



# Combining *in situ* chemical oxidation, stabilization, and anaerobic bioremediation in a single application to reduce contaminant mass and leachability in soil



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## HIGHLIGHTS

- Portland cement and lime activated persulfate by increasing pH and temperature.
- Chemical oxidation achieved BTEX and PAH removal ranging from 55% to 75%.
- Activating persulfate with ISS amendments reduced leachability more than NaOH.
- Native sulfate-reducing bacteria degraded PAHs within weeks after ISCO finished.
- ISCO, ISS, and anaerobic bioremediation were combined in a single application.

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## ABSTRACT

Laboratory batch reactors were maintained for 32 weeks to test the potential for an *in situ* remedy that combines chemical oxidation, stabilization, and anaerobic bioremediation in a single application to treat soil from a manufactured gas plant, contaminated with polycyclic aromatic hydrocarbons (PAH) and benzene, toluene, ethylbenzene, and xylenes (BTEX). Portland cement and slaked lime were used to activate the persulfate and to stabilize/encapsulate the contaminants that were not chemically oxidized. Native sulfate-reducing bacteria degraded residual contaminants using the sulfate left after persulfate activation. The ability of the combined remedy to reduce contaminant mass and leachability was compared with NaOH-activated persulfate, stabilization, and sulfate-reducing bioremediation as stand-alone technologies. The stabilization amendments increased pH and temperature sufficiently to activate the persulfate within 1 week. Activation with both stabilization amendments and NaOH removed between 55% and 70% of PAH and BTEX. However, combined persulfate and stabilization significantly reduced the leachability of residual BTEX and PAH compared with NaOH activation. Sulfide, 2-naphthoic acid, and the abundance of subunit A of the dissimilatory sulfite reductase gene (*dsrA*) were used to monitor native sulfate-reducing bacteria, which were negatively impacted by activated persulfate, but recovered completely within weeks.

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## 1. Introduction

All site remediation technologies have inherent strengths and limitations, which has recently stimulated interest in synergistically combining multiple technologies to optimize performance and reduce costs. Combining treatment technologies can maximize the strengths and reduce or eliminate the weaknesses of individual technologies. Remedies can be combined by applying at different times or locations at a site, or by introducing amendments in a single application that simultaneously trigger multiple remediation

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processes in one location. This paper presents laboratory research on a combined remedy that can achieve *in situ* chemical oxidation (ISCO), *in situ* stabilization (ISS), and enhanced bioremediation (EB) with a single application. This specific combined remedy results in short-term reductions in both contaminant mass and leachability, and enhances the potential for long-term biodegradation.

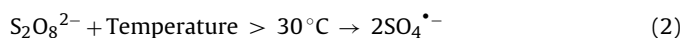
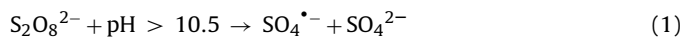
The selection of individual technologies used in a combined remedy should be based on the type and distribution of contaminants, the physical attributes of the site, and the remediation objectives or performance standards. The test soil in this study was from a former manufactured gas plant (MGP), with contaminant mass consisting primarily of polycyclic aromatic hydrocarbons (PAH) and benzene, toluene, ethylbenzene, and xylenes (BTEX). Reducing off-site contaminant migration was a priority because the area abuts the site boundary and occupied structures are present in the down-gradient direction. The primary goal was to achieve performance standards that would allow the site to be redeveloped by reducing: (1) contaminant mass, and (2) contaminant leachability, quantified using the synthetic precipitation leaching procedure (*i.e.*, SPLP, using EPA Method 1312). *In situ* soil mixing was the application chosen because contamination is relatively shallow and buildings and subsurface obstructions in the treatment zone had previously been removed.

The combined remedy developed and tested in the laboratory consisted of adding sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ , abbreviated as SPS) and ISS amendments in a single application to initiate the following sequence of processes; (1) persulfate activation by the ISS amendments, (2) chemical oxidation of a portion of the contaminant mass with the activated persulfate, (3) reduced leachability of residual contaminants *via* stabilization, and (4) long-term biodegradation of any remaining biodegradable contaminants *via* stimulation of native sulfate-reducing bacteria (SRB), which can use the residual sulfate released from persulfate activation [8]. Depending upon the remediation goals for the site, the extent of contaminant mass reduction *via* chemical oxidation and reduced leachability of remaining contaminants with stabilization can be controlled by varying the doses of SPS and/or ISS amendments [8].

ISS has been used as a stand-alone remedy to treat and redevelop many MGP, brownfield, and Superfund sites contaminated with organics [32,15]. ISS consists of adding cementitious reagents to soils that reduce physically and/or chemically the solubility, bioavailability, and leachability of the contaminants. Cementing agents (*e.g.*, Portland cement, blast furnace slag, fly ash, and lime) are commonly used. Quick lime ( $\text{CaO}$ ) in cementing agents reacts with water to precipitate slaked lime ( $\text{Ca}(\text{OH})_2$ ), which encapsulates sorbed contaminants and reduces leachability. Crane et al. [38] showed that common cementing agents reduced the leachability of BTEX and naphthalene in soil. Cementation reactions also reduce leaching by decreasing permeability, which diverts groundwater flow [15]. ISS treatment also improves soil characteristics, including unconfined compressive strength, which is desirable for geotechnical considerations related to redevelopment. Often organic contaminants at higher concentrations reduce the effectiveness of ISS by interfering with cementation reactions [36], but this limitation can be overcome with the proposed combined remedy, which degrades organic contaminants *via* chemical oxidation.

Activated persulfate is an effective ISCO technology for MGP waste, including PAHs and BTEX [29]. The persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) can be activated to form the sulfate radical anion ( $\text{SO}_4^{\bullet-}$ ) under alkaline conditions (Reaction (1)), which requires a minimum pH 10.5 and with heat (Reaction (2)), which requires a minimum temperature of 30°C [2].  $\text{SO}_4^{\bullet-}$  is a strong oxidant that degrades most organic contaminants, having an oxidation reduction potential (ORP) of 2.6 V [29]. In addition,  $\text{SO}_4^{\bullet-}$  also forms the hydroxyl radical (Reaction (3)), which has an ORP of 2.8 V. Activated persulfate has been demonstrated to oxidize PAH [37,19] and BTEX [6,17].

Normally alkaline activation is achieved with NaOH [2]. However, ISS amendments containing  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  (*e.g.*, Portland cement, blast furnace slag, fly ash, quick lime, slaked lime) increase pH and release heat upon reaction with water, which can achieve both alkaline and heat activation. Although ISS amendments have been used in the field to activate persulfate, no peer-reviewed publications could be found demonstrating this.



Persulfate activated with NaOH was also tested to simulate ISCO as a stand-alone remedy. Whereas, ISS leaves contaminants in place, ISCO degrades organic contaminants, and particularly targets the more soluble contaminants [33]. However, ISCO often requires high oxidant doses and multiple injections to achieve cleanup criteria, and the residual contaminants are not prevented from leaching. These limitations can be overcome by combining ISCO with ISS. The more soluble (and hence mobile) contaminants are preferentially oxidized, and the leachability of the contaminants not oxidized is reduced by ISS treatment [8]. Persulfate activation is typically complete within days [29], while cementation reactions associated with ISS amendments continue for weeks [15], resulting in reduced leachability over time.

The third process incorporated into this combined remedy is enhanced bioremediation using SRB. Native SRB use the sulfate (the terminal product of persulfate activation) as an electron acceptor and can degrade PAH [26,1] and BTEX [9,10,4,34]. Adding sulfate to stimulate native SRB is an effective stand-alone technology for some sites, but slow degradation rates requires years to decades to achieve cleanup criteria, during which leaching and off-site migration of contaminants would be a concern. In the proposed remedy, ISCO would degrade a large portion of the contaminants, and SRB would provide long-term degradation of contaminants after ISCO and ISS processes are complete. Sulfate is soluble enough to migrate with leached contaminants, creating a down-gradient “halo” of bioremediation by SRB [8]. The cost of bioremediation was not assessed for this site. However, bioremediation is one of the five most common treatment technologies selected for Superfund Sites [32,31]. However, when used as a stand-alone technology at MGP sites, bioremediation generally involves long treatment times [12,14].

The effectiveness of the combined remedy described above to treat the test soil was tested in a batch reactor by activating SPS with a mixture of Portland cement and slaked lime. The performance of this reactor was compared with ISCO, ISS, and bioremediation with SRB as stand-alone remedies, by maintaining reactors treated with; (1) NaOH-activated SPS, (2) ISS amendments, and (3) gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to stimulate native SRB. The reactors were monitored for 32 weeks. The pH, temperature, ORP, and persulfate concentrations were monitored to characterize persulfate activation. PAH and BTEX were measured in soil and in SPLP extracts to quantify contaminant degradation and the reduction in contaminant leachability. SRB activity was characterized by measuring concentrations of sulfide, 2-naphthoic acid, and the abundance of subunit A of the dissimilatory sulfite reductase gene (*dsrA*).

## 2. Materials and methods

### 2.1. Test soil and groundwater

Soil and groundwater samples were collected from the former Wisconsin Natural Gas–Manufactured Gas Plant Site in Racine, Wisconsin. The soil at the site is predominantly silty sand, with some

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