

Persulfate Oxidation of Petroleum Hydrocarbons

**Cindy G. Schreier (PRIMA Environmental,
Sacramento, California, USA)**

**Gary Cronk (Tait Environmental Management, Inc.,
Santa Ana, California, USA)**

ABSTRACT

Laboratory testing demonstrated that catalyzed sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) could degrade gasoline-range petroleum hydrocarbons (TPHg) and BTEX. $\text{Na}_2\text{S}_2\text{O}_8$ and iron citrate were added to site soil and water. Within 72 hours, 87-91% of TPHg was removed, while 82-100% of BTEX was removed. $\text{Na}_2\text{S}_2\text{O}_8$ was easy to use and did not generate noticeable amounts of heat or significant off-gases.

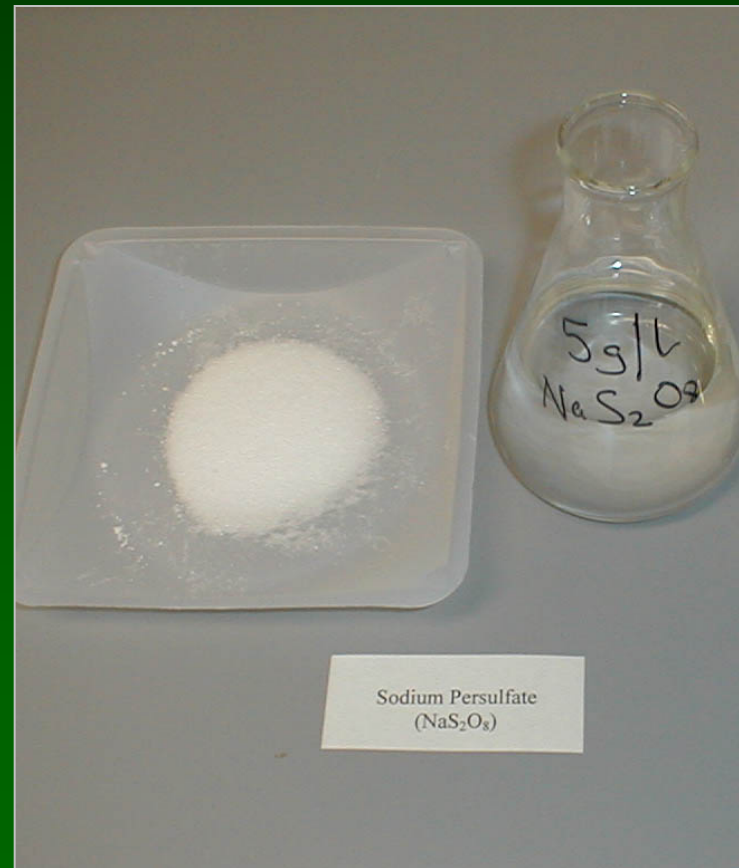
INTRODUCTION

Site Background

- **Former gasoline station in Southern California**
- **Groundwater contains up to 65,000 $\mu\text{g/L}$ of TPH-g and 2,000 $\mu\text{g/L}$ total benzene, toluene, ethylbenzene and xylenes (BTEX)**
- **Soil composed of silty sands and some clay**

Persulfate Basics

- **Strong oxidant** ($E_{1/2}=2.12\text{V}$)
- **Water soluble** (~760 g/L), granular material
- **Used extensively in manufacturing and cosmetic industries**
- **Effective toward BTEX, MTBE, chlorinated solvents** (catalyst may be required)



Persulfate Reactions

- Persulfate can oxidize compounds directly:



- Radical reactions possible with catalyzed persulfate:



- Decomposition products are sulfuric acid and/or sulfate

Factors to Consider When Evaluating Persulfate

- Contaminants are **destroyed**, not moved from one compartment to another
- Persulfate is non-selective
- **Catalyst** may be required
- Treatment may affect pH and sulfate
- Persulfate is an **emerging** remediation technology
 - Optimum dose requirements not known
 - Effect of field conditions on efficacy of oxidation uncertain

Study Objectives

- **Determine whether catalyzed persulfate can degrade TPHg and BTEX in site materials**
- **Determine appropriate catalyst dose**

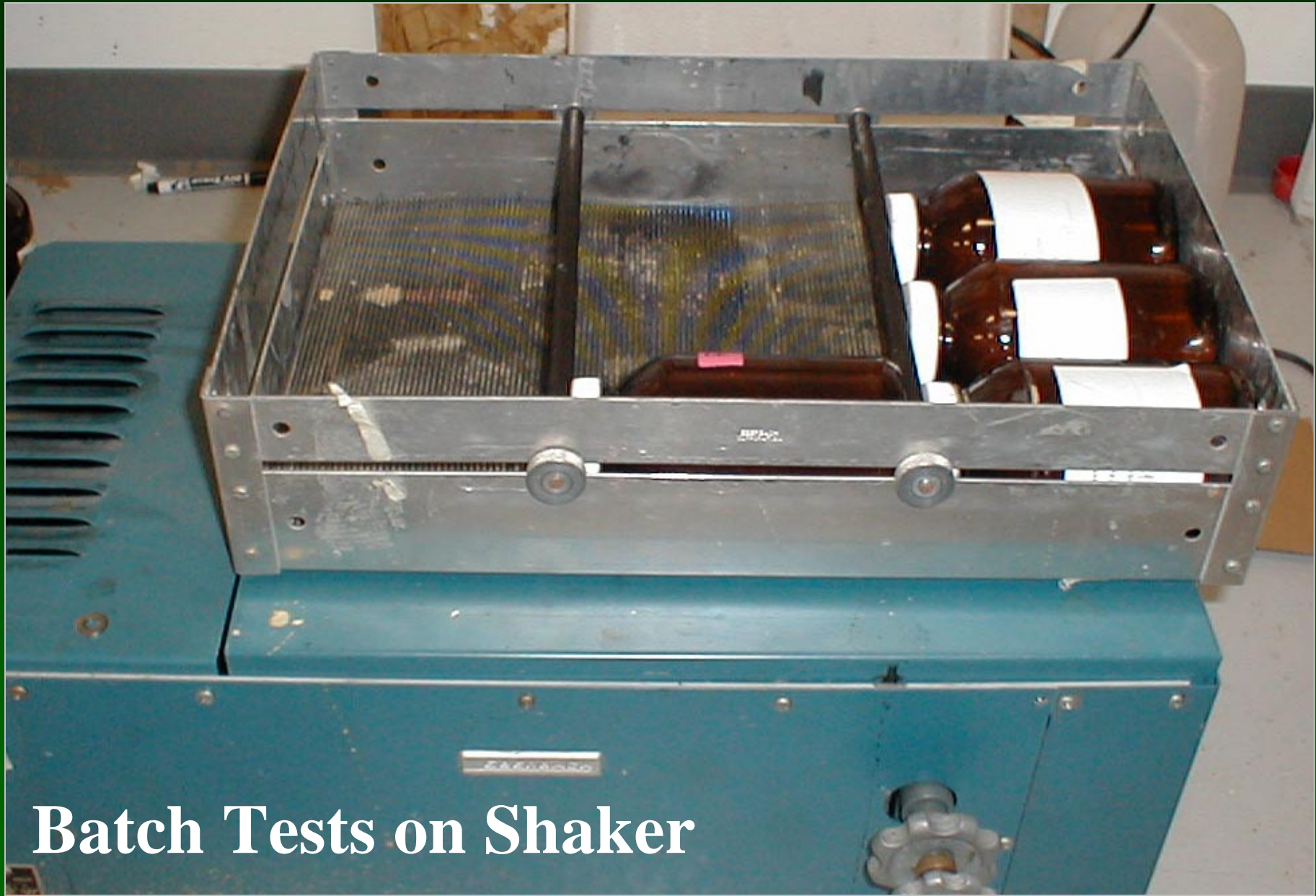
EXPERIMENTAL PROCEDURES

Batch Test Procedures

- Soil and groundwater added to amber bottle in a 4.5:1 liquid to soil ratio
- Concentrated $\text{Na}_2\text{S}_2\text{O}_8$ and iron citrate catalyst added to give initial concentrations listed in Table 1.
- Placed on shaker table and mixed for 72 hrs
- Aqueous phase analyzed for TPHg (EPA Method 8015M), BTEX (EPA Method 8260B), and pH

Table 1. Initial Test Conditions

Test	Na₂SO₄, mg/L	Iron-Citrate mg/L Fe
Control	0	0
Low Dose	5,000	140
High Dose	5,000	280



Batch Tests on Shaker

RESULTS AND DISCUSSION

- **87-91%** of TPHg was removed compared to the Control
- **99.4%** of Benzene and **100%** of toluene, ethylbenzene and xylenes removed with higher catalyst dose (280 mg/L Fe²⁺).
- **82-97%** of BTEX compounds were removed at lower catalyst dose (140 mg/L Fe²⁺)
- Both treatments reduced pH by 2-3 pH units.
- Reactions **did not generate** noticeable **heat**
- **Small amounts of off-gases were generated** as evidenced by release of pressure upon sampling

Figure 1. Effect of Treatment on TPH-g

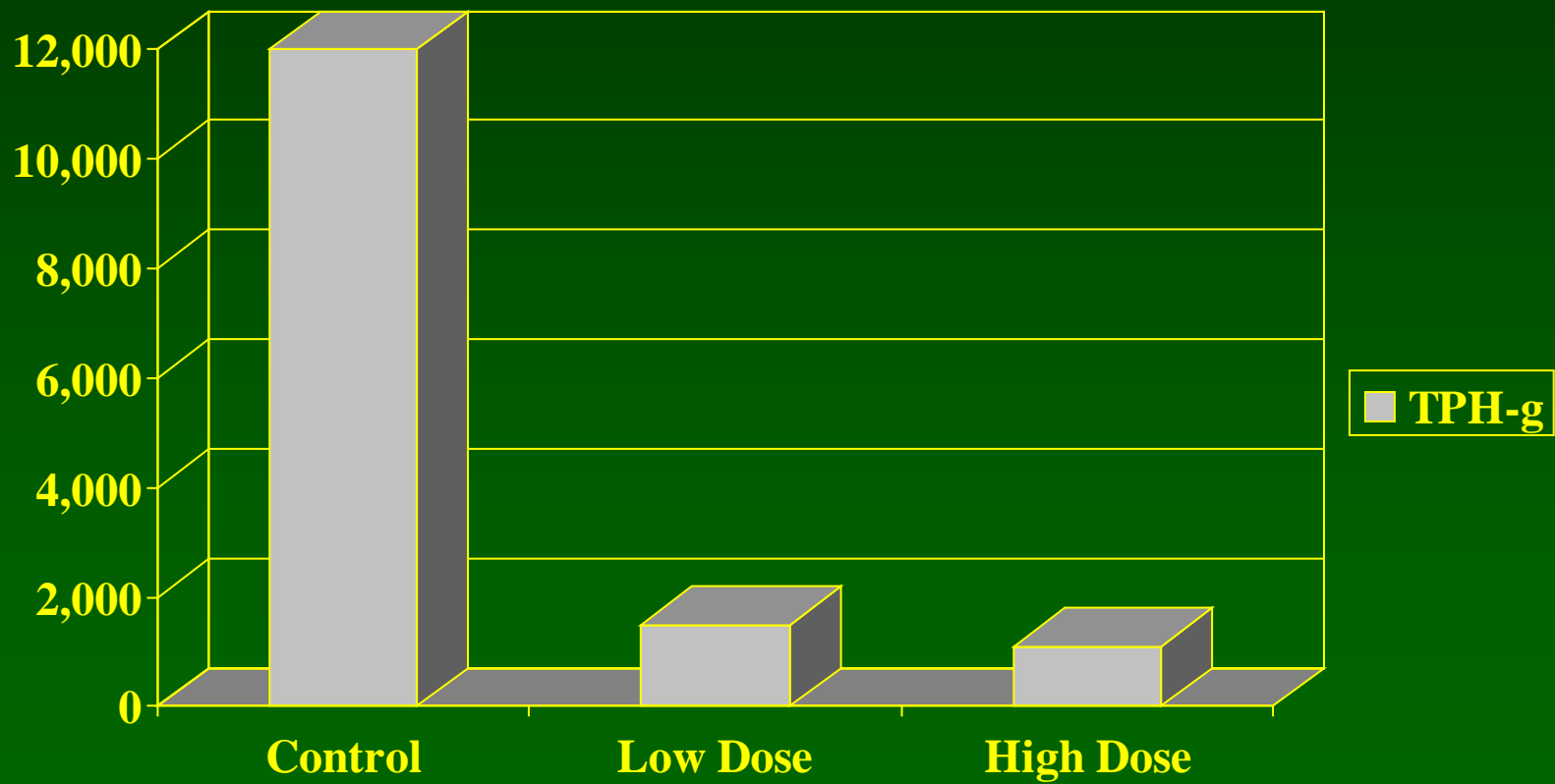


Figure 2. Effect of Treatment on BTEX

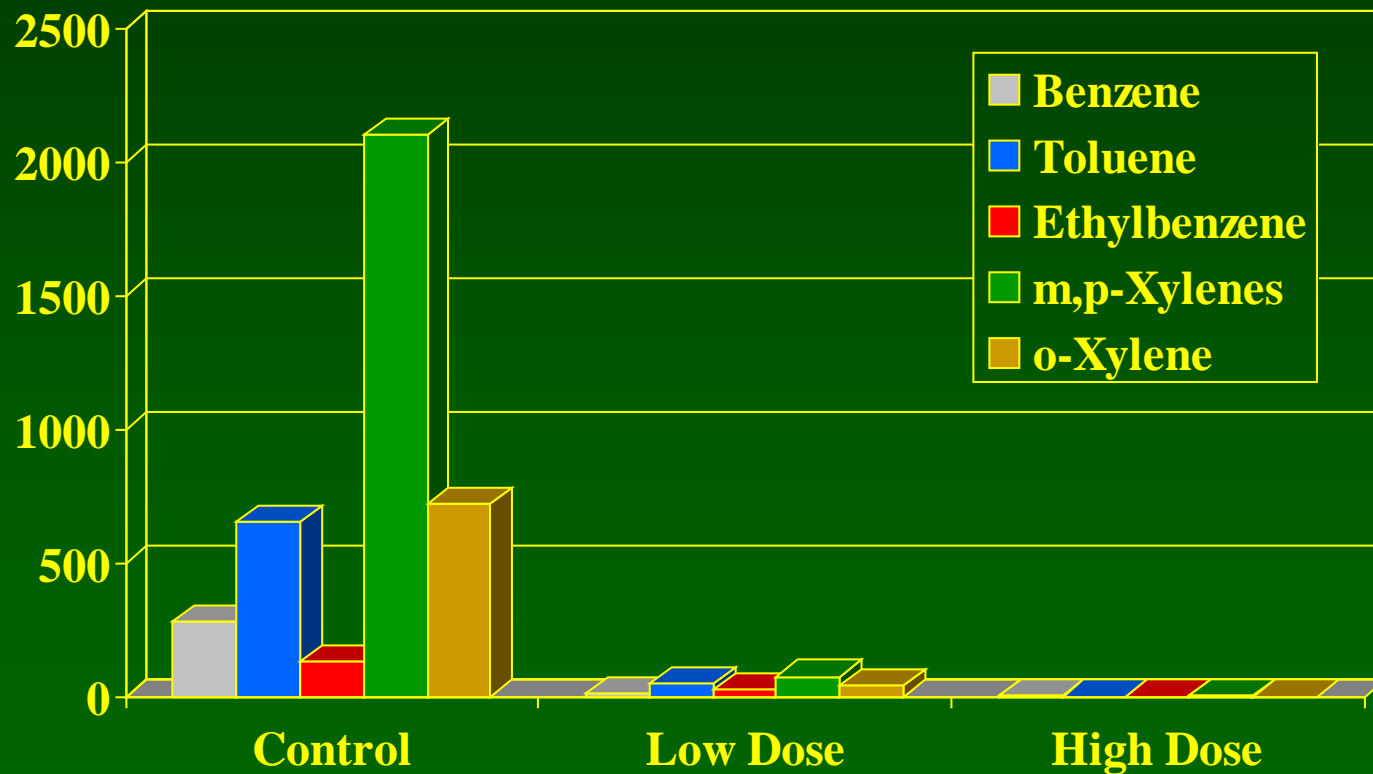
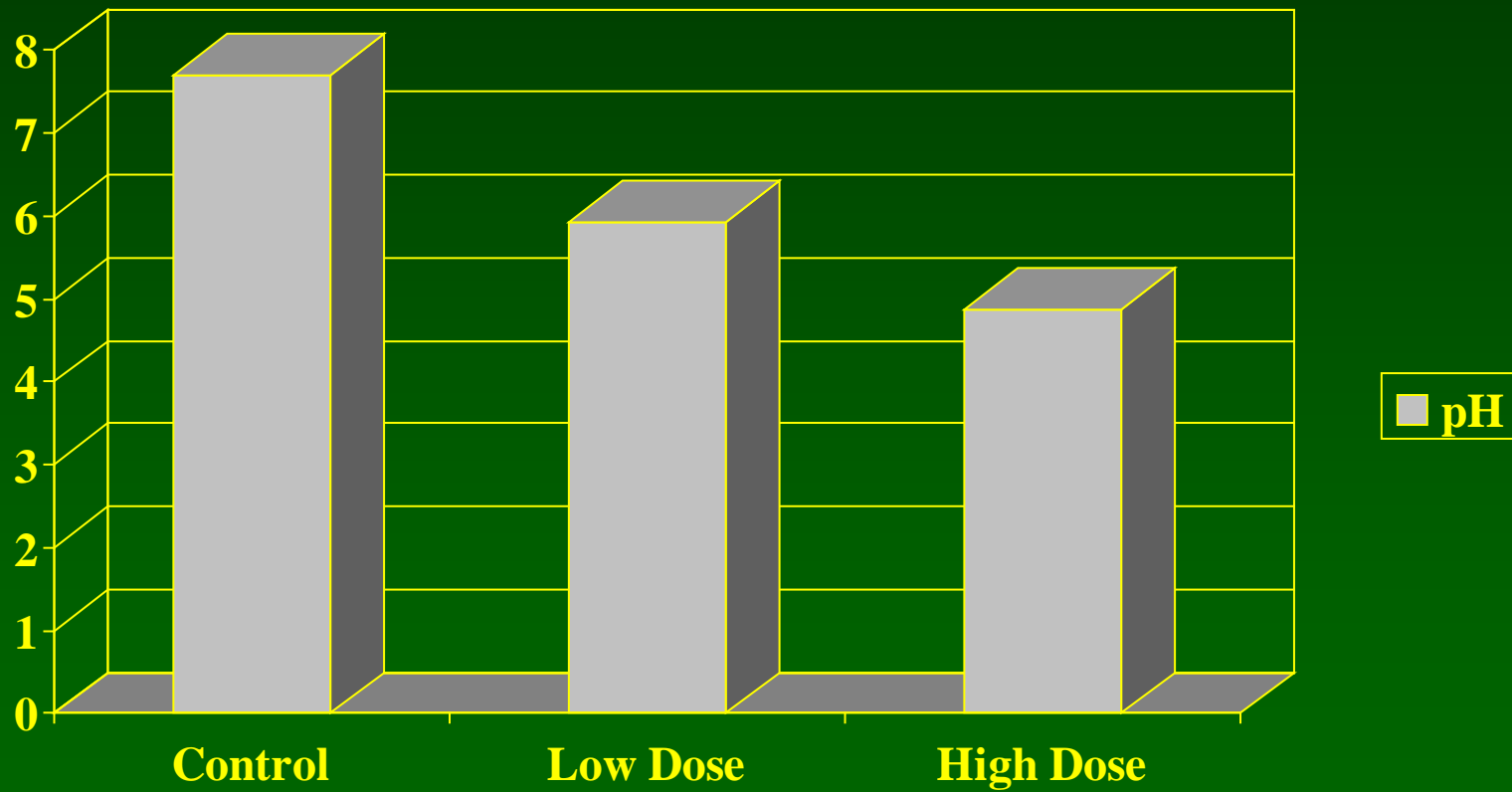


Figure 3. Effect of Treatment on pH



CONCLUSIONS

- Catalyzed persulfate **significantly reduced** the concentrations of TPH-g and BTEX from site soil and groundwater
- 280 mg/L Fe (added as iron citrate) was more effective than 140 mg/L Fe
- Catalyzed persulfate **should be added** to the list of potential *in situ* chemical oxidants because
 - it was **effective**
 - it **did not** generate noticeable heat or a significant amount of off-gas, and
 - it was **easy to use**