Remediation Using In Situ Solidification/Stabilization of a Contaminated Source at an Industrial Landfill in Brazil with Various Reagents

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ABSTRACT: A pilot study was developed for an industrial landfill located in Brazil using in situ solidification/stabilization (ISS). The objective of the pilot study was to treat and stabilize the source zone contamination in the subsurface soils with sodium persulfate, Portland cement and other reagents via in situ soil mixing with a single large diameter auger. The main contaminants of concern were BTEX and naphthalene, specifically benzene occurring at concentrations of 7 to 7000 mg/kg. A bench-scale laboratory study was developed to test and optimize varying mixtures of reagents with the site soils to develop an ISS combination approach that was field implementable, in order to achieve gross contaminant and leachability reduction, strength and permeability. This paper presents an overview of soil mixing as it relates to environmental remediation as a "new" local technology and highlights the application of up to 30 different mix combinations to address the high level benzene concentrations. A pilot study was performed focusing on the improvement of the oxidation reagent performance by varying reaction time, number of treatment strokes at a location and use of lime or Portland cement to activate the sodium persulfate.

INTRODUCTION

ISS, also known as "Soil Mixing", is a proven environmental remediation technology that has been implemented to address soil, sediment, and groundwater remediation projects throughout the United States and is growing internationally. In Brazil, the use of this technology is a new approach for in situ treatment for the environmental market.

One of the primary objectives in treating the source area is to decrease the amount of contaminant flux coming from the source area and migrating down gradient through groundwater flow. The use of ISS involves two different concepts: Solidification, a physical process where the reagents are mixed with the soil, sediment or sludge creating a solid monolithic where the contaminants are entrapped or encapsulated (Moran et al., 2017); and Stabilization where chemical reactions occur between the reagents and contaminated material, reducing leachability into a stable insoluble form and immobilizing contaminated materials or reducing their solubility through a chemical reaction (Bates and Hills, 2015).

The target site is an industrial landfill at a former steel mill located in Brazil. Several subareas of the site have been identified for remedial activities, including 13 different disposal cells (or reactors) containing a heterogeneous composition of impacted media with each cell containing various soil types, waste disposal/generation variability, underground obstructions and wide ranges of contaminant concentrations.

The contaminants of concern at the site include petroleum hydrocarbons. Of these, benzene, toluene, ethylbenzene, xylenes (BTEX) and naphthalene (N) have been identified as the primary contaminants of concern (COCs) and they were the focus of treatment.

The ISS of organic contaminated waste may involve the alteration/transformation of organic compounds or their participation in physical processes, such as absorption or encapsulation. The outcome of ISS is to retard the movement of the hazardous constituents within prescribed safe limits, defined by leachate quality (Bates and Hills, 2015). The use of combined technologies with ISS, such as chemical oxidation, decreases the contaminant mass before the immobilization, avoiding a possible post-treatment leaching if the contaminant mass is too high.

The pilot study was designed to evaluate the use of two remedial technologies, in situ chemical oxidation (ISCO) and ISS. ISCO using activated persulfate is a destructive technology commonly used for treatment of contaminated soil and groundwater. Activated persulfate has been demonstrated as effective for treating BTEX and naphthalene in numerous studies including Huang et al. (2005); Crimi and Taylor (2007); and Sra et al. (2008). One means of activating persulfate is elevation of pH to > 11. For this approach, typically a strong base such as potassium sodium hydroxide is added to elevate pH to a range of 11 to 12. Other approaches for elevating pH, such as use of lime, are also viable, as long as the pH can be elevated and maintained above pH 11. This favors generation of hydroxyl radicals capable of destroying many fuel hydrocarbons (Liang et al., 2007). Because the stoichiometric demand that high concentrations of hydrocarbons exert for persulfate is high, multiple injections are typically necessary to treat a site to completion (Krembs, 2008), which can result in very high treatment costs.

ISCO and ISS are complementary and compatible technologies for treating sites with significant contaminant mass. ISCO can be implemented to significantly reduce mass; however, it would be too expensive to achieve low concentration treatment goals alone. ISS can be implemented to immobilize mass; however, if concentrations of contaminant are too high, post-treatment leaching may occur. By reducing contaminant mass prior to immobilization, the potential for leaching is lessened. Furthermore, the high pH of lime or cement used for ISS can effectively activate persulfate, making their combination synergistic. Finally, the aggressive mechanical mixing approaches used for ISS have been demonstrated as effective for the introduction of solid phase oxidants (Siegrist et al., 2011).

PROJECT BACKGROUND

In May 2017, the pilot study was performed through soil mixing technologies (ISS and ISCO) using large diameter augers. Soil mixing in this application consisted of injecting prepared reagent combinations in a wet-based delivery (mixed in an on-site batch plant) through a hollow stem kelly bar and auger using an excavator-mounted drill rig. The drill rig would rotate the auger while advancing in depth and evenly delivering reagents while simultaneously breaking apart the soil matrix. With this approach, reagents are homogenized with in situ soils with even delivery of the reagents over the depth of an individual auger location (referred to as a “column”).

The facility consists of an industrial landfill classified as hazardous waste (or “Class 1” according to Brazilian standards). The waste originated from the steel mill carbochemical plant and is often described as a tar. Tar was mixed into five reactors with slag and lime to be “stabilized”. The stabilized tar was then disposed of on site within one of the eight cells. The project area consisted of 13 different heterogeneous hot spot contaminant areas (8 cells and 5 reactors). Each hot spot characteristic varied in contaminant concentration, waste thickness and composition. Each area contained a thin layer of clean soil cover around 20 inches (51 cm). Pilot study columns were installed through the soil cover, waste materials and thin bottom slab (Figure 1). Obstructions, if encountered, were removed with the aid of a support excavator.

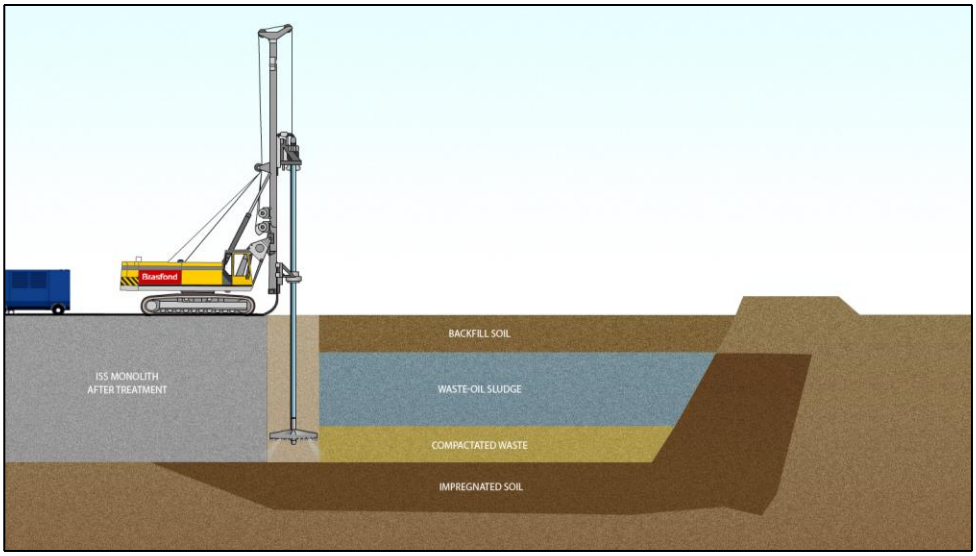

FIGURE 1. ISS drilling process schematic

Cells and reactors varied in size from 828 square feet to 26,446 square feet (77 to 2,459 m^2) with observable waste from 9.8 feet to 18 feet deep (3 to 5.5m). Further details of the size and volume composition of the disposal cells and reactors are included in Table 1 and Table 2.

Cell ID	Area (ft^2)	Waste Layer (ft)	Waste Volume (yd^3)	Waste Depth (ft)	Total Volume (soil + waste) (yd^3)
1	25,252	14.76	13,808	1614	15,342
2	23,960	14.76	13,101	1614	14,557
3	17,512	9.84	8,349	13.12	8,512
4	20,860	9.84	7,604	13.12	10,139
5	16,834	11.48	7,159	13.12	8,182
6	24,143	11.48	10,268	18.04	16,135
7	26,446	14.76	14,461	16.4	16,068
8	14,788	9.84	5,387	11.48	6,285
	169,795		**80,137**		**95,220**

TABLE 1. Cell dimension and volume

Reactor ID	Area (ft^2)	Waste Layer (ft)	Waste Volume (yd^3)	Waste Depth (ft)	Total Volume (soil + waste) (yd^3)
R1	2,109	14.76	1,153	16.4	1,281
R2	2,055	11.48	874	13.12	999
R3	1,119	9.84	408	11.48	476
R4	828	11.48	352	13.12	402
R5	882	8.2	268	9.84	321
	6,993		**3,055**		**3,479**

TABLE 2. Reactor dimension and volume

A bench-scale study was performed to evaluate potential ISS mix designs prior to the execution of the pilot study and also to test the effectiveness of sodium persulfate (SPS) addition to the impacted site soils. Samples were collected of in situ soils and tested for geotechnical characteristics. The samples obtained, were classified via the Unified Soil Classification System (USCS). SM, OL, and GM classified soils were encountered, which equate to silty sands, organic silts and silty gravels. Oxidant demand testing was also performed and showed that SPS was fully consumed within the first three days of reaction. The sodium persulfate addition to the soils in the tests performed resulted in significant reductions in the total concentrations of the contaminants of concern related to alkaline pH controls. Also, the geotechnical tests from the bench scale were also favorable, showing the achievement of target unconfined compressive strength (UCS) of 20 psi for all mixes at 7 days of cure time and well exceeded the target at 28 days. The target permeability of less than $1x10^{-5}$ cm/s was met by all mixes at 28 days and bentonite was added to several of the mixes to asses reduction of the permeability of the monolith to aid in reducing leachability. In summary, the results from the bench-scale test confirmed the feasibility of the technology and warranted the execution of the pilot study.

The ISS pilot study was implemented from the pre-excavation work platform to a depth between 19.7 to 32.8 feet (6 to 10 m) below ground surface (bgs). A test pit or pre-excavation was conducted prior to ISS to remove subsurface obstructions and to locate the perimeter (limits) of the cells and reactors at the landfill.

In total, 112 columns were installed among the various reactor and cell locations. For the purposes of this study, the Project Team utilized a 1.5 m (5-foot) diameter auger and a 2.4 m (8-foot) auger for the purpose of assessing the feasibility of mixing with the larger diameter auger.

The soil mixing rig that was used for this work was a MAIT 300 with large diameter mixing tools capable of pumping fluid through the Kelly bar and mixing head (Figure 2). It was equipped with a mast inclination measuring system with an automatic mast adjustment. This assured that the soil mixed columns are installed within strict verticality tolerances.

FIGURE 2. Drill rig & large diameter auger

REMEDIAL OBJECTIVES

In order to evaluate the remedial approach, the following objectives were established prior to the implementation of the pilot study:

- Assess the successful field application of ISS for each of the discrete cells/reactors.
- Evaluate the impact of activated sodium persulfate and ISS with Portland cement through the following metrics:
  - Mass destruction of the petroleum hydrocarbons (specially BTEX-N);
  - Reduction in leachability of the petroleum hydrocarbons;
  - Reduction of soil hydraulic conductivity;
  - Increase unconfined compressive strength soil to greater than 20 psi (0,137 MPa).

MATERIAL AND METHODS

To assess the ability to achieve the remedial objectives, the project team developed a pilot study work plan that included varying several key parameters:

- Reagent combinations and addition rates consisting of:
  - Portland cement;
  - Sodium persulfate (Klozur SP);
  - Bentonite;
  - Lime.
- Number of reagent doses/treatment passes at an individual column location;
- Allowable reaction time between reagent doses/passes;
- Based on the depth of impacted materials, site access, availability of equipment in Brazil and an evaluated most economical means of implementation, large diameter auger based soil mixing via an excavator mounted drill was selected as the method to deliver the reagents/mixes.

As shown in Table 3, different reagent strategies were applied. The design mixes were tested at 12 different locations (cells) and, in total, 5,513 cubic yards (4,215 m^3) of material was treated. Total reagent utilization consisted of 38 tons of Sodium Persulfate, 36 tons of hydrated lime, 633 tons of Portland cement, and 21 tons of bentonite.

Reagents were applied in the field at each column location. Reagent addition was calculated as a percent (%) by weight of soil. Application rates of sodium persulfate, Portland cement, lime and bentonite were applied at various rates as depicted in Table 2. In each column location, Portland cement was always added in either the first or second dose of a location as with ISCO via soil mixing, without the addition of a binder material, the remaining soil mixed product remains geotechnically unstable.

Portland Cement	Sodium Persulfate	Lime	Bentonite	Reaction Duration between Applications (days)
8%	0.00%	0.0%	0.0%	0
12%	0.27%	0.5%	0.5%	1
-	0.54%	1.0%	1.0%	5
-	0.81%	-	-	-
-	1.08%	-	-	-
-	1.61%	-	-	-
Note: Reagent addition was measured as a % by weight of soil.				

TABLE 3. Pilot Study mix designs

In general, other additives may be applied for ISS applications including blast furnace slag, flyash, cement kiln dust, activated carbon, bentonite clay, organic clay, zero valent iron (ZVI), potassium permanganate, etc (see Andromalos, Ruffing and Peter). However, the focus reagents were on those that have shown favorable outcomes to other sites with similar contaminants of concern and on reagents that are readily available in Brazil.

The pilot study also evaluated the sequence in which the reagents were introduced. Three different reagent addition sequences were tested. The sequences included: introducing all the reagents in one dose, introducing half the sodium persulfate in the first dose activated with lime and waiting 1 day to introduce the remaining reagents, and introducing half the sodium persulfate in the first dose activated with lime and waiting 5 days to introduce the remaining reagents.

RESULTS AND DISCUSSION

The pilot study included an extensive quality control (QC) process including post treatment testing for UCS, hydraulic conductivity, mass reduction analyses and leachability. The QC procedures and testing allowed for proper assessment of the viability ISS and ISCO at the site. Laboratory testing confirmed that the soils were well mixed and that the reagents were well distributed throughout the soil columns.

Baseline chemistry consisting of totals and leaching were compared to ISS/ISCO samples. Wet grab samples were molded from freshly mixed ISS columns. Samples were analyzed with a focus on BTEX and naphthalene for mass reduction and leachability. Leachability test results were compared against local Brazilian regulatory standards for hazardous waste. From a geotechnical perspective, samples were compared from a UCS and hydraulic conductivity stand point.

Destruction of Petroleum Hydrocarbons. Alkaline activated SPS was applied at the site in an effort to decrease the contaminant mass. Within the dataset provided, there are 27 columns with both baseline and post application data and 26 of those columns received treatment with alkaline activated SPS. Comparing the post application results to baseline data, 77 percent (20 of the 26 results) of the columns treated with SPS had a decreasing trend. So, 77% of the post application results indicate a reducing trend and only 23% (6 of 26) of the results indicate an increasing trend. This indicates that the concentration of measured petroleum hydrocarbons decreased as a result of the remedial activities.

As shown in Table 4, 20 column locations indicated a decreasing post-treatment contaminant trend, 16 of the 20 showed reductions of greater than 50% compared to baseline, 14 of the 20 showed reductions of greater than 75%, and 8 of the 20 had reductions of greater than 90% compared to the baseline concentrations.

Columns with Aggregate Mass Reduction: Klozur SP						
Number of Columns						
Reduction	Total SP	0.27%	0.54%	0.81%	1.08%	1.62%
>90%	8	8	6	3	2	0
>75%	14	14	11	6	4	1
>50%	16	16	13	7	5	1
>1%	20	20	17	11	7	1
Increase	6	6	6	1	1	0
Percent of Total Columns						
Reduction	Total SP	0.27%	0.54%	0.81%	1.08%	1.62%
>90%	31%	31%	26%	25%	25%	0%
>75%	54%	54%	48%	50%	50%	100%
>50%	62%	62%	57%	58%	63%	100%
>1%	77%	77%	74%	92%	88%	100%
Increase	23%	23%	26%	8%	13%	0%

TABLE 4. Contaminant mass reduction analysis

Leachability Testing. Out of the 112 mixed columns, 51 columns had post ISS leachability testing assessed. On average, the leachate contaminant concentrations (BTEX and naphthalene) in the treated cells decreased by 91.6% compared to the baseline sample analyzed at the time of the bench scale study.

Evaluating the results of the 51 columns from which the leachability tests were carried out, for the five contaminants of interest mentioned, the total of 255 results were evaluated. Of these, 37 were above the Brazilian environmental resolution (CONAMA N.420/2009) Brazilian environmental agency intervention limit and consequently 218 or 85% of these analyses were below the limits defined for groundwater.

It can be highlighted that one of the objectives of the study was to achieve reductions of the contaminant leaching concentration that reach the Brazilian Standard classified as hazardous waste "ABNT NBR 10.004 de 2004" (based on USEPA - Environmental Protection Agency 40 CFR - Part 261 - 24 - "Toxicity Characteristics"). According to this regulation, just benzene presents a specific goal of 500 µg/L. Based on this goal, just one of the treated column presented results above the limits, which means that 98% achieved the standard goal. Table 5 includes an analysis of the percentage of leachability samples that achieved the local regulatory limits.

	Benzene		Ethylbenzene	Naphthalene	Toluene	Xylenes	Total
	5µg/L*	500µg/L*	300µg/L*	140µg/L*	700µg/L*	500µg/L*	
Total number of analyses	51	51	51	51	51	51	255
Results Above limits	45%	2%	0%	27%	0%	0%	15%
Results Bellow limits	55%	98%	100%	73%	100%	100%	85%

* CONAMA N.420/2009 ** ABNT NBR 10.004/2004

TABLE 5. Leachability reduction comparison of ISS/ISCO to Brazilian regulation limits

Unconfined Compressive Strength and Hydraulic Conductivity. The intent of ISS is to help immobilize the contaminants of concern. Hydraulic conductivity is a measurement of the ease by which water moves through soils. The lower the hydraulic conductivity, the greater the resistance and the less mobile groundwater tends to be. Hydraulic conductivities of lower than 10^{-6} cm/sec are typical of silts and clay materials and are generally considered to be impervious.

The data from the pilot study show that most hydraulic conductivities were in the range between 10^{-5} cm/sec and as low as 10^{-10} cm/sec. This indicates that post treatment of the soils contained a hydraulic conductivity similar to or lower than soils such as silts and clays. In 96% of the executed columns, the hydraulic conductivity post reagent application was < $1.0x10^{-06}$ cm/sec.

The UCS target to this site is considering that the site has no future re-use determined other than to support a cap/soil cover for a controlled landfill. Such an application would require only 20-25 psi. A UCS of > 20 psi was achieved after 7 days of cure in 91% of the executed columns and in 95% after 28 days of cure.

General Results. An analysis of the data from the pilot study indicates the following:

- The addition of alkaline activated SPS (Klozur SP) helped decrease contaminant mass during the pilot study by as much as 99% in certain columns;

- On average, the leachate contaminant concentrations (BTEX and naphthalene) in the treated cells decreased by 91.6% compared to the baseline sample taken from the bench scale;
- Increasing concentration of Portland cement resulted in decreasing leachate concentrations of the site contaminants;
- Increasing concentration of bentonite resulted in decreasing leachate concentrations of site contaminants when combined with Portland cement;
- Increasing concentration of alkaline activated persulfate resulted in decreasing leachate contaminant concentrations:
    - Leachate contaminant concentrations were further decreased when the alkaline activated persulfate was delivered in two separate dosages compared to a singular dose.
- The remedies as applied resulted in targeted geotechnical soil characteristics such as compressive soil strength and hydraulic conductivity.

CONCLUSIONS AND RECOMMENDATIONS

The performance of the pilot study combining ISS and ISCO technologies was successfully applied at the site. Based on the analyses of the ISS quality control testing adopted during project execution, significant mass reduction, leachability and geotechnical property improvement confirmed the applicability of this remediation approach for a full-scale application.

It is recommended that for each remediation area, the sodium persulfate should be introduced in two doses with the first dose being activated by lime. For example, if the target persulfate is 1% by weight of soil, it is introduced in two doses of 0.5% each with the first activated with lime and the second with Portland cement.

The dataset provided indicates that the remedial activities including the addition of alkaline activated sodium persulfate, effectively decreased the concentration of BTEX and naphthalene.

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