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## Influence of Persulfate on Solidification/Stabilization Characteristics of ISS Treatment

Jeffrey M. Hudson

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INFLUENCE OF PERSULFATE ON SOLIDIFICATION/STABILIZATION CHARACTERISTICS OF ISS  
TREATMENT

by

Jeffrey M. Hudson

A thesis submitted to the Graduate College  
in partial fulfillment of the requirements  
for the degree of Master of Science  
Geosciences  
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# INFLUENCE OF PERSULFATE ON SOLIDIFICATION/STABILIZATION CHARACTERISTICS OF ISS TREATMENT

Jeffrey M. Hudson, M.S.

Western Michigan University, 2016

Two environmental remediation technologies that lend themselves well to being combined in a single application are *In Situ* Chemical Oxidation (ISCO) using activated persulfate (PS), and *In Situ* Stabilization (ISS). Persulfate can be activated by increasing the pH to 10.5 and/or increasing temperatures to 30°C. Many common ISS amendments increase temperature to 30°C and/or pH to 10.5 when in contact with soil water. Laboratory experiments were conducted with various soils to determine the ability of eight ISS amendments to activate persulfate. All eight ISS amendments activated persulfate. This work also showed that the relative contribution of heat vs. alkaline activation increased with CaO content of the ISS amendment. Portland cement (PC) was also isolated as an ISS amendment to determine the doses of PS required to be completely activated. Ten different doses completely activated PS within 2.5 hours of mixing. After allowing 28-day curing times in all ISS treated samples, two important ISS parameters were measured and compared to background (i.e., untreated) samples; (1) unconfined compressive strength (UCS), and (2) hydraulic conductivity (K). All ISS amendments increased UCS, along with decreasing K, even when combined with PS. In addition to these parameters, testing was done to determine the effect of various doses of water, PC, and PS on soil swell of two soils. Variation of amendment dose had little to no effect on final soil swell, or variation of soil/grout workability and viscosity.

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## CHAPTER I

### INTRODUCTION

#### *Background*

Site remediation technologies are numerous and vary in application. All technologies have intrinsic strengths and weaknesses, depending on post remedial goals. Advanced urbanization and industrialization has led to the optimization and development of individual remediation technologies. Combining multiple treatment technologies can maximize strengths and minimize weaknesses of individual technologies. Multiple technologies can be applied concurrently, separately in a temporal manner, or even spatially in different locations on a site to synergistically optimize remediation goals. Enhancement of remediation goals can include improved reduction of contaminant mass or concentration, minimization of treatment time, and lowered cost associated with treatment.

When combining individual remediation technologies, specific field characteristics need to be considered in order to determine a fitting remedial strategy. Local geology, which includes soil or sediment type, governs contaminant reactions, mobility, and bioavailability. Hydrogeological parameters at a local site also impact treatment strategies. Groundwater flow can affect contaminant distribution and how a contaminant flows or disperses throughout the subsurface. If contaminated, areas with a large hydraulic gradient can often experience a large spread of contaminant, based on the rapid Darcian flow of groundwater. Furthermore, contaminants themselves play a critical role in determining an appropriate remediation strategy, due to incompatibilities associated with certain remediation technologies. For instance, solubility and mobility of a contaminant can greatly constrain treatment options for any particular pollutant.

A combined remedy of interest incorporates *in situ* stabilization (ISS) and *in situ* chemical oxidation (ISCO). This remedy results in short-term reductions in both contaminant mass and leachability. A reduction in treated contaminant mass through chemical oxidation occurs using ISCO reagents. ISS amendments then improve soil characteristics by reducing permeability and hydraulic conductivity (K), which can address and inhibit potential off site migration of contaminants via contaminant leachability. Treatment also increases unconfined compressive strength (UCS) of soil. Post remediation processes also have the potential for long-term enhanced biodegradation (Cassidy et al., 2015). Combining the two processes can improve time spent on site remediation, and improve costs associated with treatment.

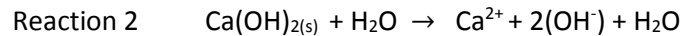
#### *In Situ Solidification/Stabilization (ISS)*

*In situ* solidification/stabilization techniques have long been utilized in the environmental remediation industry as a stand-alone remedy to redevelop many MGP, brownfield, and U.S. EPA Superfund sites (ITRC, 2011). ISS amendments, which can include Portland cement, fly ash, lime kiln dust, and lime, are used primarily to treat sites with shallow soil contamination (between 15-30 m) composed mainly of metals. Although organic wastes were initially thought to be detrimental to ISS functionality (Eaton et al., 1986; M. C. Lo, 1986), increasing attention has been appropriated to the ability of ISS amendments to remediate other common MGP site contaminants, which include organics like PAH's and BTEX monoaromatics (Crane et al., 2014; Cassidy et al., 2015, Paria and Yuet, 2006). ISS remediation is a frequently used and attractive technology due to associated low treatment costs and the relatively easy application of this technology in the field.

Stabilization additives are mixed physically with water and then mixed into contaminated soils via augers or other soil mixing equipment on site. Cementing agents reduce

the solubility, bioavailability, and mobility of contaminants in soils, both physically and chemically. In a physical sense, cementing agents encapsulate contaminants in a solid medium that reduces contaminant interaction with water in soil pore spaces. This encapsulation also reduces leaching of water through the soil medium due to reduced permeability and hydraulic conductivity (K), which diverts groundwater flow (ITRC, 2011). Due to physical encapsulation of the soil contaminants after mixing, geotechnical soil characteristics are also improved due to an increase in unconfined compressive strength (UCS).

Most ISS cementing agents, such as Portland cement, are composed of a significant percentage of lime (CaO) (Table 1). Chemically, lime in cementing agents reacts with water to precipitate slaked, or hydrated lime (Ca(OH)<sub>2</sub>) (Cassidy et al., 2015) [Reaction 1].



The addition of water generates large amounts of heat, due to the creation and destruction of chemical bonds during cement reactions. This heat dissipates after 36 hours, although complete cementation reactions associated with ISS amendments may continue for weeks (ITRC, 2011). Reaction pH also rises quickly over 12 due to the release of hydroxide anions as this acid-base reaction proceeds [Reaction 2]. Alkaline soils could inhibit Reaction 1 due to the buffering capacity of CaCO<sub>3</sub>, resulting from disseminated source material, such as limestone. Additionally, leached water containing Ca<sup>2+</sup> from disseminated CaCO<sub>3</sub> could also inhibit Reaction 1. Treated water with Ca<sup>2+</sup> would be less likely to yield Ca(OH)<sub>2</sub> in Reaction 1 due to a shift in reaction equilibrium. In order to compensate for alkalinity and hardness, more alkaline ISS amendment would need to be applied.

Following reactions, precipitated hydrated lime then coats the surface of soil particles that already contain sorbed organic contaminants, blocking these organics from water access, which reduces contaminant leaching. ISS effectively encapsulates contaminants and prevents further mobility and interaction with pore water. Cementing agents do not chemically absorb or alter organic contaminants. Therefore, ISS technologies are ineffective against organic contaminants in a dissolved or nonaqueous phase liquid (NAPL) form. Also, it is well established that organics, particularly petroleum hydrocarbons, can interfere with the setting time and properties of cements used in ISS (Eaton et al., 1986; M. C. Lo, 1986, Coz et al., 2009). This issue is typically resolved by adding more amendment on a weight basis, although organic contaminants still remain unaltered and are only immobilized.

One final characteristic of ISS treatment is the occurrence of soil swell. Most soils swell naturally when inundated with water, which is primarily related to a soil's clay content (Basma and Tuncer, 1991). Upon the addition of ISS amendments to a soil, soils can increase in size volumetrically. Volumetric increase in soil can have a detrimental effect on treatment strategy, due to cost associated with an increase in treated soil volume. Many ISS amendments containing lime (CaO) are added in order to combat natural swell (Basma and Tuncer, 1991).

#### *In Situ Chemical Oxidation (ISCO) with Persulfate (PS)*

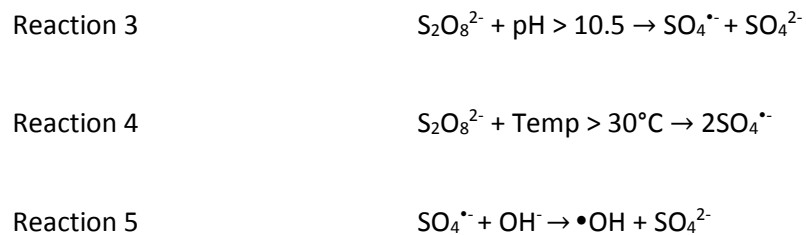
Like ISS technologies, *In Situ Chemical Oxidation* (ISCO) is a proven technology that is used in the field. ISCO involves the injection of a chemical oxidant or oxidants into a contaminated subsurface to transform an organic contaminant into harmless by-products upon contact. Upon contact with a contaminant, injected chemical reagents induce redox reactions. These reactions produce a series of products that include free radicals with high redox

potentials. These radicals break down organics into byproducts, such as carbon dioxide and water.

ISCO processes react quickly and are used to treat source contamination, usually highly concentrated contaminant plumes that exist in an aqueous phase in the saturated zone or the capillary fringe. Hydrogen peroxide, permanganate, ozone, and persulfate are four common oxidants used in ISCO, each having intrinsic strengths and limitations. Oxidant choice during treatment depends on cost, feasibility, and the local natural constraints within the system being treated for contamination. ISCO demands contaminant contact in order for contaminant degradation to occur, and ISCO treatment can be unfavorable when dealing with hydrophobic or lipophilic contaminants that are sorbed onto soil particles; i.e. not in aqueous phase. Oxidants can also react with natural soil constituents that exist in the native soil, such as iron, or elements of soil organic matter, before they reach contaminants (Huling, Pivetz, 2006). Furthermore, certain oxidation reactions, particularly catalyzed hydrogen peroxide (Fenton's/Modified Fenton's Reagent) occur very rapidly due to soil matrix elements. These reactions can terminate by the time they actually travel through the soil substrate and reach the target contaminants (Huling, Pivetz, 2006).

Persulfate (PS) is an emerging oxidant that is utilized for ISCO due to favorable characteristics. Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8^{2-}$ ) is advantageous in application, due to low cost (\$1.20/lb (Brown and Robinson, 2004)), and high solubility (73g/100g  $\text{H}_2\text{O}$  at 25°C) (Huling, Pivetz, 2006). PS is also denser than water, making density driven transport in the subsurface possible (Huling, Pivetz, 2006). Stability of PS in the subsurface is higher than other chemical oxidants, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ozone ( $\text{O}_3$ ) and has a low natural oxidant demand, allowing it to persist for weeks in the subsurface (Huang et al., 2002). Chemically, the

persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) can be activated via several mechanisms to form a sulfate anion radical ( $\text{SO}_4^{\bullet-}$ ). The sulfate anion radical is a strong oxidant with a high oxidation reduction potential (ORP) of 2.6, making it one of the strongest oxidants in all ISCO treatments (Huling, Pivetz, 2006). Traditionally, catalysis of persulfate has been achieved with ferrous iron ( $\text{Fe(II)}$ ) (Ahmad et al., 2010), Fe-EDTA complexes (Ahmad et al., 2011), photo (UV) activation (Huling, Pivetz 2006), and base activation via NaOH (Furman et al., 2010). Alkaline activation of PS can also be achieved when pH is greater than 10.5 [Reaction 3]. Another mechanism of persulfate activation is heat activation, which requires a minimum temperature of 30°C [Reaction 4]. Furthermore,  $\text{SO}_4^{2-}$  has the ability to react with a hydroxide anion to form a hydroxyl radical ( $\bullet\text{OH}$ ) [Reaction 5].



Hydroxyl radicals have an ORP of 2.8, making it yet another strong oxidant that can treat organic contaminants along with sulfate anion radicals. Stoichiometrically, heat activated persulfate [Reaction 3] is considered to be more favorable for contaminant reduction due to the production of two sulfate anion radicals per every persulfate anion (Srivastava et al., 2015).

#### *Combining ISS/ISCO*

ISS amendments containing quicklime ( $\text{CaO}$ ) or  $\text{Ca(OH)}_2$  have been shown to both increase pH above 10.5 and raise temperature to 30°C or above upon interaction with water (Cassidy et al., 2015) (Block, 2012). Portland cement and other common ISS amendments, such as fly ash, lime kiln dust, and lime, can therefore achieve alkaline and heat activation of

persulfate upon addition of water, making them candidates for simultaneous application with persulfate. Combining *in situ* solidification/stabilization additives with persulfate ( $S_2O_8^{2-}$ ) has in fact been shown to be effective in bench-scale and field studies (Cassidy, 2015) (Block, 2012), whereas several treatment goals are achieved:

1. Persulfate activation via ISS amendments ( $pH > 10.5$ ,  $30^\circ C$ )
2. Chemical oxidation of a portion of organic contaminants in aqueous phase
3. Reduced leachability of other contaminants via *in situ* stabilization
4. Improved soil characteristics (UCS, lower K)

Furthermore, long term biodegradation of any contaminants remaining after ISS/ISCO treatment has been shown to occur in laboratory studies. Residual sulfate released from initial persulfate activation has the ability to stimulate native sulfate-reducing bacteria, which can further degrade organic contaminants within the soil matrix (Cassidy et al., 2015). Combining ISS/ISCO technology not only allows for potential contaminant remediation, but overall improvement in soil characteristics. Due to the synergy demonstrated by using the persulfate reagent with ISS treatment, combining these two scenarios appears to be a useful, new remediation technology for soils, and appeared to be worthwhile for investigation within this study, as well as further future investigations in bench-scale and field settings.

### *Purpose of Study*

An in depth investigation was performed to determine how combining sodium persulfate with different ISS amendments effected persulfate activation, as well as two final ISS treatment parameters, hydraulic conductivity (K) and unconfined compressive strength (UCS). Quicklime (QL), ordinary Portland cement (PC), lime kiln dust (LKD), blast-furnace slag (BFS), fly ash – class C (FAC), fly ash – class F (FAF), cement kiln dust (CKD), and hydrated lime (HL) were



the eight ISS amendments examined. Additionally, ordinary (Type 1) Portland cement (PC) was isolated and investigated individually as an ISS amendment. The objective of this was to quantify the ability of a wide range of doses of PC to activate PS, and to observe the effect of dose amount on two ISS performance parameters, unconfined compressive strength (UCS) and hydraulic conductivity (K). Grout mixtures of all ISS cementing agents were mixed and allowed to cure for a typical ISS cementing reaction period (28 days). Following curing periods for all reaction scenarios (those involving the eight ISS amendments, those involving PC), UCS and hydraulic conductivity were measured. In addition to these ISS parameters, bench scale testing was completed to determine appropriate and relatable grout mixtures of Portland cement, persulfate, and water that are easy for practitioners to handle in the field. Measurements that were made included slump cone testing of soil-grout mixtures and Marsh funnel testing of grout viscosities. Finally, soil swell was observed upon the addition of the stand-alone ISS and PS/ISS mixtures to soils. Swell measurements were observed to determine if the addition of the PS anion created any change in swell in comparison with stand-alone ISS amendment treatment.

## CHAPTER II

### MATERIALS AND METHODS

#### *Test Soils*

Soil samples used in this study were collected from two former manufactured gas plant (MGP) sites, one located in Racine, Wisconsin, and the other located in Ashland, Wisconsin. The Racine soil was predominantly composed of sand and gravel, while the Ashland soil was a finer grained soil composed of a silt majority (Figure 1). The soil was sieved to remove particles larger than 0.5 cm in diameter and homogenized to ensure that different batches of ISS amendments tested would be used on similar contaminant concentrations. The particle size distribution of the homogenized soils after being sieved was 67% sand ( $>0.063\text{mm}$ ), 31% silt ( $0.002\text{ mm}-0.063\text{ mm}$ ), and 4% clay ( $<0.002\text{ mm}$ ) for the Racine soils, and 33% sand ( $>0.063\text{mm}$ ), 45% silt ( $0.002\text{mm}-0.063\text{ mm}$ ), and 4% clay ( $<0.002\text{ mm}$ ) for the Ashland soil.

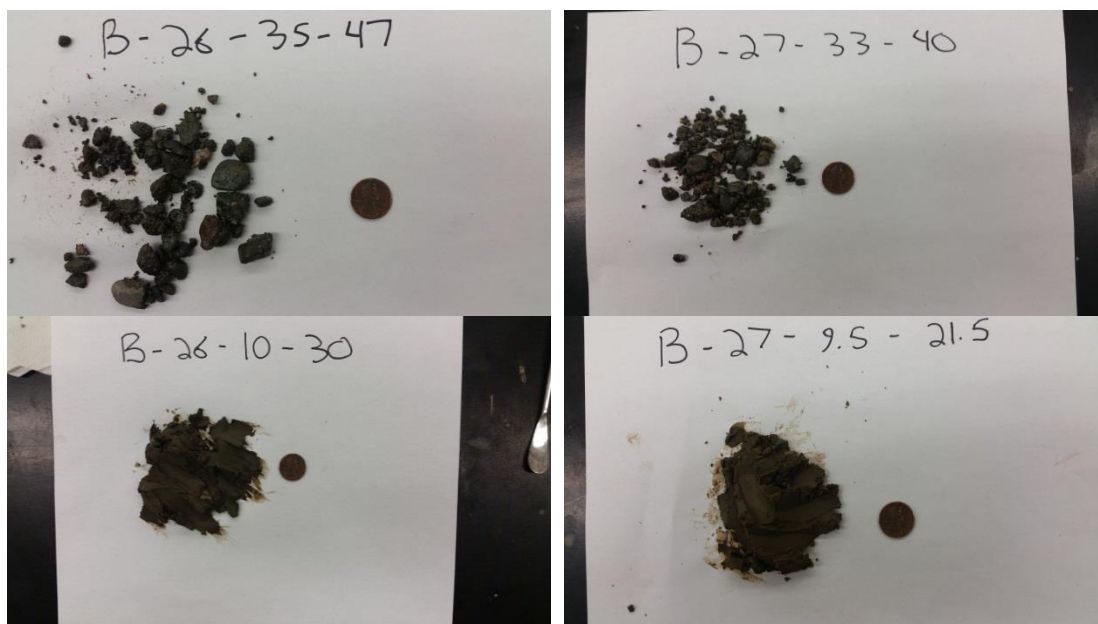


Figure 1. Soils tested: Racine soil on top, Ashland soil on bottom

### *ISS Amendments and Persulfate*

Eight different ISS amendments with varying CaO contents were used in this study (Table 1). The amendments used were quicklime (QL), Portland cement (PC), lime kiln dust (LKD), blast-furnace slag (BFS), class C fly ash (FAC), class F fly ash (FAF), cement kiln dust (CKD), and hydrated lime (HL). Additionally, ordinary Portland cement (PC) was investigated individually. Sodium persulfate was also used throughout this study, both as a stand-alone amendment, and in mixture with ISS amendments.

Table 1. Eight ISS amendments tested, abbreviation, CaO content

<b>ISS Amendment</b>	<b>Abbreviation</b>	<b>CaO Content(%)</b>
Quick Lime (CaO)	QL	100%
Ordinary Portland Cement	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) <sub>2</sub> )	HL	0%

Kosmatka et al. (2002), Struble et al. (2011), Pacheco-Torgal et al. (2015)

### *Mixing Reactors*

Mixing reactors were used to mix soil, water, and amendments of varying dose (Tables 2, 3, 4). Bench scale use of mixing reactors was able to effectively mimic field scale application of ISS/ISCO technology on a much smaller scale. Field-scale soil mixing involves larger mixing equipment, such as augers or other heavy equipment in order to mix alkaline ISS amendments with persulfate. Laboratory reactors were 2.5 L closed, glass vessels with lids containing a central port and three peripheral ports (Figure 2). The central port housed the shaft of a

propeller attached to an IKA Eurostar 200 mixer, which represented larger-scale equipment used in field mixing. The mixer was set at 200 rpm to blend the soils and homogenize the soils and reactor amendment contents. On the reactors, one of the peripheral ports contained a check-valve to allow gas to escape the reactor but none to enter. Gas released from this port was issued through a Tenax® Anasorb tube to capture volatilized contaminants, although data from those parameters was omitted from this study. The second peripheral port was used for sampling reactor contents and inserting pH and temperature probes. The third peripheral port was kept closed with a rubber stopper to prevent gas escape from the mixing vessel.



Figure 2. 2.5 L reaction vessels

Each reactor contained 3 kg of dry weight soil. The water content of the homogenized soil was 10%. In addition to the 0.33 L of retained soil water, 0.67 L of tap water was added, bringing the total water volume to approximately 1 L. Table 2 lists 20 reaction scenarios tested for the eight ISS amendments. Table 2 also lists the doses of PS ( $\text{S}_2\text{O}_8^{2-}$ ), ISS amendment, and NaOH added. The ISS amendment doses in Table 2 are on a weight basis (wt. amendment/wt. dry soil), and were added directly to the soil and water already mixing in the reactors. Previous

screening studies that had been conducted (data not shown) had established that the dose of PS tested (1.5%) was completely activated by the dose of each ISS amendment (3%). The control reactor had no ISS amendments or PS added to the soil and water mixes. The reactors that received PS were first dosed with PS, and then mixed for 30 minutes to allow the PS powder to completely dissolve before starting the activation reactions by adding ISS amendments. These reactors received 45 g of sodium persulfate, which yields a concentration of PS ion ( $\text{S}_2\text{O}_8^{2-}$ ) of approximately 36 g/L when dissolved in the water in the reactors (Srivastava et al., 2015). To test the effect of unactivated PS on the soil, one reactor received PS without any activator. To test the effectiveness of activated PS as a stand-alone ISCO technology, the NaOH-PS reactor was dosed with PS and used NaOH as an activator, added in solid form. NaOH is often used as an alkaline activation method for persulfate (Block et al., 2004). Eight combined remedy treatments were tested using the ISS amendments listed in Table 1 to activate PS. Eight ISS-only treatments were also tested as stand-alone methods by omitting PS doses in these individual reactor scenarios.

The amendments were mixed into the soil and water for 3 hours within the reactors. During mixing, time samples of pH and temperature were taken and monitored by inserting probes into reactors in order to track these two conditions that control PS activation. All the mixing reactors were sampled and monitored in the exactly same manner. The reactors with ISS amendments but no added PS were also monitored for temperature, and pH.

Table 2. Reaction scenarios of 8 ISS amendments tested, corresponding reaction names, and amendment dose (amendment weight/dry soil weight)

Reaction Scenario	Reactor Name	PS(%)	ISS(%)	NaOH (%)
Control (nothing added)	Control	0	0	0
Unactivated PS	PS	1.5	0	0
NaOH-activated PS	NaOH-PS	1.5	0	3
Heat-Activated PS	Heat-PS	1.5	0	0
QL-activated PS	QL-PS	1.5	3	0
PC-activated PS	PC-PS	1.5	3	0
LKD-activated PS	LKD-PS	1.5	3	0
BFS-activated PS	BFS-PS	1.5	3	0
FAC-activated PS	FAC-PS	1.5	3	0
FAF-activated PS	FAF-PS	1.5	3	0
CKD-activated PS	CKD-PS	1.5	3	0
HL-activated PS	HL-PS	1.5	3	0
QL	QL	0	3	0
PC	PC	0	3	0
LKD	LKD	0	3	0
BFS	BFS	0	3	0
FAC	FAC	0	3	0
FAF	FAF	0	3	0
CKD	CKD	0	3	0
HL	HL	0	3	0

After 3 hours, the contents of the mixing reactors were transferred to concrete test cylinders (7.6 cm ID x 15.2 cm L, and compliant with ASTM C31 and ASTM C39), where the treatment reactions continued. After a 28 day curing period within the cylinders, the treated soil samples were then analyzed for hydraulic conductivity (K), and unconfined compressive strength (UCS), important geotechnical parameters that govern ISS treatment.

Furthermore, another 22 reactor scenarios were created to determine the effect of varying ISS amendment dose on PS activation and ISS treatment characteristics. Unlike previous

reactors, which investigated eight different ISS amendments, ordinary (Type 1) Portland cement was isolated and tested at various doses to determine PS activation. Reactor scenarios were similar to the aforementioned setup, where each reactor was charged with 3 kg of soil (dry weight). The water content of the homogenized soil was 10%. In addition to the 0.33 L of retained soil water, 0.67 L of tap water was added, bringing the total water volume to approximately 1 L. Table 3 lists 22 reaction scenarios tested with PC, the reactor names, and the doses of PS and PC used. The amendment doses are on a weight basis (wt. amendment/wt. dry soil), and were added directly to the slurry in the reactors. Srivastava et al. (2015) and screening studies established that a ratio of PC:PS equal to 2:1 achieved complete activation of PS in this soil. A negative Control reactor had nothing added to the soil and water. The reactors that received PS were first dosed with PS, and then mixed for 30 minutes to allow the PS powder to completely dissolve before initiating activation by adding PC. To serve as a control for the effect of unactivated PS on the soil, one reactor received 5% PS without any activator. There were ten reaction scenarios testing the combined ISCO/ISS remedy, with PS doses ranging from 0.25% to 5%, and PC doses ranging from 0.5% to 10%. There were also ten reaction scenarios with the same range in ISS doses, but without added PS, to test ISS as a stand-alone treatment.

The amendments were mixed into the soil and water for 3 hours, during which time samples were taken to measure PS ( $S_2O_8^{2-}$ ) concentrations to monitor activation. All the mixing reactors were sampled and monitored in the exactly same manner. The reactors with ISS amendments but no added PS were also monitored for PS concentrations. After 3 hours, the contents of the mixing reactors were transferred to four concrete test cylinders (7.6 cm ID x 15.2 cm L, and compliant with ASTM C31 and ASTM C39), where the treatment reactions continued. After 28 days of curing in the cylinders, samples were analyzed for hydraulic conductivity (K), and unconfined compressive strength (UCS).

The PS anion was analyzed for activation by being quantified in 0.20  $\mu\text{m}$ -filtrate from reactor contents, using the spectrophotometric method described by Liang et al. (2008b). The detection limit for PS was 10 mg/L.

Table 3. PC used in 22 reaction scenarios, the corresponding reactor names, and the amendment doses on a weight basis (amendment weight/dry soil weight)

<b>Reaction Scenario</b>	<b>PS (%)</b>	<b>PC (%)</b>
<b>Control Reactions</b>		
Control (nothing added)	0.00	0.00
5% PS (unactivated)	5.00	0.00
<b>ISCO/ISS Treatments</b>		
0.25% PS-0.5% PC	0.25	0.50
0.5% PS-1% PC	0.50	1.00
0.75% PS-1.5% PC	0.75	1.50
1% PS-2% PC	1.00	2.00
1.25% PS-2.5% PC	1.25	2.50
1.5% PS-3% PC	1.50	3.00
2% PS-4% PC	2.00	4.00
3% PS-6% PC	3.00	6.00
4% PS-8% PC	4.00	8.00
5% PS-10% PC	5.00	10.00
<b>ISS Treatments</b>		
0.5% PC	0.00	0.50
1% PC	0.00	1.00
1.5% PC	0.00	1.50
2% PC	0.00	2.00
2.5% PC	0.00	2.50
3% PC	0.00	3.00
4% PC	0.00	4.00
6% PC	0.00	6.00
8% PC	0.00	8.00
10% PC	0.00	10.00

#### *Unconfined Compressive Strength (UCS) and Hydraulic Conductivity (K)*

Two important parameters that quantify ISS performance are unconfined compressive strength (UCS) and hydraulic conductivity. Unconfined compressive strength (UCS) is defined as a composite stress at which an unconfined, cylindrical specimen will fail in a compression test. In



this study, soil compression measurements of soil monoliths were taken following 28-day curing periods involving the ISS treatment to quantify UCS. Monoliths were removed from curing containers, and placed into a soil compression apparatus for testing (ASTM D2166 standard test method for unconfined compressive strength of cohesive soil). Following ISS treatment, most soils must exceed a minimum EPA regulation UCS of 50 psi (345 kPa). The UCS is taken at a maximum load attained per unit area or 15% axial strain, whichever occurs first during the test.

During this study, strain-controlled application of an axial load is placed on a vertical soil column, or monolith, providing an approximate value of the strength of the cohesive soil (Figure 3).



Figure 3. Soil compression device

Initial readings of samples were taken before deformation occurred. Induced axial strain was applied at 0.5% per minute, correlating with established ASTM standards. Load, deformation,

and time values at sufficient intervals were recorded and increased until the subsequent load values start to decrease with increasing strain, or until 15% strain was reached. Calculations used to observe parameters during testing were as follows:

Axial Strain ( $\epsilon$ ):  $\epsilon_1 = \frac{\Delta L}{L_0} \times 100$        $\Delta L$  = Length Change of specimen,  $L_0$  = Initial length of specimen

Average Cross Sectional Area (A):

$A = \frac{A_0}{(1 - \frac{\epsilon_1}{100})}$        $A_0$  = initial average cross sectional area ( $\text{mm}^2$ ),  $\epsilon_1$  = Axial strength for given load

Compressive Stress ( $\sigma$ ) in kPa:

$\sigma_c = \frac{P}{A}$        $P$  = given applied load,  $A$  = corresponding average cross sectional area ( $\text{mm}^2$ )

In addition to using a compressive device, a pocket penetrometer was utilized to determine compressive strength of various amendment monoliths within the non-stick columns during 28-day curing periods.

Another important parameter that quantifies ISS performance is hydraulic conductivity. Hydraulic conductivity decreases following 28-day curing times associated with ISS treatment, due to cementitious reactions associated with solidification/stabilization processes. One of the routes of contaminant release involving ISS treatment is through dissolution and flow of bulk wastes through the treated soil (Conrad, Shumborski, 1993). As alkaline precipitation of ISS amendments takes place, flow of water through ISS amended soil becomes limited, due to crystallization of cement minerals. Hydraulic conductivity is therefore important, and be calculated on monoliths using ASTM Method D5084 for falling head:

$$K = \frac{aL}{At} \ln\left(\frac{h_1}{h_2}\right)$$

where K is hydraulic conductivity, a is a cross-sectional area of the stand pipe, L is the height of the soil sample column, A is the monolith cross section, t represents the recorded time for the water column to drip through the sample, and (h<sub>1</sub>/h<sub>2</sub>) represents a gradient (often denoted dh/dl). Following 28-day cement curing reactions in molds, permeameters were set up to analyze hydraulic conductivity values for all 20 reaction scenarios involved in the experimentation with eight different ISS amendments, experimentation of dose variation with PC as a stand-alone and PS-mixed ISS amendment, and experimentation PC and PS as it pertained to soil swell (Figure 4).

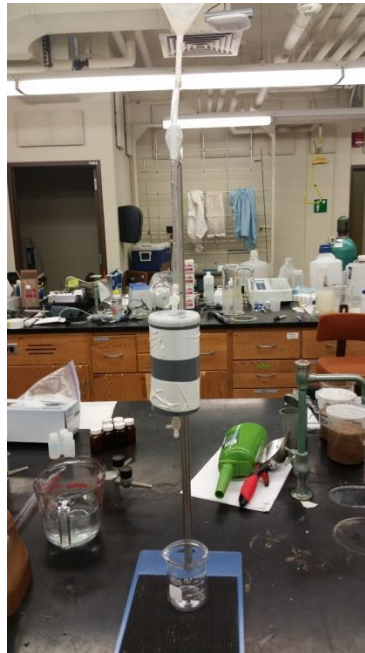


Figure 4. Falling head permeameter

### *Soil Swell, Grout Workability and Viscosity*

A second, major component to this study is soil swell. Swell results due to a change in soil volume associated with moisture content. As soil becomes wet, it expands in volume due to the abilities of clay within the soil to retain water (Thomas et al., 2000). The higher the clay content within a soil, the larger the extent of potential swell. Soil swell will be measured on the Racine and Ashland soil samples to determine the effect of various doses of water, PS and PC amendments on volumetric soil change following treatment. Ten reaction scenarios will be utilized to determine and single out the ability of variation in persulfate dose, Portland cement dose, and water on resulting soil swell (Table 4).

In order to quantify swell, initial soil density measurements will be taken using a proctor method ASTM D698 for determining soil density. Following a 28-day curing period associated with treatment, soil densities will then be measured using a mud balance (Figure 5). Due to soil volume increase during treatment, it is likely that density after treatment will be less than initial densities measured, due to the fact that volume has increased, based on the relationship provided by the formula:

$$D = M/V$$

Table 4. Ten reaction scenarios used to amend two test soils

Reaction	PS (%)	PC (%)	Water (%)
R1	0	0	5
R2	0	5	5
R3	0	10	10
R4	1	5	5
R5	1	7	7
R6	2	5	5
R7	2	8	8
R8	4	8	8
R9	4	10	10
R10	6	12	12

Final density subtracted from initial density, divided by the initial density will represent a percentage increase in soil volume.

$$((\rho_o - \rho)/\rho_o)$$

Soil swell will be calculated for two soils of each soil type, the sandy Racine soil, and the finer, Ashland soil.

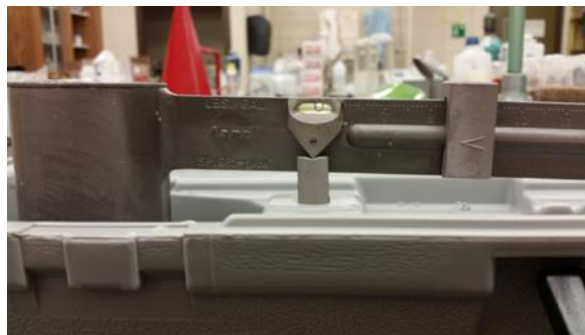


Figure 5. Mud balance used to calculate final density

Concrete slump tests, or cone slump tests, are a simple method developed in order to measure the workability or viscosity of concrete or other stabilization amendment grout mixtures. Workability is the ease at which concrete will flow, and slump tests measure the workability by observing the consistency of concrete within a specific batch. Certain mixtures, depending on water content within the mixture, tend to be more workable than other mixtures. Wetter mixes with higher water content are more workable; however, strength following cementitious curing processes with higher water content tends to be compromised. In this study, slump tests were used to determine the workability of ISS amendments, and ISS/PS grout mixtures when mixed with water.



Figure 6. Slump test procedure

Behavior of compacted ISS amendments and ISS/PS grout mixtures under the action of gravity were monitored. Procedurally, a cone was placed on a hard, non-absorbent surface filled with batch mixtures in three stages. Each time the cone was filled, it was tamped down with a

rod 25 times to ensure its conformity to the shape of the cone. The cone mold was then lifted vertically upward, so as not disturb the concrete inside. Batch mixtures experienced subsidence, or “slump”, which were then interpreted to gain an understanding of its consistency (Figure 6). Test procedures resulting in true slump were interpreted following the slump tests. ISS amendments and ISS/PS mixtures were categorized based on determined standards, whereas a very dry mixture results in slump ranging from 0-25 mm, low workability mixtures result in slump ranging from 10-40 mm, and medium workability batches results in slump ranging from 50-90 mm. Slump was measured to the nearest 5 mm if overall slump was less than 100mm, and to the nearest 10 mm if overall slump was greater than 100 mm (Gambhir, 2004).

A marsh funnel was also used to test the workability of various amendment doses when they were in an initial fluid, grout mixture with water and sodium persulfate (PS). A marsh funnel is a simple device used for measuring viscosity in a non-Newtonian fluid by observing the time it takes a known volume of liquid to flow from a cone through a short tube. Specific test procedures in this study followed protocol as defined by ASTM C939-10, Standard Test Method for Flow of Grout for Preplaced-Aggregate Concrete (Flow Cone Method). When using a marsh funnel, the funnel is held vertically while with the end tube being held by a finger or stopper. The liquid measured, in this case the grout mixture, was poured through the mesh screen at the top of the funnel to remove particulates that might block the bottom of the tube (Figure 7). Measurements were initiated when the finger or stopper is released from the bottom of the funnel tube, and a stopwatch is simultaneously started. Liquid was allowed to flow into a measuring container, and the flow time through the funnel (in seconds) was recorded as the Marsh funnel time, or  $t$ . Effective viscosity of a fluid can be determined following a simple formula:

$$\mu = \rho(t - 25)$$

Where:

$\mu$  = effective viscosity in centipoise

$\rho$  = density of fluid in g/cm<sup>3</sup>

t = Marsh funnel time in seconds



Figure 7. Marsh funnel device



## CHAPTER III

### RESULTS AND DISCUSSION

#### *Persulfate Activation*

The eight ISS amendments used to activate persulfate (PS) were QL, PC, LKD, BFS, FAC, FAF, CKD, and HL, are listed in Table 1. Persulfate activation over time can be directly correlated to the decrease in the concentration of the PS anion (Figure 8). PS concentrations in the Control reactor were zero throughout the 3-hour period, because no PS was added and none was generated. PS concentrations in the eight ISS reaction scenarios at the bottom of Table 2 were also zero, because PS was not added in order to test ISS amendments in a stand-alone situation. Concentrations in the unactivated PS reactor remained near 36 g/L, which was approximately the original concentration of PS resulting from the 1.5% dose added on a weight basis (Table 2). This demonstrates that PS was not activated by the soil during the 3-hour period. In contrast, NaOH, heat, and the 8 ISS amendments achieved complete PS activation within 3 hours or less. Heat activation was complete within 30 minutes, whereas NaOH activation required 3 hours. In reactions involving PS and the 8 ISS amendments, a correlation developed where the rate of PS activation decreased directly with decreasing CaO content in the activator (see Table 1). Specifically, QL achieved complete activation in 30 minutes, PC in 1 hour, LKD in 1.5 hours, BFS in 2 hours, FAC in 2.5 hours, and FAF, CKD, and HL in 3 hours. It is also interesting to note that the time profile of PS disappearance was nearly identical for QL-PS and Heat-PS. This correlation suggests that between heat and alkaline activation, the predominant activation mechanism of PS with QL is heat activation.

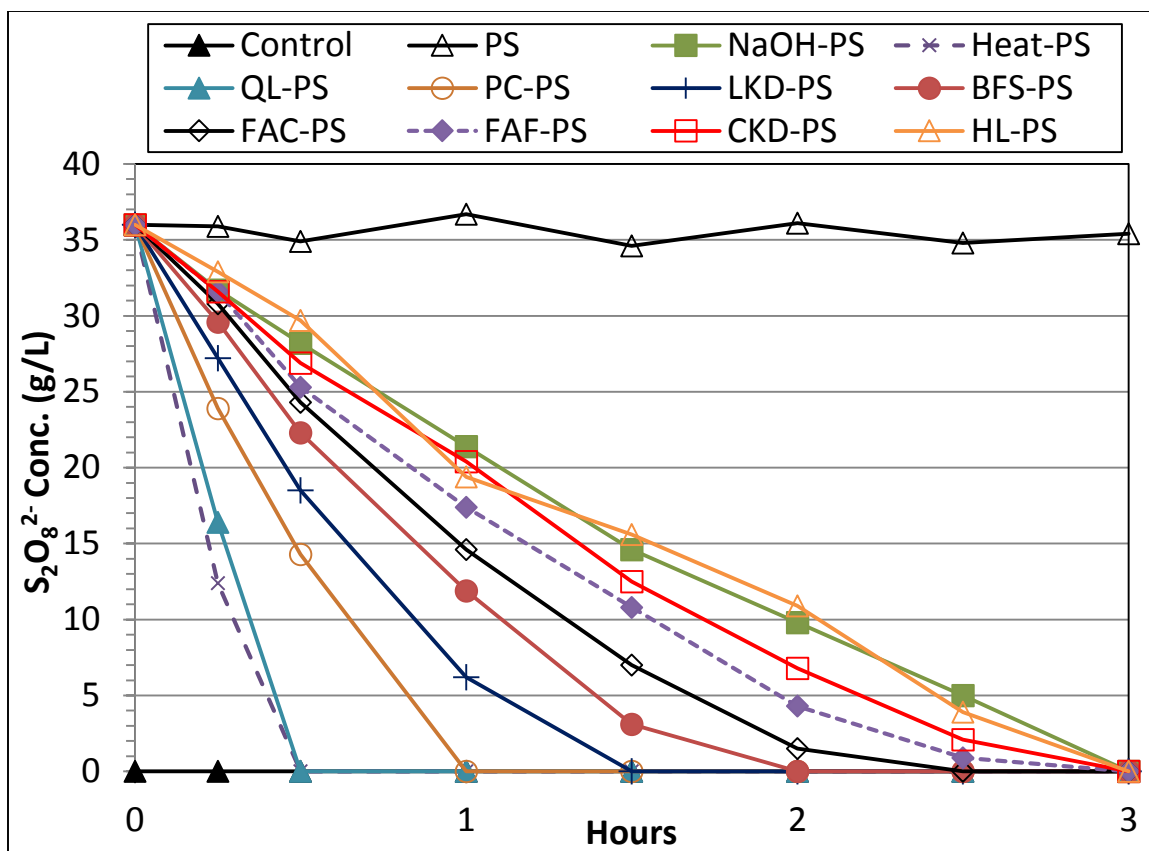


Figure 8. Concentration of the PS anion ( $S_2O_8^{2-}$ ) in control and all the reactors dosed with PS and eight ISS amendments during 3 hour mixing period

Time profiles of temperature and pH during the 3-hour PS activation period are shown in Figures 9 and 10, respectively. The temperature and pH data for the eight ISS reaction scenarios are not included in Figures 9 and 10. In the Heat-PS reaction, the temperature spiked from the background value of 35°C to nearly 50°C within the first 30 minutes (not shown). Temperatures in the Control and the unactivated PS reactor remained near the background values of 15°C throughout the 3-hour period. However, all PS activations showed a marked temperature increase from background temperature values. As was observed with rates of PS activation, the maximum temperatures attained in the activation reactions were directly related to the CaO content of the activator (Table 1). For instance, the highest maximum temperature reached with ISS activation (over 40°C) was in the QL-PS reactor. Quick lime is composed of

100% CaO (Table 1). This was then followed by PC-PS, LKD-PS, and so on as CaO content decreases from 100% content. The reaction of CaO with water [Reaction 1] releases a significant amount of heat. Despite containing no CaO, the HL-PS and NaOH-PS reactions still increased in temperature to values near 29°C. As expected, temperatures increased from background values for all activations, because both alkaline and heat activation cause the rupture of the O-O bond in PS (Kolthoff and Miller, 1951; Negi and Anand, 2007), which releases 140 kJ/mol [Reaction 1]. Reactions involving the chemical oxidation of contaminants are also exothermic (Kolthoff and Miller, 1951; Mora et al., 2009). The heat released during PS activation also explains why maximum temperatures in the reactors dosed only with ISS amendments (data not shown) were 3°C to 4°C lower than the in the reaction with each respective ISS amendment with PS. Coupling exothermic processes involved in chemical oxidation with heat produced by ISS activators increased total heat involved in reactions that would be 3°C to 4°C lower in isolated situations.

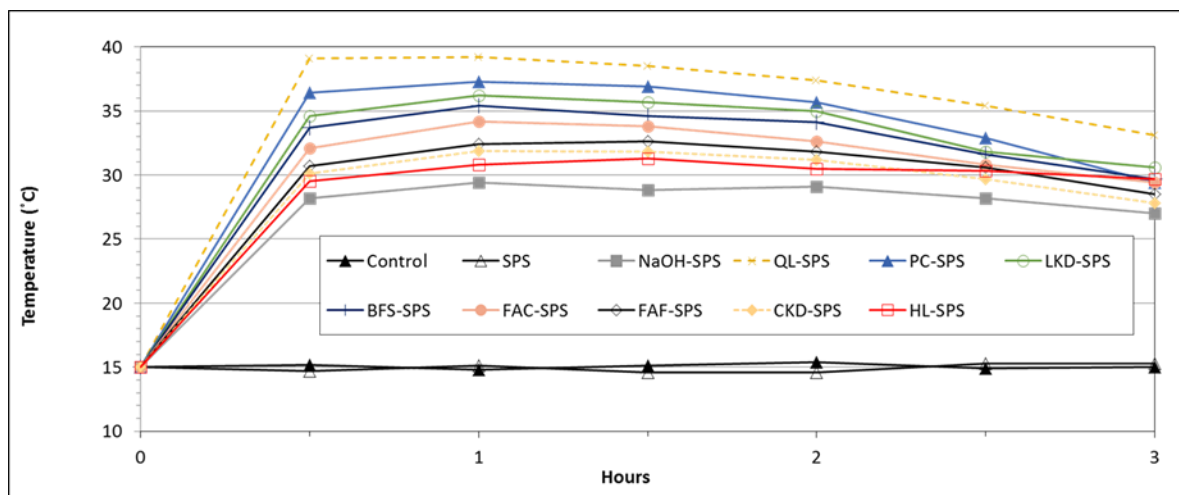


Figure 9. Temperature (°C) associated with reaction mixing scenarios over 3 hours

The pH values in Figure 10 also help explain the time profiles of PS activation in Figure 8. The pH in the Control and the unactivated PS reactor remained near the background value of 7.3

throughout the 3-hour period. In the Heat-PS reaction the pH values decreased below the background soil pH, to values near 6 (not shown in figure 10). With the exception of Heat-PS, all the activation scenarios reached a pH above 11 during the 3 hour period, well above the minimum pH (10.5) for alkaline PS activation. The highest pH values (> 13) were observed in NaOH-PS, QL-PS, and HL-PS reactions. Complete activation of PS was observed in the NaOH-PS and HL-PS reactions (Figure 8), despite having maximum temperatures below 29°C. Therefore, this can only be attributed to alkaline activation caused by the high pH values, which are shown in Figure 10. Among the ISS amendments, the maximum pH values observed increased with increasing  $\text{Ca(OH)}_2$  content, with maximum pH values achieved for Hydrated Lime (HL) and pure  $\text{Ca(OH)}_2$  (HL).

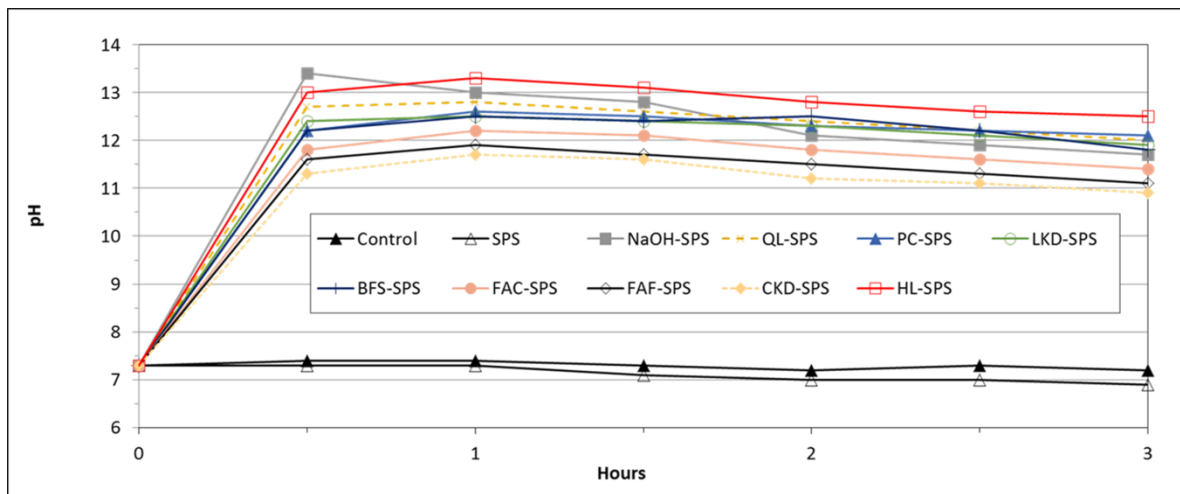


Figure 10. pH values associated with reaction mixing scenarios over a 3 hours

Cassidy et al. (2015) reported that adding 50% PC and 50% HL had an ability to activate PS in a contaminated soil, but this is the first study to demonstrate that a wide variety of ISS amendments can achieve PS activation. Cassidy et al. (2015) were also unable to distinguish alkaline activation of PS [Reaction 2] from heat activation [Reaction 3], which is important

because heat activation generates 2 moles of oxidizing radicals per mole of PS [Reaction 3], whereas alkaline activation produces only 1 mole [Reaction 2].

Based on the data in Figures 8 through 10, three different PS activation regimes can be defined:

- (1) Activation purely by the heat mechanism
- (2) Activation purely by the alkaline mechanism
- (3) Combination of heat and alkaline activation.

The Heat-PS reaction achieved temperatures well above 35°C, with pH values below 7, allows us to conclude that little or no alkaline activation occurred in the Heat-PS reaction, and that heat was the primary activation mechanism (House, 1962; Huang et al., 2002; Killian and Bruell, 2003). In contrast, NaOH-PS and HL-PS did not attain the minimum temperature required for heat activation (30°C), but did increase the pH well above 10.5 (the minimum pH for alkaline activation). It can therefore be concluded that the NaOH-PS and HL-PS reactions activated PS solely via alkaline activation, with no contribution from heat activation. Apart from HL, all the other ISS activators increased the temperature above 30°C for some period of time, but also increased the pH above 10.5. Therefore, some combination of alkaline and heat activation occurred in reaction scenarios QL-PS, PC-PS, LKD-PS, BFS-PS, FAC-SPS, FAF-PS, and CKD-PS. For these 7 ISS activations, it is reasonable to assume that the contribution of heat activation relative to alkaline activation increased as the maximum temperature increased, and as the period of time during which the temperature remained above 30°C increased (House, 1962; Killian and Bruell, 2003). For example, the contribution of heat activation relative to alkaline

activation would be expected to be greater for QL-PS, PC-PS, and LKD-PS than for BFS-PS, FAC-PS, FAF-PS, and CKD-PS (Figure 9).

Among the eight ISS-activated PS reactions, the extent of chemical oxidation (not presented in this study) of contaminants has been shown to increase as the maximum temperature during the 3-hour mixing period increased (Figure 9), which is directly related to the CaO content of the ISS amendment (Table 1) (Srivastava et al., 2015). This can be explained by an increased contribution of heat activation of PS relative to alkaline activation as the CaO content of the ISS amendment, and the accompanying maximum temperatures increase. Heat activation of PS is more efficient for contaminant oxidation than alkaline activation because it yields two times more oxidizing radicals (Reactions 3 through 5) per mole. When considered together, Figures 8 through 10 clearly indicate that the relative contribution of heat activation relative to alkaline activation increased as the CaO content of the ISS amendments increased. Work by Srivastava et al. has also shown that Heat-PS and QL-PS reactions are nearly identical in contaminant removal of BTEX, NAP and of PAH, and have very similar rates of PS activation (Figure 1). QL has the highest CaO content of all the ISS amendments (100%), and achieved significantly higher temperatures than the other seven ISS amendments (Figure 2). Srivastava et al. showed other ISS amendments achieved decreasing degrees of contaminant oxidation as the CaO content decreased. Put together, these results also demonstrate the advantage of promoting heat activation of PS for contaminant oxidation, and that the CaO content and the dose of ISS amendments should be identified to achieve temperatures above 30°C.

Portland cement was also isolated to test the effect of dose variation on persulfate activation. Figure 11 shows concentrations of the PS anion ( $S_2O_8^{2-}$ ) in the Control and all the reactors dosed with PS during the 3-hour mixing period. PS disappearance is a direct measure of

its activation. PS concentrations in the Control were zero throughout the 3-hour period, because no PS was added and none was generated. PS concentrations were also measured in the ten ISS reactors not dosed with PS, but the data are not shown in Figure 4 because all concentrations were below detection, as expected. Concentrations in the unactivated 5% SPS reactor remained near 116 g/L, indicating that PS was not activated appreciably by the soil during the 3-hour period. In contrast, all the reaction scenarios with PC showed an immediate decrease in PS concentrations, and reached levels below detection within 3 hours, demonstrating that each dose of PS was completely activated by the dose of PC used. The time required to achieve complete activation increased as the dose of PS increased, from 30 minutes in the 0.25% SPS-0.5% PC reactor to 2.5 hours in the 5% SPS-10% PC reactor. Distinguishing alkaline vs. heat activation of PS was not an objective in this part of the study, but pH measurements throughout the 3-hour mixing period (data not shown) were above 11, which is sufficient for PS activation.

These results show that a dose ratio of PC:PS of 2:1 (by weight) in the test soil was sufficient to activate persulfate within 2.5 hours, over a wide range of PS doses. However, the minimum ratio of PC required to completely activate PS in other soils that have been tested show that this ratio varies, and that the time required for complete activation can also vary, in some cases taking longer than 3 hours. In some soils, the minimum PC:PS ratio for complete activation varies with PS dose, typically increasing as the PS dose decreases. When using ISS amendments to activate PS, it is desirable to achieve complete activation as soon as possible, and in any case within 24 hours, because after this time the  $\text{Ca(OH)}_2$  generated from CaO (Reaction 1) coats soil grains sufficiently that sorbed contaminants are shielded from the desired chemical oxidation reactions (Reactions 2, 3, and 4). For a given dose of PS, increasing the dose of ISS amendment tends to decrease the time required for complete activation.

Based on work by Srivastava et al., the difference in BTEX and NAP contaminant removal is greatest at the lower PS doses, and becomes less pronounced with increasing PS dose, particularly above 1%. Likewise, the percent NAP removal was between 8% and 64% greater than the percent 17PAH oxidized (Srivastava et al., 2015). These findings can be explained by the increase in molecular weight from BTEX to NAP and from NAP to 17PAH. Organic contaminants of low molecular weight are more soluble, and therefore more available to oxidation in the aqueous phase (Schwarzenbach et al., 2003).

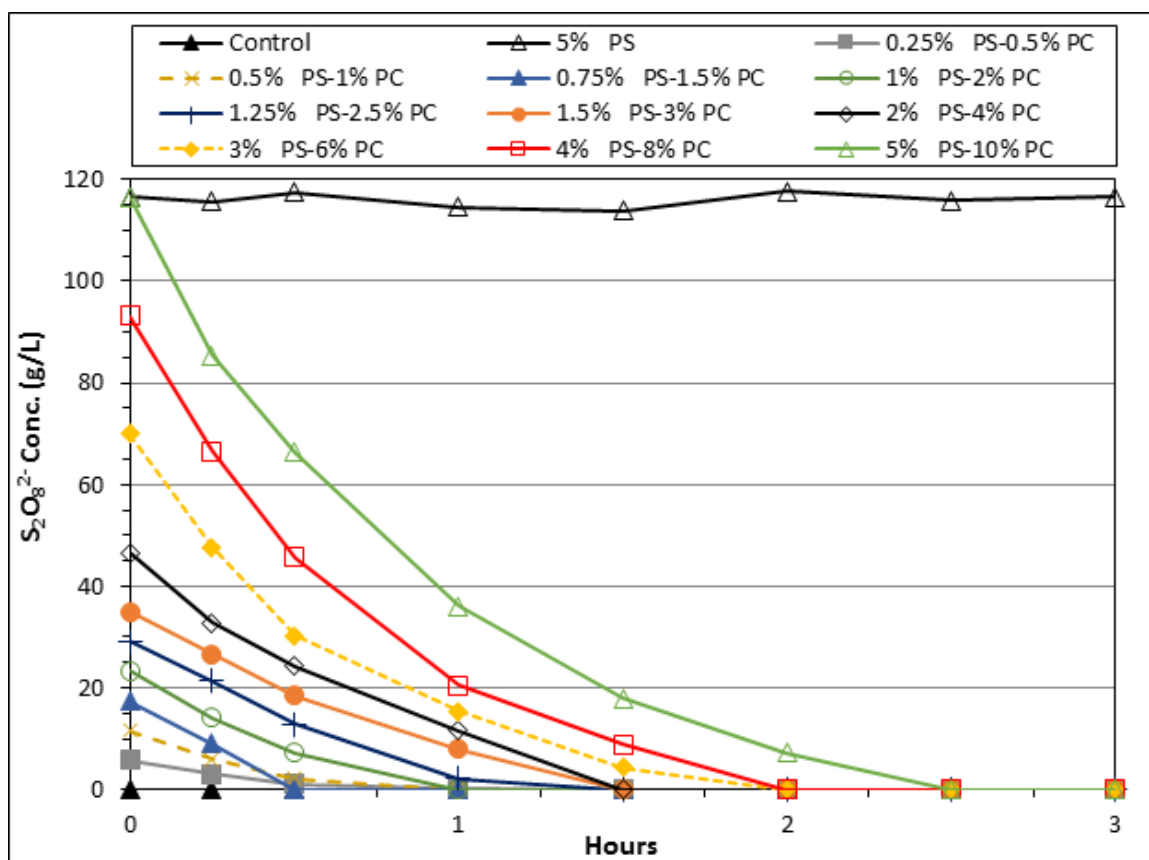


Figure 11. Concentrations of the PS anion ( $S_2O_8^{2-}$ ) during the 3-hour mixing period in the control and all reaction scenarios dosed with PS and PC



### *Unconfined Compressive Strength (UCS) and Hydraulic Conductivity (K)*

Unconfined compressive strength (UCS) and hydraulic conductivity (K) values measured in the ISS amendment-PS reaction scenarios are listed in Tables 5. Also, UCS and K values measured with PC-PS dose scenarios are listed in Table 6. UCS is an important geotechnical property for site redevelopment, and a common minimum target UCS following ISS treatment is 345 kPa (50 psi) (ITRC, 2011; U. S. EPA, 2013). A minimum UCS of 345 kPa improves the compressive strength of soils, but also allows soils to still be workable for additional redevelopment purposes. Reducing hydraulic conductivity (K) is also an important performance parameter of ISS, because it decreases the infiltration of rainwater in the treated soil materials. This diminishes contaminant leachability and prevents contaminant mobility in groundwater. The UCS of the untreated soil in this study was approximately 62 kPa, and the K value was  $2.74 \times 10^{-2}$  cm/s. The PS, NaOH-PS, and Heat-PS reactions showed very little or noticeable changes in UCS or K compared with the Control and with background soil values. However, all of the reactors treated with ISS amendments, both with PS and without PS, increased the UCS to values between approximately 755 kPa to 1,136 kPa. These reported UCS values all meet and exceed the minimum target of 345 kPa (50 psi) and still render the soil workable for redevelopment. All 16 reaction scenarios receiving ISS amendments (with and without PS) decreased K to values between  $3.03 \times 10^{-4}$  cm/s to  $8.14 \times 10^{-6}$  cm/s. This represents a large reduction in K of between 2 to 4 orders of magnitude. There was not a significant difference in UCS or K values between the ISCO/ISS treatments and stand-alone ISS treatments, indicating that the reactions associated with activated PS did not negatively impact these two ISS performance parameters. This indicates that PS could be used effectively without detrimental effects in a combined remedial treatment with ISS agents.

Table 5. Values of unconfined compressive strength (UCS) and hydraulic conductivity (K) associated with different ISS amendment-PS reaction scenarios

Reactor	UCS (kPa)	K (cm/sec)
Control	62	3.74E-02
PS	71	5.02E-02
NaOH-PS	48	4.91E-02
Heat-PS	57	2.59E-02
QL-PS	841	9.91E-04
PC-PS	1136	8.14E-06
LKD-PS	977	2.96E-05
BFS-PS	810	6.49E-04
FAC-PS	755	3.03E-04
FAF-PS	835	5.59E-05
CKD-PS	989	8.22E-04
HL-PS	865	6.43E-04
QL	927	1.96E-05
PC	841	5.97E-06
LKD	986	6.41E-04
BFS	1024	2.88E-04
FAC	810	5.03E-04
FAF	792	7.02E-05
CKD	862	4.94E-04
HL	958	1.03E-05

Table 6 also shows UCS and K values that are associated with reactor treatment scenarios, although this table represents the selection of PC as the stand alone ISS amendment studied in these reaction scenarios. The UCS of the untreated soil was approximately 60 kPa, and the K was 2.74E-02 cm/s. The Control and the 5% unactivated PS reactions showed no appreciable changes in UCS or K compared with the background values. However, all the ISCO/ISS and ISS treatments caused UCS values to increase K values to decrease. UCS values increased consistently as the PC dose increased, and K values decreased with increasing PC dose, as would be expected. The maximum PC dose of 10% increased UCS measurements to over 3,000 kPa and decreased K values to between 7.7E-08 cm/s and 9.4E-08 cm/s. Doses of PC of 1.5% and above increased the UCS to more than 345 kPa. There was not an appreciable

difference between UCS and K values with ISCO/ISS and ISS treatment for homologue treatments that received the same dose of PC. These results indicate that the dose of PC controlled UCS and K values achieved with treatment, and that the reactions accompanying activated PS in the ISCO/ISS treatments did not negatively impact these two critical ISS performance parameters.

Table 6. Unconfined compressive strength (UCS) and hydraulic conductivity (K) of varying PS-PC doses, measured in 28-day curing samples

<b>Reaction Scenario</b>	<b>UCS (kPa)</b>	<b>K (cm/s)</b>
Control	46	1.63E-02
5% PS	55	9.96E-01
0.25% PS-0.5% PC	79	5.38E-02
0.5% PS-1% PC	205	1.38E-03
0.75% PS-1.5% PC	402	5.76E-03
1% PS-2% PC	632	3.03E-04
1.25% PS-2.5% PC	748	2.24E-05
1.5% PS-3% PC	913	8.73E-05
2% PS-4% PC	1,340	1.43E-06
3% PS-6% PC	1,637	8.76E-06
4% PS-8% PC	2,178	4.38E-07
5% PS-10% PC	3,065	9.44E-08
0.5% PC	87	3.93E-02
1% PC	192	5.21E-03
1.5% PC	421	8.98E-03
2% PC	614	6.36E-04
2.5% PC	711	6.55E-05
3% PC	985	2.52E-06
4% PC	1,298	7.95E-06
6% PC	1,662	3.32E-07
8% PC	1,974	8.04E-07
10% PC	3,135	7.71E-08

### *Soil Swell, Grout Workability and Viscosity*

Soil swell is an important property of all treatment scenarios involving ISS technology. Soil volume increase can be experienced during treatment implementation, which is detrimental for treatment cost and efficiency. In this study, four soils from two sites, the first from an MGP plant in Racine, Wisconsin, and the other, an MGP plant in Ashland, Wisconsin, were amended with different doses of water and Portland cement as a stand-alone ISS amendment, as well as water, PC, PS mixtures (R1 through R9) to determine effects of soil swell (Table 4).

The first two soil samples, each from Racine, were treated. Each soil sample was treated with nine treatment scenarios, including one water only scenario, two scenarios using only Portland cement and water mixtures, and six scenarios using persulfate, PC, and water mixtures of varying dose. Following treatment and a standard 28-day curing period associated with ASTM method D2166, UCS values and hydraulic conductivity (K) were measured, in accordance with the previous amendments in this study. Reaction Scenario 1 (R1) showed no distinct change in soil compression strength during and following treatment time (Table 7,8). For all treatment scenarios involving Portland cement (R2 through R9), UCS was increased to a point which exceeded EPA minimum standards (50 psi), and hydraulic conductivity was greatly reduced (Table 7,8). Additionally, UCS values taken on day 5 of the 28-day curing period showed an increase in soil UCS that exceeded EPA minimum parameters of 50 psi in all of these scenarios. Reaction scenarios involving a larger percentage of PC dose (amendment wt./dry soil wt.) showed the most significant increase in UCS and decrease in hydraulic conductivity. Overall, the addition of persulfate as an amendment to PC and water had no deleterious effects on UCS and

hydraulic conductivity, as UCS still exceeded minimum psi, and hydraulic conductivity values still were greatly decreased relative to soil background values.

Table 7. Racine soil test results following reaction scenarios, soil 1

Reaction	PS(%)	PC (%)	Water (%)	UCS ASTM D2166 28-day (psi)	UCS 5-day pocket penetrometer (psi)	Hydraulic Conductivity K (cm/s)	Density before (kg/m <sup>3</sup> )	Density After (kg/m <sup>3</sup> )	Swell (%)	Marsh Funnel Time (sec)	Slump (inches)
R1	0	0	5	0	30	7.24E-01	1,832	1,290	29.6%	40	6
R2	0	5	5	246	132	4.49E-03	1,832	1,240	32.3%	38	4
R3	0	10	10	307	156	6.07E-05	1,832	1,280	30.1%	42	4
R4	1	5	5	238	157	1.85E-04	1,832	1,280	30.1%	39	5
R5	1	7	7	250	172	4.18E-05	1,832	1,260	31.2%	44	4
R6	2	5	5	261	130	3.16E-04	1,832	1,250	31.8%	36	5
R7	2	8	8	273	138	9.35E-05	1,832	1,290	29.6%	41	6
R8	4	8	8	261	144	2.72E-05	1,832	1,270	30.7%	41	4
R9	4	10	10	328	236	4.02E-06	1,832	1,200	34.5%	38	5

Table 8. Racine soil test results following reaction scenarios, soil 2

Reaction	PS(%)	PC (%)	Water (%)	UCS ASTM D2166 28-day (psi)	UCS 5-day pocket penetrometer (psi)	Hydraulic Conductivity K (cm/s)	Density before (kg/m <sup>3</sup> )	Density After (kg/m <sup>3</sup> )	Swell (%)	Marsh Funnel Time (sec)	Slump (inches)
R1	0	0	5	0	0	6.93E-01	1,811	1,300	28.2%	42	5
R2	0	5	5	251	140	5.51E-03	1,811	1,270	29.9%	40	4
R3	0	10	10	320	159	3.28E-05	1,811	1,240	31.5%	39	4
R4	1	5	5	249	138	6.67E-04	1,811	1,250	31.0%	39	6
R5	1	7	7	266	135	5.35E-04	1,811	1,270	29.9%	40	5
R6	2	5	5	273	115	8.80E-04	1,811	1,220	32.6%	42	4
R7	2	8	8	286	108	7.47E-05	1,811	1,240	31.5%	42	6
R8	4	8	8	306	157	2.66E-05	1,811	1,210	33.2%	39	5
R9	4	10	10	358	174	9.40E-05	1,811	1,250	31.0%	41	5

Marsh funnel and slump parameters of soil/grout mixtures were also recorded before 28-day curing periods took place. In both Racine soils, marsh funnel values ranged from 36 seconds to 44 seconds, and 39 seconds to 42 seconds, respectively (Table 7,8). There was no distinct correlation between amendment dose and marsh funnel time, and there was small variance in marsh funnel time even with large dose variance. This implies that soil/grout

viscosities weren't greatly affected by the presented amendment doses, all of which were 10% or below. Slump ranged from 4 to 6 inches in all reaction scenario mixtures (Table 7,8). Slump variation with dose was also minimal and showed little or no correlation to amendment dose in both Racine soils.

Soil swell values were calculated following treatment by finding the difference between original soil densities and soil densities following treatment. Swell in both Racine soils varied little with amendment dose over all of the reaction scenarios presented in each Racine soil. Swell varied from 29.6% to 34.5%, and 28.2% to 33.2% in both soils, respectively (Table 7,8). There appears to be little correlation between dose of PS, PC, or water with swell.

An additional two soil samples, each from Ashland, were also treated and measured for ISS treatment parameters. Ten reaction scenarios were used on two treated soils (R1 through R10) (Table 4). Like the soil from Racine, UCS was increased and exceeded EPA minimum values following treatment, and hydraulic conductivity was greatly decreased. Reaction scenarios involving a larger percentage of PC dose (amendment wt./dry soil wt.) showed the most significant increase in UCS and decrease in hydraulic conductivity (Table 9, 10). Overall, the addition of persulfate as an amendment to PC and water had no negative effects on UCS and hydraulic conductivity, as UCS still exceeded minimum psi, and hydraulic conductivity values still were greatly decreased relative to soil background values.

Marsh funnel and slump parameters of soil/grout mixtures were also recorded before 28-day curing periods took place. In both Racine soils, marsh funnel values ranged from 36 seconds to 42 seconds for both soils, respectively (Table 9, 10). There was no distinct correlation between amendment dose and marsh funnel time, and there was small variation in marsh funnel time even with large dose variance. This implies that soil/grout viscosities weren't greatly

affected by a variety of amendment doses, all of which were 12% or below. Slump ranged from 4 to 6 inches in all reaction scenario mixtures (Table 9, 10). Slump variation with dose was also minimal and showed little or no correlation to amendment dose in both Racine soils.

Table 9. Ashland soil test results following reaction scenarios, soil 1`

Reaction	PS(%)	PC (%)	Water (%)	UCS ASTM D2166 28-day (psi)	UCS 5-day pocket penetrometer (psi)	Hydraulic Conductivity K (cm/s)	Density before (kg/m <sup>3</sup> )	Density After (kg/m <sup>3</sup> )	Swell (%)	Marsh Funnel Time (sec)	Slump (inches)
R1	0	0	5	0	0	6.89E-01	1,545	950	38.5%	37	5
R2	0	5	5	246	145	2.40E-03	1,545	930	39.8%	39	5
R3	0	10	10	307	220	5.11E-05	1,545	900	41.7%	41	4
R4	1	5	5	235	121	3.26E-07	1,545	960	37.9%	36	6
R5	1	7	7	295	158	4.42E-04	1,545	900	41.7%	42	5
R6	2	5	5	240	140	6.76E-05	1,545	910	41.1%	37	4
R7	2	8	8	312	180	8.15E-04	1,545	930	39.8%	40	4
R8	4	8	8	326	160	1.45E-06	1,545	870	43.7%	41	6
R9	4	10	10	330	250	5.62E-05	1,545	940	39.2%	42	6
R10	6	12	12	358	290	7.72E-07	1,545	900	41.7%	39	5

Table 10. Ashland soil test results following reaction scenarios, soil 2

Reaction	PS(%)	PC (%)	Water (%)	UCS ASTM D2166 28-day (psi)	UCS 5-day pocket penetrometer (psi)	Hydraulic Conductivity K (cm/s)	Density before (kg/m <sup>3</sup> )	Density After (kg/m <sup>3</sup> )	Swell (%)	Marsh Funnel Time (sec)	Slump (inches)
R1	0	0	5	42	37	2.12E-02	1,486	950	36.1%	40	5
R2	0	5	5	183	130	4.95E-04	1,486	910	38.8%	42	6
R3	0	10	10	212	140	2.37E-05	1,486	890	40.1%	42	4
R4	1	5	5	257	190	8.29E-06	1,486	900	39.4%	37	6
R5	1	7	7	207	125	3.97E-04	1,486	870	41.5%	41	4
R6	2	5	5	245	160	6.68E-05	1,486	880	40.8%	39	5
R7	2	8	8	225	120	4.55E-04	1,486	890	40.1%	36	6
R8	4	8	8	247	150	8.92E-06	1,486	900	39.4%	42	4
R9	4	10	10	358	200	4.64E-06	1,486	880	40.8%	39	6
R10	6	12	12	252	240	2.77E-08	1,486	860	42.1%	40	5

Ashland soil swell values were calculated following treatment by finding the difference between initial soil densities and soil densities following treatment. Swell in both soils varied little with amendment dose over all of the reaction scenarios presented in each Racine soil.

Swell varied from 37.9% to 43.7%, and 36.1% to 42.1% in both soils, respectively (Table 9, 10).

There appears to be little correlation between dose of PS, PC, or water with swell.

Overall, resulting treatment parameters of both the Racine and Ashland soils appeared to be similar. UCS in both soils was increased and hydraulic conductivity decreased following treatment. Both treated soils showed little to no variation in soil/grout mixture viscosity and slump with variation in amendment dose. Soil swell also wasn't affected by PC dose variation, but differed between the Racine and Ashland MGP soils, with the Ashland soil samples experiencing a much greater swell (Figure 12). This is likely due to the fine-grained nature of the Ashland soil (silt ~40%), with it having higher silt and clay content than the Racine soil, which was primarily a gravely sand (Sand and Gravel ~ 70%). Soils with a higher composition percentage of silt and clay have a greater tendency to swell due to the ability of clays to retain water (Thomas et al., 2000). Larger volumetric soil change experienced with Ashland was expected, and was experienced, due to its higher silt content.

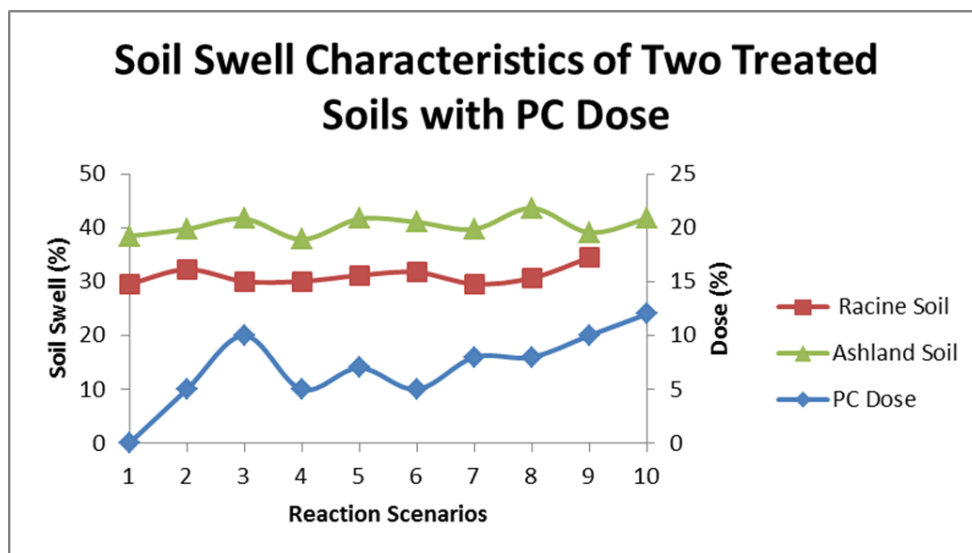


Figure 12. PC dose and soil swell of two different soils following 10 reaction scenarios



## *Conclusion*

All eight of the ISS amendments tested were able to activate persulfate (PS) within 3 hours. Quick lime had the highest CaO content (100%) and hydrated lime the lowest CaO content (0%). The maximum temperatures achieved with ISS-activated PS increased as the CaO content of the ISS amendments increased. This translated to work done by Srivastava et al., showing a higher percentage of contaminants oxidized via higher reaction temperatures. For the same PS dose, contaminant oxidation was enhanced to the extent that heat activation was favored relative to alkaline activation of PS, because the heat mechanism yields two times more oxidizing radicals per mole than the alkaline mechanism (Srivastava et al., 2015). With the doses of PS and ISS amendments used in this study, it can be concluded that PS activation with quick lime occurred purely via the heat mechanism, because the extent of contaminant oxidation was nearly identical to an activation using heat at a pH below 7 (Srivastava et al., 2015). In contrast, activation with hydrated lime (0% CaO) can be attributed almost exclusively to the alkaline mechanism because the percentage of contaminant oxidation was very similar to activation using NaOH, with temperatures maintained below 30°C (Srivastava et al., 2015).

Portland cement was also isolated as an ISS amendment. A PC:PS ratio of 2:1 was selected to activate PS doses ranging from 0.25% to 5% (by weight). For all ISCO/ISS treatment scenarios, PS activation was complete within 2.5 hours. The presence of PS did not negatively impact the increase in UCS and decrease in K achieved with each dose of PC.

Soil swell was also investigated on two soils, utilizing different doses of persulfate, Portland cement, and water. UCS, hydraulic conductivity, marsh funnel time, and slump of these varying doses were also examined. Dose rates had no effect on swell, UCS, hydraulic conductivity, marsh funnel time, or slump. Soil swell was greater for the second soil type

sampled, but this was ultimately determined to be due to the individual soil's higher clay content. UCS in all dose treatment scenarios exceeded EPA minimum standards, and hydraulic conductivities were greatly reduced on both soils treated. Marsh funnel viscosity and slump all had little to no variation or correlation with dose variation in treatment scenarios. This particular exercise also demonstrated that variation of PS dose has little to no effect on ISS treatment parameters. All together, the results from this study clearly show that a combined ISCO/ISS remedy can achieve a profound synergy for site cleanup compared with using either ISCO or ISS as stand-alone technologies.

## BIBLIOGRAPHY

- Ahmad, M., Teel, A. L., Furman, O. S., Reed, J. I., & Watts, R. J. (2011). Oxidative and reductive pathways in iron-ethylenediaminetetraacetic acid-activated persulfate systems. *Journal of Environmental Engineering*.
- Ahmad, M., Teel, A. L., & Watts, R. J. (2010). Persulfate activation by subsurface minerals. *Journal of contaminant hydrology*, 115(1), 34-45.
- Basma, A. A., & Tuncer, E. R. (1991). Effect of lime on volume change and compressibility of expansive clays. *Transportation Research Record*, (1295).
- Block PA, Brown RA, and Robinson D. (2004). Novel activation technologies for sodium persulfate in situ chemical oxidation. In: *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA., (Eds. AR Gavaskar and ASC Chen). Columbus, Ohio: Battelle Press.
- Block, P. (2012). *The Use of Lime and Cement as Activators of Persulfate Chemical Oxidation* (1st ed., pp. 1-33). Retrieved from <http://file:///C:/Users/User/Downloads/11%20Block%20Presentation.pdf>
- Brown, R.A., and Robinson, D., 2004. Response to naturally occurring organic material: permanganate versus persulfate, In: *Proceedings of the Fourth International Conference of Remediation of Chlorinated and Recalcitrant Compounds* (Monterey, CA, May 24-27, 2004), (Gavaskar, A.R., and Chen, A.S.C., Eds.), Battelle Press, Columbus, Ohio.
- Cassidy, D. P., Srivastava, V. J., Dombrowski, F. J., & Lingle, J. W. (2015). Combining In-Situ Chemical Oxidation, Stabilization and Anaerobic Bioremediation in a Single Application to Reduce Contaminant Mass and Leachability in Soil. *Journal of Hazardous Materials*.
- Conrad, D. J., & Shumborski, S. (1993). Parameters Affecting the Measurement of Hydraulic Conductivity for Solidified/Stabilized Wastes.
- Coz, A., Andrés, A., Soriano, S., Viguri, J. R., Ruiz, M. C., & Irabien, J. A. (2009). Influence of commercial and residual sorbents and silicates as additives on the stabilisation/solidification of organic and inorganic industrial waste. *Journal of hazardous materials*, 164(2), 755-761.
- Crane, R. E., Cassidy, D. P., & Srivastava, V. J. (2014). Activated Carbon Preconditioning to Reduce Contaminant Leaching in Cement-Based Stabilization of Soils. *Journal of Environmental Engineering*.

- Eaton, H. C., Walsh, M. B., Tittlebaum, M. E., Cartledge, F. K., & Chalasani, D. (1987). Organic interference of solidified/stabilized hazardous wastes. *Environmental monitoring and assessment*, 9(2), 133-142.
- Furman, O. S., Teel, A. L., Ahmad, M., Merker, M. C., & Watts, R. J. (2010). Effect of basicity on persulfate reactivity. *Journal of Environmental Engineering*.
- Gambhir, M. L. (2004). *Concrete technology*. Tata McGraw-Hill. Retrieved 2010-12-11.
- House D. (1962). Kinetics and mechanism of persulfate oxidation. *Chem. Rev.*, 62: 185-203.
- Huang, KC, Couttenye, R, and Hoag, GE. (2002). Kinetics of Heat-Assisted Persulfate Oxidation of methyl tert-butyl ether (MTBE). *Chemosphere*, 49, 4, 413-420.
- Huling, S. G., & Pivetz, B. E. (2006). *In-situ chemical oxidation* (No. EPA/600/R-06/072). ENVIRONMENTAL PROTECTION AGENCY WASHINGTON DC OFFICE OF WATER.
- ITRC, Development of Performance Specifications for Stabilization/Solidification, Interstate Technology & Regulatory Council, 2011  
[http://www.itrcweb.org/documents/solidifaction\\_stabilization/ss-1.pdf](http://www.itrcweb.org/documents/solidifaction_stabilization/ss-1.pdf)
- Killian PF, Bruell CJ. (2003). Thermally activated peroxydisulfate oxidation of polychlorinated biphenyls (PCBs). In: Calabrese EJ, Kostecki PT, Dragun J. (Eds.), *Contaminated Soils*, Vol. 8, pp. 27–38, Amherst Scientific Publishing, Amherst, Massachusetts, USA.
- Kolthoff IM, Miller IK. (1951). "The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium". *J. Am. Chem. Soc.* **73**(7): 3055-3059.
- Kosmatka S, Kerkhoff B, Panerese W. (2002). *Design and Control of Concrete Mixtures*, 14<sup>th</sup> ed. Portland Cement Association, Skokie, Illinois.
- Liang, C., Huang, C. F., Mohanty, N., & Kurakalva, R. M. (2008). A rapid spectrophotometric determination of persulfate anion in ISCO. *Chemosphere*, 73(9), 1540-1543.
- Lo, I. M. C. (1996). Solidification/stabilization of phenolic waste using organic-clay complex. *Journal of Environmental Engineering*, 122(9), 850-855.
- Mora VC, Rosso JA, Carrillo Le Roux G, Mártire DO, Gonzalez MC. (2009). Thermally activated peroxydisulfate in the presence of additives: A clean method for the degradation of pollutants, *Chemosphere*, 75: 1405-1409.
- Negi AS, Anand SC. (2007). *A Textbook of Physical Chemistry*, New Age International, 961 pages.
- Pacheco-Torgal F, Labrincha J, Leonelli C, Palomo A, Chindaprasit P. (2015). Handbook of Alkali-Activated Cements, Mortars and Concretes. Woodhead Publishing Series in Civil and Structural Engineering, Number 54. Woodhead Publishing. Elsevier, Cambridge, UK.

- Paria, S., & Yuet, P. K. (2006). Solidification-stabilization of organic and inorganic contaminants using Portland cement: a literature review. *Environmental Reviews*, 14(4), 217-255.
- Schwarzenbach RP, Gschwend PM, Imboden DM. (2003). Environmental Organic Chemistry, 2<sup>nd</sup> Edition, 1328 pages, Wiley-Interscience, Hoboken, NJ.
- Srivastava, V.J., Hudson, J.M., Cassidy, D.P. (2015) In Situ Solidification (ISS) and In Situ Chemical Oxidation (ISCO) Combined in a Single Application to Reduce Contaminant Mass and Leachability in Contaminated Soil. In Review for Journal of Hazardous Materials.
- Srivastava, V.J., Hudson, J.M., Cassidy, D.P. (2015) Achieving Synergy between Chemical Oxidation and Stabilization in a Contaminated Soil. In Review for Chemosphere.
- Struble L, Livesey P, Strother PD, Bye G. (2011). Portland Cement, 3rd edition: Composition, Production and Properties. ICE-Institution of Civil Engineers, 230 pp.
- Thomas, P. J., Baker, J. C., & Zelazny, L. W. (2000). An expansive soil index for predicting shrink-swell potential. *Soil Science Society of America Journal*, 64(1), 268-274.
- US EPA. 2009. Technology Performance Review: Selecting and Using Solidification/ Stabilization. EPA/600/R-09/148
- U.S. EPA (2013). *Superfund Remedy Selection Report*, 14<sup>th</sup> Edition, EPA-542-R-13-016.