RemRx™ CRP

Prescriptive Groundwater Remediation

RemRx™ CRP Persulfate:

comparative analysis of persulfate ISCO products

Persulfate for ISCO

Sodium persulfate ($Na_2S_2O_8$) has been utilized for In Situ Chemical Oxidation (ISCO) since the early 2000s. Persulfate ($S_2O_8^{2-}$) itself is a potent oxidant, but it is kinetically recalcitrant and selectively reactive (eq 1). Activation of persulfate with heat, base, or reductant (eqs 2-4) results in the formation of reactive radical species (e.g. sulfate radical anion, $SO_4^{\bullet-}$) that are kinetically and thermodynamically capable of contaminant degradation. Radical chain propagation results from reactions of $SO_4^{\bullet-}$ with other species (e.g. contaminants, water), forming additional oxidizing species (hydroxyl radical, $OH^{\bullet}$; eq 5). Persulfate and persulfate radical anion are effective oxidants for a variety of contaminants, listed below.[1, 2]

$S_2O_8^{2-} + RH \rightarrow SO_4^{\bullet-} + R^{\bullet} + HSO_4^-$ (eq 1)

$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-}$ (eq 2)

$SO_4^{\bullet-} + OH^- \rightarrow OH^{\bullet} + SO_4^{2-}$ (eq 3)

$S_2O_8^{2-} + Fe^{2+/3+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+/4+}$ (eq 4)

$SO_4^{\bullet-} + H_2O \rightarrow OH^{\bullet} + SO_4^{2-}$ (eq 5)

Target Contaminants

PCE, TCE, DCE, VC

BTEX, chlorobenzene, phenols

1,4-dioxane, MTBE, TBA

PAHs, explosives, pesticides, PCBs

amenable

reluctant

RemRx™ Controlled Release Polymers (CRP)

RemRx™ CRP is a patented controlled release system that provides a prescriptive oxidant dosage for sustained delivery into the subsurface. RemRx™ CRP Persulfate is a controlled release system for persulfate designed to minimize rebounding effects after a single dose (**Figure 1**). As a result, RemRx™ CRP Persulfate aims to bring sites to closure with fewer applications than typical ISCO approaches, with the goal of increasing treatment efficiency and decreasing total project costs.

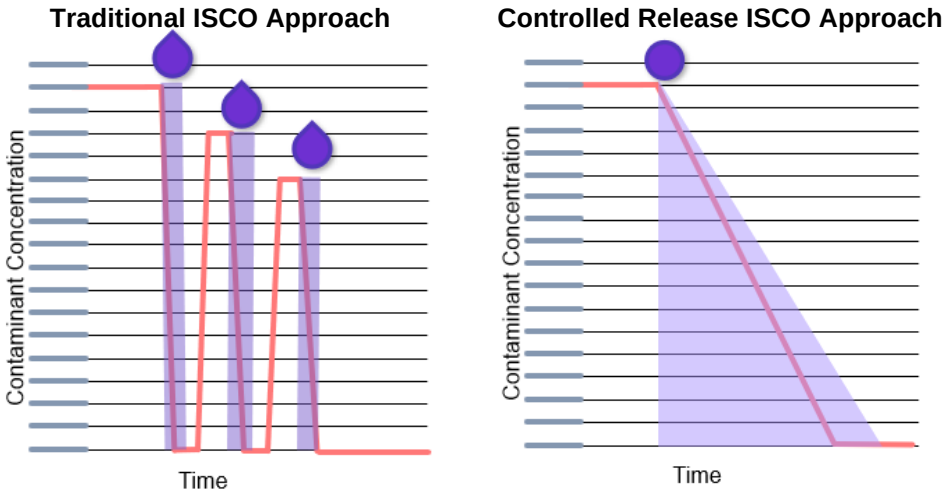

FIGURE 1. (**LEFT**) Traditional ISCO treatments require multiple oxidant injections to address rebounding, where contaminant concentrations initially decrease but then increase over time. (**RIGHT**) A controlled release ISCO approach leads to sustained oxidant delivery over time, mitigating rebound.

The CRP Solution

RemRx™ offers a series of controlled release remediation products with several advantages over other ISCO products on the market today (**Table 1**). RemRx™ CRP Persulfate is manufactured as small pellets that are straightforward to deploy using standard techniques (e.g. well socks, back-fill borings, excavation). RemRx™ CRP Persulfate benefits from multiple release mechanisms and mitigates rebounding by releasing oxidant over extended periods of time. These benefits are discussed in further detail below.

① **Mechanism of release**. RemRx™ CRP Persulfate utilizes 3 different release mechanisms to deliver oxidant to the subsurface over a timescale of months to years. Like other persulfate salts on the market today, RemRx™ CRP Persulfate releases persulfate into the deployment area for contaminant degradation. However, the novel controlled release functionality of RemRx™ CRP Persulfate comes from two additional mechanisms: (1) restricted diffusion of water into the CRP, and (2) gradual biodegradation of the polymer matrix. Both of these mechanisms greatly extend persulfate release in order to address rebounding with the goal of making remediation efforts more efficient.

② **Addressing rebounding.** Rebounding is a ubiquitous challenge in any ISCO deployment. Rebounding occurs because of the inherent equilibrium between contaminant in the dissolved and undissolved phase (**Figure 2**). We have performed extensive testing in both the laboratory and at pilot-scale field test sites to ensure that our CRP products release over extended periods of time to address rebounding. Data from a pilot scale deployment of CRP Persulfate show average percent contaminant changes that are trending downward over the course of a year.

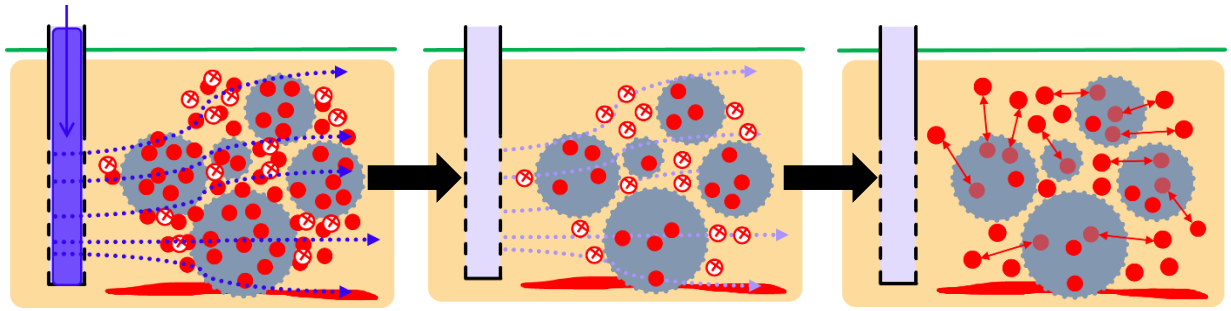

FIGURE 2. Graphic representation of rebounding with traditional ISCO products. (**LEFT**) Oxidant is injected. (**CENTER**) Contaminants in dissolved phase degrade. (**RIGHT**) Back diffusion causes contaminant concentrations to rebound. With traditional ISCO products, oxidant is no longer present to address rebounding.

③ **Time to total release.** RemRx™ CRP Persulfate can be formulated to access a range of release rates, which can be tuned as a function of oxidant and polymer. Figure 3 compares sodium persulfate (SPS) and potassium persulfate (KPS) in powder and CRP pellet form. The SPS powder releases within 2 hours, SPS pellet within 7 days, and KPS pellet within 14 days in aqueous batch reactors. RemRx™ CRP release rates can be tuned to specific site needs to extend release and match the timescale of contaminant degradation in the field. These laboratory studies are corroborated by field data, which indicates that RemRx™ CRP Persulfate is still releasing a year after deployment.

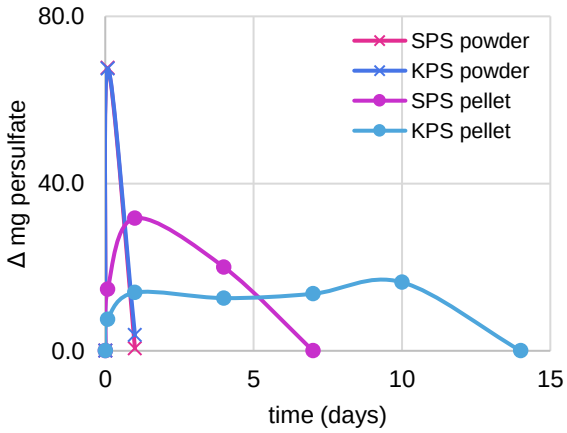

FIGURE 3. Comparison of persulfate release of SPS and KPS powder, SPS pellet, and KPS pellet. Release is plotted as change in milligrams persulfate released.

Table 1. Comparison of selected persulfate-based ISCO reagents.

Product ➢ Feature ⩛	RemRx™ CRP [3]	Klozur® KP [4]	Klozur® CR [6]	Klozur® SP [8]
Form **Components**	*pellets* Sodium/potassium persulfate and polymer	*granular powder* Potassium persulfate	*granular powder* Sodium persulfate, calcium peroxide, calcium hydroxide	*granular powder* Sodium persulfate
Field application	✓ suspension in wells ✓ back-fill borings ✓ slurry injection ✓ soil blending ✓ excavation	✗ suspension in wells ✗ back-fill borings ✓ slurry injection ✓ soil blending ✓ excavation	✗ suspension in wells ✗ back-fill borings ✓ slurry injection ✓ soil blending ✓ excavation	✗ suspension in wells ✗ back-fill borings ✓ slurry injection ✓ soil blending ✓ excavation
Minimum applications needed	1	1–3[5]	>3	>3
Time to total release	months to years	several months	weeks to months[7]	weeks to months
Mechanism of release	① oxidant dissolution ② restricted diffusion of water into polymer ③ matrix degradation	① oxidant dissolution (based on solubility)	① oxidant dissolution ② slow H_2O_2 production	① oxidant dissolution

1 Siegrist, R. L.; Crimi, M.; Simpkin, T. J., *In situ chemical oxidation for groundwater remediation*. Springer Science & Business Media: 2011; Vol. 3.
2 *Technical and regulatory guidance for in situ chemical oxidation of contaminated soil and groundwater*; Interstate Technology & Regulatory Council, In Situ Chemical Oxidation Team: Washington, D.C., 2005.
3 https://www.remrxremediation.com/
4 http://www.peroxychem.com/chemistries/persulfates/products/klozur-kp
5 Case study where a single application was needed: http://www.peroxychem.com/media/241921/peroxychem-klozur-kp-case-study-napthalene-btex-to-nd-88-01-esd-17.pdf
6 http://www.peroxychem.com/chemistries/persulfates/products/klozur-cr
7 After in situ chemical oxidation, calcium peroxide can release oxygen for up to one year to enhance aerobic bioremediation.
8 http://www.peroxychem.com/media/247760/PeroxyChem-Klozur-SP-Product-Sheet-02-03-ESD-14.pdf