Klozur® Persulfate Soil Mixing Recommendations and Application Guidelines

Klozur® persulfate is a high purity environmental grade product used as an *in situ* chemical oxidation (ISCO) technology to treat a wide variety of contaminants of concern in soil and groundwater around the world. Klozur persulfate can be activated using PeroxyChem's patented technologies[1] to form the powerful oxidative and reductive radicals that aggressively treat targeted contaminants. This technology is well established having been successfully applied in thousands of field applications and scientifically validated in hundreds of independent peer-reviewed journal articles and conference presentations.

The Klozur persulfate portfolio includes several high purity products:

- **Klozur SP** is based on sodium persulfate which is highly soluble and has been used for over a decade to treat contaminated source areas.
- **Klozur One** is a blend of Klozur SP with carefully crafted activator technologies combined into a single all-in-one product. Klozur One makes applying Klozur SP more convenient than ever before.
- **Klozur KP** is based on potassium persulfate which has over an order of magnitude lower solubility than Klozur SP. This allows it to serve as an extended release oxidant to treat low permeable soils and in permeable reactive barriers.
- **Klozur CR** provides a combined remedy of chemical oxidation and bioremediation. The product is a blend of Klozur SP and PermeOx® Ultra, typically used to treat low to moderately contaminated site source zones, plumes, and in excavation backfill applications.

Klozur products are typically applied using an injection, soil mixing or backfill strategies to establish contact between Klozur SP and the contaminants of concern. This document discusses the soil mixing strategies for applying Klozur products.

Soil Mixing

A soil mixing strategy typically involves the mechanical agitation of subsurface soils blending in both Klozur persulfate and the necessary activator reagents. The mechanical agitation breaks apart the natural soil structure and helps to establish contact between activated Klozur persulfate and the contamination found in the soils. This contact is key for successful remediation. A soil mixing application strategy can be particularly useful in treating source zones and lower permeable soils such as silts or clays.

ISCO works by establishing contact between sufficient mass of activated persulfate with the mass of contamination

Soil mixing has been used to target:

- Source areas as the primary method of treatment
- Residual contamination after excavation as a secondary method of treatment
- Combined with *in situ* stabilization (ISS) and other technologies
- To blend in reagents to form a permeable reactive barrier

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Key Advantages of Soil Mixing

- Very effective in establishing contact between the activated persulfate and contaminant on soils
- Can be used to breakup low permeability materials allowing better contact minimizing the impact of site soil heterogeneity.
- Helps establish contact of reagents with zones of high concentration including non-aqueous phase liquids (NAPLs)
- Rapid process that is well suited for source zones
- Amendments can be added to increase soil strength and decrease contaminant flux from soils

In situ soil mixing of activated Klozur persulfate can be combined with a second remedial technology: *in situ* stabilization (ISS). The combination of ISCO and ISS occurs when Portland cement, bentonite, or other solidification compounds are blended in with the activated persulfate. The benefit of combining both technologies into a single application is that ISCO can be used to reduce the contaminant mass while ISS can be used to reduce the potential contaminant mass flux coming from the blended area. In addition, ISS using Portland cement can increase soil strength following a soil mixing application, providing surface support.

Methods of Soil Mixing

There are several different methods that can be used to mix the Klozur persulfate with soil to establish contact with the contamination.


Courtesy of CH2M

Excavation Buckets

The buckets on backhoes and excavators can be used to mix the reagents with the soils. This method typically has a low mobilization costs, but tends to be less efficient, have a limited depth range, and reagents tend to be applied at the surface and blended down into the target depth interval. Because of these limitations, excavation bucket mixing is typically used for smaller and shallow sites.


Courtesy of ISOTEC

Excavator Mounted Drum Mixers

Excavator mounted drum mixers have become more advanced and their use more commonplace. These drum mixers typically have a method to inject liquid or slurried reagents from the drum allowing for the placement of the reagents at depth and have teeth that rotate on a drum to mix the reagents with the soil. Many drum mixers allow the drum itself to rotate creating multiple axis of rotation. Drum mixers can have lower mobilization costs since they are typically on arms that can be mounted on excavators. The functional depth of drum mixers without benching or terracing of the soils is limited to reach of the excavator arm (typical: 15 to 25 ft; 4.5 to 7.5 m). These mixers tend to be efficient, mixing between 200 to 600 tons of soil per day.

<u>Rotary Augers</u>

Rotary augers are circular devices mounted to various rigs or cranes. The augers rotate mixing in the reagents and soils. Some rotary augers allow injection of liquid or slurried reagents at depth typically through injection ports in the rotary blades. Mobilization costs of rotary augers typically increase with the size and depth of which the auger is capable of treating. However, rotary augers can be used to soil mix at depths well below the other soil mixing methods and tend to be used for soil mixing projects where the tool needs to reach deeper than 25 to 30 ft. bgs (8 to 9 m bgs).

Courtesy of GeoSolutions

<u>Screening</u>

Dry reagents can be blended with excavated soils above ground and reapplied to the excavation area.

Soil mixing is usually accomplished by dividing a site area into cells. These cells will vary in size as needed, but are typically squares with sides of 10 to 15 feet (3 to 4.5 meters). If augers are to be used, the cell is typically defined by the auger diameter. If liquid or slurry reagents and tooling allow injection at depth, vertical intervals are also established with different mass of reagents being applied as required to each vertical interval. Another common approach is to mix the entire vertical target interval sufficiently assuming an average distribution of both the contaminant and reagent. This method allows the treatment of the entire vertical interval with a single approach and reagents can be added at the surface and blended down.

Soil mixing has been conducted in both saturated and unsaturated (vadose) zones. However, vadose zone applications may require the addition of water depending on the bound moisture content of the soil. If excess water is applied then additional time may be required for the soil to drain. Please see “Lessons Learned” section of this document for a discussion regarding post application drainage.

Persulfate Activation

Activated persulfate can generate powerful radicals capable of treating most contaminants of concern. Common activation methods include alkaline or high pH, iron-chelate, di-valent iron, zero valent iron, heat, and hydrogen peroxide. While all of PeroxyChem’s recommended activation methods can be used with an *in situ* mixing application strategy, materials compatibility with *in situ* mixing projects is often an important consideration, since mixing equipment typically has components that contain carbon steel, which is reactive with Klozur persulfate at neutral and acidic pH values.

<u>Alkaline activated persulfate</u> is the most common activation method used for *in situ* soil mixing projects because carbon steel has a significantly lower rate of corrosion under alkaline conditions. Any equipment contacting reagents

needs to be chemically compatible with those reagents. Please consult PeroxyChem's Corrosion and Materials Compatibility with Klozur Persulfate guide for more information.

Combining ISCO with ISS

In situ soil mixing of activated Klozur persulfate can be combined with *in situ* stabilization (ISS) to reduce the contaminant mass, enhance the soil characteristics post soil mixing, and to minimize the contaminant mass flux from the treated area. The combination of ISCO and ISS occurs when Portland cement, bentonite, or other solidification compounds are blended in with the activated Klozur persulfate. The amount and type of solidification agent can be varied depending upon the desired soil characteristics.

Solidification Agents

Several different compounds can be used to help with soil structure following a soil mixing project by partially or completely solidify the soils. These compounds include:

- Portland Cement
- Calcium hydroxide ($Ca(OH)_2$); hydrated, slaked, or caustic lime)
- Calcium Oxide (CaO; quicklime)
- Fly Ash (Class C & F)
- Blast Furnace Slag
- Cement Kiln Dust
- Lime Kiln Dust
- Other pozzolans
- Bentonite

Always consider the purity and impurities of the above substances to make sure they are appropriate for your site specific needs.

Key Design Considerations and Parameters

Design considerations are site specific. Among the most critical design parameters are the loading rates of the different reagents to be added. Loadings can vary both horizontally from cell to cell or column to column or vertically if using a mixing technology that allows placement of the reagents at depth.

Common loading parameters include:

- Persulfate loading
- Activator loading
- Stabilization agent loading

Soil design loadings are typically reported as grams reagent per Kg soil (g/Kg) or % reagent weight per soil weight (% w/w). While it is common to specify an average loading for each area, it can be beneficial to also specify a minimum loading and, if needed, a maximum loading. It is important to specify when using dry soil weight or wet soil weight. Dry soil weights are commonly used in calculations and laboratory reported data since this methodology eliminates the potential variability that a soil's moisture content can introduce. However, some environmental professionals prefer to specify reagent loading in terms of wet soil weight to aide in field monitoring.

Courtesy of Orin

Other typical key design parameters include:

- Cell or column size
- Vertical target interval
- Number of cells and columns
- Post application geotechnical soil characteristics such as compressive strength and hydraulic conductivity

Bench Scale Tests

Bench scale tests for *in situ* soil mixing projects commonly evaluate several site specific parameters including:

- Base buffering capacity: Amount of alkali required to bring the site into alkaline range (if using alkaline activated persulfate)
- Different loadings of Klozur persulfate, activator and stabilization agent
- Treatment efficacy of combined reagent blend
- Soil strength, hydraulic conductivity and other properties
- Decrease in leachability when combined with ISS

Monitoring

Courtesy of Redox Tech

Monitoring programs are a critical aspect of applying any remedial technology. It is important to understand and develop a list of key questions and make sure the monitoring program is sufficient to generate the data to answer those questions. The exact questions will vary depending upon the site, but common questions for soil mixing with activated persulfate include:

- What was the progress toward the interim or final remedial goals?
- What was the contaminant mass reduction due to ISCO (soil, groundwater and NAPL)?
- Were the Klozur persulfate and activator uniformly blended?
- Were the desired reagent application rates achieved?
- What are the new groundwater flow patterns at the site?
- Are anaerobic oxidation or biogeochemical treatment occurring post ISCO?

For sites combining ISCO with ISS, or otherwise, using a solidification agent to help with geotechnical soil characteristics, other common goals for a monitoring program include:

- What is the resulting compressive soil strength and hydraulic conductivity of post application soils?
- What is the immediate change in contaminant leachability?
- What is the long term change in contaminant leachability after exposure to multiple volumes of water?

The frequency and time intervals of sample points are site specific. Generally speaking, PeroxyChem recommends waiting until more than 95 percent of the persulfate has been consumed or until persulfate concentrations have fallen to less than 1 g/L before collecting soil samples. It is important to insure sufficient time for the contaminant to re-equilibrate between soil and groundwater before monitoring groundwater. This equilibration process typically takes between 1 to 3 months (post-application) for soil samples and 2 to 4 months (post-application) for groundwater samples.

Case Studies

In situ soil mixing has been used as an application strategy for Klozur persulfate for the past decade. The following is a sampling of available case studies.

In Situ Mixing

In situ mixing has been used to apply Klozur persulfate at a large number of sites and as a result there are numerous case studies which have been presented at conferences. Some of these case studies include:

Courtesy of Bill Lang

- Fulkerson et al (2016) presented on a number of different soil mixing applications including two lime activated Klozur SP projects.
- Perlmutter et al (2017) presented on a site where over 740,000 lbs of Klozur SP and 260,000 lbs of hydrated lime that resulted in greater than 90 percent treatment of the contaminants of concern as measured 2 to 4 weeks post treatment.
- Morris et al (2012) used hydrated lime with Klozur SP to treat a complex mixture of pesticides.
- Trichloroethene (TCE) was reduced by 96 to 99.9 percent in 18 of 21 sampling locations at another alkaline activated Klozur persulfate site (Tarmann et al., 2012).
- Soils with up to 2,300 mg/Kg of mixed cVOCs were reduced to 1 mg/Kg at a site in New Jersey by soil mixing with activated persulfate (Dyson and Palko, 2012).

ISS with ISCO

A combination of Portland cement, lime and 760,000 lbs of Klozur SP were applied at Turtle Bayou using auger mixers and summarized in Wiley and Block (2010). The ratio of the cement was maintained so that the soil had structure but was still sufficiently malleable to allow multiple applications. The application met its remedial goal of greater than 80 percent treatment. Combining ISS with activated persulfate was also discussed in Cassidy et al (2015) this research showed treatment by activated persulfate, a reduction in contaminant leaching due to ISS, and then anaerobic oxidation of petroleum hydrocarbons from a single application of Portland cement and Klozur SP.

Lessons Learned

As with any technology, there have been lessons learned during field applications. A few of lessons learned from *in situ* soil mixing of activated persulfate are summarized below:

Dusting
Applying reagents in winds, from height or a combination can result in reagent dust. Mitigation measures for the various possible field conditions should be considered. Common mitigation measures include having staff in proper PPE, minimizing drop height of the reagents, misting, applying hydrated reagents, and avoiding exposing dry reagents if winds are above a certain velocity.

Soil Expansion
Soils are typically not as compacted following a soil mixing application and high plasticity clays can expand. This can result in excess soils that will no longer fit in the excavation area that is referred to as fluff. The excess materials are either typically stockpiled to the side of or on top of the excavation area, or removed for disposal. Material stockpiled on top of the excavation may partially or completely return to the excavation area as the mixed soils compress over time. Site management during an application may include building of berms around the treatment area.

Drainage
Soil mixing in the vadose zone, especially if significant amounts of water are added, can result in mostly dry soils becoming a soil slurry. These conditions may persist especially if drainage from the mixing area is limited. This issue is most common when soil mixing low permeability vadose zone soils that can remain a slurry for an extended period of time as the added water slowly moves out of the area.

Soil Strength
The resulting soil strength or compressive characteristics of soils following an *in situ* soil mixing project may not be suited for subsequent site activities. These characteristics may make moving machinery or building upon the soil following an *in situ* soil mixing project more challenging. This can be mitigated by increasing soil strength with the addition of a solidification agents such as a calcium source (calcium hydroxide, etc.) to form gypsum with the residual sulfate, Portland cement, or another bulking agent. Varying degrees of the solidification agents can be used to obtain different soil characteristics.

Mitigation of ISCO by ISS

While ISS and ISCO have been successfully applied together, if the ISS solidifies the soils too quickly it could interfere with the ISCO oxidation processes. This can occur if a significant concentration of Portland cement is added to the mixture or if the mixture contains too little water and the Portland cement effectively dries the soils. The rate of solidification and the percent treatment by ISCO can be evaluated on a bench scale test.

Health and Safety

Klozur persulfate has been applied safely and effectively at thousands of sites. However, as with any chemical, proper procedures and equipment are recommended in its use. When working with Klozur persulfate, ensure to have adequate ventilation and use the appropriate personal protective equipment, including safety glasses, suitable protective clothing, boots (steel toed or equivalent), chemical resistant gloves, hard hat, and hearing protection (when direct push is used). For dust, splash, mist, or spray exposures wear a filtering dust mask and chemical protective goggles. A face shield can also be used in addition to goggles.

Dust	**When applying any solid reagent, dust could evolve. PeroxyChem recommends proper consideration of this potential including personal protective equipment (PPE), and dust mitigation measures.**
Contaminant Vapors	The mixing process can expose contaminated soils to the atmosphere and allow vapors to escape potentially causing a health and safety hazard. Some mixing technologies have developed hoods to help minimize this risk.

Please consult the appropriate safety data sheets (SDS) for guidelines regarding proper handling procedures. Klozur persulfate SDS's can be found at http://www.peroxychem.com/remediation. Additional safety equipment may be required for mechanical and site operations.

Please contact PeroxyChem for additional guidance.

Notes

1. A limited use license is included with the purchase of Klozur Persulfate for PeroxyChem's suite of national and international patents for the *in situ* activation of persulfate to remediate environmental contaminants of concern including US 6019548, US 6474908, US 7524141, US 7576254B2, US 7785038, and US 9375768B2.

References

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