



FLORIDA DEPARTMENT OF Environmental Protection

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Tallahassee, FL 32399-2400

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Governor

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Secretary

September 13, 2019

Via Electronic Mail to Patrick Hicks at patrick.hicks@peroxychem.com

Mr. Patrick Hicks, PhD
PeroxyChem LLC
One Commerce Square
2005 Market Street
Suite 3200
Philadelphia, PA 19103

Re: **Klozur® KP**
The FDEP Innovative Technology Application Number: 1728

Dear Mr. Hicks:

The Florida Department of Environmental Protection's Division of Waste Management (Division) hereby accepts Klozur® KP for remediation of petroleum, chlorinated hydrocarbons, and other suitable contaminants in groundwater and soil, in situ and ex situ, via oxidation-reduction (redox) chemical reaction. Klozur® KP consists of potassium persulfate with a small amount of ammonia persulfate that is used in combination with an activator to form oxidative and reductive radicals for treatment of organic contaminants. The activator can be divalent metals such as ferrous sulfate, chelated metals such as chelated iron, hydrogen peroxide, pH modifiers, or heat.

Enclosure 1 contains regulatory information. Enclosure 2 provides calculation of an Alternative Groundwater Cleanup Target Level (AGCTL) for un-ionized ammonia.

For vadose remediation, where the underlying groundwater will not be affected by the leaching of Klozur® KP, there are no special concerns beyond those that would normally need to be addressed in preparing a Remedial Action Plan and conducting a cleanup in accordance with Chapters 62-780 and 62-777, F.A.C. However, for in situ groundwater remediation, via direct injection of Klozur® into an aquifer, there are underground injection control regulations that must be observed. Since injection-type, in situ aquifer remediation is likely to be the most common application of Klozur® KP, the bulk of the regulatory requirements discussed herein will be directed to that topic.

While the Florida Department of Environmental Protection (FDEP) does not provide endorsement of specific or brand name remediation products or processes, it does recognize the need to determine their acceptability from an environmental standpoint with respect to applicable rules and regulations, and the interests of public health safety. Vendors, upon receipt of an acceptance, must market their product or process on its merits regarding performance, cost, and safety in comparison to competing alternatives

in the marketplace. This acceptance letter shall not be construed as either an approval of the product or a certification of its performance.

Additionally, Department acceptance of any product or process does not imply it has been deemed applicable for all cleanup situations, or that it is preferred over other treatment or cleanup techniques in any particular case. A site-specific evaluation of applicability and cost-effectiveness must be considered for any product or process, whether conventional or innovative, and adequate site-specific design details must be provided in a Remedial Action Plan.

It is not a requirement that a remediation product or process obtain an acceptance from the Department in order to be proposed for use in a site-specific Remedial Action Plan, but the plan must contain information to show that it meets all applicable and appropriate rules and regulations. For Klozur® KP listed in this letter, a copy of this acceptance letter containing regulatory compliance advice should be included in the appendix of each site-specific Remedial Action Plan that proposes its use.

The Department reserves the right to revoke its acceptance of a product or process if it has been falsely represented.

If you have any questions, contact Elena Compton at (850) 245-8911, through Mail Station 4535 at the letterhead address, or by e-mail at Elena.Compton@dep.state.fl.us.

Sincerely,



Elena Compton, M.S., P.E.
Professional Engineer III
PRP Team 2, FDEP
850-245-8911

Enclosures: (1) Regulatory Information; (2) Calculation of AGCTL for Ammonia

06-29-2018: FDEP e-mail

09-13-2019: Burlab # 1728

ENCLOSURE 1
REGULATORY INFORMATION

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1. Groundwater cleanup standards: The onus shall be on users of Klozur® KP to ensure that all applicable groundwater standards will be met at the time of project completion for the contaminants of concern being remediated, and any by-products produced as a result of chemical or biochemical reactions induced or assisted by Klozur® KP listed in the subject letter. The following chapters of the Florida Administrative Code (F.A.C.) are cited: Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C., for groundwater classes and standards; Chapter 62-522, F.A.C., for groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects; Chapters 62-780, F.A.C., for cleanup criteria, allowance of alternative cleanup target levels and conditional closure requirements; and Chapter 62-777, F.A.C., for cleanup target levels.
2. Injection well permit: Per Rule 62-528.630(2)(c), F.A.C., the issuance of an enforceable, site-specific Remedial Action Plan Approval Order by the Department for injection-type aquifer remediation constitutes the granting of a Class V injection well construction/clearance permit.
3. Underground Injection Control (UIC): Remedial Action Plans proposing injection-type aquifer remediation shall include the information required by Rules 62-528.630(2)(c)1 through 6, F.A.C., for the purposes of the UIC program. Reviewers of those plans, upon issuance of a Department-enforceable Remedial Action Plan Approval Order, must transmit this information to the UIC program in Tallahassee by submitting a completed copy of the "UIC Notification". The notification is in the form of a memorandum currently located on the Internet at <https://floridadep.gov/waste/petroleum-restoration/forms/uic-notification-remediation-hazardous-waste>.
4. General information about temporary Zones of Discharge (ZOD): For groundwater remediation, the composition of a fluid to be injected must meet the primary and secondary drinking water standards set forth in Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C. [and Chapter 62-777], pursuant to UIC Rule 62-528.600(2)(d), F.A.C. Aquifer remediation products that do not meet these requirements must seek relief from water quality criteria by one of two mechanisms as follows. Permission for a temporary ZOD may be obtained via Rule 62-520.310(8)(c), F.A.C. If permission for a ZOD cannot be obtained by rule, then it will be necessary to seek a variance from Department rules in accordance with Section 120.542, Florida Statutes.

Rule 62-520.310(8)(c), F.A.C., allows for a temporary ZOD for closed-loop re-injection systems, for the prime constituents of the reagents used to remediate site contaminants, and for groundwater secondary standards. In order to obtain permission for a temporary ZOD by rule, a site-specific Remedial Action Plan must indicate: (a) the chemical ingredients of concern in the fluid to be injected that will be present in excess of groundwater standards; (b) the size of the ZOD that is needed; (c) the amount of time that the ZOD will be needed; and (d) a plan for monitoring the injected chemical ingredients of concern.

The size of the temporary ZOD will usually be the injection well radius of influence when the treatment system is a single injection point. For a multiple point system, the ZOD can usually be

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expressed and illustrated as the total area covered by all the injection points, located side-by-side with overlapping radii of influence.

5. Upon expiration of the time-period granted for the ZOD by way of Rule 62-520.310(8)(c), F.A.C., the concentrations of the above referenced analytes must meet their respective groundwater standards or their natural-occurring background values at the specific cleanup site, whichever is less stringent.

Conditional closure is also allowable provided the closure criteria of Rule 62-780.680, F.A.C., are met and there are no exceedances of a primary standard due to impurities in the product. Note that such conditional closure may require a modification of the size or duration of the ZOD. This modification must be approved in an enforceable order of the department, such as a conditional Site Rehabilitation Completion Order.

6. Site-specific Remedial Action Plans shall describe the volume and concentration of Klozur® KP reagents that will be injected.

7. Specific ZOD information for Klozur® KP:

- a. For the pre-injection concentrations of Klozur® KP suspension 35 % and below (percent by weight), required UIC ZOD compliance monitoring for to comply with Rule 62-520.310(8)(c), F.A.C.: Sulfate, TDS (Total Dissolved Solids), pH, and Ammonia, reviewers of Remedial Action Plans, when filling out the UIC Notification memorandum, should check the box labeled as follows:

“☐ ZOD permission by rule 62-520.310(8)(c), F.A.C., for reagent chemical species and/or parameter(s) in the fluid to be injected (or re-injected) that exceed secondary groundwater standards. ...”.

- b. For the pre-injection concentrations of Klozur® KP suspension greater than 35 % (percent by weight), required UIC ZOD compliance monitoring for to comply with Rule 62-520.310(8)(c), F.A.C.: Sulfate, TDS, pH, Iron, and Ammonia, reviewers of Remedial Action Plans, when filling out the UIC Notification memorandum, should check the box labeled as follows:

“☐ ZOD permission by rule 62-520.310(8)(c), F.A.C., for reagent chemical species and/or parameter(s) in the fluid to be injected (or re-injected) that exceed secondary groundwater standards. ...”.

9. Quarterly monitoring should suffice in most cases. Upon expiration of the time period granted for the ZOD by way of Rule 62-520.310(8)(c), F.A.C., the concentrations of the above referenced analytes must meet their respective groundwater standards or their natural-occurring background values at the specific cleanup site, whichever is less stringent, or appropriate controls are put in place to allow conditional closure under rule 62-780.680, F.A.C.

Sulfate, TDS, pH, and Iron have the following secondary drinking water standards: Sulfate = 250,000 ug/L (microgram per liter), TDS = 500,000 ug/L, pH = range from 6.5 to 8.5, and Iron = 300,000 ug/L. Ammonia is currently identified in Chapter 62-777, F.A.C., as a “minimum criteria systemic toxicant” and it has a Groundwater Cleanup Target Level (GCTL) of 2,800 ug/L. However, the oral reference dose upon which this number is based has been withdrawn from the U.S.

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Environmental Agency's (EPA) Integrated Risk Information System (IRIS) database. Therefore, the FDEP has calculated an alternative groundwater cleanup target level in accordance with Chapter 62-780, F.A.C. This Alternative Groundwater Cleanup Target Level (AGCTL) calculation is attached as Enclosure 3. The Department recommends using the referenced AGCTL for ammonia.

10. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Division of Waste Management has no objection to the use of some wells for the injection of Klozur® KP if the wells are suitable for the purpose. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply Klozur® KP product. This will avoid a premature conclusion that the entire site meets cleanup goals. By making sure that designated tracking wells are not used for treatment, there will be more assurance that the treatment process has permeated the entire site and that it did not remain localized to the area immediately surrounding each injection well.
11. Three categories of groundwater monitoring:
 - a. Active remediation monitoring for a cleanup site's contaminants of concern:
During the period of active remediation, groundwater shall be monitored in accordance with the requirements set forth in Section 62-780.700, F.A.C.
 - b. Post Active Remediation Monitoring for a cleanup site's contaminants of concern:
At least one (1) year of quarterly post remediation groundwater monitoring for the contaminants of concern shall be conducted at a minimum of two (2) wells: one located in the area of highest contamination, the other at the downgradient edge of the contamination plume, pursuant to Section 62-780.750, F.A.C.
 - a. Monitoring of the UIC zone of discharge for Sulfate, TDS, pH, and Ammonia, as discussed in paragraph 7a (seven a) above, or, when applicable, monitoring of the UIC zone of discharge for Sulfate, TDS, pH, Iron, Ammonia, as discussed in paragraph 7b (seven b) above.
12. Injection operations:
 - a. Avoidance of migration: For injection-type in-situ aquifer remediation projects, injection of Klozur® KP shall be performed in such a way and at such a rate and volume that no migration of either the Klozur® KP or the contaminants of concern in the aquifer or surface water results, pursuant to Rule 62-528.630(3), F.A.C.
 - b. Underground Injection Control operating permit: Although an operating permit is not required for aquifer remediation wells pursuant to Rule 62-528.640(1)(b), and 62-528.640(1)(c), F.A.C., since no movement of the contamination plume is expected to accompany the treatment process, the Department requests that the information items listed in Rule 62-528.640(1)(b), F.A.C., be considered and included in Remedial Action Plan proposals as a matter of good and thorough design practice. Briefly summarized, they are: quality of water in the aquifer, quality of the injected fluid, existing and potential uses of the affected aquifer, and well construction details.
13. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order or a declaration of "No Further Action", injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C.

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The Underground Injection Control Section of the Department shall be notified so that the injection wells can be removed from the inventory-tracking list.

14. Open-pit application: There is no objection to the introduction of Klozur® KP to an open excavation pit in which the groundwater has been exposed. Open-pit application is not injection, and it is not necessary to notify the Underground Injection Control Section, but this should not be construed as carte blanche to introduce to the pit any substance at any concentration with no regard to potential toxicological effects. The Division of Waste Management therefore recommends that the groundwater in the area of the pit be monitored for the same zone of discharge parameters that would have been monitored (if any) had the application actually been an injection.

September 1, 2015

Brian Dougherty, PhD
Office of District and Business Support
Division of Waste Management
Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Re: Calculation of an alternative groundwater cleanup target level for un-ionized ammonia

Dear Dr. Dougherty:

At your request, we have calculated alternative groundwater cleanup target levels (AGCTL) for total ammonia based on water temperature and pH. As you know, calculation of an AGCTL necessitates consideration of exposure from oral, dermal, and inhalation pathways (Chapter 62-780, FAC). The GCTL equation promulgated in Chapter 62-777, FAC calculates a criterion for groundwater based on the oral route, but does not consider other routes of exposure. The FDEP has not specified a preferred methodology for calculating exposure for the inhalation and dermal routes from groundwater. Therefore, to aid our calculation, we utilized the USEPA regional screening level (RSL) tap water equation, which includes exposure from the inhalation and dermal routes.

We reviewed current toxicity values available for ammonia using the hierarchy of toxicity sources promulgated in Chapter 62-780, FAC. No oral reference dose (RfD_o) is currently available for ammonia. An inhalation reference concentration (RfC) of 0.1 mg/m³ is available from the USEPA's IRIS database.¹ This value was based on a lack of decreased pulmonary function or changes in subjective symptomatology in humans (USEPA, 1991). As this effect is route specific to inhalation, an RfD_o cannot be extrapolated from the RfC. Without an oral reference dose, the toxicity from exposure by the oral and dermal routes cannot be estimated. While it is possible for ammonia to cause direct irritation of the skin due to its alkaline properties, quantitative data are lacking and it is not possible to calculate with any certainty the concentration of ammonia in groundwater that would cause irritation from direct contact (ATSDR, 2004). Therefore, the AGCTL was calculated based on inhalation exposure to ammonia volatilized from groundwater.

¹ The USEPA has recently proposed an updated RfC of 0.3 mg/m³, but this has not been approved or posted on IRIS. The time frame for completing this update is unknown.

To calculate an AGCTL for total ammonia, it was first necessary to estimate the risk-based concentration of un-ionized ammonia that would be of concern (since this is the fraction that will volatilize). We utilized the USEPA equation for tap water for non-carcinogenic effects by the inhalation route to calculate a risk-based concentration for un-ionized ammonia (Figure 1). Calculation of an AGCTL under Chapter 62-780, FAC also requires the consideration of sensitive sub-populations. Because ammonia is a non-carcinogen, children are the appropriate receptor of concern.

Figure 1: USEPA RSL equation for inhalation exposure from tap water for a non-carcinogen

$$NH_3 \left(\frac{\mu g}{L} \right) = \frac{THQ \times AT \times CF}{EF \times ED \times ET \times \left(\frac{1 \text{ day}}{24 \text{ hours}} \right) \times \left(\frac{1}{RfC} \right) \times K}$$

Parameter	Definition (units)	Default Value
NH ₃	un-ionized ammonia (μg/L)	--
THQ	target hazard quotient	1
AT	child averaging time (days)	2190
CF	conversion factor (μg/mg)	1000
EF	exposure frequency (d/y)	350
ED	exposure duration (years)	6
ET	resident water exposure time (hours/day)	24
RfC	inhalation reference concentration (mg/m ³)	0.1
K	Andelman Volatilization Factor (L/m ³)	0.5

The risk-based concentration of un-ionized ammonia was calculated as:

$$NH_3 \left(\frac{\mu g}{L} \right) = \frac{1 \times 2190 \times 1000}{350 \times 6 \times 24 \times \left(\frac{1 \text{ day}}{24 \text{ hours}} \right) \times \left(\frac{1}{0.1} \right) \times 0.5}$$

$$NH_3 \left(\frac{\mu g}{L} \right) = 208.57 \text{ (rounded to 210)}$$

In groundwater, ammonia concentrations are reported as total ammonia. The reported value is the sum of both the un-ionized (NH₃) and ionized (NH₄⁺) forms. The FDEP has a manual for the calculation of un-ionized ammonia based on total ammonia concentrations in fresh water, pH, and temperature (FDEP, 2001). The concentration of unionized ammonia can be calculated using the FDEP Unionized Ammonia Calculator v1.2 or using the equations below. Based on the methodology presented in the FDEP manual, the mole fraction of un-ionized ammonia is calculated using the following equations:

$$f = 1 / (10^{(pKa - pH)} + 1)$$

$$pKa = 0.0901821 + 2729.92/T_k$$

$$T_k = ^\circ C + 273.2$$

where:

f = the mole fraction of un-ionized ammonia

T_k = temperature in degrees Kelvin

°C = temperature in degrees Celsius

The mole fraction of un-ionized ammonia is used to determine the concentration of un-ionized ammonia using the following equation:

$$Ammonia_{total} \times f \times \left(\frac{17}{14}\right) = NH_3$$

where:

Ammonia_{total} = total ammonia (µg/L)

NH₃ = un-ionized ammonia (µg/L)

Table 1 (attached) lists AGCTLs for total ammonia based on a range of common pH values and temperatures for Florida groundwater. The AGCTLs listed in Table 1 do not consider organoleptic effects. The odor threshold for total ammonia in tap water is 1,500 µg/L and for taste is 35,000 µg/L (ATSDR, 2004). Based on Table 1, the risk-based concentration of total ammonia will likely exceed the odor threshold and will exceed the taste threshold at pH less than 7.0.

Because the concentration of un-ionized ammonia increases with water temperature, showering/bathing represents an acute exposure scenario where residents are exposed for short periods of time to relatively higher concentrations of un-ionized ammonia in air. We could not find any published data regarding the average temperature of water used for showering. However, 120°F (48.9°C) is considered a safe hot water temperature (Shields et al., 2013). Exposure to 48.9°C water takes 10 minutes to cause a serious burn and therefore can be used as the maximum likely shower temperature (Shields et al., 2013). Using the equations above, at water temperature of 48.9°C and a pH of 7.5 (chosen because it produces the largest fraction of un-ionized ammonia), the fraction of un-ionized ammonia available for inhalation would be 7.9%. The maximum airborne concentration of ammonia below which it is believed nearly all individuals could be exposed for up to one hour without experiencing anything other than mild, transient effects or without perceiving a defined odor is 25 ppm (AIHA, 2015). Using maximum allowable air concentration of 25 ppm for un-ionized ammonia and a water temperature of 48.9°C results in an acute AGCTL of 260,000 µg/L. Therefore, the AGCTLs in Table 1 were limited to a maximum concentration of 260,000 µg/L to protect against acute exposures.

Please let us know if you have any questions regarding the derivation of this AGCTL.

Sincerely,



Leah D. Stuchal, Ph.D.



Hannah M. Neeley, MPH



Stephen M. Roberts, Ph.D.

References:

AIHA (2015) *2015 ERPG Levels*. American Industrial Hygiene Association, Emergency Response Planning Guidelines, Falls Church, VA.

ATSDR (2004) *Toxicological Profile for Ammonia*. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

FDEP (2001) *Calculation of Un-Ionized Ammonia in Fresh Water*. Florida Department of Environmental Protection, Chemistry Laboratory Methods Manual, Tallahassee.

Shields, WC, McDonald, E, Frattaroli, S, Zhu, J, Perry, EC, and Gielen, AC. (2013) Still too hot: Examination of water temperature and water heater characteristics 24 years after manufacturers adopt voluntary temperature setting. *J Burn Care Res.* 34(2): 281-287.

USEPA (1991) *Ammonia (CASRN 7664-41-7)*. United States Environmental Protection Agency, Integrated Risk Information System, <http://www.epa.gov/iris/subst/0422.htm>

Table 1 – AGCTLs in µg/L (ppb) for total ammonia based on a range of common pH and temperatures for Florida groundwater

pH	20°C	21°C	22°C	23°C	24°C	25°C	26°C	27°C	28°C	29°C	30°C
5.5	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.6	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.7	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.8	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.9	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
6.0	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
6.1	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
6.2	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
6.3	220,000	200,000	190,000	180,000	160,000	150,000	140,000	130,000	120,000	120,000	110,000
6.4	170,000	160,000	150,000	140,000	130,000	120,000	110,000	110,000	98,000	92,000	86,000
6.5	140,000	130,000	120,000	110,000	100,000	96,000	90,000	84,000	78,000	73,000	68,000
6.6	110,000	100,000	95,000	88,000	82,000	77,000	71,000	67,000	62,000	58,000	54,000
6.7	87,000	81,000	75,000	70,000	65,000	61,000	57,000	53,000	49,000	46,000	43,000
6.8	69,000	64,000	60,000	56,000	52,000	48,000	45,000	42,000	39,000	37,000	34,000
6.9	55,000	51,000	48,000	44,000	41,000	38,000	36,000	33,000	31,000	29,000	27,000
7.0	44,000	41,000	38,000	35,000	33,000	31,000	28,000	27,000	25,000	23,000	22,000
7.1	35,000	32,000	30,000	28,000	26,000	24,000	23,000	21,000	20,000	18,000	17,000
7.2	28,000	26,000	24,000	22,000	21,000	19,000	18,000	17,000	16,000	15,000	14,000
7.3	22,000	20,000	19,000	18,000	17,000	15,000	14,000	13,000	13,000	12,000	11,000
7.4	18,000	16,000	15,000	14,000	13,000	12,000	11,000	11,000	10,000	9,300	8,700
7.5	14,000	13,000	12,000	11,000	10,000	9,800	9,200	8,500	8,000	7,500	7,000

* - acute exposure AGCTL

AGCTLs were calculated using an f value rounded to 5 significant digits and an un-ionized ammonia concentration of 210 µg/L