

CASE STUDY | KLOZUR® KP

KLOZUR® KP IN SITU CHEMICAL OXIDATION REACTIVE BARRIER FOR THE TREATMENT OF 1,4-DIOXANE

SITE INFORMATION

Site: Confidential Former Industrial location in New York State
Lead Consultant: AECOM

CONTAMINANTS OF CONCERN

1,4-Dioxane, 1,1,1-TCA, 1,1-DCA, 1,2-DCA, and 1,1-DCE

REMEDIAL APPROACH

Injected Permeable Reactive Barrier using Klozur® KP for treatment of a contaminated Plume.

RESULTS

99% Reduction in bench and field pilot tests.



Photo credit: AECOM and ISOTEC

SUMMARY

Alkaline activated Klozur® KP was used to treat a plume containing 1,4-Dioxane and chlorinated ethanes using an injected permeable reactive barrier (PRB) design. Bench and field pilot test results indicated a greater than 99 percent reduction in groundwater concentrations often to below the detection limit. The Klozur® KP and hydrated lime activator were observed to persist longer than their 6 month design persistence. The destruction of 1,4-Dioxane and the dichloroethane(s) illustrates the unique ability of alkaline activated Klozur® persulfate to treat contaminants with both oxidative and reductive pathways.

BACKGROUND

This former industrial facility in New York state used chlorinated solvents, including 1,1,1-Trichloroethane (TCA), in its manufacturing process. The site became contaminated with TCA along with common daughter products including; 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), and 1,1-dichloroethene (DCE). 1,4-Dioxane, which was commonly used as a TCA stabilizer, was also present. The plume of the contaminants migrated away from the industrial source area and extended beneath a wetland area. The target for this remedial pilot application was to demonstrate a remedy for the contaminant plume beneath the wetlands.

REGULATORY ISSUES

The site was managed under New York's Inactive Hazardous Waste Disposal Site Program and the groundwater was subject to restricted use cleanup objectives. Remedial action objectives for the site included groundwater target concentrations of 5 micrograms per liter ($\mu\text{g/L}$) for 1,1,1-TCA, 1,1-DCA, and 1,1-DCE and 0.6 $\mu\text{g/L}$ for 1,2- DCA.

PREVIOUS TECHNOLOGY EVALUATION

The contaminant plume was originally controlled using a groundwater extraction system which was operated for 15 years before being deactivated. A soil vapor extraction system was used to address portions of the upgradient source area. Despite these efforts, a contaminant plume consisting of 1,4-dioxane, chloroethanes and chloroethenes above the remedial goals was identified. Initially, bioremediation including enhance reductive dechlorination (ERD) with emulsified vegetable oil and aerobic co-metabolic bioremediation were evaluated.

A bench scale test found that neither technology successfully remediated the entire suite of contaminants, with ERD successfully treating the chlorinated compounds but with little impact to 1,4-dioxane, and aerobic co-metabolic based on propane and bioaugmentation demonstrating little to no treatment of the contaminants, likely due to inhibitory effects of the chlorinated compounds. Sequential application of ERD followed by aerobic co-metabolic bioremediation was considered but eliminated due to the operational complexity associated with implementation.

KLOZUR® PERSULFATE BENCH TEST

Following bioremediation bench scale test results, an evaluation of alkaline activated Klozur® KP, potassium persulfate, to remediate the commingled contaminant plume was initiated. Alkaline activated persulfate generates both the oxidative and reductive pathways; therefore remediates 1,4-dioxane, which is treated via an oxidative pathway, and the chlorinated ethanes, which are most efficiently treated using a reductive pathway (chloroethenes are known to be treated via either pathway).

A series of column studies to evaluate alkaline activated potassium persulfate were performed. Klozur® KP was used instead of Klozur® SP, sodium persulfate, due to its significantly lower solubility. This lower solubility allows Klozur® KP to be applied as a solid which then dissolves over an extended period of time as groundwater fluxes past. Calcium hydroxide (hydrated lime) was selected to create alkaline activated conditions and match the extended release profile of the Klozur® KP. In the control column, an interval of sand was inserted in between two intervals of contaminated site soils. In the reactive column, the sand interval was replaced with a blend of hydrated lime, Klozur® KP, and sand. The influent feed into both columns was untreated site groundwater. The effluent of each column was evaluated for pH, residual persulfate, and contaminant concentrations using EPA Method 8260. The data showed that the hydrated lime maintained a pH of >12 over the duration of the test while the pH in the control column remained circumneutral. All contaminants of concern were treated to below the detection limit (2 to 4 $\mu\text{g/L}$) for each of the three time points collected in the column with hydrated lime and Klozur® KP while the contaminant levels in the control column effluent remained $>1,100 \mu\text{g/L}$.

Table 1 | Column Bench Scale Test Results

Approximate Pore Volumes	Contaminant Concentrations (µg/L)							
	1,4-Dioxane		DCA(s) ³		1,1-DCE		Total VOCs ⁴	
	Control	AAP ^{1,2}	Control	AAP ^{1,2}	Control	AAP ^{1,2}	Control	AAP ^{1,2}
5	390	ND	353	ND	400	ND	1,177	ND
15	450	ND	385	ND	500	ND	1,545	ND
25	360	ND	461	ND	460	ND	1,632	ND

1. AAP: Alkaline activated Klozur KP with hydrated lime
 2. Detection limits: 2µg/L for 1,1-DCA, 1,2-DCA, 1,1-DCE and 4µg/L for 1,4-dioxane
 3. DCA(s) include 1,1-DCA and 1,2-DCA
 4. Additional detected compounds include: 1,1,1-TCA, 1,1,2-TCA, benzene, chloroethane, trichloroethene, trichlorofluoromethane, and vinyl chloride
- ND: Non-detect

FIELD PILOT TEST

Based on the successful bench study, the Klozur® KP PRB was pilot tested at a location slightly upgradient from the wetlands. The pilot test included injecting Klozur® KP, calcium hydroxide (hydrated lime), Klozur® SP and 25% NaOH. All reagents were combined into a single injection solution. The additional of Klozur® SP into the injection solution served two purposes: 1) reducing the rate of dissolution of the Klozur® KP in the injection solution and 2) treating the non-target oxidant demand found at the site. The solid slurry injectate was applied via 6 injection points along a 40 ft transect from 23 to 33 feet below ground surface. The average flow rate of the solid slurry into fine sands was 5 gallons per minute under pressures ranging from 20 to 100 pounds per square inch (psi). Given the estimated groundwater flux across the transect the mass of Klozur® KP had been calculated to persist for up to 6 months.

The monitoring network consisted of three wells screened in an interval corresponding to the injection interval. The first well was placed within the expected radius of influence of the injection locations, approximately 3 ft downgradient of the transect line. This allowed for an evaluation of the performance and longevity of the reagents at the PRB. The second and third monitoring locations were located 10 ft and 25 ft down gradient of the PRB transect and were intended to monitor downgradient impacts.

The monitoring data showed that all contaminants of concern were successfully treated at the PRB. Data from (MW-1) demonstrated a 99.8% reduction for all contaminants and treatment of 1,4-dioxane to non-detect. The data also showed that residual persulfate and alkaline conditions persisted for up to eight months after the pilot test application within the PRB. This indicated that the geochemical conditions for alkaline activated persulfate were maintained at the PRB for longer than the designed 6 month time-frame. Low levels of persulfate were observed downgradient from the PRB, however the pH was unchanged at both downgradient locations. This indicated that the alkaline conditions generated to activate the persulfate within the PRB transect were not sustained downgradient of the PRB. Despite the loss of alkaline conditions, the contaminants of concern were reduced by over 80 percent at the monitoring location 10 ft down gradient and by over 60 percent at the monitoring location 25 ft downgradient. The increase in DCA concentrations moving further downgradient suggested that most of the treatment occurred at the PRB and the remediated groundwater was likely re-contaminated as contaminants repartitioned off soils downgradient from the PRB prior to the monitoring wells.

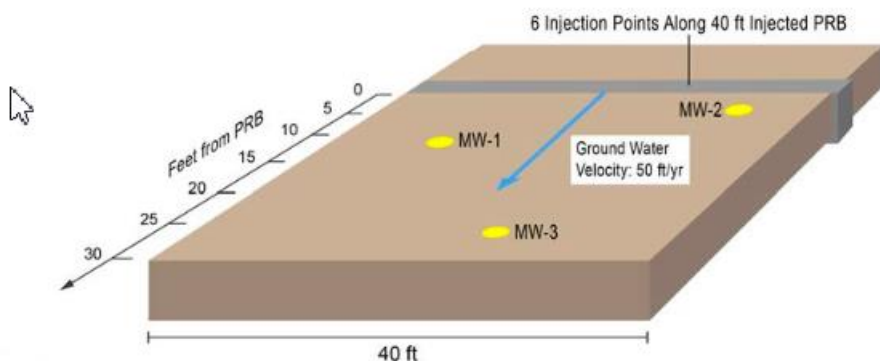


Figure 1 | Pilot Test Area

Table 2 | Pilot Test Results

Event	Klozur Persulfate (g/L)	pH	Contaminant Concentrations (µg/L)					Reduction VOCs (%)
			DCA	DCE	1,4-Dioxane	VOCs*		
MW-1 (3 ft downgradient of PRB transect)								
Baseline	NA	6.9	21	40	30	115		
3 month	7.2	12	0.2	ND	ND	0.2	99.8%	
6 month	NA	NA	0.2	ND	ND	0.2	99.8%	
8 month	14.2	12	NA	NA	NA	NA	NA	
MW-2 (10 ft downgradient of PRB transect)								
Baseline	NA	7.2	44	72	55	184		
3 month	3	6	10	11	ND	26	86%	
6 month	NA	NA	16	ND	16	34	82%	
8 month	2.5	6.8	NA	NA	NA	NA	NA	
MW-3 (25 ft downgradient of PRB transect)								
Baseline	NA	7.2	89	270	200	610		
3 month	NA	NA	46	82	69	216	65%	
6 month	NA	NA	63	30	110	230	62%	
8 month	8	6.5	NA	NA	NA	NA	NA	

* VOCs listed. Not including acetone | ND: Non-detect, NA: Not analysed

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