.

## **Controlled Vadose Zone Saturation and Remediation (CVSR) Using Chemical Oxidation**

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Presentation at the Battelle 7<sup>th</sup> International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 24-27, 2010

### **Abstract**

Controlled Vadose Zone Saturation and Remediation (CVSR) is essentially a long overdue advancement of standard in-situ treatment methods that have been traditionally used in the saturated zone. Unsaturated zone treatment technologies are not new, but they normally revolve around mechanical operations such as soil vapor extraction (SVE). While the cost of CVSR is comparable to SVE, it can generally be performed within a much shorter timeframe (6 months). To our knowledge, this is only the second published report combining CVSR with in-situ chemical oxidation (ISCO).

CVSR technology was successfully applied to an active industrial site in Illinois. Alkaline activated sodium persulfate using sodium hydroxide was used to treat the shallow soils to a depth of 15 feet. The vadose zone soils were contaminated with a variety of VOC constituents including PCE, TCE, methylene chloride, ethylbenzene, toluene, and total xylenes. Prior to the field injections, a soil buffering test was performed in the laboratory in order to determine the amount of sodium hydroxide needed to raise the pH of the soil to above 10.5 units and maintain it for five days.

Because chemical oxidation relies on diffusion of oxidants in an aqueous medium, the vadose zone soils were saturated using a combination of vertical injection wells, an infiltration gallery, and horizontal injection wells installed beneath two small buildings. The infiltration gallery and the horizontal wells were initially used to percolate water into the vadose zone to achieve saturation. The vertical and horizontal wells were then used to inject the hydroxide and oxidant. A total of 12 vertical injection wells were installed in two treatment areas along with the infiltration gallery. Due to the presence of low permeability silts and clays, each vertical injection well had an estimated radius of influence of 10 feet. Approximately 4,700 gallons of sodium hydroxide (25% concentration) and 11,500 pounds of sodium persulfate were injected over a 27 day period in November and December of 2008. A second injection of activated persulfate was performed in Area 1 in August 2009.

The concentrations of the compounds of concern, PCE, TCE, methylene chloride, ethylbenzene, toluene, and total xylenes, all decreased from 88% to 99% within 180 days after treatment. The ISCO injections attained the site-specific soil cleanup criteria, in conjunction with an engineered barrier, established by the State of Illinois EPA.

### **Project Site Description**

The project site is located in a suburb located just north of Chicago, Illinois. The site was impacted by various volatile organic constituents, including toluene, ethylbenzene, total

xylenes, acetone, methylene chloride, PCE, and TCE. Two areas of concern exist at the site; the Filling Room (Area 1) and the Fill Pipe area (Area 2). The Filling Room Area measured approximately 3,850 ft<sup>2</sup> and the Fill Pipe Area measured 1,200 ft<sup>2</sup>. Depth to groundwater beneath the site is approximately 5 feet below ground surface (bgs) beneath the Filling Room Area and 15-16 feet bgs in the Fill Pipe Area. Soils were predominantly silty clays and clayey silts with some sandy stringers. No visual LNAPL or DNAPL was present in the monitoring wells prior to the ISCO treatment, although the high concentrations in the soil and groundwater (over 1% saturation level) indicate that LNAPL or DNAPL could be present at the site.

The vadose zone soils in the two areas of concern were the primary target for remediation. At the Filling Room Area (Area 1), the target treatment zone was from 2 feet to 8 feet bgs. At the Fill Pipe Area (Area 2), the target treatment zone was from 2 feet to 15 feet bgs

### **Project Objectives**

The objective of the ISCO injection was to reduce the soil concentrations of VOCs at the Site to concentrations below site-specific Tier 2 Soil Remediation Objectives established by the State of Illinois EPA. To accomplish the ISCO treatment, the vadose zone soils were initially saturated with water using an infiltration gallery and horizontal injection wells in order to create an aqueous media and allow for dispersion of oxidants.

### **Infiltration Gallery and Injection Well Construction**

JAG Consulting Group designed and installed an infiltration gallery in Areas 1 and 2 to saturate the vadose zone and to provide an aqueous medium for dispersion and diffusion of the persulfate radicals and to provide oxidant contact with all the soil particles and VOCs within the vadose zone. In addition, eight horizontal wells were drilled under the two small buildings located in Area 1 in order to treat VOC contamination under the buildings (see Figure 1). The horizontal borings were drilled with a horizontal boring machine, as shown in Figure 2.

ENVIRON installed eleven new vertical injection wells, designated IW-1 to IW-11, within the two treatment areas on November 5 to 7, 2008 (see Figure 1). Eight of the new injection wells in Area 1 were screened from approximately 3 feet to 8 feet bgs, while the remaining three injection wells in Area 2 were screened from 3 feet to 15 feet bgs. The injection wells were constructed of 2-inch schedule 40 PVC casing and screen. At ground surface, each injection well was completed with a concrete pad and a flush-mounted steel well box. Based on the low permeability silts and clays, each injection well had an estimated radius of influence of 10 feet. Following installation, the injection wells were developed by ENVIRON by surging the sand pack and removal of water until clear water was produced.

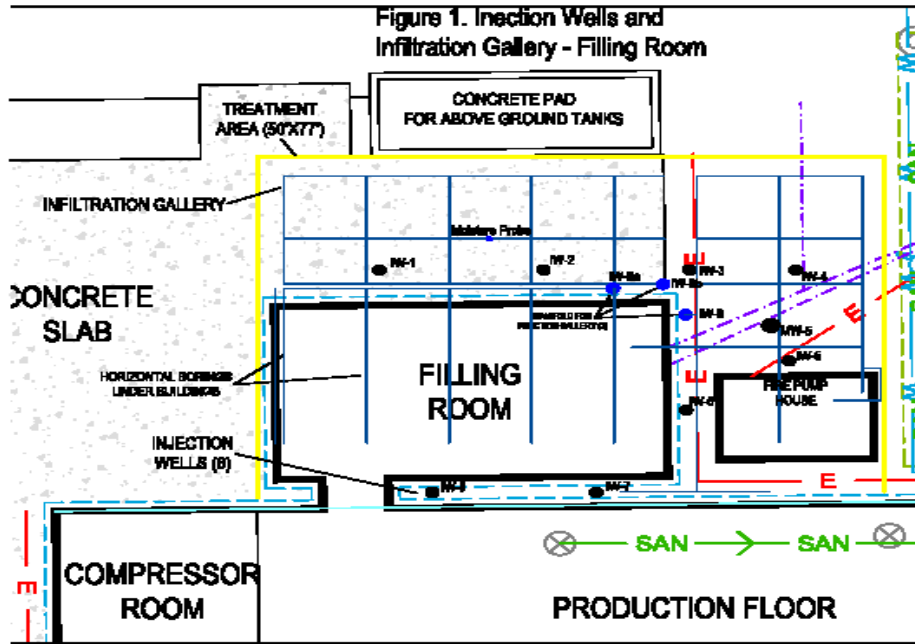


Figure 2. Drilling of Horizontal Wells (Area 1)



### **Bench Scale Testing**

A soil buffering test in the laboratory was performed and confirmed that the soils beneath the site are highly buffered. The buffering test was performed by determining the amount of sodium hydroxide required to raise and maintain the pH of the soil above 10.5 units for a period of five days. This provided a scale-up quantity of sodium hydroxide that would be required in the field.

A laboratory bench scale soil oxidant demand (SOD) test was also performed. The results indicate SOD values (3.0 to 4.5 g/kg) to be in the normal to slightly elevated range. Contributors to SOD include naturally occurring organics in the soil, the presence of reduced metals, and high alkalinity and total dissolved solid (TDS) levels which can cause scavenging of oxidants. The SOD results were interpreted to mean that some slight amount of interference with oxidation may occur and additional injection events of persulfate may be required to attain the low cleanup objectives for the soil.

### **Injection Events**

The first injection event occurred from November 18 to December 15, 2008 (27 day period). Approximately 4,700 gallons of sodium hydroxide (25%) and 11,500 pounds of sodium persulfate (5,320 gallons at 24%) were injected into the wells over this period. Freezing temperatures and snowfall caused many delays in early December 2008 which extended the injection period. For safety reasons, no excess pressure (less than 20 psi) was applied during the injections (only gravity feed pressures were used).

During the ISCO injections, ground surfacing of chemicals (daylighting) was observed often and was immediately controlled by turning off the flow valve leading to the nearest injection well. Neutralization of the caustic sodium hydroxide that bubbled to the surface was accomplished by use of a mild muriatic acid (HCl) solution, while the persulfate was neutralized using a mild solution of sodium bisulfite (reducing agent). Field personnel inspected the injection areas and observed no visible signs of subsurface degradation, subsidence, or bulging of pavement.

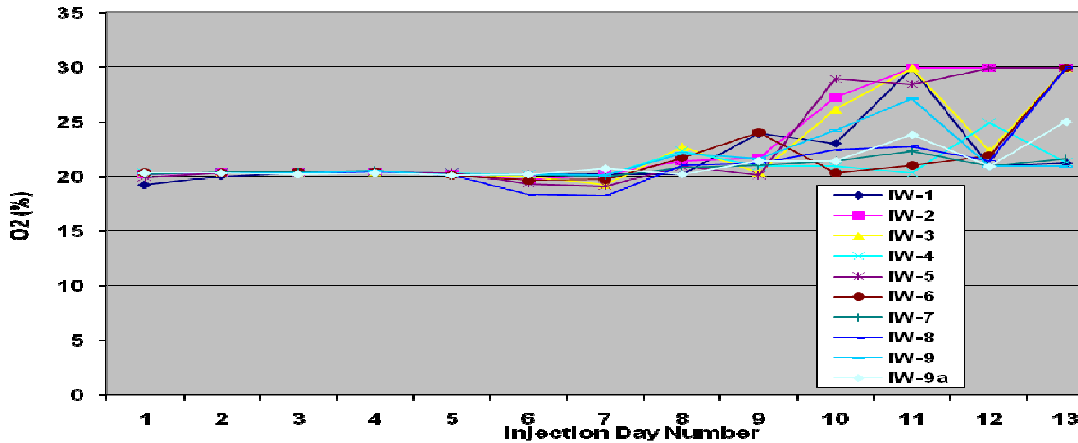
The second injection event was only performed in Area 1 and occurred from August 4 to August 16, 2009 (12 day period). A total of 2,600 gallons of sodium hydroxide was injected into Area 1 and 2,475 gallons of sodium persulfate (at 24% solution) was injected during this injection event.

### **Air Quality Monitoring Data**

To protect the health and safety of field personnel, facility employees, and the public during field activities, and to monitor for the potential migration of subsurface gas vapors, JAG Consulting Group implemented an air monitoring program. The emissions from each injection well and various points in and around the work area were monitored periodically throughout each workday with a four gas air quality meter that monitored for oxygen, carbon dioxide, carbon monoxide, and lower explosive limit.

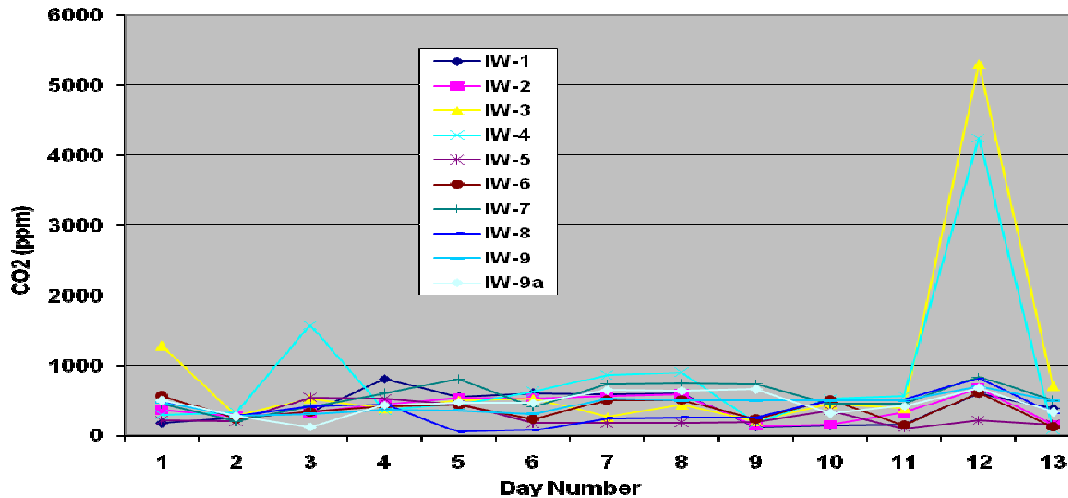
During the sodium hydroxide injections, (Days 1 through 6) only minor fluctuations in oxygen levels were detected (see Figure 3.). However, during the persulfate injections starting on Day 9 and 10, an immediate increase in oxygen level up to 23% to 29% was detected in the injection wells and generally stayed elevated throughout the ISCO injection. This observation was expected, as persulfate is known to release small quantities of oxygen gas as it degrades VOCs.

**Figure 3. Oxygen Levels During ISCO Injections**



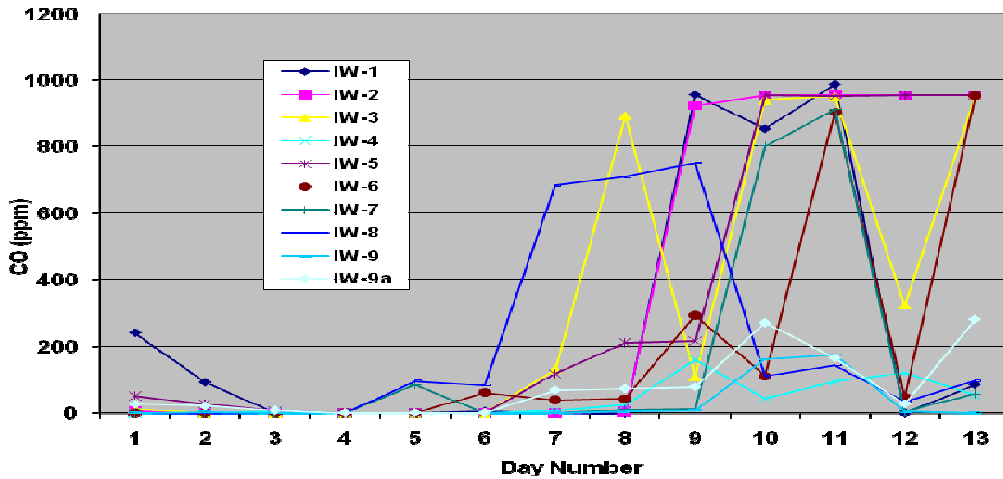
Carbon dioxide (CO<sub>2</sub>) levels were observed to generally remain at moderate levels (200 ppm to 500 ppm) for the first 11 days of injections. Starting on Day 12, the carbon dioxide levels increased dramatically to levels above 4,000 ppm in injection wells IW-3 and IW-4 (see Figure 4). Carbon dioxide gas is formed as a breakdown product as hydrocarbon bonds are destroyed by the persulfate.

**Figure 4. Carbon Dioxide Levels During ISCO Injections**



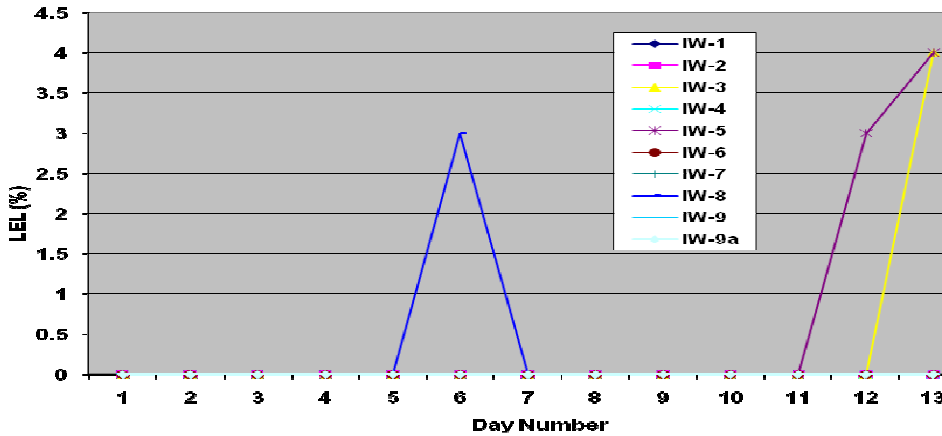
Carbon monoxide (CO) levels generally remained at low levels (less than 200 ppm) for the first 6 to 8 days. Starting on Day 8 and 9, the carbon monoxide levels increased to levels above 800 ppm in the injection wells (see Figure 5). Carbon monoxide gas is also formed as a breakdown product as hydrocarbon bonds are destroyed.

**Figure 5. Carbon Monoxide Levels During ISCO Injections**



The lower explosive limit (LEL) levels were generally non-detectable during most days of ISCO injections. The only detected readings were 4% LEL on Day 13 in injection well IW3, 4% LEL on Days 12 and 13 in injection well IW-5, and 3% LEL in injection well IW-8 on Day 6 (see Figure 6). The LEL readings are most likely caused by the displacement of VOC gases inside the well casing.

**Figure 6. LEL Levels During ISCO Injections**



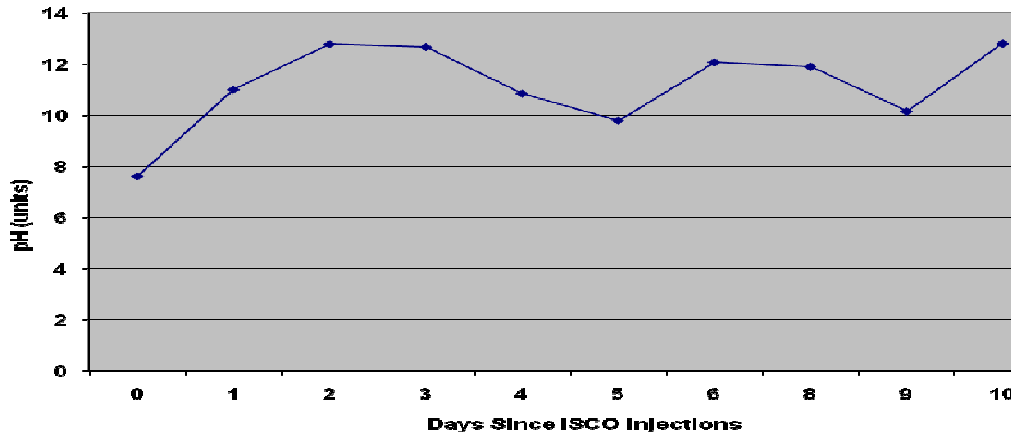
**Water Quality Monitoring Data**

Water quality monitoring data was also collected on a daily basis during the injections from monitoring wells MW-5 and MW-6. The water quality parameters collected from these wells were used to verify that the persulfate and hydroxide were fully dispersing into the treatment zone and were also used to verify the radius of influence.

In monitoring well MW-6, the pH immediately increased to over pH 11 during the hydroxide injections and stayed in that range during the entire period (see Figure 7). pH levels above 10.5 are required to activate the sodium persulfate. However, in monitoring well MW-5, no significant change in the pH occurred during the injection period. Note that monitoring well MW-6 was located approximately 4 feet from the nearest injection well, while monitoring well MW-5 was located approximately 15 feet from the nearest injection well. It is suspected that a pH increase was not monitored in well MW-5,

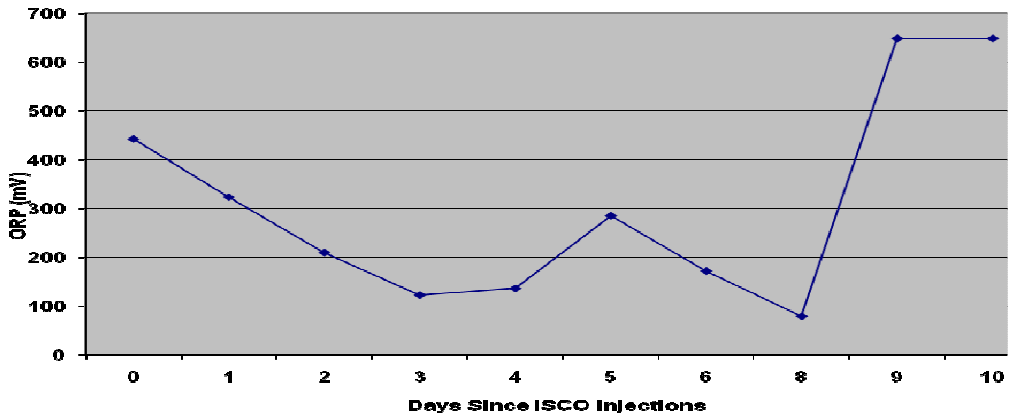
because the ROI was much less than 15 feet and the surface percolation of oxidants was not reaching the screened area of the monitoring well (below 5 feet depth).

**Figure 7. pH In Monitoring Well MW-6**



In monitoring well MW-6, the oxidation reduction potential (ORP) level decreased slightly during the hydroxide injections, but then rose to over 600 mV during the persulfate injections (starting at Day 9, see Figure 8). In general, elevated ORP levels above 300 mV indicate that oxidative conditions were prevalent and confirm that the persulfate was activated.

**Figure 8. ORP In Monitoring Well MW-6**



**Contaminant Reductions**

All of the soil VOCs showed a significant reduction in concentration as a result of the ISCO injections. With only a few exceptions, most all of the VOC concentrations in Area 1 and Area 2 were decreased from 88% to 99%. The VOC concentration reductions are summarized in Tables 1 and 2 below.

**Table 1. Reduction of VOCs in Area 1**

Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
SB-7	SB-48	PCE	8,800	2,800	68.2%
		TCE	1,200	10	99.2%
		Methylene Chloride	2,200	10	99.5%
		Ethylbenzene	240,000	97,000	59.6%



Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
		Xylenes (Total)	1,400,000	470,000	66.4%
		Toluene	370,000	150,000	59.5%
<b>SB-12</b>	<b>SB-38</b>	PCE	48,000	2,300	95.2%
		TCE	2,400	100	95.8%
		Methylene Chloride	9,300	350	96.2%
		Ethylbenzene	260,000	9,400	96.4%
		Xylenes (Total)	1,300,000	47,000	96.4%
		Toluene	1,100,000	38,000	96.5%
<b>SB-14</b>	<b>SB-58</b>	PCE	45,000	14,000	68.9%
		TCE	1,700	10	99.4%
		Methylene Chloride	620	440	29.0%
		Ethylbenzene	72,000	27,000	62.5%
		Xylenes (Total)	430,000	160,000	62.8%
		Toluene	87,000	120,000	-37.9%
<b>SB-15</b>	<b>SB-40</b>	PCE	52	470	-803.8%
		TCE	23	5	78.3%
		Methylene Chloride	640	5	99.2%
		Ethylbenzene	12,000	4.8	100.0%
		Xylenes (Total)	39,000	10	100.0%
		Toluene	45	4.8	89.3%

Table 2. Reduction of VOCs in Area 2

Baseline Boring No.	Corresponding Confirmation Boring No.	Constituent	Initial Concentration (ug/kg)	After ISCO Concentration (ug/kg)	Percent Reduction
<b>SB-17</b>	<b>SB-33</b>	PCE	160,000	180	99.9%
		TCE	5,900	10	99.8%
		Methylene Chloride	360	1	99.7%
		Ethylbenzene	880	12	98.6%
		Xylenes (Total)	1,200	82	93.2%
		Toluene	52,000	1,400	97.3%
<b>SB-20</b>	<b>SB-35</b>	PCE	220,000	1,900	99.1%
		TCE	4,500	280	93.8%
		Methylene Chloride	620	10	98.4%
		Ethylbenzene	250	19	92.4%
		Xylenes (Total)	1,900	10	99.5%
		Toluene	1,900	10	99.5%
<b>SB-8</b>	<b>SB-34</b>	PCE	1,700,000	190,000	88.8%
		TCE	16,000	4,200	73.8%
		Methylene Chloride	5,900	10	99.8%
		Ethylbenzene	2,900	850	70.7%
		Xylenes (Total)	220,000	7,000	96.8%
		Toluene	200,000	22,000	89.0%

In Area 2, the ISCO injections, in conjunction with the use of an engineered barrier attained the site-specific soil cleanup criteria established by the State of Illinois EPA after the first injection. A second injection of persulfate was performed in treatment Area 1 in August 2009 and this area has also attained the State of Illinois soil cleanup levels.

# Mechanism of Base Activation of Persulfate

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Base is the most commonly used activator of persulfate for the treatment of contaminated groundwater by in situ chemical oxidation (ISCO). A mechanism for the base activation of persulfate is proposed involving the base-catalyzed hydrolysis of persulfate to hydroperoxide anion and sulfate followed by the reduction of another persulfate molecule by hydroperoxide. Reduction by hydroperoxide decomposes persulfate into sulfate radical and sulfate anion, and hydroperoxide is oxidized to superoxide. The base-catalyzed hydrolysis of persulfate was supported by kinetic analyses of persulfate decomposition at various base:persulfate molar ratios and an increased rate of persulfate decomposition in D<sub>2</sub>O vs H<sub>2</sub>O. Stoichiometric analyses confirmed that hydroperoxide reacts with persulfate in a 1:1 molar ratio. Addition of hydroperoxide to basic persulfate systems resulted in rapid decomposition of the hydroperoxide and persulfate and decomposition of the superoxide probe hexachloroethane. The presence of superoxide was confirmed with scavenging by Cu(II). Electron spin resonance spectroscopy confirmed the generation of sulfate radical, hydroxyl radical, and superoxide. The results of this research are consistent with the widespread reactivity reported for base-activated persulfate when it is used for ISCO.

## Introduction

In situ chemical oxidation (ISCO) has become a widely used technology for the remediation of contaminated soils and groundwater. The most common ISCO processes are catalyzed H<sub>2</sub>O<sub>2</sub> propagations (i.e., modified Fenton's reagent—CHP), permanganate, and activated persulfate (1). Each of these ISCO processes has limitations. CHP is often ineffective because hydrogen peroxide decomposes rapidly in the subsurface, which limits contact between the reactive oxygen species generated and the contaminants. Permanganate is consumed by soil organic matter and other reduced species (i.e., natural oxidant demand) and is characterized by limited reactivity; it is reactive only with alkenes and benzene derivatives containing ring activating groups (2). Persulfate is an increasingly popular ISCO reagent because it is significantly more stable than hydrogen peroxide, providing the potential for transport from the point of injection to contaminants in lower permeability regions of the subsurface. Furthermore, it appears to degrade most contaminants of concern, including trichloroethylene, 1,1,1-trichloroethane, methyl *tert*-butyl ether, polychlorinated biphenyls, and components of gasoline (3–9). The primary

limitation of activated persulfate is the minimal knowledge of its reaction pathways in the subsurface.

Persulfate is usually activated to increase its reactivity; laboratory activators include uv light and heat, but the most common activators used for ISCO applications are chelated iron and base. Base activation of persulfate has been used at approximately 60% of sites where persulfate ISCO has been employed (10). Base-activated persulfate technology has successfully destroyed highly chlorinated methanes and ethanes in groundwater and soil systems when base was used in excess (11, 12). Several mechanisms have been proposed for the base activation of persulfate (13–15). Kolthoff and Miller (14) hypothesized that persulfate decomposes homolytically into two sulfate radicals, which are then transformed to hydroxyl radicals through subsequent reactions. In contrast, Singh and Venkatarao (15) proposed that persulfate first decomposes to peroxomonosulfate, which then collapses to sulfate and molecular oxygen. However, no proposed mechanisms of persulfate decomposition under alkaline conditions have been thoroughly evaluated and confirmed.

The objective of this study was to elucidate the mechanism of base activation of persulfate. The first step of the proposed mechanism is the base-catalyzed hydrolysis of persulfate to hydroperoxide, which was investigated through kinetic analysis of persulfate decomposition. The second step of the mechanism involves the reduction of another persulfate molecule by the hydroperoxide, which was investigated by adding exogenous hydroperoxide.

## Experimental Section

**Materials.** Sodium persulfate (98%), hexachloroethane (HCA) (99%), diethylenetriamine pentaacetic acid (DTPA) (97%), and deuterated water (D<sub>2</sub>O) were purchased from Sigma-Aldrich (St. Louis, MO). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) (≥99%) was obtained from Axxora LLC (San Diego, CA). DMPO was purified with activated charcoal followed by filtration until no extraneous electron spin resonance spectroscopy (ESR) signals were observed (16). Magnesium chloride (99.6%), hydrogen peroxide (50%), sodium hydroxide (98%), sulfuric acid (96.1%), acetic acid (>99%), sodium bicarbonate (>99%), ammonium sulfate (>99%), and starch were obtained from J.T. Baker (Phillipsburg, NJ). Stock solutions of peroxomonosulfate (SO<sub>5</sub><sup>2-</sup>) were prepared from oxone (2KHSO<sub>5</sub>•KHSO<sub>4</sub>•K<sub>2</sub>SO<sub>4</sub>) (Alfa Aesar; Ward Hill, MA). Potassium iodide (99%) was also purchased from Alfa Aesar (Ward Hill, MA), and titanium sulfate was obtained from GFS Chemicals, Inc. (Columbus, OH). Mixed hexanes and sodium thiosulfate (>99%) were purchased from Fisher Scientific (Fair Lawn, NJ). Double-deionized water was purified to >18 MΩ•cm using a Barnstead E-pure system. Sodium hydroxide solutions were purified to remove transition metals by the addition of magnesium chloride followed by stirring for 8 h and then filtering through 0.45 μm hydrophilic polypropylene membrane filters (17, 18).

**Persulfate Decomposition Studies.** Persulfate decomposition reactions were conducted in 40 mL borosilicate vials containing 20 mL of 0.5 M persulfate activated by 1 M, 1.5 M, 2 M, and 3 M NaOH. Persulfate concentrations were measured by iodometric titration with 0.01 N sodium thiosulfate (19). Persulfate decomposition was also measured in D<sub>2</sub>O versus H<sub>2</sub>O to examine the kinetic effect of deuterium isotopes on base-catalyzed persulfate hydrolysis; these reactions consisted of 0.5 M persulfate and 3 M NaOH. The pH was monitored over time in all reactions and did not change by more than 0.2 pH units.

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### Stoichiometry of Hydroperoxide-Persulfate Systems.

Persulfate and total hydrogen peroxide species ( $\text{H}_2\text{O}_2 + \text{HO}_2^-$ ) concentrations were monitored simultaneously in reactions containing 0.5 M persulfate, 1.5 M NaOH, and 0.5 M  $\text{H}_2\text{O}_2$ , which dissociates to hydroperoxide ( $\text{HO}_2^-$ ) in alkaline systems ( $\text{p}K_a = 11.75$ ), to examine the stoichiometry of the reaction of hydroperoxide and persulfate. At the 3:1 base:persulfate ratio of the reactions, the initial pH was 12.5; therefore, approximately 85% of the added hydrogen peroxide was in the form of hydroperoxide.  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  decomposition was also investigated in reactions containing different ratios of  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  to persulfate. These reactions consisted of 20 mL of 0.5 M persulfate, 1.5 M NaOH, and 0.5 and 1 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ .

**Generation of Superoxide in Persulfate-NaOH- $\text{H}_2\text{O}_2 + \text{HO}_2^-$  Systems.** HCA was used as a probe to detect superoxide (20). Although HCA is unreactive with superoxide in deionized water, its reactivity increases significantly in aqueous systems containing electrolytes such as hydrogen peroxide (18). Reactions contained 20 mL of 2  $\mu\text{M}$  HCA, 0.5 M persulfate, 1 M NaOH, and 0.1 M–0.5 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ . At the 2:1 base:persulfate ratio of the reactions, the initial pH was 12.1; therefore, approximately 70% of the added hydrogen peroxide was in the form of hydroperoxide. Control reactions were performed in parallel with double deionized water in place of  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ . Reactions were conducted in borosilicate vials capped with PTFE-lined septa in the dark at  $20 \pm 2$  °C. A triplicate set of reactors was established for each time point in the experiment; as the reactions proceeded, the total reactor contents were extracted with hexane, and the extracts were analyzed for HCA by gas chromatography.

**Dismutation of Superoxide.** Copper(II) was used to dismutate superoxide ( $k = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) as a means of confirming superoxide generation in base-activated persulfate systems (21, 22). The base-activated persulfate decomposition of HCA was repeated using 0.5 M persulfate, 1 M NaOH, 0.5 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ , and 2  $\mu\text{M}$  HCA with the addition of 2  $\mu\text{M}$   $\text{CuCl}_2$  to dismutate superoxide. This low concentration of Cu(II) did not promote persulfate decomposition and activation, as documented in parallel control reactions conducted without the addition of Cu(II).

**Detection of Radicals Using ESR Spectroscopy.** Radicals generated in base-activated persulfate systems were detected by ESR spectroscopy using DMPO as a spin trap agent. Reactions consisted of 3 mL of 0.05 M persulfate, 0.1 M NaOH, 0.05 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ , and 0.09 M DMPO. The reactants were injected into an aqueous sample cell (Bruker, AquaX high sensitivity) 1 min after the reaction was initiated. All spectra were obtained using a Bruker 6/1 spectrometer with a resonance frequency of 9.86 GHz, microwave power of 2.0 mW, modulation frequency of 100 kHz, modulation amplitude of 1.0 G, sweep width of 100 G, time constant of 164 ms, sweep time of 168 s, and receiver gain of  $2.0 \times 10^5$ .

**Measurement of Oxygen Evolution.** A U-tube manometer filled with water was used to measure the differential pressure in reactions containing 0.5 M persulfate and 3 M NaOH. A reactor was attached to one end of the U-tube manometer, and the other end of the U-tube was open to the atmosphere. The ideal gas law was applied to calculate the moles of gas evolved during the reaction. Persulfate concentrations were quantified in parallel by iodometric titration as the reactions proceeded. The presence of oxygen in the manometer tubes was confirmed by conducting reactions in parallel in Ex-tainer vials equipped with a pierceable rubber septum. The headspaces of the vials were sampled with a gastight syringe and introduced into a vacuum line where water and  $\text{CO}_2$  were cryogenically removed (23). Collected gas samples were analyzed using an isotope-ratio mass spectrometer (Delta Plus XP, ThermoFinnigan, Bremen, Germany); the evolved gas was found to be >99%  $\text{O}_2$ .

**Analysis.** Persulfate concentrations in systems with no hydrogen peroxide addition were measured using iodometric titration with 0.01 N sodium thiosulfate (19). In reactions containing both persulfate and hydrogen peroxide, iodometric titration was used to measure the total peroxy oxygen concentrations, and  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  concentrations were quantified by complexation with titanium sulfate followed by visible spectrophotometry at 407 nm using a Spectronic 20 Genesys spectrophotometer (24, 25); the  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  concentration was then subtracted from the total peroxy oxygen concentration to obtain the concentration of persulfate.

Peroxomonosulfate concentrations were measured in activated persulfate reactions using a Metrohm 690 ion chromatograph equipped with a Super-Sep anion-exchange column. The mobile phase consisted of a degassed solution of 2.0 mmol/L phthalic acid containing 5% (v/v) acetonitrile (pH 3); its flow rate was 1.5 mL/min (26).

Hexane extracts were analyzed for HCA using a Hewlett-Packard 5890A gas chromatograph fitted with a 0.53 mm (i.d.)  $\times$  60 m Equity 1 capillary column and electron capture detector (ECD). Chromatographic parameters included an injector temperature of 220 °C, detector temperature of 270 °C, initial oven temperature of 100 °C, program rate of 30 °C/min, and final temperature of 240 °C.

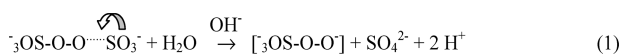
Statistical analyses were performed using SAS software version 9.1 (27). Linear regressions were performed to calculate first-order rate constants for persulfate decomposition. Contrast tests were conducted using a general linear model to compare regression coefficients (first-order rate constants for persulfate decomposition) across different treatments. Pearson's correlation test was used to determine correlations between measured and predicted oxygen evolved in base-activated persulfate systems.

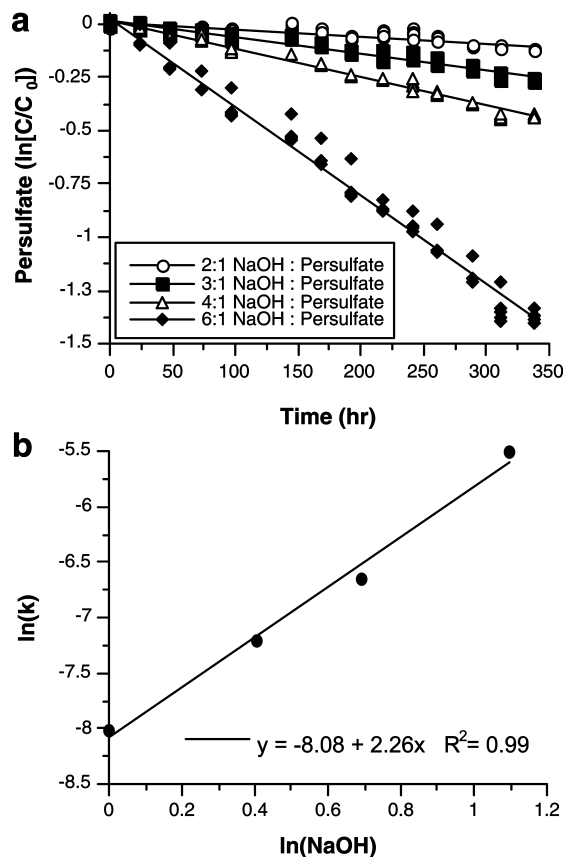
## Results and Discussion

**Base-Activated Persulfate Decomposition Kinetics.** The pseudo-first-order loss of persulfate in solutions with a range of base:persulfate molar ratios is shown in Figure 1a. Persulfate decomposition rates increased with increasing concentrations of NaOH, demonstrating that the rate of persulfate decomposition is a function of basicity. Therefore, the relationship between the first-order persulfate decomposition rate and NaOH concentration was evaluated to determine the reaction order with respect to NaOH. When  $\ln[\text{NaOH}]$  was plotted as a function of  $\ln[\text{persulfate}]$  (Figure 1b), the slope was 2.2, indicating a second-order reaction with respect to NaOH (28).

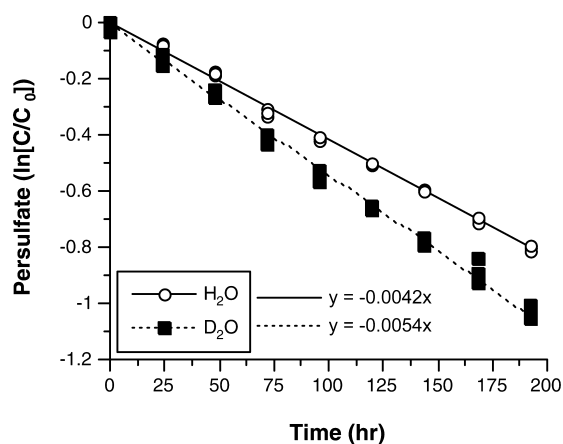
These results suggest that base-catalyzed hydrolysis of persulfate is the first step in the activation of persulfate under alkaline conditions (29). To confirm the base-catalyzed hydrolysis of persulfate, persulfate decomposition reactions were conducted in  $\text{D}_2\text{O}$  vs  $\text{H}_2\text{O}$ . The results of Figure 2 show greater persulfate decomposition in  $\text{D}_2\text{O}$ , with  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.3$ ; these results are consistent with the kinetics of base-catalyzed hydrolysis of esters and amides (30, 31). Because the  $\text{D}_2\text{O}/\text{DO}^-$  system provides stronger nucleophilic activity than the  $\text{H}_2\text{O}/\text{HO}^-$  system (31), the inverse deuterium kinetic isotope experimental value of 1.3 derived from Figure 2 confirms a hydroxide-catalyzed direct nucleophilic attack on persulfate.

**Proposed Mechanism.** Based on the results of Figures 1 and 2, the initial step of the proposed mechanism is the base-catalyzed hydrolysis of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) to peroxomonosulfate ( $\text{SO}_5^{2-}$ ) and sulfate ( $\text{SO}_4^{2-}$ ). Persulfate likely forms an activated complex with hydroxide that weakens the S–O bond



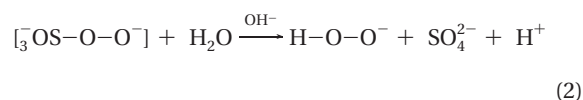


**FIGURE 1.** a) First-order decomposition of base-activated persulfate with varying molar ratios of NaOH:persulfate (reactors: 0.5 M persulfate, 1 M, 1.5 M, 2 M, or 3 M NaOH; 20 mL total volume;  $T = 20 \pm 2$  °C). b) First-order rate constants for persulfate decomposition in base-activated systems as a function of initial NaOH concentration.



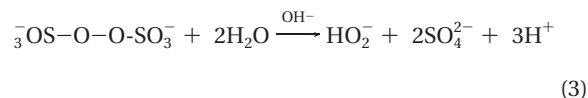
**FIGURE 2.** First-order decomposition of base-activated persulfate in  $D_2O$  vs  $H_2O$  (reactors: 0.5 M persulfate and 3 M NaOH in 20 mL total volume of  $D_2O$  or  $H_2O$ ;  $T = 20 \pm 2$  °C).

As a result, the S–O bond undergoes fission. A similar fission of the remaining S–O bond in peroxomonosulfate results in the formation of sulfate and hydroperoxide ( $HO_2^-$ ), the conjugate base of hydrogen peroxide

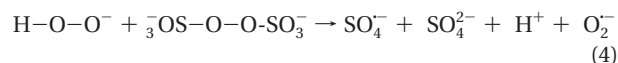


In reaction 1, peroxomonosulfate is formed as a transient intermediate during the base-catalyzed hydrolysis of per-

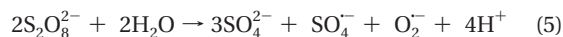
sulfate; however, it was not detected by ion chromatography in solutions containing persulfate and any of numerous NaOH concentrations. Peroxomonosulfate rapidly decomposes to hydroperoxide and sulfate at basic pH (32–34); therefore, no detectable peroxomonosulfate is expected in base-activated persulfate systems. Summing reactions 1 and 2 provides the following net reaction for the base-catalyzed hydrolysis of persulfate



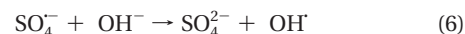
Preliminary experiments using HCA as a superoxide probe (20, 35) showed the presence of superoxide in base-activated persulfate systems, suggesting that superoxide may be generated during persulfate activation. In the proposed mechanism, the hydroperoxide formed from the hydrolysis of one persulfate molecule then reduces another persulfate molecule, generating sulfate radical ( $SO_4^{\cdot-}$ ) and sulfate anion, while hydroperoxide is oxidized to superoxide ( $O_2^{\cdot-}$ )



Reduction and initiation of an oxidant by hydroperoxide is not without precedent; Staehelin and Hoigné (36) documented the reduction of ozone by hydroperoxide in ozone/ $H_2O_2$  systems. Summing reactions 3 and 4 yields the following net reaction for persulfate activation under basic conditions



Furthermore, in highly alkaline conditions, sulfate radical reacts with hydroxide to form hydroxyl radical ( $OH^{\cdot}$ ) (37)

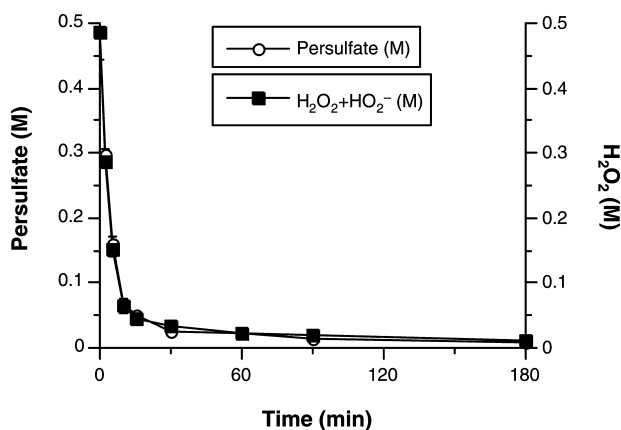


To confirm the proposed mechanism described in reactions 4–6, the reduction of persulfate by hydroperoxide, the generation of superoxide, and the stoichiometric evolution of oxygen were evaluated in base-activated persulfate systems.

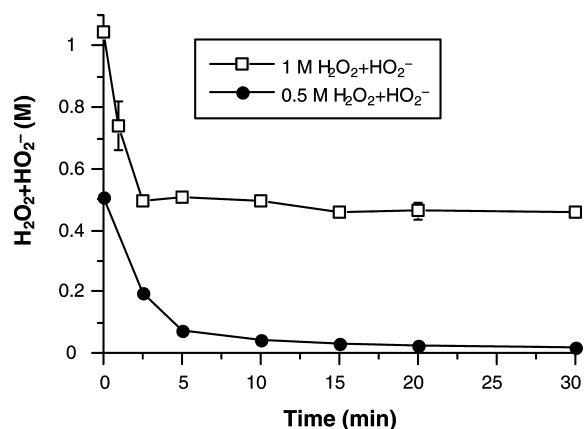
**Reduction of Persulfate by Hydroperoxide Anion.** In the proposed mechanism, hydroperoxide is generated through reaction 2; however, hydroperoxide was nondetectable by Ti(IV) sulfate complexation or ion chromatography (24). Other methods typically used to detect  $H_2O_2 + HO_2^-$ , such as iodometric titration or catalase, could not be used because of positive interference from persulfate. Persulfate decomposes relatively slowly, with a rate of  $\sim 3.3 \times 10^{-3}$  mM/min in a solution of 0.5 M persulfate and 3 M NaOH (Figure 1). Therefore, hydroperoxide would be generated through reaction 2 at approximately the same low rate; because hydroperoxide is likely consumed by reduction of persulfate at a rate significantly more rapid than its production, it is undetectable in base-activated persulfate systems. To confirm the rapid rate of reaction of hydroperoxide,  $3.3 \times 10^{-3}$  mM  $H_2O_2 + HO_2^-$  was added to a basic persulfate system (0.5 M persulfate and 3 M NaOH) and was assayed with titanium sulfate complexation; no  $H_2O_2 + HO_2^-$  was detected.

To evaluate the fate of hydroperoxide generated through base-catalyzed hydrolysis of persulfate, external hydroperoxide addition was investigated from two perspectives: 1) the fate of  $H_2O_2 + HO_2^-$  after its addition to basic persulfate systems and 2) the effect of adding excess  $H_2O_2 + HO_2^-$  on the generation of superoxide.  $H_2O_2 + HO_2^-$  concentrations decreased rapidly when hydrogen peroxide was added to basic persulfate solutions (Figure 3) with 95% loss after 15 min, confirming that hydroperoxide reacts rapidly with





**FIGURE 3.** Decomposition of persulfate and hydrogen peroxide in a 1:1 persulfate:H<sub>2</sub>O<sub>2</sub> system (reactors: 0.5 M persulfate, 0.5 M H<sub>2</sub>O<sub>2</sub>, 1.5 M NaOH; 20 mL total volume;  $T = 20 \pm 2$  °C). Error bars represent the standard error of the mean.



**FIGURE 4.** Stoichiometry for the degradation of added hydroperoxide in base-activated persulfate systems (reactors: 0.5 M persulfate, 1.5 M NaOH, 0.5 or 1 M H<sub>2</sub>O<sub>2</sub>; 20 mL total volume;  $T = 20 \pm 2$  °C). Error bars represent the standard error of the mean.

persulfate. Furthermore, both persulfate and H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> decomposed at the same rate, with >98% degradation by 180 min; because the starting masses were equivalent, the degradation stoichiometry of hydroperoxide:persulfate was 1:1. The rate of persulfate decomposition in the presence of added H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> in Figure 3 was significantly faster than that shown in Figure 1a, which is expected based on reaction

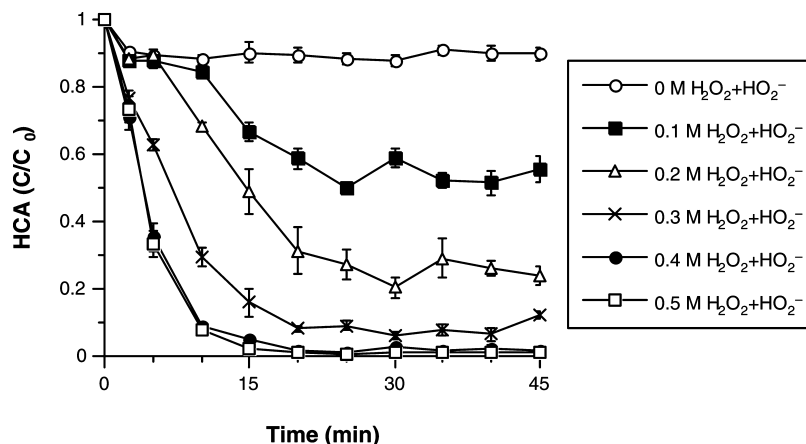
4 of the proposed mechanism in which hydroperoxide rapidly reduces persulfate.

The stoichiometry of the reaction of hydroperoxide with persulfate was further investigated (Figure 4). When 0.5 M H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> was added to 0.5 M persulfate, nearly all of the H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> was consumed over 30 min, confirming the results of Figure 3. However, when 1 M H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> was added to 0.5 M persulfate, the reaction stalled after 3 min when ~0.5 M H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> was consumed. These results confirm a molar ratio of 1:1 for the reaction of hydroperoxide with persulfate.

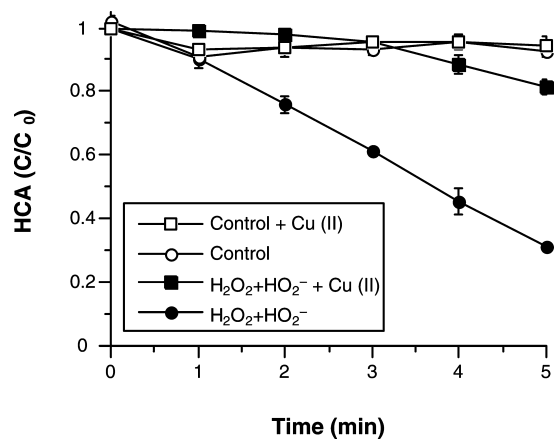
**Generation of Superoxide Anion.** The effect of increasing H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> concentrations on degradation of the superoxide probe HCA in base-activated persulfate systems is shown in Figure 5. (Hydroperoxide reacts at a negligible rate with HCA; the loss of HCA in the presence of hydroperoxide was no different than in deionized water control systems (20)). As the concentration of added H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> increased, HCA degradation increased proportionately. These results are consistent with the proposed mechanism of the oxidation of hydroperoxide to superoxide as persulfate is reduced to sulfate anion and sulfate radical; i.e., HCA degradation by superoxide proceeds in proportion to the mass of hydroperoxide added to the system.

To distinguish between reduction of HCA by superoxide and reduction of HCA by any alkyl radicals that might be formed in the system, copper(II) was used to dismutate superoxide formed in reaction 4 (21, 22) (Figure 6). Without copper addition, the superoxide probe HCA degraded 70% within 5 min. However, when 2 μM Cu(II) was added to the system, HCA degradation was only 15% after 5 min and was similar to control reactions without the addition of hydrogen peroxide. These results provide additional support that superoxide is formed in reaction 4.

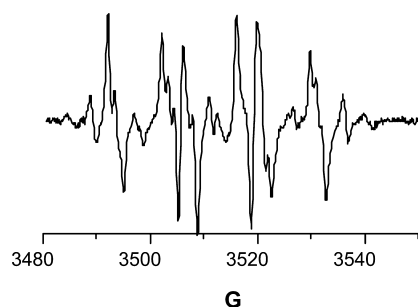
To confirm the identity of the reactive species generated in reaction 4 as well as reaction 6, ESR spectroscopy was used with DMPO as a spin trap agent to identify the radicals present in base-activated persulfate systems containing a 1:1 ratio of H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup>:persulfate. A peak for hydroxyl radical was evident in the ESR spectra (Figure 7); however, the presence of sulfate radical and superoxide was difficult to determine, likely due to low fluxes of these radicals in the system. Detection of superoxide in the system by ESR is also further limited by its low rate of reaction with DMPO ( $k = 10-18 \text{ M}^{-1} \text{ s}^{-1}$ ) (38, 39). Therefore, the software WinSim 2002 was used to analyze the ESR spectra. The simulated ESR spectra that fit the actual spectra best, with a Spearman's rank correlation coefficient of  $R = 0.97$ , included all three predicted reactive oxygen species: hydroxyl radical, sulfate



**FIGURE 5.** Relative rates of superoxide generation measured by the probe molecule hexachloroethane with varying masses of H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup> added to base-activated persulfate systems (reactors: 0.5 M persulfate, 1 M NaOH, 0–0.5 M H<sub>2</sub>O<sub>2</sub>+HO<sub>2</sub><sup>-</sup>, 2 μM HCA; 20 mL total volume;  $T = 20 \pm 2$  °C). Error bars represent the standard error of the mean.



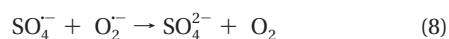
**FIGURE 6.** Effect of copper(II) scavenging of superoxide on HCA degradation in base-activated persulfate systems with added  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  (reactors: 0.5 M persulfate, 1 M NaOH, 0.5 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ , 2  $\mu\text{M}$  HCA, 0 and 2  $\mu\text{M}$  Cu(II); 20 mL total volume; controls:  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  replaced by deionized water;  $T = 20 \pm 2$  °C). Error bars represent the standard error of the mean.



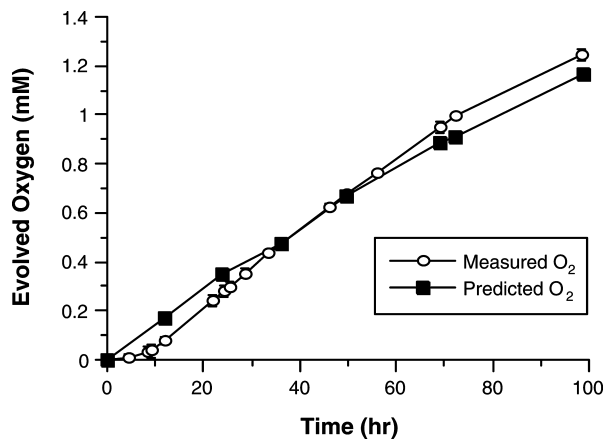
**FIGURE 7.** ESR spectrum for a base-activated persulfate system with added  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  (reactors: 0.05 M persulfate, 0.1 M NaOH, 0.05 M  $\text{H}_2\text{O}_2 + \text{HO}_2^-$ , and 0.09 M DMPO;  $T = 20 \pm 2$  °C).

radical, and superoxide. On the basis of the hyperfine splitting constant values obtained by the simulation, adducts were identified as  $\text{DMPO-OH}$  ( $A_N = 15.21$ ,  $A_H = 15.77$  gauss),  $\text{DMPO-SO}_4$  ( $A_N = 13.97$ ,  $A_H = 9.94$ ,  $A^{\beta}_H = 1.44$ , and  $A^{\alpha}_H = 0.79$ -gauss), and  $\text{DMPO-OOH}$  ( $A_N = 14.49$ ,  $A^{\beta}_H = 10.83$ ,  $A^{\alpha}_H = 1.31$ -gauss). These results are consistent with ESR spectra and hyperfine splitting constants reported for hydroxyl radical, sulfate radical, and superoxide in other studies (40, 41) and are consistent with the proposed mechanism.

**Stoichiometric Oxygen Evolution.** The final step in confirming the proposed mechanism was to quantify the stoichiometry of molecular oxygen generated from the decomposition of base-activated persulfate. The sulfate radical, superoxide, and hydroxyl radical generated in reactions 4 and 6 proceed through propagation and scavenging reactions in base-activated persulfate systems, resulting in the generation of molecular oxygen



Superoxide is likely scavenged by hydroxyl radical through reaction 7 as well as by sulfate radical in reaction 8, resulting in the generation of one mole of molecular oxygen per mole of superoxide decomposed. Because the superoxide generated through reaction 5 eventually collapses to molecular oxygen, the mass of oxygen evolved would be expected to follow the stoichiometry



**FIGURE 8.** Measured vs predicted oxygen evolution in persulfate-NaOH reactions (reactors: 0.5 M persulfate and 3 M NaOH; 12 mL total volume;  $T = 20 \pm 2$  °C). Error bars represent the standard error of the mean.

To investigate the stoichiometry of oxygen evolution during base-activated persulfate decomposition, oxygen evolution was measured in reactions with a 6:1 molar ratio of base:persulfate (Figure 8). Persulfate decomposition was also quantified in the reactions, and the predicted oxygen evolution based on the persulfate loss is also shown in Figure 8. The actual oxygen evolution correlated highly with the predicted evolution of 2 moles of oxygen per mole of persulfate decomposed ( $R_{\text{Pearson}} = 0.99$ ). The results of Figure 8 provide additional confirmation of the proposed mechanism.

The results of this research provide data that are consistent with a mechanism for the base activation of persulfate in which 1) persulfate decomposes to hydroperoxide through base-catalyzed hydrolysis, and 2) hydroperoxide reduces another persulfate molecule resulting in the formation of sulfate radical and sulfate while the hydroperoxide is oxidized to superoxide. Sulfate radical then oxidizes hydroxide, resulting in the formation of hydroxyl radical. Kinetic analyses of persulfate decomposition are consistent with its base-catalyzed hydrolysis, and hydroperoxide decomposition dynamics are also consistent with the proposed mechanism. Probe compound and scavenging studies supported the generation of superoxide in base-activated persulfate reactions, and ESR spectroscopy confirmed the presence of all three predicted species: sulfate radical, hydroxyl radical, and superoxide. One half mole of molecular oxygen was produced per mole of persulfate decomposed, which is consistent with the stoichiometry of the proposed mechanism.

Base-activated persulfate is now used extensively for the ISCO remediation of contaminated soils and groundwater. Recent findings have documented that base-activated persulfate can destroy not only compounds that react with sulfate radical and hydroxyl radical (e.g., alkenes and aromatic compounds) but also highly oxidized perhalogenated compounds as well (e.g., carbon tetrachloride) (4, 35). The mechanism proposed in this study explains the widespread reactivity of base-activated persulfate. Furthermore, understanding the mechanism of base activation of persulfate and the reactive oxygen species generated will aid in screening persulfate process conditions (e.g., base-activated persulfate vs iron chelate-activated persulfate), designing persulfate ISCO treatability studies, and determining dosages of base and persulfate for activated persulfate ISCO applications.

### Acknowledgments

The authors thank David Sedlak for discussions of superoxide dismutation using copper. Funding for this research was provided by the Strategic Environmental Research and Development Program (SERDP) through Project No. ER-1489.



## Supporting Information Available

Figure S1: effect of ionic strength on persulfate degradation rate (further supports the base-catalyzed hydrolysis of persulfate) and Figure S2: effect of varying base:persulfate ratio on the degradation rate of added  $\text{H}_2\text{O}_2 + \text{HO}_2^-$  (further supports the role of hydroperoxide in persulfate degradation). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ES1013714



# MATERIAL SAFETY DATA SHEET

Prepared to U.S. OSHA, CMA, ANSI and Canadian WHMIS Standards

## BASIC CHEMICAL SOLUTIONS

### **PART I** *What is the material and what do I need to know in an emergency?*

#### 1. PRODUCT IDENTIFICATION

**TRADE NAME (AS LABELED):** **BCS SODIUM HYDROXIDE LIQUID**  
(1% - 50%)

**CHEMICAL NAME/CLASS:** Sodium Hydroxide Solution

**PRODUCT USE:** Metal finishing, neutralization, industrial cleaners, chemical processing.

**SUPPLIER/MANUFACTURER'S NAME:** **BASIC CHEMICAL SOLUTIONS**

**ADDRESS:** **Corporate Office**  
525 Seaport Blvd.  
Redwood City, CA 94063

**BUSINESS PHONE:** 800-411-4227

**EMERGENCY PHONE:** **CHEMTREC:** 800-424-9300

**DATE OF PREPARATION:** May 7, 2003

Si usted no entiende las Hojas de Informacion de Seguridad sobre Materials, busque a alguien para que se la explique a usted en detalle.

(If you do not understand the Material Safety Data Sheet, find someone to explain it to you in detail.)

#### 2. COMPOSITION AND INFORMATION ON INGREDIENTS

CHEMICAL NAME	CAS #	%w/w	EXPOSURE LIMITS IN AIR					
			ACGIH		OSHA			OTHER mg/m <sup>3</sup>
			TLV mg/m <sup>3</sup>	STEL mg/m <sup>3</sup>	PEL mg/m <sup>3</sup>	STEL mg/m <sup>3</sup>	IDLH mg/m <sup>3</sup>	
Sodium Hydroxide	1310-73-2	1-50	2, C	NE	2, C (Vacated 1989 PELs)	NE	10	NIOSH REL: 2 DFG MAKs: 2
Water and other ingredients. The other ingredients are each present in less than 1 percent concentration in this product.		Balance	The components present in the balance of this product do not contribute any significant, additional hazards. All hazard information pertinent to this product has been presented in the remaining sections of this Material Safety Data Sheet, per the requirements of Federal Occupational Safety and Health Hazard Communication Standard (29 CFR 1910.1200).					

NE = Not Established. C = Ceiling Limit. See Section 16 for Definitions of Terms Used.

NOTE: All WHMIS required information is included. It is located in appropriate sections based on the ANSI Z400.1-1993 format.

### 3. HAZARD IDENTIFICATION

**EMERGENCY OVERVIEW:** This product is a clear to turbid liquid solution. This solution is corrosive, and can be damaging to contaminated tissue. Ingestion of large quantities can be fatal. In the event of fire or spill, adequate precautions must be taken. This solution reacts with water to generate heat. If involved in a fire, this product may decompose to produce sodium oxides and a variety of other compounds (i.e. carbon monoxide and carbon dioxide). Emergency responders must wear the proper personal protective equipment suitable for the situation to which they are responding.

**SYMPTOMS OF OVER-EXPOSURE BY ROUTE OF EXPOSURE:** This solution can damage skin, eyes, mucous membranes, and other contaminated tissue. Burns may not be immediately painful or visible.

**INHALATION:** If mists or sprays of this solution are inhaled, this product may cause pulmonary irritation, irritation of the mucous membranes, coughing, and a sore throat. Damage to the tissues of the respiratory system may occur.

**CONTACT WITH SKIN or EYES:** Severe irritation and/or burns can occur following eye exposure. Contact may cause impairment of vision and corneal damage possibly blindness. Skin contact may result in a "soapy" feel and cause reddening, discomfort, and irritation. Prolonged exposure may result in ulcerating burns which could leave scars.

**SKIN ABSORPTION:** Skin absorption is not anticipated to be a significant route of over-exposure to any component of this product.




**INGESTION:** Though ingestion is not anticipated to be a significant route of over-exposure to this product, if ingestion does occur burning and irritation of the mouth, throat, esophagus, and other tissues of the digestive system will occur immediately upon contact. Ingestion of large quantities may be fatal.

**INJECTION:** Though injection is not anticipated to be a significant route of over-exposure to this product, if it occurs, may cause local reddening, tissue swelling, and discomfort.

**HEALTH EFFECTS OR RISKS FROM EXPOSURE:** An Explanation in **Lay Terms**.

**ACUTE:** This solution is corrosive, and can burn and damage eyes, skin, mucous membranes, and any other exposed tissue. If inhaled, irritation of the respiratory system may occur, with coughing, and breathing difficulty. Though unlikely to occur during occupational use, ingestion of large quantities may be fatal.

**CHRONIC:** Repeated skin contact with this product may result in dermatitis (inflammation and reddening of the skin).

HAZARDOUS MATERIAL INFORMATION SYSTEM			
HEALTH		(BLUE)	3
FLAMMABILITY		(RED)	0
REACTIVITY		(YELLOW)	1
PROTECTIVE EQUIPMENT			D
EYES	RESPIRATORY	HANDS	BODY
	SEE SECTION 8		
For routine industrial applications			

## PART II *What should I do if a hazardous situation occurs?*

### 4. FIRST-AID MEASURES

**SKIN EXPOSURE:** If the product contaminates the skin, immediately begin decontamination with running water. Minimum flushing is for 15 minutes. Remove contaminated clothing, taking care not to contaminate eyes. Washing with large amounts of clean water should continue until affected skin surface no longer feels slippery. Victim must seek medical attention.

**EYE EXPOSURE:** If this product enters the eyes, open victim's eyes while under gentle running water. Use sufficient force to open eyelids. Have victim "roll" eyes. Minimum flushing is for 15 minutes. Do not attempt to neutralize. Oils or ointments should not be used at this time. Victim must seek immediate medical attention.

**INHALATION:** If vapors, mists, or sprays of this product are inhaled, remove victim to fresh air. If necessary, use artificial respiration to support vital functions. Remove or cover gross contamination to avoid exposure to rescuers.

**INGESTION:** If this product is swallowed, **CALL PHYSICIAN OR POISON CONTROL CENTER FOR MOST CURRENT INFORMATION**. If professional advice is not available, do not induce vomiting. Victim should drink milk, egg whites, or large quantities of water. Never induce vomiting or give diluents (milk or water) to someone who is unconscious, having convulsions, or who cannot swallow.

Victims of chemical exposure must be taken for medical attention. Rescuers should be taken for medical attention, if necessary. Take copy of label and MSDS to health professional with victim.

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## 5. FIRE-FIGHTING MEASURES

FLASH POINT, °C (method): Not flammable.

AUTOIGNITION TEMPERATURE, °C: Not flammable.

FLAMMABLE LIMITS (in air by volume, %): Lower (LEL): Not applicable.

Upper (UEL): Not applicable.

FIRE EXTINGUISHING MATERIALS:

Water Spray: YES

Carbon Dioxide: YES

Foam: YES

Dry Chemical: YES

Halon: YES

Other: Any "ABC" Class.

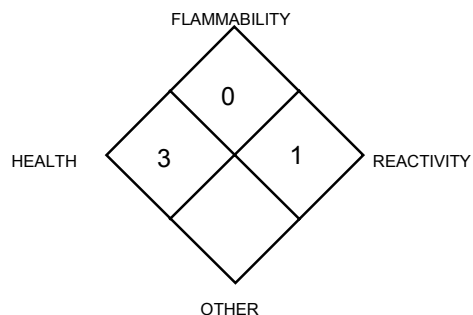
UNUSUAL FIRE AND EXPLOSION HAZARDS: Not considered flammable or combustible. Does not support combustion. However, contact with water or acids may generate sufficient heat to ignite nearby combustible materials. Contact with aluminum, tin or zinc will result in the generation of heat and release of hydrogen gas. Run-off from fire control may cause pollution. Keep fire-exposed containers cool with water spray to prevent rupture due to excessive heat. High pressure water hose may spread product from broken containers increasing contamination. When involved in a fire, this material may decompose and produce irritating fumes and toxic gases (including carbon monoxide, carbon dioxide and sodium oxides). Products of combustion are irritating to the respiratory tract and may cause breathing difficulty. Symptoms may be delayed several hours or longer depending upon the extent of exposure.

Explosion Sensitivity to Mechanical Impact: Not sensitive.

Explosion Sensitivity to Static Discharge: Not sensitive.

SPECIAL FIRE-FIGHTING PROCEDURES: Incipient fire responders should wear eye protection. Structural fire fighters must wear Self-Contained Breathing Apparatus and full protective equipment. If possible, prevent run-off water from entering storm drains, bodies of water, or other environmentally sensitive areas.

### NFPA RATING



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## 6. ACCIDENTAL RELEASE MEASURES

SPILL AND LEAK RESPONSE: Uncontrolled releases should be responded to by trained personnel using pre-planned procedures. Proper protective equipment should be used. In case of a spill, clear the affected area, protect people, and respond with trained personnel.

The proper personal protective equipment for incidental releases (e.g.-1 L of the product released in a well-ventilated area) use impermeable gloves, specific for the material handled, goggles, face shield, and appropriate body protection. In the event of a large release, use impermeable gloves, specific for the material handled, chemically resistant suit and boots, and hard-hat. Self Contained Breathing Apparatus or respirator may be required where engineering controls are not adequate or conditions for potential exposure exist. When respirators are required, Select NIOSH/MSHA approved based on actual or potential airborne concentrations in accordance with latest OSHA and/or ANSI recommendations.

Absorb spilled liquid with polypads or other suitable absorbent materials. Neutralize residue with citric acid or other caustic neutralizing agent. Decontaminate the area thoroughly. Test area with litmus paper to confirm neutralization. Place all spill residue in a suitable container. Dispose of in accordance with Federal, State, and local hazardous waste disposal regulations (see Section 13, Disposal Considerations).

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## PART III *How can I prevent hazardous situations from occurring*

### 7. HANDLING and STORAGE

WORK PRACTICES AND HYGIENE PRACTICES: As with all chemicals, avoid getting this product ON YOU or IN YOU. Wash hands after handling this product. Do not eat or drink while handling this material. Remove contaminated clothing immediately. Discard contaminated clothing items, or launder before re-use. Inform anyone handling such contaminated laundry of the hazards associated with this product. Use ventilation and other engineering controls to minimize potential exposure to this product.

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## 7. HANDLING and STORAGE (Continued)

**STORAGE AND HANDLING PRACTICES:** All employees who handle this material should be trained to handle it safely. Avoid breathing mists or sprays generated by this product. It is best to never add water to this product, always add product, with constant stirring, slowly to surface of lukewarm (80-100 °F, 27-38 °C) water, to assure product is being completely dispersed as it is added. Only trained personnel can add water to this product. Never add more product than can be absorbed by solution while maintaining temperatures below 200 °F(93 °C) to prevent boiling and spattering of caustic solution. Use in a well-ventilated location.

**For Non-Bulk Containers:** Open containers slowly, on a stable surface. Containers of this product must be properly labeled. Store containers in a cool, dry location, away from direct sunlight, sources of intense heat, or where freezing is possible. Material should be stored in secondary containers, or in a diked area, as appropriate. Store containers away from incompatible chemicals. Keep container tightly closed when not in use. Wash thoroughly after using this material. Storage areas should be made of fire-resistant materials. If appropriate, post warning signs in storage and use areas. Inspect all incoming containers before storage, to ensure containers are properly labeled and not damaged. Empty containers may contain residual liquid, therefore, empty containers should be handled with care.

**Bulk Containers:** All tanks and pipelines which contain this material must be labeled. Perform routine maintenance on tanks or pipelines which contain this product. Report all leaks immediately to the proper personnel.

**Tank Car Shipments:** Tank cars carrying this product should be loaded and unloaded in strict accordance with tank-car manufacturer's recommendation and all established on-site safety procedures. Appropriate personal protective equipment must be used (see Section 8, Engineering Controls and Personal Protective Equipment.). All loading and unloading equipment must be inspected, prior to each use. Loading and unloading operations must be attended, at all times. Tank cars must be level, brakes must be set or wheels must be locked or blocked prior to loading or unloading. Tank car (for loading) or storage tank (for unloading) must be verified to be correct for receiving this product and be properly prepared, prior to starting the transfer operations. Hoses must be verified to be clean and free of incompatible chemicals, prior to connection to the tank car or vessel. Valves and hoses must be verified to be in the correct positions, before starting transfer operations. A sample (if required) must be taken and verified (if required) prior to starting transfer operations. All lines must be blown-down and purged before disconnecting them from the tank car or vessel.

**PROTECTIVE PRACTICES DURING MAINTENANCE OF CONTAMINATED EQUIPMENT:** Follow practices indicated in Section 6 (Accidental Release Measures). Make certain application equipment is locked and tagged-out safely. Always use this product in areas where adequate ventilation is provided. Decontaminate equipment before maintenance begins by a triple-rinse with water followed, if necessary, by using caustic neutralizing agent and an additional rinse. Collect all rinsates and dispose of according to applicable Federal, State, or local procedures.

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## 8. EXPOSURE CONTROLS - PERSONAL PROTECTION

**VENTILATION AND ENGINEERING CONTROLS:** If required use a corrosion-resistant ventilation system separate from other exhaust ventilation systems to ensure that there is no potential for overexposure to sprays, or mists of this product and that exposures are below those in section 2 (Composition and Information on Ingredients). Ensure eyewash/safety shower stations are available near areas where this product is used.

**RESPIRATORY PROTECTION:** Maintain airborne contaminant concentrations below exposure limits listed in Section 2 (Composition and Information on Ingredients). If respiratory protection is needed, use only protection authorized in 29 CFR 1910.134, or applicable State regulations. If adequate ventilation is not available or if there is potential for airborne exposure above the exposure limits (listed in Section 2) a respirator may be worn up to respirator exposure limitations, check with respirator equipment manufactures recommendations/limitations. For a higher level of protection use positive pressure supplied air respiration protection or Self Contained Breathing Apparatus or if oxygen levels are below 19.5% or are unknown.

**EMERGENCY OR PLANNED ENTRY INTO UNKNOWN CONCENTRATIONS OR IDLH CONDITIONS:**

Positive pressure, full-facepiece Self Contained Breathing Apparatus; or positive pressure, full-facepiece Self Contained Breathing Apparatus with an auxiliary positive pressure Self Contained Breathing Apparatus.

**EYE PROTECTION:** Splash goggles or safety glasses. Face-shields are recommended when the operation can generate splashes, sprays or mists.

**HAND PROTECTION:** Wear appropriate gloves for routine industrial use. Use appropriate gloves for spill response, as stated in Section 6 of this MSDS (Accidental Release Measures).

**BODY PROTECTION:** Use body protection appropriate for task. Cover-all, rubber aprons, or chemical protective clothing made from natural rubber are generally acceptable, depending upon the task.

## 9. PHYSICAL and CHEMICAL PROPERTIES

Physical and chemical properties for various concentrations of **Sodium Hydroxide**, the main component of this product are as follows:

	Series			
	10	20	30	50
PHYSICAL STATE:	Liquid			
BOILING POINT @ 760 mm Hg:	110°C	113°C	119°C	140°C
FREEZING POINT:	-12°C 10°F	-26°C -14°F	0°C 32°F	12°C 53.6°F
VAPOR PRESSURE mm Hg @ 60°C:	135	110	76	13
SPECIFIC GRAVITY @ 15.6°C	1.11	1.22	1.33	1.53
DENSITY – lb-gal @ 15.6°C:	9.26	10.17	11.09	12.76
VAPOR DENSITY:	Not Determined			
EVAPORATION RATE (water = 1):	Similar to or slower than water depending upon weight percent.			
pH:	14.0 pH @ 7.5% solution			
SOLUBILITY in H <sub>2</sub> O - % by wt:	Completely Soluble			

ODOR THRESHOLD: Not available.

APPEARANCE AND COLOR: This product is a clear light straw to turbid liquid solution.

HOW TO DETECT THIS SUBSTANCE (warning properties): Litmus paper will turn blue-purple upon contact with this solution even with low concentrations.

## 10. STABILITY and REACTIVITY

STABILITY: Stable.

DECOMPOSITION PRODUCTS: Thermal decomposition products of this solution can include carbon monoxide, carbon dioxide, and sodium compounds.

MATERIALS WITH WHICH SUBSTANCE IS INCOMPATIBLE: This product reacts with strong acids. Additionally, it is incompatible with organic halogen compounds, organic nitro compounds, aluminum, zinc, tin, and other metals. Avoid contact with leather and wool. **Reactions with various food sugars may form carbon monoxide.**

HAZARDOUS POLYMERIZATION: Will not occur.

CONDITIONS TO AVOID: Avoid exposure or contact to extreme temperatures and incompatible chemicals.

## PART IV *Is there any other useful information about this material?*

## 11. TOXICOLOGICAL INFORMATION

TOXICITY DATA: Additional toxicology information for components greater than 1 percent in concentration is provided below.

### SODIUM HYDROXIDE:

Eye Irritancy (monkey) = 1% solution, 24 hr, Severe.

Skin Irritancy (rabbit) = 500 mg, 24 hr, Severe.

Eye Irritancy (rabbit) = 4 g, Mild.

Eye Irritancy (rabbit) = 1% solution, Severe.

Eye Irritancy (rabbit) = 50 :g, 24 hr, Severe.

Eye Irritancy (rabbit) = 1 mg, 24 hr, Severe.

Eye Irritancy (rabbit) = 100 mg with rinse, Severe.

Cytogenic Analysis System (grasshopper, parenteral) = 20 mg

LD<sub>50</sub> (intraperitoneal, mouse) = 40 mg/kg.

LDLo (oral, rabbit) = 500 mg/kg.



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## 11. TOXICOLOGICAL INFORMATION (Continued)

**SUSPECTED CANCER AGENT:** The components of this product's ingredients are not found on the following lists: FEDERAL OSHA Z LIST, NTP, IARC, CAL/OSHA; and therefore are not considered to be, nor suspected to be, cancer-causing agents by these agencies.

**IRRITANCY OF PRODUCT:** This product is severely irritating to contaminated tissue.

**SENSITIZATION TO THE PRODUCT:** No component of this product is known to be a sensitizer.

**REPRODUCTIVE TOXICITY INFORMATION:** Listed below is information concerning the effects of this product and its components on the human reproductive system.

**Mutagenicity:** This product is not reported to produce mutagenic effects in humans. Mutation data is available for the Sodium Hydroxide (component of this product), obtained during clinical studies on animal tissues exposed to high doses of this compound.

**Embryotoxicity:** This product is not reported to produce embryotoxic effects in humans.

**Teratogenicity:** This product is not reported to cause teratogenic effects in humans.

**Reproductive Toxicity:** This product is not reported to cause reproductive effects in humans.

*A **mutagen** is a chemical which causes permanent changes to genetic material (DNA) such that the changes will propagate through generational lines. An **embryotoxin** is a chemical which causes damage to a developing embryo (i.e. within the first eight weeks of pregnancy in humans), but the damage does not propagate across generational lines. A **teratogen** is a chemical which causes damage to a developing fetus, but the damage does not propagate across generational lines. A **reproductive toxin** is any substance which interferes in any way with the reproductive process.*

**BIOLOGICAL EXPOSURE INDICES:** Currently there are no Biological Exposure Indices (BEIs) associated with the components of this product.

**MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE** Skin disorders can be aggravated by over-exposure to this product. Inhalation of this products mists may aggravate respiratory conditions.

**RECOMMENDATIONS TO PHYSICIANS:** Treat symptoms and eliminate over-exposure to this product.

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## 12. ECOLOGICAL INFORMATION

ALL WORK PRACTICES MUST BE AIMED AT ELIMINATING ENVIRONMENTAL CONTAMINATION.

**ENVIRONMENTAL STABILITY:** The components of this product are relatively stable in the environment; they may degrade, after time, into other organic and inorganic constituents. Additional environmental data is available for the components of this product as follows:

**SODIUM HYDROXIDE:**  $K_{ow}$  = too low to be measured. Water solubility = 9 g/0.9 ml water. BOD: None.

**EFFECT OF MATERIAL ON PLANTS or ANIMALS:** This product is harmful to plant and animal life if this product is released into the environment. As with all chemicals, work practices should be aimed at eliminating environmental releases.

**EFFECT OF CHEMICAL ON AQUATIC LIFE** This product can substantially raise the pH of an aquatic environment and can be extremely toxic to fish and aquatic plants. As with all chemicals, work practices should be aimed at eliminating environmental releases. Additional aquatic data for the components of this product is available as follows:

**SODIUM HYDROXIDE:**

LC<sub>100</sub> (*Cyprinus carpio*) = 180 ppm/24 hr/25 °C

TL<sub>m</sub> (mosquito fish) = 125 ppm/96 hr (fresh water)

TL<sub>m</sub> (bluegill) = 99 mg/L/48 hr (tap water)

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## 13. DISPOSAL CONSIDERATIONS

**PREPARING WASTES FOR DISPOSAL:** Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority.

**EPA WASTE NUMBER:** D002 (Characteristic, corrosive), applicable to wastes consisting only of this solution.

## 14. TRANSPORTATION INFORMATION

THIS MATERIAL IS HAZARDOUS AS DEFINED BY 49 CFR 172.101 BY THE U.S. DEPARTMENT OF TRANSPORTATION.

PROPER SHIPPING NAME: Sodium Hydroxide solution  
HAZARD CLASS NUMBER and DESCRIPTION: 8 (Corrosive Material)  
UN IDENTIFICATION NUMBER: UN 1824  
PACKING GROUP: II  
DOT LABEL(S) REQUIRED: Corrosive

NORTH AMERICAN EMERGENCY RESPONSE GUIDEBOOK NUMBER (2000): 154

MARINE POLLUTANT: This product does not contain any components which are designated by the Department of Transportation to be Marine Pollutants. (49 CFR 172.101, Appendix B).

TRANSPORT CANADA TRANSPORTATION OF DANGEROUS GOODS REGULATIONS: THIS MATERIAL IS CONSIDERED AS DANGEROUS GOODS. Use the above information for the preparation of Canadian Shipments.

Note: The latest DOT information is provided, please verify all DOT information as it is subject to change without notice.

## 15. REGULATORY INFORMATION

SARA REPORTING REQUIREMENTS: The components of this product subject to the reporting requirements of Sections 302, 304 and 313 of Title III of the Superfund Amendments and Reauthorization Act are as follows.

COMPONENT	SARA 302	SARA 304	SARA 313
Sodium Hydroxide	No	Yes	No

SARA Threshold Planning Quantity: Not applicable.

TSCA INVENTORY STATUS: The components of this product are listed on the TSCA Inventory.

CERCLA REPORTABLE QUANTITY (RQ): Sodium Hydroxide = 1000 lbs.

OTHER FEDERAL REGULATIONS: Not applicable.

STATE REGULATORY INFORMATION: Components of this product are covered under specific State regulations, as denoted below:

**Alaska - Designated Toxic and Hazardous Substances:** Sodium Hydroxide.

**California - Permissible Exposure Limits for Chemical Contaminants:** Sodium Hydroxide.

**Florida - Substance List:** Sodium Hydroxide.

**Illinois - Toxic Substance List:** Sodium Hydroxide.

**Kansas - Section 302/313 List:** Sodium Hydroxide.

**Minnesota - List of Hazardous Substances:** Sodium Hydroxide.

**Missouri - Employer Information/Toxic Substance List:** Sodium Hydroxide.

**New Jersey - Right to Know Hazardous Substance List:** Sodium Hydroxide.

**North Dakota - List of Hazardous Chemicals, Reportable Quantities:** Sodium Hydroxide.

**Pennsylvania - Hazardous Substance List:** Sodium Hydroxide.

**Rhode Island - Hazardous Substance List:** Sodium Hydroxide.

**Texas - Hazardous Substance List:** Sodium Hydroxide.

**West Virginia Substance List:** Sodium Hydroxide.

**Wisconsin - Toxic and Hazardous Substances:** Sodium Hydroxide.

CALIFORNIA PROPOSITION 65 No component of this product is on the California Proposition 65 lists.

LABELING (Precautionary Statements): **DANGER! CORROSIVE MATERIAL! LIQUID AND MIST CAUSE SEVERE BURNS TO ALL BODY TISSUE. MAY BE FATAL IF SWALLOWED. HARMFUL IF INHALED. MAY CAUSE LUNG DAMAGE. REACTS VIOLENTLY WITH ACIDS. REACTS WITH WATER TO GENERATE HEAT. AVOID SPATTERING BY SLOWLY ADDING TO SOLUTION.** Do not get into eyes, on skin or clothing. Avoid breathing spray or mist. Do not take internally. Use with adequate ventilation and employ respiratory protection when exposed to the mist or spray. When handling, wear chemical splash goggles, face shield, rubber gloves and protective clothing. Do not transfer to unlabeled containers. Use with adequate ventilation. Wash thoroughly after handling, Keep container closed when not in use. **FIRST-AID:** In case of contact, immediately flush skin or eyes for at least 15 minutes. If inhaled, move to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Do not induce vomiting. **IN CASE OF FIRE:** Use water, dry chemical, CO<sub>2</sub>, or alcohol foam. **IN CASE OF SPILL:** Dike area to contain spill. Only trained personnel equipped full acid- protective gear should be permitted in this area. Spilled material may be absorbed into an appropriate absorbent material. Spills should be removed using a vacuum truck. Neutralize remaining traces of material with any dilute inorganic acid or citric acid and then flush with water. If necessary a liberal covering of sodium bicarbonate should then be applied and then rinsed with water. Do not wash into storm or sanitary sewer system.

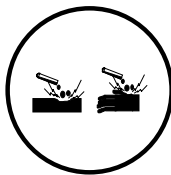
TARGET ORGANS: Skin, eyes and respiratory system.

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## 15. REGULATORY INFORMATION (Continued)

WHMIS SYMBOLS:

E- Corrosive Material



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## 16. OTHER INFORMATION

INFORMATION SOURCE:

CHEMICAL SAFETY ASSOCIATES, Inc.

PREPARED BY:

BASIC CHEMICAL SOLUTIONS

THIS INFORMATION IS DRAWN FROM RECOGNIZED SOURCES BELIEVED TO BE RELIABLE. BASIC CHEMICAL SOLUTIONS MAKES NO GUARANTEES NOR ASSUMES ANY LIABILITY IN CONNECTION WITH THIS INFORMATION. THE USER SHOULD BE AWARE OF CHANGING TECHNOLOGY, RESEARCH, REGULATIONS AND ANALYTICAL PROCEDURES THAT MAY REQUIRE CHANGES HEREIN. THE ABOVE DATA IS SUPPLIED UPON THE CONDITION THAT PERSONS WILL EVALUATE THIS INFORMATION AND THEN DETERMINE ITS SUITABILITY FOR THEIR USE.
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## DEFINITIONS OF TERMS

A large number of abbreviations and acronyms appear on a MSDS. Some of these which are commonly used include the following:

**CAS #:** This is the Chemical Abstract Service Number which uniquely identifies each constituent. It is used for computer-related searching.

### EXPOSURE LIMITS IN AIR:

**ACGIH** - American Conference of Governmental Industrial Hygienists, a professional association which establishes exposure limits.

**TLV - Threshold Limit Value** - an airborne concentration of a substance which represents conditions under which it is generally believed that nearly all workers may be repeatedly exposed without adverse effect. The duration must be considered, including the 8-hour **Time Weighted Average (TWA)**, the 15-minute **Short Term Exposure Limit**, and the instantaneous **Ceiling Level**. Skin adsorption effects must also be considered.

**OSHA** - U.S. Occupational Safety and Health Administration.

**PEL - Permissible Exposure Limit** - This exposure value means exactly the same as a TLV, except that it is enforceable by OSHA. The OSHA Permissible Exposure Limits are based in the 1989 PELs and the June, 1993 Air Contaminants Rule (Federal Register: 58: 35338-35351 and 58: 40191). Both the current PELs and the vacated PELs are indicated. The phrase, "Vacated 1989 PEL," is placed next to the PEL which was vacated by Court Order.

**IDLH - Immediately Dangerous to Life and Health** - This level represents a concentration from which one can escape within 30-minutes without suffering escape-preventing or permanent injury. The **DFG - MAK** is the Republic of Germany's Maximum Exposure Level, similar to the U.S. PEL. **NIOSH** is the National Institute of Occupational Safety and Health, which is the research arm of the U.S. Occupational Safety and Health Administration (**OSHA**). NIOSH issues exposure guidelines called **Recommended Exposure Levels (RELs)**. When no exposure guidelines are established, an entry of **NE** is made for reference.

### FLAMMABILITY LIMITS IN AIR:

Much of the information related to fire and explosion is derived from the **National Fire Protection Association (NFPA)**. **LEL** - the lowest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source. **UEL** - the highest percent of vapor in air, by volume, that will explode or ignite in the presence of an ignition source.

### TOXICOLOGICAL INFORMATION:

Possible health hazards as derived from human data, animal studies, or from the results of studies with similar compounds are presented. Definitions of some terms used in this section are: **LD<sub>50</sub>** - Lethal Dose (solids & liquids) which kills 50% of the exposed animals; **LC<sub>50</sub>** - Lethal Concentration (gases) which kills 50% of the exposed animals; **ppm** concentration expressed in parts of material per million parts of air or water; **mg/m<sup>3</sup>** concentration expressed in weight of substance per volume of air; **mg/kg** quantity of material, by weight, administered to a test subject, based on their body weight in kg. Data from several sources are used to evaluate the cancer-causing potential of the material. The sources are: **IARC** - the International Agency for Research on Cancer; **NTP** - the National Toxicology Program, **RTECS** - the Registry of Toxic Effects of Chemical Substances, **OSHA** and **CAL/OSHA**. IARC and NTP rate chemicals on a scale of decreasing potential to cause human cancer with rankings from 1 to 4. Subrankings (2A, 2B, etc.) are also used. Other measures of toxicity include **TDLo**, the lowest dose to cause a symptom and **TCLo** the lowest concentration to cause a symptom; **TDo**, **LDLo**, and **LDo**, or **TC**, **TCo**, **LCLo**, and **LCo**, the lowest dose (or concentration) to cause death. **BEI** - Biological Exposure Indices, represent the levels of determinants which are most likely to be observed in specimens collected from a healthy worker who has been exposed to chemicals to the same extent as a worker with inhalation exposure to the TLV.

### REGULATORY INFORMATION:

This section explains the impact of various laws and regulations on the material. **EPA** is the U.S. Environmental Protection Agency. **WHMIS** is the Canadian Workplace Hazardous Materials Information System. **DOT** and **TC** are the U.S. Department of Transportation and the Transport Canada, respectively. Other acronyms used are: **Superfund Amendments and Reauthorization Act (SARA)**; the **Toxic Substance Control Act (TSCA)**; Marine Pollutant status according to the **DOT**; California's Safe Drinking Water Act (**Proposition 65**); the **Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)**; and various state regulations. This section also includes information on the precautionary warnings which appear on the materials package label.