



Achieving synergy between chemical oxidation and stabilization in a contaminated soil



Vipul J. Srivastava^a, Jeffrey Michael Hudson^b, Daniel P. Cassidy^{b,*}

^a CH2M HILL, 125 S. Wacker, Suite 3000, Chicago, IL 60606, USA

^b Department of Geosciences, Western Michigan University, Kalamazoo, MI 49006, USA

HIGHLIGHTS

- Eight ISS amendments activated persulfate in soil by increasing temperature and/or pH.
- Activated persulfate ISCO removed 47%–84% of the BTEX & NAP, and 13%–33% PAH.
- ISS-activated persulfate reduced the leachability of BTEX & NAP by 76%–91% and of the 17 PAH by 83%–96%.
- ISCO/ISS treatment reduced contaminant leachability far more than ISCO or ISS alone.

ARTICLE INFO

Article history:

Received 11 December 2015

Received in revised form

27 March 2016

Accepted 4 April 2016

Available online 17 April 2016

Handling Editor: X. Cao

Keywords:

Combined remedies

BTEX

ISCO

ISS

Naphthalene

Persulfate

ABSTRACT

Eight *in situ* solidification/stabilization (ISS) amendments were tested to promote *in situ* chemical oxidation (ISCO) with activated persulfate (PS) in a contaminated soil. A 3% (by weight) dose of all ISS amendments selected for this study completely activated a 1.5% dose of PS within 3 h by raising temperatures above 30 °C (heat activation) and/or increasing pH above 10.5 (alkaline activation). Heat is released by the reaction of CaO with water, and pH increases because this reaction produces Ca(OH)₂. Heat activation is preferred because it generates 2 mol of oxidizing radicals per mole of PS, whereas alkaline activation releases only 1. The relative contribution of heat vs. alkaline activation increased with CaO content of the ISS amendment, which was reflected by enhanced contaminant oxidation with increasing CaO content, and was confirmed by comparing to controls promoting purely heat or alkaline (NaOH) activation. The test soil was contaminated with benzene, toluene, ethylbenzene, and xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAH), particularly naphthalene (NAP). ISS-activated PS oxidized between 47% and 84% of the BTEX & NAP, and between 13% and 33% of the higher molecular weight PAH. ISS-activated PS reduced the leachability of BTEX & NAP by 76%–91% and of the 17 PAH by 83%–96%. Combined ISCO/ISS reduced contaminant leachability far more than ISCO or ISS treatments alone, demonstrating the synergy that is possible with combined remedies.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Combining multiple remediation technologies can offer many benefits when used to exploit the strengths and minimize the weaknesses inherent in each individual technology. Synergy is realized when a combined remedy enhances remediation performance and/or reduces costs compared to individual technologies used alone. Remedies can be combined by applying reagent

amendments at different times in sequence/series (i.e. sequential technology applications), or by introducing multiple reagent amendments in a single application that trigger more than one remediation reaction (i.e. simultaneous technology application).

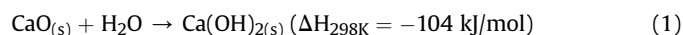
The combined remedy investigated in this work is a single application of amendments used for both *in situ* solidification/stabilization (ISS) and *in situ* chemical oxidation (ISCO), specifically activated persulfate (PS). Cassidy et al. (2015) recently documented that adding 50% Portland cement and 50% hydrated lime was able to activate PS in a contaminated soil, which chemically oxidized a significant portion of the contaminants. The sulfate released by PS activation promoted long-term bioremediation of residual contaminants by the native sulfate-reducing bacteria. The leachability

* Corresponding author.

E-mail addresses: vipul.srivastava@ch2m.com (V.J. Srivastava), jeffrey.m.hudson@wmich.edu (J.M. Hudson), daniel.cassidy@wmich.edu (D.P. Cassidy).

of the residual contaminants that were not oxidized was greatly reduced compared to treatment with ISS, ISCO, or enhanced bioremediation treatments alone.

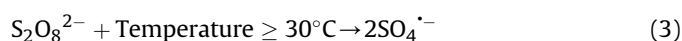
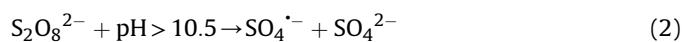
ISS has been used as a stand-alone remedy to treat and redevelop many MGP, brownfield, and Superfund sites contaminated with organics (ITRC, 2011; U.S. EPA, 2013). ISS consists of mixing cementitious reagents to contaminated soils that reduce physically and/or chemically the solubility, bioavailability, and leachability of contaminants, and improve soil characteristics (ITRC, 2011). Cementing agents containing CaO (quick lime) are commonly used. Table 1 lists the eight ISS amendments tested in this study, the abbreviation used throughout this paper for each, and the CaO content of each. Quick lime reacts with water to form hydrated lime (Ca(OH)_2) (Reaction (1)). This reaction releases a significant amount of heat (104 kJ/mol) (Cot-Gores et al., 2012) and increases the pH by generating Ca(OH)_2 . The Ca(OH)_2 from Reaction (1) also combines with silicic acid in the ISS amendment and/or the native soil to promote pozzolanic reactions, which encapsulates sorbed contaminants and reduces their leachability. Crane et al. (2014) showed that common cementing agents reduced the leachability of BTEX and naphthalene in soil. Cementation reactions also reduce leaching by decreasing the hydraulic conductivity (K), which diverts groundwater flow away from the stabilized contaminants (ITRC, 2011). ISS treatment also increased unconfined compressive strength (UCS), which is an important geotechnical consideration for redevelopment. In general, ISS does not result in contaminant stripping during mixing because it is a wet mixing process (Siegrist, 1996). Soluble organic contaminants present at high concentrations can sometimes reduce the effectiveness of ISS by interfering with cementation reactions (Zain et al., 2010). However, this limitation can be overcome with the proposed remedy because it degrades organic contaminants via chemical oxidation.



Sodium persulfate (SPS) is an effective ISCO technology for MGP waste, including PAHs and BTEX (Tsitonaki et al., 2010). The PS anion ($\text{S}_2\text{O}_8^{2-}$) is activated to form the sulfate radical anion ($\text{SO}_4^{\cdot-}$). Alkaline activation takes place at a pH above 10.5, via Reaction (2), and heat activation requires temperatures above 30 °C, via Reaction (3) (Block et al., 2004; Huang et al., 2005). $\text{SO}_4^{\cdot-}$ is a strong oxidant with an oxidation reduction potential (ORP) of 2.6 V, capable of degrading BTEX, PAHs, and many other contaminants (Tsitonaki et al., 2010). $\text{SO}_4^{\cdot-}$ can also react with water to form the hydroxyl radical (Reaction (4)), which has an ORP of 2.8 V, and also oxidizes a wide variety of organic contaminants, including BTEX and PAHs. Activated PS is a proven technology for the oxidation of PAH (Zhao et al., 2013; Liao et al., 2014) and BTEX (Crimi and Taylor, 2007; Liang et al., 2008a).

NaOH is most commonly used for alkaline activation (Block

et al., 2004). However, all the ISS amendments in Table 1 contain Ca(OH)_2 , or generate it via Reaction (1), and can therefore be used to achieve alkaline activation of PS. With the exception of hydrated lime, all the ISS amendments in Table 1 also contain CaO, and can also activate PS by the heat released in Reaction (1). Heat activation and alkaline activation can proceed simultaneously as long as both meet the minimum conditions described in Reactions (2) and (3). Heat activation is better for contaminant oxidation because it generates two moles of $\text{SO}_4^{\cdot-}$ per mole of PS (Reaction (3)), compared to one mole of $\text{SO}_4^{\cdot-}$ with alkaline activation (Reaction (2)). However, higher temperatures also promote stripping of volatile contaminants. For a given dose of ISS amendments, the higher the CaO content, the greater the increase in temperature. Hydrated lime and NaOH do not contain CaO, but can increase the temperature somewhat because of the heat released as they dissolve in water. However, the heats of hydration for both Ca(OH)_2 and NaOH are approximately 40 kJ/mol (CRC, 2015), which is significantly less than the heat released by the reaction of CaO with water (Reaction (1)).



ISCO degrades organic contaminants, particularly the more soluble contaminants (Watts and Teel, 2006; Cassidy et al., 2015). However, ISCO for source area often requires very high oxidant doses and multiple injections to achieve cleanup criteria, and the residual contaminants are not prevented from leaching. Combined technologies to overcome the limitations of ISCO has been investigated for many years when ISCO was combined with biological treatment to improve the efficiency of the combined treatment (Srivastava et al., 1994). Moreover, because chemical oxidants are generally more expensive than ISS amendments as investigated in this study, and while ISS leaves most contaminants in place, but it does reduce contaminant leachability potential and improves soil properties. The limitations of both ISCO and ISS can be minimized by combining the two technologies. The more soluble and volatile (and hence mobile) contaminants are preferentially degraded by ISCO, and the leachability of the contaminants left behind is reduced by ISS, as first shown in a CH2M HILL report to EPRI (EPRI, 2013). PS activation is typically complete within hours or days (Tsitonaki et al., 2010; Cassidy et al., 2015), while cementation reactions associated with ISS continue for weeks (ITRC, 2011), resulting in reduced leachability over time.

The contaminated soil tested in these laboratory studies was from a former manufactured gas plant (MGP) site. The contaminants were benzene, toluene, ethylbenzene, and xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAH), primarily naphthalene (NAP). The primary remediation goal was to minimize off-site migration of contaminants in groundwater and soil vapor. Of particular concern were the BTEX, and NAP, the most soluble and volatile contaminants at the site. The application selected was *in situ* soil solidification because the contamination was relatively shallow and subsurface obstructions in the treatment zone had been removed. Initial treatability studies (not presented here) were conducted to evaluate both ISS treatment and various ISCO technologies (i.e., activated PS, permanganate, and several modified Fenton formulations) as stand-alone remedies. Even though ISCO removed a considerable portion of the contaminant mass, the leachability of BTEX and NAP were not reduced sufficiently unless high, cost-prohibitive oxidant doses were used. This same

Table 1
The eight ISS amendments tested, the abbreviation used, and the CaO content.

ISS amendment	Abbreviation	CaO content ^{a,b,c} (%)
Quick Lime (CaO)	QL	100%
Ordinary Portland cement (Type I)	PC	60–68%
Lime kiln dust	LKD	50–56%
Blast-furnace slag	BFS	40–45%
Fly ash (Class C)	FAC	21–27%
Fly ash (Class F)	FAF	6–14%
Cement kiln dust	CKD	5–10%
Hydrated lime (Ca(OH)_2)	HL	0%

^a Kosmatka et al. (2002).

^b Struble et al. (2011).

^c Pacheco-Torgal et al. (2015).

Download English Version:

<https://daneshyari.com/en/article/6306728>

Download Persian Version:

<https://daneshyari.com/article/6306728>

[Daneshyari.com](https://daneshyari.com)