Application of Alkaline Activated Persulfate to Treat Petroleum Hydrocarbon Contamination Beneath the Active Construction of a 32-Story High-Rise Residential Tower

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ALKALINE ACTIVATED PERSULFATE
Introduction to Klozur® Persulfate

Klozur® Persulfate is:

• Based on the sodium persulfate molecule

• A strong oxidant used for the destruction of contaminants in soil and groundwater

• Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution

• Applicable across a broad range of organic contaminants

• Highly soluble in water (significant oxidant mass is smaller volumes)
Fundamental Chemistry

- Klozur® Activated Persulfate is based upon the persulfate anion:

\[
\text{Na}^+ \cdot \overset{\text{O}}{\text{S}} - \overset{\text{O}}{\text{O}} \cdot \overset{\text{O}}{\text{S}} - \overset{\text{O}}{\text{O}} \cdot \overset{\text{S}}{\text{O}}^3^- \cdot \text{Na}^+
\]

- Persulfate is a peroxygen, and similar to hydrogen peroxide, it can be split at the O-O bond forming the sulfate radical:

\[
\overset{\text{O}}{\text{S}} - \overset{\text{O}}{\text{O}} - \overset{\text{O}}{\text{SO}}_3^- \rightarrow \overset{\text{O}}{\text{S}} - \overset{\text{O}}{\text{O}}\cdot \cdot \overset{\text{O}}{\text{S}} - \overset{\text{O}}{\text{O}}\cdot \cdot \overset{\text{SO}}_3^-
\]
Alkaline Activation: Chemistry

- Sodium persulfate is activated when the solution is raised to pH > 10.5

- Alkaline Activation - **simple version**:  
  \[ \text{pH >10.5} \quad \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4\cdot \]

- Alkaline Activation - **complex version** (Furman et al., 2010):
  \[
  \text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow \text{HO}_2^- + 2\text{SO}_4^{2-} + 3 \text{H}^+ \\
  \text{HO}_2^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4\cdot^- + \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2\cdot^- \\
  \text{SO}_4\cdot^- + \text{OH}^- \rightarrow \text{OH}\cdot + \text{SO}_4^{2-}
  \]
  (note: $\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^- + \text{H}^+ \text{pK}_a = 11.7$)

- Complex version of the reaction results in the transient oxygen species of $\text{SO}_4\cdot^-$, $\text{OH}\cdot$, $\text{O}_2\cdot^-$, and $\text{HO}_2^-$

- Analogous to the chemistry that has been studied with catalyzed hydrogen peroxide (CHP)
SITE BACKGROUND
• Located in the Chelsea neighborhood of New York City.

• Site uses included lumber yard, metal works facility, auto-repair facility, coal yard, piano manufacture, livery car service, and gasoline station.

• Leaking underground storage tanks observed at site.
Target Area

• Approximately 6,500 ft\(^2\) (185 ft x 35 ft).

• Treatment Interval of 9 to 14 ft bgs.

• Sandy and silty-sandy material.
Contaminants of Concern

- Average Concentration of Petroleum Hydrocarbons:
  - 3,000 µg/L BTEX
  - 140 µg/L Naphthalene
  - 1,400 mg/kg GRO + DRO

- DRO and GRO up to 3,760 and 4,180 mg/kg, respectively.

- Variable GRO to DRO distribution indicated possible multiple releases.
Bench-Scale Tests

- Evaluated catalyzed hydrogen peroxide (CHP) and alkaline activated persulfate (AAP).

- CHP eliminated as peroxide decomposed rapidly even with stabilizing reagents, likely limiting subsurface distribution and resulting in rapid release of gas.

- Alkaline activated persulfate selected for effectiveness and chemical compatibility.
  - Reduced BTEX by 64-77%.
  - Reduced total TPH by 50%, with 50% percent of persulfate mass remaining.
FIELD APPLICATION
Field Application Design

- Designed based on multiple applications with emphasis on achieving remedial goals in single application.
- Injection wells installed to be accessible upon completion.
- Design called for 100,000 to 180,000 lbs of persulfate.
  - 72,700 lbs in first application
  - 60,300 lbs of 50% sodium hydroxide
  - Approximately 35,000 gallons of reagent solution (250 g/L persulfate)
- Design incorporated the RemMetrik process utilizing Wavefront technology.
Field Application Logistics

- Difficult spatial constraints from construction activities
- Temporarily closed lane of W. 28th St. each day for batching. Road was open during injection.
- Over 400 daily construction personnel
- Total access window of 9 days.
Batching
Mixing and Distribution Areas
Well Field
Field Application

• Occurred May 7 to 17, 2013

• Performed by XDD in cooperation with ZEBRA Environmental and Fleming-Lee Shue.

• 72,372 lbs of alkaline activated Klozur persulfate injected in 35,432 gallons of solution.

• Completed on schedule and within budget, with no impact to construction activities.
Groundwater Results

- Monitoring conducted approximately 5 months after the application in three quarterly events.

- BTEX and naphthalene GW concentrations decreased by 92 to 95%.

Rebound was Not Observed
Soil Results

- Soil sampled approximately 5 months after the application.
- BTEX concentrations reduced by 99.9%.

DRO/GRO Soil Concentrations were reduced by an Average of 99.2 percent
Conclusions

• Single application of alkaline activated persulfate effectively treated BTEX, DRO and GRO
  – Up to 4,000 mg/Kg DRO and GRO

• No rebound observed after 3 quarterly monitoring events.

• Site closed by NY-DEC
Questions

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