



The Safe Use of Klozur® Persulfate Activators

Activators are used with Klozur Persulfate to convert the persulfate anion, a strong but kinetically slow oxidant, into the sulfate radical, a much stronger and kinetically faster oxidative species capable of destroying a wide range of organic contaminants. PeroxyChem is the owner or exclusive licensee of several patented methods to activate persulfate: heat, high pH, metals and chelated metals, hydrogen peroxide and zero valent iron (ZVI). The choice of activator system is dependent on several criteria, including the type of contaminants targeted, the application method, site hydrogeology and lithology, and other site conditions such as the presence of structures and underground utilities. Contact PeroxyChem and we can provide technical support for your selection of the activator chemistry for your project. Additional information can be found at peroxychem.com/remediation. The subject of this month's Peroxygen Talk is the safe use of these Klozur Persulfate activation chemistries.

High pH Activation

High pH activation currently represents the most favored method for activation in the field. High pH – activated persulfate has been demonstrated effective on a wide range of contaminants, including chlorinated solvents (PCE, TCE, DCE, TCE, DCA, vinyl chloride, carbon tetrachloride), petroleum hydrocarbons (BTEX, GRO, DRO), aromatic hydrocarbons, chlorinated benzenes, pesticides and others (examples include MTBE, 1,4-dioxane). The target pH range for effective persulfate activation is 10.5 – 12, with efficacy dropping significantly below a pH of 10. Sodium hydroxide (NaOH) is often the chemical of choice for injection applications, whereas lime is often used as the pH modifier when *in situ* or *ex situ* soil blending is performed.

Chemicals with very high pH's can be corrosive to the skin and may cause severe burns and / or blindness. As a result, it is very critical that the appropriate SDS be reviewed by all staff that may come in contact with the NaOH or lime, and that the proper protective equipment be utilized at all times, including chemically resistant gloves, clothing and boots, and face shields and goggles to protect the eyes. NaOH can be purchased in many forms, including solid (pellets or prills) or in solution with concentrations ranging up to 70% or more. Care must be taken when mixing NaOH into tanks of water, as NaOH has a very high heat of mixing or dilution, -44.45 kJ / mol, and can release significant quantities of heat when diluted. Mixing highly concentrated solutions of NaOH, or solid NaOH, requires long addition periods and large heat reservoirs to dissipate the generated heat. It is always recommended to use NaOH in solutions of 25% or less. At or below these concentrations, the majority of the heat of mixing is gone, and the product is much safer to use. The sale of Klozur Caustic is offered, a 25% environmental grade NaOH solution to our customers.

Klozur persulfate and low concentrations of NaOH can be injected into the subsurface in a sequential manner or they can be pre-mixed in a tank prior to application. If pre-mixed, it is suggested that the resulting solution be injected into the ground within a couple of hours to prevent loss of persulfate through decomposition. Recent field experience has indicated the potential of concentrated mixtures of Klozur persulfate and NaOH to form crystals, both in the mix tank and within injection wells. Individually, the onset of crystallization of Klozur Caustic occurs at 10.4 °F and Klozur

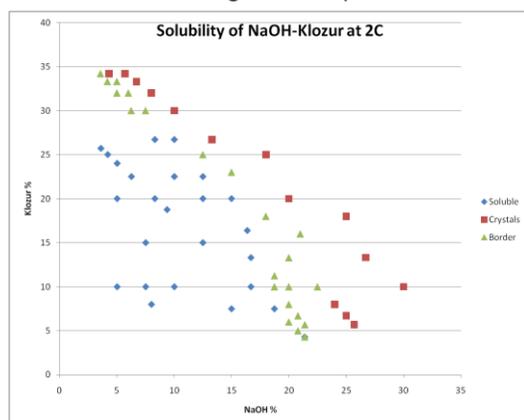


Figure 1 Onset of Crystallization for Combinations of Klozur Persulfate and NaOH

Persulfate solutions can be made up to 37 wt% at 32 °F before crystallization occurs. Environmental Labs tested various concentration combinations of Klozur Persulfate and Klozur Caustic at 36 and 68 °F (2 and 20 °C) to



investigate under which conditions crystallization occurs. The results for the 36 °F data are shown in Figure 1 (the 68 °F data is very similar). As a result, the following mixing guidelines have been developed to prevent the formation of crystals.

Klozur Persulfate wt %	Recommended Maximum NaOH wt%	Klozur SP weight per 100 gallons of solution (lb)	Recommended Maximum gallons of Klozur Caustic per 100 gallons of solution
5	20	43.0	16.2
10	20	87.7	16.2
15	18	136.8	15.5
20	16	190.3	13.5
25	12	248.2	11.2
30	8	310.5	6.8
35	0	377.1	0

Table 1: Recommended maximum NaOH addition rates to Klozur persulfate solutions to prevent crystal formation.

NaOH solutions are denser than water (10.6 lb / gal at 25 wt%, 9.27 lb /gal at 20 wt%). As a result, whether injected into the subsurface by itself or in combination with Klozur persulfate, the resulting solution may be more dense than the groundwater and will have a tendency to sink within the aquifer. This should be noted and designed for, as the density of the solution may result in the persulfate and activator dropping below the target treatment zone. Injecting lower weight percentage solutions or injecting nearer the top of the treatment zone may allow for longer contact times between the oxidant and contaminants of concern.

FeEDTA Activation

Klozur Persulfate can be activated with chelated iron for the oxidative destruction of organic contaminants of concern, including PCE, TCE, DCE, vinyl chloride, BTEX, low molecular weight aromatic hydrocarbons, methyl-*tert*-butyl ether (MTBE), 1,4-dioxane and others. For chelated iron activation of Klozur Persulfate, the iron concentration in the groundwater needs to be maintained between 150 mg / L (ppm) and 600 mg / L (ppm). Iron concentrations below 150 ppm will result in kinetics that may not be favorable for the oxidation of various contaminants, and concentrations in excess of 600 ppm may lead to increased persulfate auto-decomposition. One example of a chelated iron is Dissovline® Fe – EDTA, which is 13% iron by weight, thus requiring between 1,154 ppm and 4,615 ppm FeEDTA to maintain the desired groundwater iron concentrations. FeEDTA has a relatively low solubility, and at 32 °F, will only be soluble up to 5.1 wt%. The solubility only increases to 9 wt% at 68 °F. Other chelated iron complexes are available, such as iron citrate. It is recommended to add chelated iron when iron activation is selected, even if there is iron already present in the sub-surface. Measured iron concentrations present in soils may not be available for persulfate activation or the iron may not be distributed evenly enough through the treatment zone to insure adequate activation of the persulfate.

The target groundwater FeEDTA concentration is not dependent upon the amount of Klozur persulfate being applied, but rather on the volume of groundwater being treated. As a result, the ratio of FeEDTA to persulfate will vary from project to project, leading to the potential for the need to combine high concentrations of Klozur persulfate and FeEDTA to achieve the desired groundwater concentrations for a given application. FeEDTA is



comprised of iron as the activator and an organic ligand (EDTA, ethyldiaminetetracetic acid) which itself is oxidizable. Because of this, addition of high levels of FeEDTA to concentrated persulfate solutions may lead to decomposition of the Klozur persulfate at certain concentration combinations. This would lead to loss of the oxidant and potentially generate excessive heating of the activated persulfate solution. It is not well defined under which combinations of FeEDTA and persulfate concentrations leads to persulfate decomposition. Consequently, it is recommended that the Klozur persulfate and the FeEDTA, or any other type of chelated iron, be made into solution in separate batch tanks and only combined in-line prior to the well head or injected into the subsurface in a sequential manner.

Hydrogen Peroxide Activation

Hydrogen peroxide – activated persulfate has been demonstrated effective in the field on a wide range of organic contaminants, including chlorinated ethenes, ethanes and methanes, BTEX, petroleum hydrocarbons, MTBE, aromatic hydrocarbons and others. The target molar ratio of hydrogen peroxide to Klozur persulfate is 5:1 to 10:1, or 0.7:1 – 1.4:1 on a pound (100% peroxide) to pound basis. The higher the hydrogen peroxide loading as compared to the amount of persulfate, the faster the contaminant reaction kinetics will be, but the shorter the persulfate lifetime.

Hydrogen peroxide is sold commercially in a variety of concentrations. Common concentrations include 70%, 50%, 17.5%, and 8%. Highly concentrated forms of hydrogen peroxide may generate extreme exothermic reactions upon injection into the subsurface or when contacting high levels of contamination, potentially liberating significant quantities of gas. Care must be taken to avoid excessive heat and gas evolution as this may cause damage to utilities, buildings and represents a safety hazard if not properly controlled. It is recommended that hydrogen peroxide solutions of no more than 8% by weight be used to activate Klozur persulfate. This will help to minimize the generation of heat and gas upon injection of hydrogen peroxide into the subsurface. Use of concentrated hydrogen peroxide solutions in excess of 8 wt% may increase the risk of injury, loss of product containment and equipment damage. Hydrogen peroxide can be applied with persulfate either in a sequential manner, with the persulfate typically being injected first, or pre-mixed in a tank and co-injected. It is always safer to inject the materials sequentially. For co-injection, it is recommended that the following maximum ratios of hydrogen peroxide and persulfate than can be pre-mixed:

- No more than 5 gallons of 8% hydrogen peroxide should be added per gallon of 30% Klozur solution
- No more than 3 gallons of 8% hydrogen peroxide should be added per gallon of 20% Klozur solution
- No more than 2 gallons of 8% hydrogen peroxide should be added per gallon of 10% Klozur solution

Always use clean water and clean mixing and handling equipment. Transition metals in the supply water, such as iron, can result in rapid decomposition of the hydrogen peroxide. It is recommended that oxidant solutions be injected promptly into the subsurface and avoid delays resulting in the solutions remaining in mix tanks for extended periods of time. Also use vented tanks and piping when using oxidizing solutions. Always drain lines to empty and avoid trapping solution between valves for extended periods of time. Do not “dead head” pumps. When injecting hydrogen peroxide solutions, it is recommended that temperature and back-pressure be monitored and controlled to prevent highly exothermic, subsurface reactions. Clean all equipment with a water flush after use to remove any residual oxidant.



One final note, which comes to us by way of an e-mail from a Klozur persulfate customer, regards our being mindful of our environment and the wildlife in it. Many wild animals are attracted to salt as part of their diets. Thus it is important that any chemical in dry or liquid form that you are using, including Klozur persulfate, be properly stored and secured, and all equipment, including shovels, handling equipment and hoses be rinsed and cleaned after use in order to prevent access to foraging by the local wildlife. We strive to promote good stewardship to our environmental and all those that live within it. If you have any anecdotal information that we can share to promote the safe use of our products, please let us know.

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