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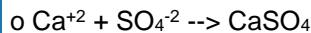
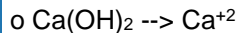
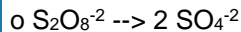
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March 2010 - The Use of Lime to Activate Klozur Persulfate and Its Impact on Contaminant Soil Concentrations

Hydrated lime, $\text{Ca}(\text{OH})_2$, and in some instances quicklime, CaO , have been used successfully as an activator for Klozur® Persulfate for the treatment of petroleum and chlorinated solvent contaminated soils. Due to its relatively low solubility, the most common method of use with Klozur persulfate is soil blending, either *in situ* or *ex situ*. Lime provides several benefits as an activator, including:

- Relative low cost
- Broad availability
- Ease of use, especially for soil blending applications
- Generation of an alkaline environment, providing high pH activation of Klozur persulfate ($\text{pK}_a = 11.3$ for hydrated lime)
- Generation of heat upon hydration, providing thermal activation of Klozur persulfate
- Reduction of residual sulfate groundwater concentrations through precipitation of gypsum



However, over the past couple of years, several laboratory and field pilot scale studies have indicated that lime addition only, with no Klozur persulfate, is as effective as the addition of lime and persulfate together in reducing contaminant soil concentrations. In other words, there is an apparent lack of benefit from the Klozur persulfate in lime + persulfate treatment applications. Most recently this was observed by Waisner *et al*¹ in studies on the reduction of energetic compounds by lime and lime / persulfate systems. Yet, there is no clear mechanism for the alkaline chemical destruction of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). In fact, the literature demonstrates that PCBs and PAHs are merely encapsulated by a coating of precipitated $\text{Ca}(\text{OH})_2^{2-4}$ or in the case of the use of quicklime through volatilization due to the heat generated by hydration⁵⁻⁷.

If the primary mechanism for the apparent lime reduction of contaminants is through $\text{Ca}(\text{OH})_2$ encapsulation, then a reduction in pH would result in dissolution of the lime, releasing the contaminants back into the environment. In essence, lime encapsulation is reversible and non-permanent with a drop in pH. However, the standard US EPA methods for analysis of PCBs and PAHs concentrations in soil (US EPA SW846 Method 3545) does not require the pH to be lowered to circum-neutral values prior to extraction of the soil. As a result, these methods are not sensitive to actual contaminant oxidative destruction versus encapsulation.



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Archive

Oct 2010 - Activated Persulfate Chemistry: Combined Oxidation and Reduction Mechanisms

August 2010 - The Safe Use of Klozur® Persulfate Activators

June 2010 - Sulfate Revisited: The Fate of Sulfate in the Groundwater

March 2010 - The Use of Lime to Activate Klozur Persulfate and Its Impact on Contaminant Soil Concentrations

Jan 2010 - Use of Compound Specific Isotope Analysis to Enhance In Situ Chemical Oxidation Performance Monitoring and Project Management

Nov 2009 - Determination of the Klozur® Persulfate Demand

In an effort to elucidate the impact of lime on lime-activated persulfate chemical oxidation, a study was commissioned at Western Michigan University with Professor Dan Cassidy (daniel.cassidy@wmich.edu). The full report of the study can be found at the Klozur Resource Center at www.klozur.com. For the study, sediment from the Kalamazoo River (KRS) and soil from Montreal, Canada (MCS) heavily contaminated with polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were used. The KRS mean contaminant concentrations were 6445 mg / kg PCB and 8301 mg / kg PAH. For the MCS, mean contaminant concentrations were 3847 mg / kg PCB and 6602 mg / kg PAH.

Two experiments were carried out. The first consisted of a lime dosing study to determine the amount of lime needed to maintain a pH greater than 11 with and without persulfate present. This study was performed in 500 mL Erlenmeyer flasks under continuous shaking. The second experiment was performed in slurry reactor vessels, utilizing the lime dosing determined in the first experiment. The contaminant reduction rates from the lime dosing study were consistent with the results from the slurry reactors, and thus only the results from the slurry reactors will be presented here. Results from the lime dosing study can be found in the full report on the Klozur website.

The slurry reactors consist of a five liter, closed glass reaction vessel with a mechanical mixer and multiple sampling ports. The sampling ports were used to measure pH temperature, and for slurry sampling. One port housed two Tenex® activated carbon tubes in series to quantify off-gassing of PAHs and PCBs. The mechanical mixers were run continuously at approximately 350 rpm. For the KRS and the MCS, three reaction scenarios were tested: control with no lime or persulfate added, hydrated lime addition only, and persulfate with hydrated lime addition. Each reactor was dosed with two kilograms dry weight of soil or sediment and enough distilled water to reach the four liter mark (50% solids concentration). For the persulfate reactors, 646 g of persulfate was added (323 g persulfate / kg soil or sediment). Lime was dosed at either 2% Ca(OH)₂ for reactors without persulfate or 3% by weight for reactors with persulfate. For contaminant quantification, a triplicate sample of 20 mL of slurry was taken. The soil pellet containing 10 g of dry weight of soil was first spiked with 0.1 mL of a 2 solution of 2-fluorobiphenyl in hexane and thoroughly mixed to allow quantification of contaminant recovery. The soil pellet was then extracted for PCBs and PAHs using EPA method 3545 without pH adjustment. To investigate the potential of lime encapsulation, a second triplicate set of slurry was taken and adjusted to a pH of 6 using hydrogen chloride prior to the centrifugation and extraction steps of EPA Method 3545. Further detail on the analytical methods used can be found in the full report.

The pH of the MCS slurry with no lime or persulfate was consistent over twenty two days at 6.9. The KRS maintained a pH of 7.3 for this period. For the MCS and KRS slurries with lime and with lime plus persulfate, pH was maintained above 11 for the twenty two days of the study. The temperature profile of both the KRS and MCS slurries did not increase significantly above room temperature for the lime only addition. However, the temperature in both the KRS and MCS slurries increased significantly upon addition of lime and persulfate, with maximum temperatures around 70 °C being reached in the first several days of the experiment, dropping back to room temperature after about two weeks.

The results from the slurry reactor study are shown below (values are mean ± standard deviation for triplicate samples; ND – non-detect):

Aug2009 - Measurement of Persulfate in Solution

Jan 2009 - The Effect of Klozur® Activated Persulfate ISCO on Microbial Populations

Nov2008 - Geochemical Impacts of ISCO: A Field-Scale Assessment

July2008 - Surfactant Enhanced In Situ Chemical Oxidation

(values in mg / kg)	KRS Control	KRS Lime Only	KRS Lime with pH adj	KRS Lime + persulfate	KRS Lime + persulfate with pH adj
Initial PCB Concentration	6328 ± 502	6539 ± 523	6483 ± 527	6404 ± 523	6298 ± 531
Final PCB Concentration	6210 ± 482	2814 ± 245	6287 ± 482	467 ± 245	1470 ± 295
% total removal	2%	57%	3%	93%	77%
% volatile removal	ND	ND	ND	1.3%	

Table 1: PCB slurry reactor results for the Kalamazoo sediment

(values in mg / kg)	KRS Control	KRS Lime Only	KRS Lime with pH adj	KRS Lime + persulfate	KRS Lime + persulfate with pH adj
Initial PAH Concentration	7890 ± 532	7680 ± 499	7340 ± 546	8192 ± 502	8092 ± 532
Final PAH Concentration	7683 ± 504	3768 ± 328	7560 ± 480	1091 ± 258	2493 ± 308
% total removal	3%	51%	-3%	87%	69%
% volatile removal	0.8%	ND		2.1%	

Table 2: PAH slurry reactor results for Kalamazoo sediment

(values in mg / kg)	MCS Control	MCS Lime Only	MCS Lime with pH adj	MCS Lime + persulfate	MCS Lime + persulfate with pH adj
Initial PCB Concentration	3768 ± 401	3940 ± 462	3812 ± 420	4121 ± 440	4208 ± 444
Final PCB Concentration	3892 ± 433	1241 ± 214	3786 ± 466	958 ± 213	1661 ± 262
% total removal	-3%	69%	1%	77%	61%
% volatile removal	ND	ND		1.1%	

Table 3: PCB slurry reactor results for Montreal soil

(values in mg / kg)	MCS Control	MCS Lime Only	MCS Lime with pH adj	MCS Lime + persulfate	MCS Lime + persulfate with pH adj
Initial PAH Concentration	6544	6392	6631	6117	6019

	± 514	± 427	± 451	± 427	± 455
Final PAH Concentration	5928	2282	692	739	1941
	± 522	± 248	± 469	±248	± 298
% total removal	9%	64%	2%	88%	68%
% volatile removal	0.6%	ND		2.4%	

Table 4: PAH Slurry reactor results for Montreal soil

Review of Tables 1 through 4 show that for both the KRS and MCS soils, recovery of the PCBs and PAHs was consistent over the twenty-two period demonstrating low contaminant loss in handling and assay procedures. Upon addition of lime to either the KRS or MCS soil, between 57 and 69% of the PCBs and 51 – 64% of the PAHs were not recovered after the twenty-two weeks. However, upon adjustment of the lime-treated slurry samples to a pH of 6 prior to extraction, almost all of the PAHs and PCBs were recoverable from both the soil and sediment samples (all within 97% recovered). These results demonstrate that the “treatment” mechanism by lime addition on these two soil types is through encapsulation rather than destruction, and that the encapsulation is reversible and non-permanent with a lowering of pH. In addition, it is seen that the standard EPA method 3545 does not take into account transitory entrapment of the material by lime. As a result, lime by itself does not lead to contaminant destruction, and sites treated with only lime are not truly remediated as lime encapsulation is reversible and non-permanent.

KRS and MCS soils treated with combinations of lime and Klozur persulfate also show significant reductions in PCB and PAH concentrations (77 – 93% and 87 – 88% respectively). These results show a greater destruction percentage than lime only treatment. However, unlike the lime only treatment, the lime plus persulfate treatments still show significant reductions even with adjustment of the pH to 6 (61 – 77% for PCBs and 68 – 69% for PAHs). As a result, persulfate activated with lime does lead to oxidative destruction of the PAHs and PCBs. There is still some encapsulation occurring in the lime plus persulfate treatments (the difference between the non-adjusted pH and adjusted pH values). This may be a result of an under-dosage of persulfate for these highly contaminated soils and sediments, and it would be expected that increased persulfate dosing would lead to higher contaminant destruction percentages.

In conclusion, it is evident that the standard EPA test method 3545 does not adequately account for reversible, lime encapsulation due to a lack of pH adjustment prior to extraction. This may lead to erroneous conclusions that lime application is adequate in remediating contaminated soils, and that it provides equivalent benefit to lime activated persulfate treatment. Adjusting the pH to circum-neutral levels prior to extraction will provide a more accurate estimation of the contaminant destruction that is capable with lime and lime activated persulfate.

¹Waisner, S., Medina, V.F., Morrow, A.B. and Nestler, C.C. J. **Environmental Eng.**, 134, p 743 – 749, 2008.

²Bonan, D. J. **American Ceramic Society.**, 77, p 193 – 196, 2005.

³Conner, J.R.. Chemical Fixation and Solidfication of Hazardous Wastes. Van Nostrand Reinhold, 1993.

⁴Yilmaz, O., Unlu, ., Cokca, E. **J. of Env Eng.**, 129, p 366 – 376, 2003.

⁵US EPA, EPA/600/2-91/0-52, Washington, DC, 1991.

⁶Davila, B., Whitford, W. and Saylor, E.S. EPA/540/S-93/506, Washington, DC, 1993.

⁷Schifano, V., C. MacLeod, N. Hadlow, R. Dudeney. **J. of Haz. Mat.**, 141, p 395 – 409, 2007.

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