Alkaline Activated Klozur® Persulfate

Alkaline activated Klozur® persulfate, U.S Patent No.: 7,576,254 and its foreign counterparts, is a widely used technology capable of remediating most common organic contaminants of concern. Alkaline activated persulfate forms oxidative radical species, reductants, and nucleophiles (Furman et al, 2010). This multi-radical attack allows the treatment of chlorinated ethenes (TCE, PCE, DCE, and vinyl chloride), 1,4-dioxane, MTBE, TBA, petroleum hydrocarbons (BTEX, and PAHs), pesticides, as well as more recalcitrant compounds including chlorinated methanes, such as carbon tetrachloride, and chlorinated ethanes, such as 1,1,1-trichloroethane. For a complete list, please contact your PeroxyChem technical representative or consult www.peroxychem.com/remediation.

ALKALI REAGENT SELECTION

Common reagents used to create alkaline conditions for activation of Klozur persulfate include:

- **25 Percent Sodium Hydroxide, 25% NaOH, *liquid***
  The use of 25 percent sodium hydroxide (NaOH) is recommended for safety and handling considerations as 25 percent NaOH releases less heat upon dilution and remains in solution at lower temperatures than more concentrated forms of NaOH. For more information please consult PeroxyChem's Technical Bulletin on Crystal Formation in Solutions of Klozur Persulfate and Klozur Caustic or contact your local PeroxyChem technical representative.
- **Calcium Hydroxide, $Ca(OH)_2$, *solid***
  Calcium hydroxide [$Ca(OH)_2$] is commonly referred to as slaked lime, hydrated lime, or caustic lime. Calcium hydroxide is recommended over calcium oxide (CaO) in most circumstances as calcium hydroxide releases significantly less heat (less exothermic) than calcium oxide upon hydration. Both lime products can generate the alkaline conditions to activate Klozur persulfate when dosed appropriately.
- **Calcium Oxide, CaO, *solid***
  Calcium oxide (CaO) is also commonly referred to as quicklime. Calcium oxide releases significant heat (exothermic) once hydrated as the calcium oxide consumes water to form calcium hydroxide [$Ca(OH)_2$] in a process referred to as "slaking." Even when mixed directly with hydrated soil, it can release sufficient heat energy to create heat activated conditions for persulfate. Health, safety and handling of the expected evolution of heat should be considered when using calcium oxide to activate persulfate.
- **Portland Cement, *solid***
  Portland cement contains a significant amount of calcium oxide with the other major components including silicon dioxide, aluminum oxides and gypsum. Portland cement has been applied with Klozur persulfate to improve the geotechnical characteristics of the soil post mixing. At higher dosage rates, Portland cement can provide a combined remedy that both reduces contaminant mass (via *In Situ* Chemical Oxidation, ISCO) and contaminant flux (via *In Situ* Stabilization, ISS) from a single application. As with calcium hydroxide above, it is recommended the potential heat evolution of the system be considered prior to field application.

Due to a number of health and safety concerns, the following alkali reagents are **NOT RECOMMENDED** for use with Klozur persulfate:

- High purity Sodium Hydroxide flakes, granules or powder, *solid* **Not Recommended**
  Solid forms of sodium hydroxide release significant heat (highly exothermic) upon hydration. In certain circumstances, sufficient heat may be liberated that it can boil the solution, generate steam eruptions, and damage to equipment.
- Sodium Hydroxide, >25% NaOH, *liquid* **Not Recommended**
  Sodium Hydroxide is sold commercially in a variety of concentrations. To minimize potential risk, PeroxyChem recommends NaOH solutions of no more than 25% by weight be used to activate Klozur persulfate. More concentrated forms of NaOH (50 % or greater solutions and solid form NaOH) may generate increasingly exothermic reactions upon dilution and any NaOH solution greater than 30% can solidify above the freezing point of water.
- Carbonate based lime products, *solid* **Not Recommended**
  Different types of lime exist that are not based on calcium hydroxide or calcium oxide but are instead based on carbonates or contain a significant amount of carbonates. These forms of lime, such as Agricultural lime, should not be used to create alkaline activated conditions as the carbonates can interfere with the oxidative treatment process.

There are several factors to using a lime reagent (calcium hydroxide or calcium oxide) that should be considered including:

Purity	Commercially available lime products typically include impurities. For example, high purity commercial lime products might have greater than 95 percent of the desired lime product (calcium hydroxide or calcium oxide) while other commercially available lime products could have significantly lower percentages of the desired lime product. These impurities have the potential to introduce an unexpected compound into the subsurface, such as carbonates (see below), and necessitate adjusting the total mass of product required to supply the intended amount of calcium hydroxide or calcium oxide.
Carbonates	Carbonates are common impurities in solid lime products, which have the ability to react with, or scavenge, certain oxidative radicals which could negatively impact the efficacy of the persulfate. Trace levels of carbonates are not expected to be a significant issue, however products containing significant carbonates should either be avoided or bench tested to assess their treatment efficacy.
Calcium sulfate	Residual calcium from the lime will react with residual sulfate from persulfate to form gypsum. This reaction can significantly reduce the amount of soluble sulfate in the system and it has been used to increase soil strength.

DETERMINING THE AMOUNT OF ACTIVATOR NEEDED

Alkaline activation typically requires system conditions of at least pH 10.5 be maintained throughout active treatment with the Klozur persulfate. Klozur CR is formulated with PermeOx Ultra in sufficient quantities to create alkaline conditions in typical conditions. Klozur SP (sodium persulfate) and Klozur KP (potassium persulfate) require the addition of an alkaline material.

The demand for alkalinity arises from two sources:

1) Natural demand from soil and groundwater, and
2) The neutralization of acid generated during reactions with persulfate.

Total Alkaline Demand =
(1) natural demand from soil and groundwater + (2) neutralization of generated acid

Natural Demand for Alkalinity

The amount of the 25% NaOH needed to raise soil and groundwater to pH 10.5 is best determined experimentally. PeroxyChem recommends a base buffer capacity (BBC) test be conducted to determine this amount. This test is conducted using aqueous NaOH with the results reported as grams 25 percent NaOH per Kg soil. These values can be converted to calcium hydroxide or calcium oxide instead of 25 percent NaOH using conversion factors, estimated below:

- 0.23 g calcium hydroxide per g of 25 percent NaOH
- 0.175 g calcium oxide per g 25 percent NaOH

Please contact PeroxyChem for further information or to inquire about the BBC test offered by our laboratory.

Alkalinity to Neutralize Generated Acid

PeroxyChem recommends adding sufficient alkalinity to account for the decomposition of all of the Klozur persulfate so that the persulfate system stays sufficiently alkaline until all of the Klozur persulfate is consumed. As persulfate reacts, it typically forms 2 moles of acid for every mole of persulfate that decomposes. The demand for the amount of an alkali reagent required to neutralize the acid generated during persulfate decomposition is presented in Table 1.

Alkali Reagents	Formula	Molecular Weight	Molar Ratio	Alkali Mass per Klozur SP Mass (lb per lb or Kg per Kg)	Alkali Mass per Klozur KP Mass (lb per lb or Kg per Kg)
25% Sodium Hydroxide[1]	NaOH	40	2	1.34	1.18
Calcium Hydroxide[2]	$Ca(OH)_2$	74.1	1	0.31	0.27
Calcium Oxide[2]	CaO	56.1	1	0.24	0.21
Notes: 1 - Assumes mass of 25 percent sodium hydroxide **solution**.					
2 - Assumes 100 percent solid product. Does not include hydration or impurities.					

Table 1. Dosage factors for Alkali Reagents; does not include base buffering capacity

Portland cement, pozzolans, bentonite, or other materials can be used in differing amounts to help control post soil mixing soil characteristics including in sufficient quantities to solidify the soil resulting in a combined ISCO and ISS remedy. The amount of Portland cement needed to solidify the soils may be different than the amount needed to activate the persulfate. The quantities of Portland cement required to activate persulfate and result in the desired soil characteristic should each be assessed and, typically, the greater mass used. It is also recommended that soil stability tests be run on site soils including the Klozur persulfate.

The following examples demonstrate how to estimate the amount of alkali needed at a site to create alkaline activated conditions.

Example 1:

100,000 lbs of Klozur SP is going to be applied to a site with a base buffering capacity of 5 g 25% NaOH/Kg soil. There are 8,000,000 Kg soil within the target interval of 30 ft bgs to 40 ft bgs at the site. The use of liquid activator, 25 percent NaOH, has been selected.

Calculations:

- Part 1 – BBC. The amount due to base buffer capacity of the soil can be determined by multiplying 5 g 25% NaOH per Kg soil by 8,000,000 Kg soil. This is equal to 40 million grams of 25 percent NaOH solution, or 88,105 lbs.
- Part 2 – Persulfate Neutralization. The amount of 25% NaOH needed to offset the acid generated from persulfate decomposition would be 1.34 lbs of 25% NaOH times the 100,000 lbs of Klozur SP which equals 134,000 lbs of 25% NaOH solution.
- The final amount of 25% NaOH required at the site would be the addition of the two, or 88,105 + 134,000 = 222,105 lbs of 25% NaOH.

Example 2:

25,000 Kgs of Klozur KP is going to be applied to a site with a base buffering capacity of 3 g 25% NaOH/Kg soil. There are 3,000,000 Kg soil within the target area at the site. As the target interval is 1 m bgs to 4 m bgs and 98% pure hydrated lime (calcium hydroxide) has been selected as the activator.

Calculations:

- Part 1 – BBC. The amount due to base buffer capacity of the soil can be determined by multiplying 3 g 25% NaOH per Kg soil by 3,000,000 Kg soil times the conversion factor of 0.23. This is equal to 2.07 million grams of hydrated lime, or 2,070 Kgs.
- Part 2 – Persulfate Neutralization. The amount of hydrated lime needed to offset the acid generated from persulfate decomposition would be 25,000 Kgs of Klozur KP times 0.27 Kgs of hydrated lime per Kg Klozur KP divided by 0.98 (purity) which equals 6,887 Kgs of hydrated lime.
- The final amount of calcium hydroxide (hydrated lime) required at the site would be a combination of the two, or 2,070 + 6,887 = 8,957 Kgs of hydrated lime.

Example 3:

It has been decided to apply the combined remedy of activated Klozur SP and ISS to treat a large brownfield site. It has been estimated that the site needs a minimum of 400,000 lbs of Klozur SP and has a base buffering capacity of 2 g 25% NaOH/Kg soil. There are an estimated 26,000,000 lbs of soil within the target area at the site. To stabilize the soils, Portland cement has been selected as the activator. The Portland Cement to be used was identified as being 63 percent

calcium oxide and it was determined that 8 percent Portland Cement (w/w with the soil mass only) sufficiently stabilized the soils.

Calculations:

- Part 1 – BBC. The amount due to base buffer capacity of the soil can be determined by multiplying 2 g 25% NaOH per Kg soil by 26,000,000 lbs soil, dividing by 2.204 lbs/Kg and 0.175 conversion from 25% NaOH to CaO. This is equal to 4.1 million grams of calcium oxide, or 9,100 lbs of calcium oxide.
- Part 2 – Persulfate Neutralization. The amount of hydrated lime needed to offset the acid generated from persulfate decomposition would be 0.24 lbs of hydrated lime times the 400,000 lbs of Klozur SP which equals 96,000 lbs of calcium oxide.
- The final amount of 100% pure calcium oxide (quicklime) required at the site for ISCO would be a combination of the two, or 9,100 + 96,000 = 105,100 lbs of calcium oxide. As the Portland Cement is specified as having 63 percent calcium oxide, this would be equivalent to 105,100/0.63 = 166,825 lbs of Portland Cement required to activate Klozur SP.
- The final step would be to compare the amount of Portland cement needed for alkaline activation against the amount that was determined best to stabilize soils. The amount of Portland cement needed in this example to stabilize the soils was 8 percent of the original soil mass. The total mass at the site would be 8 percent of 26,000,000 lbs of soil or 2,080,000 lbs of Portland cement. In this case the amount of Portland cement needed to stabilize the soils exceeded the amount needed to activate persulfate and should be used in the design.

SAFETY AND HANDLING

As the combination of an alkali reagent with persulfate can initiate a reaction, **PeroxyChem recommends Klozur products and alkaline products be stored separately. Even after being batched, PeroxyChem recommends that the Klozur persulfate and alkaline solutions be stored in separate chemically compatible tanks.** Contact between the alkali material and persulfate prior to injection should be limited to prevent the initiation of the reaction. This is typically accomplished by mixing the reagents inline prior to injection or injecting the reagents separately in a serial manner that creates sufficiently alkaline conditions to activate the persulfate.

Alkaline activated Klozur persulfate has been applied safely and effectively at numerous 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), 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.

Please consult the appropriate Safety Data Sheets (SDS) for guidelines regarding proper handling procedures. The SDS's for Klozur persulfate products 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.