

# The Effects of S-ISCO on Contaminant Liberation

## Summary

A frequently asked question regarding surfactant use in remediation is if desorbed soil contaminants will persist and elevate groundwater contaminant levels. Because in-situ chemical oxidation consists primarily of aqueous phase reactions, the use of surfactants for desorption and emulsification of tightly sorbed, hydrophobic contamination from soil into the aqueous phase is a crucial step toward achieving complete or near complete remediation of these contaminants. The use of surfactant alone will result in increased groundwater contaminant concentrations, which in the absence of an oxidant for destruction can lead to undesired contaminant mobilization. Field and laboratory data presented in this paper show that combined surfactant and oxidant chemistry used during Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO®) addresses this issue.

S-ISCO utilizes simultaneous injection of surfactant and oxidant to desorb and emulsify contaminants, rendering them immediately available to an oxidant for destruction. The surfactant and oxidant work together to desorb, emulsify, and destroy hydrophobic contamination from soils. Because oxidant and surfactant are injected as a homogenous solution, the oxidant immediately begins destroying emulsified contamination. The injected chemistry travels together through the subsurface with the groundwater providing continued desorption, emulsification, and oxidation of contaminants throughout the duration of the treatment, until soil and groundwater concentrations reach remedial objective levels.

Analysis of site groundwater monitoring data discussed in subsequent sections, show presence of S-ISCO chemistry in various wells at a site, throughout and after implementation. The data illustrates that surfactant and oxidant are simultaneously present in these wells, along with elevated groundwater TPH concentrations (emulsification) followed by decreased TPH levels indicating destruction of all emulsified contamination via oxidation. Post injection data demonstrates that the decreases in groundwater TPH levels are sustained once injections cease and the surfactant and oxidant have completely reacted.

Additional analysis, based on laboratory data and average groundwater velocities, provides a projection of the potential degradation of TPH contamination against the distance traveled in the subsurface. This projection illustrates how emulsified contaminants would be continuously oxidized during travel and would be brought to remedial levels before traveling a significant distance.

Finally, laboratory tests examine the interaction between surfactant and oxidant in the presence and absence of a contaminant. Graphs illustrate that contaminant is more susceptible to oxidation than the surfactant, where in the presence of contaminant the surfactant persists and in the absence of a contaminant the surfactant is oxidized.

Overall, field and laboratory data show combined surfactant and oxidant chemistry used during S-ISCO provides effective solubilization and simultaneous oxidation of soil-sorbed, hydrophobic contaminants, leaving behind remediated soil and clean groundwater that meet site cleanup criteria.

## Background

Hydrophobic organic contamination, sorbed on soils and leaching into groundwater, is a persistent problem at many contaminated sites. Traditional In Situ Chemical Oxidation (ISCO) treatments attempt to address these sites using aqueous solutions containing activated oxidants to clean the groundwater. These aqueous based reactions are limited by the mass transfer of the hydrophobic contaminants into the aqueous phase as well as the limited contaminant surface area exposed to the aqueous phase oxidants. Due to these limitations, ISCO treatments typically leave sites with temporarily clean groundwater which is subject to rebound once contaminants leach back into the aqueous phase, from the unaddressed soil-sorbed contaminants, re-establishing its equilibrium of contaminated groundwater.

S-ISCO was developed to address this issue. During a S-ISCO treatment proprietary plant-based surfactant and co-solvent blends are simultaneously injected with the oxidant in a homogeneous solution. This surfactant oxidant mixture works simultaneously to desorb and emulsify the contaminants while immediately exposing them to oxidants for destruction. By emulsifying contaminants in the aqueous phase, contaminant surface area is greatly increased thereby increasing the oxidants efficiency to contact and oxidize the contamination. The combination of a proprietary plant-based surfactant blend, VeruSOL, and an oxidant work efficiently together as the contaminants are more susceptible to oxidation than the surfactant, and therefore are primarily oxidized first, as shown in Example 2 in this document.

## S-ISCO

EthicalChem's patented S-ISCO process involves simultaneous use of surfactants with oxidants to desorb, emulsify, and destroy free phase contamination. The injected S-ISCO chemistry consists of an aqueous blend of surfactants, oxidants, and an activator, which exist in a stable homogenous solution with no risk of phase separation. This single solution travels through the subsurface exposing the sorbed contaminants to the surfactant and oxidant simultaneously. Once the surfactant has emulsified the contaminant into the aqueous phase it is immediately engaged with the oxidant for destruction. Additionally, the surfactants create a micro-emulsion, bringing the contamination into solution by encapsulating and solubilizing it in micro-sized micelles, thereby greatly increasing the surface area of the contamination that is available to oxidants for rapid destruction.

Unlike surfactant flush methods there is never a case during S-ISCO implementation where surfactant would be traveling alone through the subsurface without an oxidant. During S-ISCO injections, surfactant and oxidants are strategically dosed to minimize or eliminate the risk of surfactant outlasting the oxidant. Combined oxidant-surfactant solution will allow for destruction of emulsified contaminants before they travel a significant distance from the point of desorption, given typical groundwater velocities. Remedial activities using S-ISCO have been completed near sensitive receptors including bodies of water. Strategically placed monitoring wells around the site and off site enable monitoring movement of S-ISCO

chemistry and verify that emulsified contaminants do not approach sensitive receptors. Throughout the implementation and post-injection monitoring periods, monitoring wells are sampled and analyzed to ensure S-ISCO chemistry is flowing to the desired locations, contaminants are not traveling beyond desired boundaries, and to confirm all chemical components (surfactant and oxidant) are still present as the chemistry travels through the subsurface.

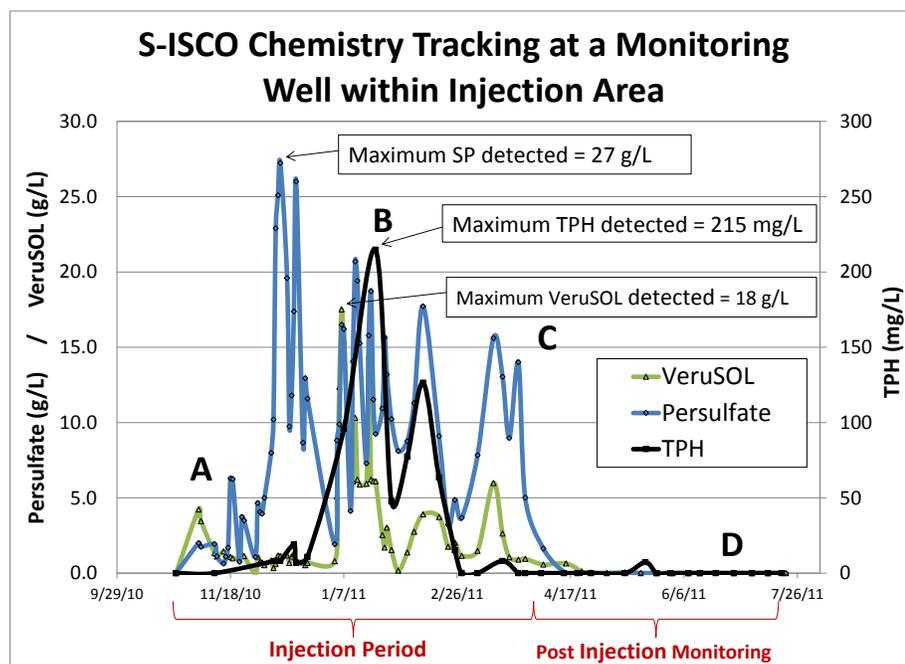
Monitoring data from a New York City area full scale implementation presented below demonstrates simultaneous travel of all S-ISCO chemicals throughout the subsurface. Additionally, a theoretical analysis was completed using a combination of laboratory treatability data from contaminated site treatability tests, along with a range of site groundwater seepage velocities. The two analyses illustrate simultaneous travel of oxidants and surfactants in the subsurface, along with the range of potential contaminant travel versus the time it takes to oxidize emulsified contaminants. Finally, laboratory data is presented which illustrates the persistence of S-ISCO surfactants when a contaminant is present, and where in the absence of a contaminant the surfactant is oxidized.

## Field and Laboratory Data

### Example 1: Site monitoring data from an MGP site located adjacent to a river

The graph below depicts S-ISCO chemicals, VeruSOL surfactant and sodium persulfate, along with aqueous phase TPH concentrations, at a monitoring well located within the treatment area. The x-axis represents the timeframe of the entire project beginning with injections in October through March, followed by post-injection monitoring through July.

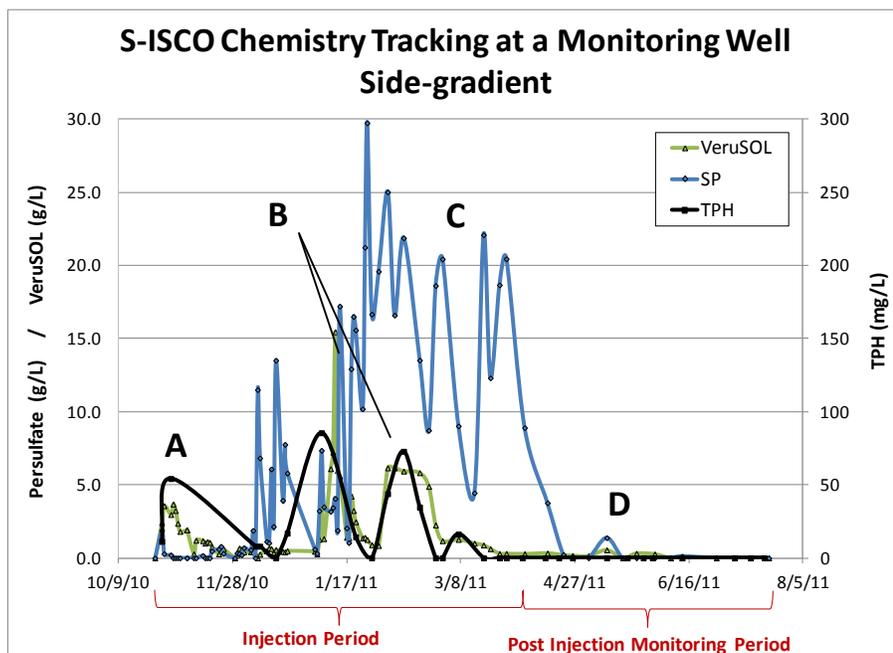
The graph shows the presence of VeruSOL and persulfate immediately after injections began (A). The surfactant and oxidant arrive together at this well, with no emulsified TPH. As the surfactant begins to desorb and emulsify contaminants from the soil matrix, the aqueous TPH concentrations spike up to a maximum of 215 mg/L in this well (B). At the same time while the TPH is elevated,



monitoring data shows surfactant and oxidant still present in this well. Throughout the injection period and a few weeks post injection, persulfate was present at this well, and was oxidizing the emulsified TPH.

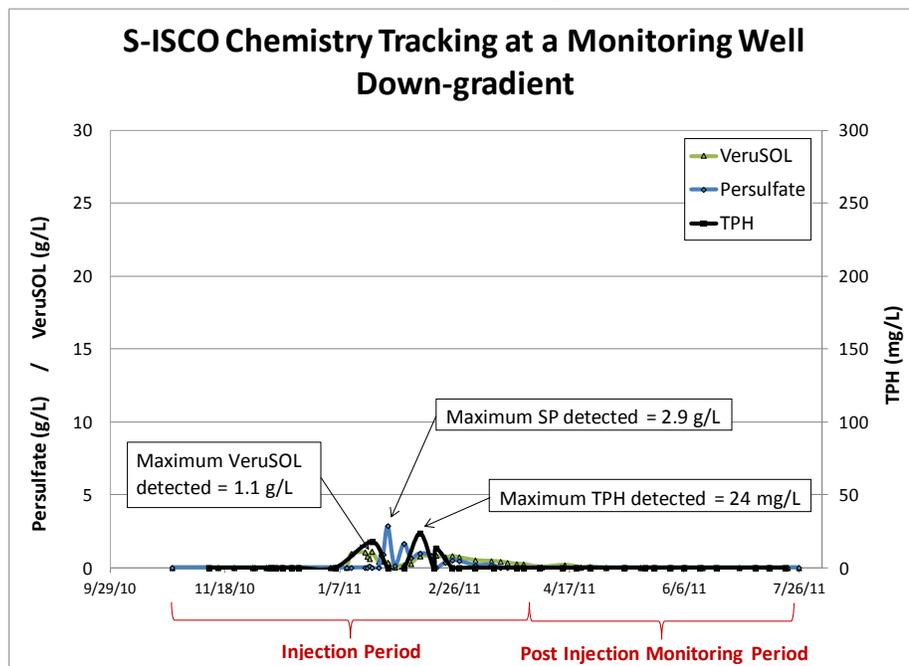
Toward the end of injections, in March, the aqueous TPH concentrations return close to non-detect levels while oxidant and low amounts of surfactant still remain present (C). The presence of surfactant along with the declining TPH indicates that the surrounding soil has been effectively cleaned of the sorbed MGP material (i.e. there is no TPH left to solubilize). Shortly after injections ceased all the groundwater parameters showed no indication of surfactant and oxidant suggesting both surfactant and oxidant have eventually been completely consumed (D).

The graph to the right illustrates the presence of S-ISCO chemistry and emulsified TPH present in a well side-gradient to the injection wells. Shortly after injections began, oxidant, surfactant, and emulsified TPH are present in this well (A). Throughout injections the surfactant and emulsified TPH remain present (B) along with a strong presence of oxidant (C). Data demonstrates how the surfactant and



emulsified TPH are eliminated toward the end of the injection period (March), however oxidant remains. Post injection monitoring parameters showed a small presence of residual oxidant and a trace of surfactant, however no sign of emulsified TPH was observed moving through this well (D).

The third graph (right) shows parameter data collected at the same site from a down-gradient well. This data shows a minor presence of all S-ISCO chemicals (VeruSOL and persulfate) continuing to work and desorb TPH from the soil down gradient from the injection wells. The maximum concentrations seen are 1.1 g/L surfactant 2.0 g/L persulfate, and 24 mg/L of emulsified TPH.

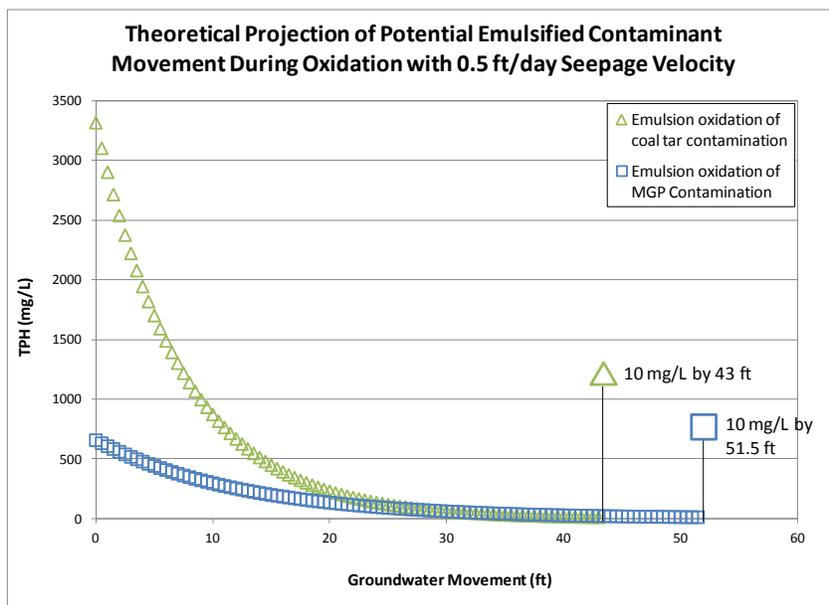
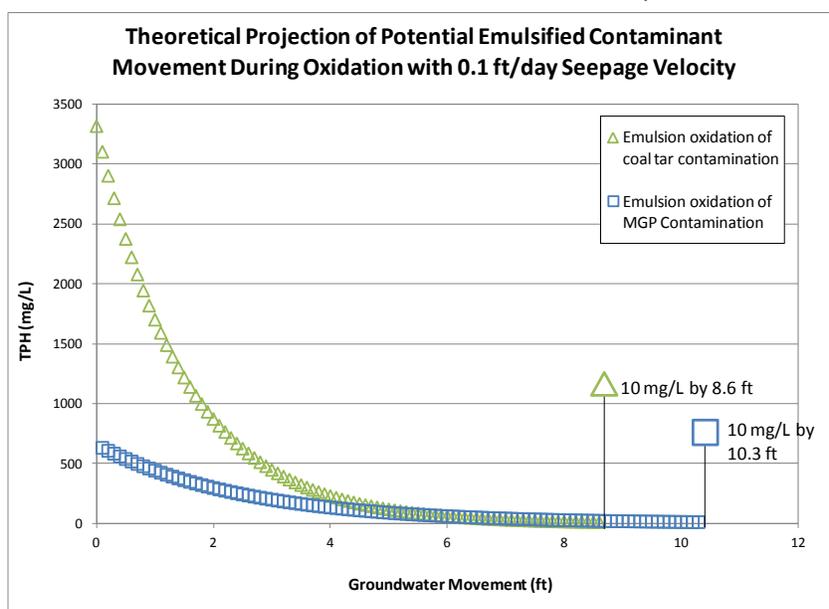


These low concentrations indicate that successful oxidation reactions took place up gradient between the injection wells and this location as the chemicals traveled. The chemistry was present in this well in early January, approximately 3 months into the injection period. Following the completion of injections, neither the injected chemistry nor elevated TPH is observed at this down gradient well, indicating all chemistry was destroyed on the site, and no residual S-ISCO material or desorbed TPH travelled further in the subsurface throughout the 4 month post-injection monitoring period.

**Example 2: Laboratory test data on oxidation of emulsified TPH and theoretical projection of travel**

Laboratory tests were completed for various sites to evaluate the oxidation of emulsified contaminants. An emulsion was prepared for each project by thoroughly shaking site soil with a VeruSOL surfactant solution. The aqueous phases were removed and treated with alkaline activated sodium persulfate; there was no soil present during this oxidation test. The evaluation of these results is intended to provide theoretical examples of the time required to destroy emulsified contaminants.

This graph on the right (top) illustrates projected movement of emulsified TPH from a contaminated site. This projection uses the rate of TPH destruction observed in the laboratory during an aqueous phase oxidation test to generate an estimate of potential contaminant movement assuming a groundwater seepage velocity of 0.1 ft/day where TPH was emulsified by surfactant from contaminated site soil. As illustrated, the emulsions began with aqueous TPH concentrations of about 3,300 mg/L and 650 mg/L. In the time it takes to oxidize the TPH down to 10 mg/L the emulsified contaminants could potentially travel between 8 – 10 ft for these two scenarios.



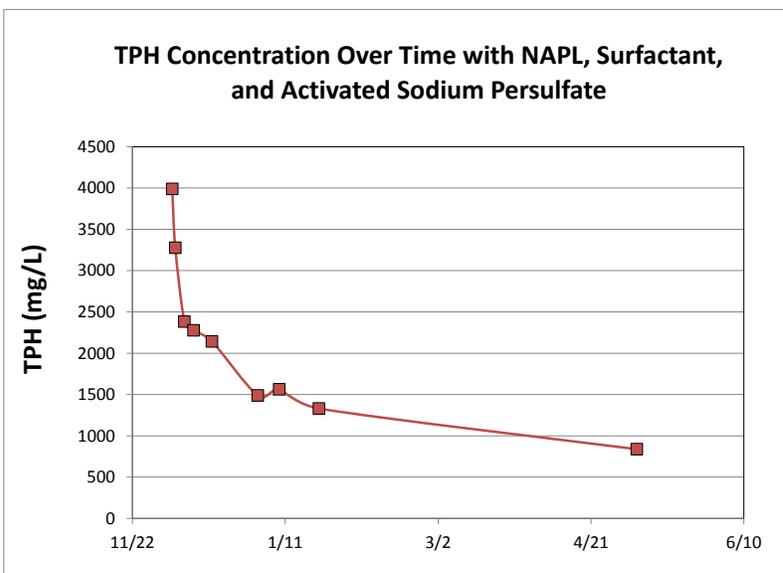
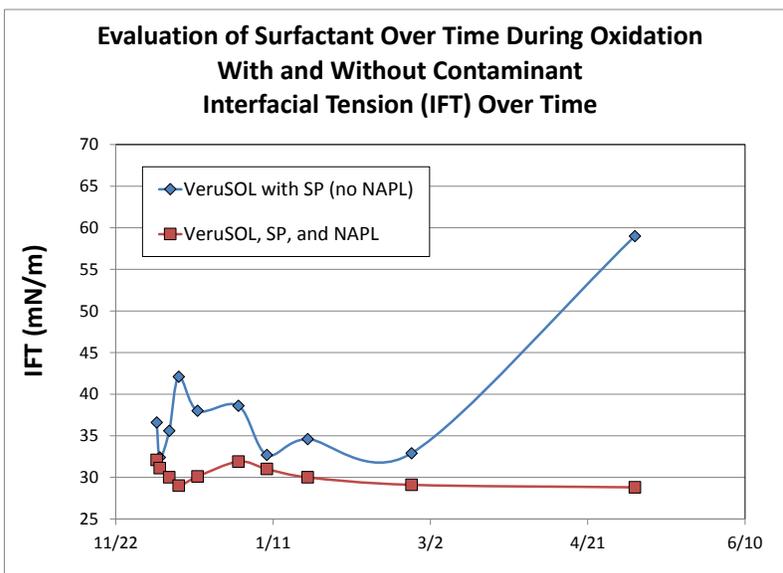
The bottom graph depicts the potential travel with a relatively high seepage velocity of 0.5 ft/day. As illustrated in this graph the potential TPH may travel between 43 – 52 ft by the time the TPH reaches 10 mg/L.

As these two theoretical graphs show, the emulsified contamination is rapidly degraded to below 100 mg/L by 24 – 26 ft in both scenarios where the ground water velocities are 0.1 ft/day and 0.5 ft/day. In a field implementation scenario it is unlikely the emulsion would travel as swiftly as predicted by this theoretical projection because unlike in the lab, emulsification and oxidation would occur simultaneously rather than sequentially, and emulsified TPH concentrations would not reach as high levels.

### Example 3: Laboratory test data on surfactant oxidation

Laboratory tests were completed to evaluate the effect of sodium persulfate (oxidant) on the surfactant in the presence and absence of a contaminant and to test the hypothesis that when surfactant, oxidant, and contaminant are all present within a system, the contaminant is primarily subject to oxidation first, before the surfactant due to the molecular characteristics of each. The contaminant used was a non-aqueous phase liquid (NAPL) consisting of diesel range total petroleum hydrocarbons (TPH). Interfacial tension (IFT) was measured to evaluate the presence of surfactant. The IFT of pure water is about 72 mN/m, and a decrease in IFT to a minimum of approximately 32 mN/m signifies the presence of surfactant. The amount of surfactant used in this test was 10 g/L. A typical field dose of surfactant during S-ISO is 5 – 25 g/L, depending on the type and quantity of contamination.

The top graph to the right shows that after 81 days (2/28) the surfactant is still present (therefore not oxidized) in both the system with NAPL and without NAPL. The next data point, collected at day 152, shows that the surfactant has been oxidized (IFT increased back towards 72 nM/m) in the reaction without NAPL, however it is still



present, stable, and effective in the reaction with NAPL. The graph on the bottom right shows the TPH concentration in the reaction with surfactant (VeruSOL), persulfate, and NAPL, and confirms that destruction of emulsified NAPL is taking place (while the surfactant remains present).

Note, this lab test is a comparison of oxidant/surfactant with and without NAPL in an aqueous solution only and the oxidant dosing was not designed for rapid destruction of the NAPL. Additionally, in the subsurface, in the presence of many other factors such as soil type, pH, inorganics, etc., the actual destruction rates will typically be faster, however the relative relationships are expected to be the same; surfactant will exist longer in the presence of contaminants versus without contaminants.

Overall this test data supports that when surfactant, oxidant, and contaminant, are all present within a system, the contaminant is subject to oxidation first, before the surfactant.

## **Conclusion**

S-ISCO is a unique remedial technology which provides destruction of tightly sorbed hydrophobic contaminants and residual source material on soil by use of simultaneous injections of surfactants and oxidants. Field experience has demonstrated that combined surfactant oxidant solutions are highly stable and are able to travel through the subsurface as a homogeneous solution to reach target contaminated areas. This solution results in simultaneous desorption, emulsification, and oxidation of contaminants. The contaminant surface area exposed to oxidants is greatly increased by emulsification into the aqueous phase. Once emulsified, the solution may continue to travel slowly with groundwater however the destruction rate of the emulsified contaminants will allow for complete or near complete destruction before contaminants are able to move very far. Additionally, laboratory tests have shown that plant-based surfactants used by EthicalChem do not directly compete with the contaminants for reaction with the oxidant during oxidation. The surfactant molecules are relatively stable, with a larger molecular structure than most organic contaminants, making them less susceptible to oxidation than the contaminants. Once most/all contaminants have been emulsified and destroyed, the remaining surfactant will be oxidized as well. If an oxidant is no longer present, the readily biodegradable surfactants will degrade.

In summary, S-ISCO is a highly sustainable, environmentally friendly technology that addresses source contamination and eliminates rebound, unlike chemical technologies which only address groundwater. With controlled implementation strategies and monitoring schedules, S-ISCO implementations have been successfully completed throughout the US and internationally near various sensitive receptors and bodies of water.