Chemical Oxidation and Inclusion Technology for Expedited Soil and Groundwater Remediation

Broad Agency Announcement Factsheet

Introduction

The Air Force Civil Engineer Center (AFCEC) Environmental Directorate Broad Agency Announcement (BAA) seeks to fund better, faster, and more sustainable environmental solutions for the Air Force. The AFCEC Environmental Restoration BAA currently focuses on solutions for Emerging Contaminants (ECs) and Emerging Issues (EIs) and is executed through the Restoration Technical Support Branch and Environmental Quality Technical Support Branch under FAR 6.102(d)(2).

AFCEC BAA 608 titled *Chemical Oxidation and Inclusion Technology for Expedited Soil and Groundwater Remediation* was funded from 2011 through 2015 to assess the efficacy of OxyZone® and XCT™ to treat mixed organic contaminants. Target contaminants included conventional volatile organic compounds, such as solvents (e.g., dichlorobenzene, trichloroethane and tetrachloroethylene) and petroleum constituents (e.g., benzene, toluene, ethylbenzene, and xylenes), as well as emerging compounds, such as perfluorinated organic compounds (PFCs) and 1,4-dioxane.

Field Demonstration

Joint Base Langley-Eustis Fire Training Area 15 was selected as the demonstration site. This site has unique hydrogeologic and geologic challenges. Situated between the James River (to the west) and a salt marsh (to the east) where groundwater under tidal influence is less than two feet below the ground surface, site lithology consists of 2-10 feet of discontinuous, interbedded low permeability silty sands and organic silts in the shallow zone overlying 10-19 feet of high permeability sands in the deep zone and a deeper clay confining unit.

Historic Aerial photo of Fire Training Area

High VOC Concentrations in the In the Site Groundwater – ug/l

Analyte (ug/L)	I-5 (Shallow)	I-6 (Shallow)	MW-2904 (Deep)	U-4 (Deep)
DCB	35,500+2	35,300	18,200	8,500
PCE	30,000	27,900	15,000	8,700
1,1,1-TCA	156,600	48,700	6,300	10,00
TPH-GRO	71,000	35,000	NM	NM
tVOCs	282,000	164,200	59,800	31,100

At the demonstration site, the most heavily contaminated soil was between 5 and 7 feet below ground surface, as shown in the **Table** above. In addition to the complex mixture of contaminants, Dense Non-Aqueous Phase Liquid (DNAPL) was detected.

Nine different PFCs were detected in the soil and groundwater with total concentrations as high as 290 (ug/l). The PFCs in the highest concentrations are PFOS (perfluorooctanesulfonic acid), PFHxS (perfluorohexanesulfonic acid), and PFOA (perfluorooctanoic acid).

In February, 2012, a baseline pre-treatment investigation was performed for site characterization. From the baseline hydrogeological and contaminant data, three (3) Test Cell locations for the in-situ treatment testing of

OxyZone® and XCT™ where identified. OxyZone is a patented oxidant mixture of EnChem Engineering, Inc. previously shown to destroy difficult to treat compounds like trichloroethanes. Thus it was decided to investigate the impact on PFCs as well as the conventional VOCs and semi-VOCs at the Site. XCT™ contains a unique biodegradable carbohydrate (XCT™ solution) to enhance contact between the oxidants and contaminant while also increasing contaminant solubility and oxidation.

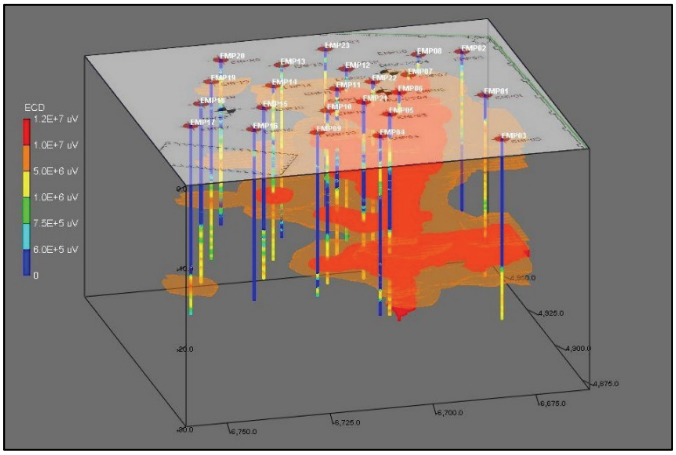
Exterior View of Trailer

Interior View of Trailer

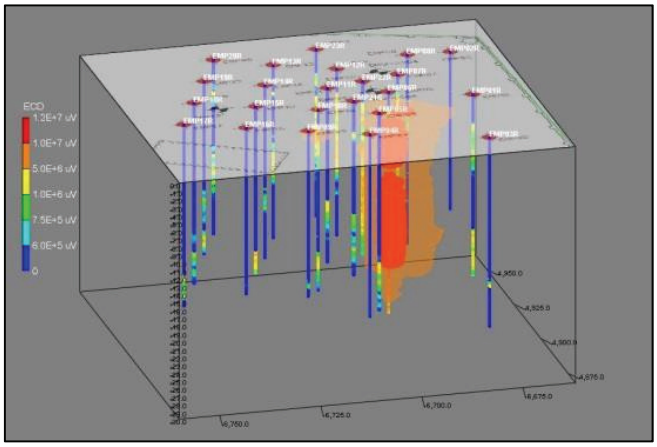
The OxyZone® and XCT™ generating equipment is entirely enclosed in a trailer with a small footprint. Only a fresh water source and an electrical source are required.

In December 2012, Test Cell #2 received sequential injection of OxyZone®, then XCT™ solution, followed by OxyZone®, in a single injection event, and Test Cell #3 received quasi-simultaneous injection of OxyZone® and XCT™ with small alternating volumes of OxyZone® and XCT™, in a single injection event. In April/May and July/August 2013, Test Cell #1 received an OxyZone® injection, followed by the XCT™ solution injection, and then a second OxyZone® injection. The two different injection events were one month apart.

Pre- and post-demonstration Membrane Interface Probe (MIP) Electron Capture Device (ECD) investigation results (March 2012 and December 2013), along with analytical results, display the overall contaminant reduction.



MIP ECD Data Isometric View – Pre-Injection

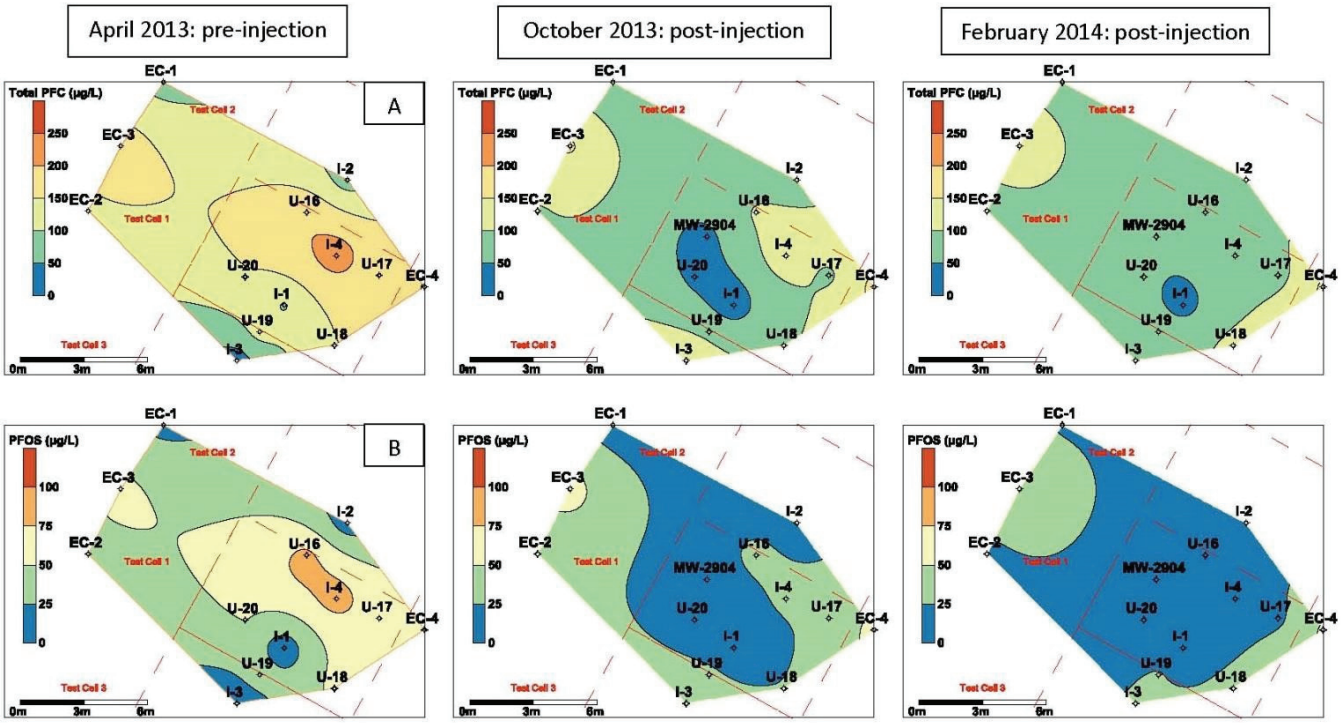


MIP ECD Data Isometric View – Post Injection

The most optimal application of OxyZone® and XCT™ was found to be a sequential injection of OxyZone®, XCT™ solution, and OxyZone®, in this order, which was evaluated in Test Cell #1.

In addition to a very significant decrease in concentrations of VOCs and semi-VOCs, concentrations of PFC also decreased from April 2013 (prior to OxyZone® and XCT™ injections) to October 2013 and February 2014 (post-injections), as shown below.

PFCs in Deep Screened Wells around Injection Test Cell # 1



Statistical evaluation of all the Site data showed the following:

1. Decrease in total PFCs concentration in groundwater.
2. PFOS:
   - highest soil concentration of all PFCs.
   - greatest decrease in groundwater (except well U-16D) of all PFCs
3. Statistical comparison of wells within Test Cell to those outside Test Cell showed PFCs concentrations decreased within the Test Cell #1 and not outside the Test Cell #1.
4. Groundwater concentrations of conservative tracer chloride showed no (dilution) impact from injections.

Laboratory Testing

Prior to fieldwork, extensive laboratory studies were performed to determine the appropriate concentrations of OxyZone® and XCT™ solution required to destroy site contaminants.

Subsequent to the field investigation that detected PFCs in the soil and groundwater, and the apparent destruction of some portion of the PFCs in the subsurface, laboratory treatability experiments were performed on spiked

deionized water and actual Site groundwater to verify the findings in a more controlled setting. The experimental results, listed below, show significant decreases and transformations of most all PFCs occurred during OxyZone® treatment, both in deionized water and in the presence of high concentrations of other contaminants exerting an oxidant demand. What was also observed was the apparent transformation of longer chained PFCs to smaller chained PFCs that therefore increased in concentration before subsequently decreasing.

Spiked Deionized Water (after 2 hours OxyZone® treatment)			
Specific PFC	Initial concentration – ppb	Final concentration – ppb	% removal
PFOS: (8 carbon sulfonate)	93	1	99%
PFOA: (8 carbon acid)	83	1	99%
PFHpS (7 carbon sulfonate)	4	0.4	90%
PFHxA (6 carbon acid)	6	6	no change
Total of 4 PFAS	186	8.4	95%

PFAS Contaminated Site GW spiked with additional PFOS and PFOA – 6 hrs. OxyZone®				
Specific PFAS	Initial concentration - ppb	Intermediate (3 hrs.) concentration - ppb	Final (6 hrs.) Concen-tration - ppb	% removal
PFOS: (8 carbon sulfonate)	138	25	3.6	97%
PFOA: (8 carbon acid)	33	22	1.6	95%
PFHpS (7 carbon sulfonate)	6.7	3.9	2.3	65%
PFHpA (7 carbon acid)	5.5	< 0.4	< 0.2	96%
PFHxA (6 carbon acid)	15	43	< 8.5	44%
PFHxS (6 carbon sulfonate)	68	99	< 0.2	99.7%
PFPeA (5 carbon acid)	11	< 2.0	< 0.9	92%
PFBS (4 carbon sulfonate)	8.7	14	< 0.4	95%
PFBA (4 carbon acid)	3.0	5.5	< 0.4	86%
Total of 9 PFAS	289	127	18	94%

Presentations and Publications

Ball, Raymond; Moore, Alan: "*Remediation of Perfluorinated Substances (PFAS) in Contaminated Groundwater with OxyZone®, a Multi-Oxidant Blend*". Fluoros 2015, an International Symposium on Fluorinated Organics in the Environment; July 13, 2015; Golden, CO.

Ball, Raymond; Moore, Alan: "*Remediation of Perfluoroalkyls with OxyZone®, a Multi-Oxidant Blend*". Emerging Contaminants Summit, March 1-2, 2016; Westminster, CO.

Ball, Raymond; Moore, Alan: "Remediation of Perfluoralkyl Compounds (PFCs) with OxyZone®, a Multi-Oxidant Blend", AEHS Soils Conference, October 18, 2016; Amherst, MA

Eberle, D., Ball, R., Boving, T.B. "*Impact of ISCO Treatment of VOCs on PFAS Co-contaminants at a Former Fire Training Area*". Environmental Science, and Technology. Manuscript re-submitted with minor revisions. March 2017.

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