Combined Remedy ISCO Treatment Approach with Klozur® SP to Reduce Modified Fenton Reagent Gas Generation

Background

In situ chemical oxidation (ISCO) using modified Fenton's reagent and alkaline activated Klozur® SP was applied at the Unipetrol RPA, s.r.o. petrochemical plant (Litvinov, Czech Republic) under the Czech Republic's "Removal of Old Ecological Burdens" national program. The contaminant plume covered approximately 33,500 m^2 (Figure 1) and the main pollutants of interest are BTEX (benzene, toluene, ethylbenzene, and xylenes), naphthalene, and other petroleum hydrocarbons from the range of C_5-C_{40} represented by the monitored parameter TPH (total petroleum hydrocarbons). The major portion of the pollution had its origin with either concealed sources (leaky underground wastewater piping) or unreported operational accidents. The starting concentrations were as high as 100 mg/L TPH inside the source area with NAPL (non-aqueous phase liquid) present. Target concentration limits (within the contamination plume area) were: benzene = 2,500 µg/L, naphthalene = 2,500 µg/L, TPH = 20 mg/L; reference concentration limits (at the contamination plume border) were: benzene = 400 µg/L, naphthalene = 1,700 µg/L, TPH = 10 mg/L. The main environmental risk recipient is the Bílina River flowing about 2 km south of the facility border.

Along with conventional pump-and-treat and venting efforts, the project deployed a combined remedy of *in situ* chemical oxidation (ISCO) using the hydrogen peroxide based MFR (Modified Fenton's Reagent) and activated Klozur® SP (sodium persulfate).

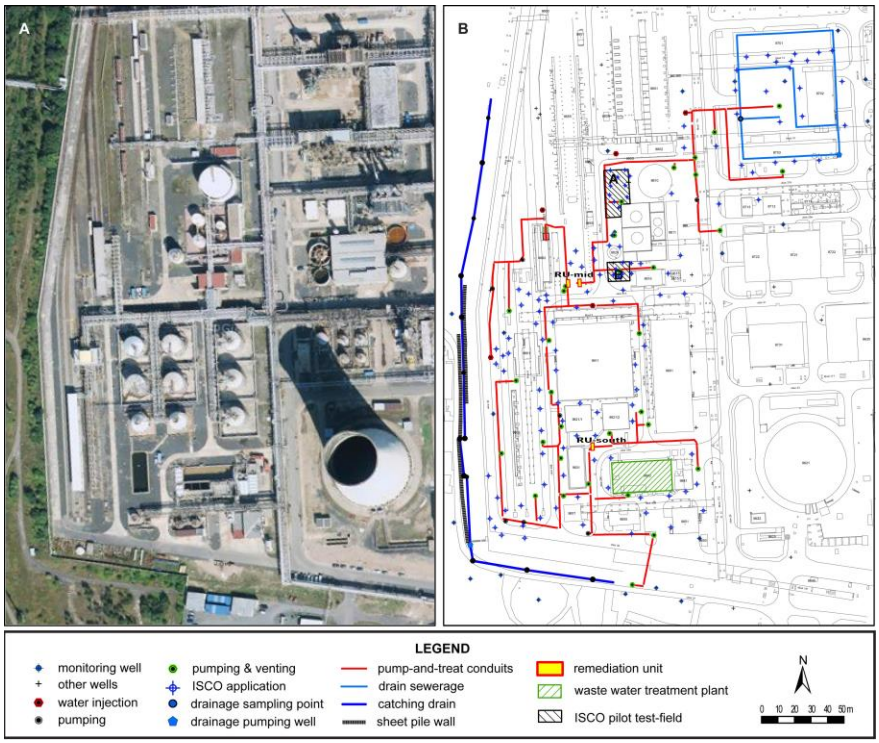

Figure 2. Aerial photograph of the petrochemical facility area impacted with the contaminant plume (www.mapy.cz); B, remediation project design.

Site Information

Site: UNIPETROL RPA, s.r.o., Litvínov, Czech Republic

Site Type: Active Petrochemical Facility

Lead Consultant: Karel Waska, EPS biotechnology, s.r.o.

Contractors: ID ekoslužby, s.r.o.

Contaminants of Concern

BTEX, Naphthalene, TPH

Remedial Approach1

Combined Remedy of Modified Fenton's Reagent and Klozur® SP

EPS biotechnology

The target unconfined sandy-gravel aquifer thickness ranges from 1.0 m to 3.0 m with estimated porosity of 0.15. It was underlaid by isolating tertiary silty-clays at the depth of 5.0 to 8.0 m bgl (below ground level). The contaminated groundwater table reaches 2.0 to 5.0 m bgl with groundwater flow generally in the NE–SW direction and average hydraulic conductivity K = 2.6 x 10^{-4} m/s.

Challenge

The site is located inside a fully operational petrochemical facility with imminent presence of class 1 explosive zones (EX-1, OSHA standard 1910.307) having rigorous safety measures enforced. There were also concerns with using a MFR-only approach due to the potential for gas generation beneath structures. The limited budget prevented the sole use of Klozur SP and demanded the stoichiometrically more favorable use of less stable MFR (exothermic reaction, acidic stabilization). While the exothermic reaction and acidic conditions were controlled by real-time on-site monitoring, the clogging of injection wells by MFR generated gases and the short reactive zone of MFR with respect to the need of remediating large tracts beneath inaccessible structures presented a difficult task.

Solution

Klozur SP was used in combination with the MFR for two main reasons: 1) greater reactive zone (better stability) suitable for remediation under large buildings and structures (e.g., bulk tank-storage courts); and, 2) negligible gas generation. Total of 400 m^3 (106,000 gallons) 35% (wt/wt) hydrogen peroxide (H_2O_2) and 5,500 kg (12,125 lbs) Klozur SP were injected into the network of application-monitoring wells to enhance and speed up the pump-and-treat remediation in action. Following the pilot assessment, a full industrial-scale remediation started in November 2015 and continued until September 2017. To minimize any interference with the petrochemical production, the ISCO applications were carried out using ~~a~~ mobile injection piping and reagent reservoirs installable and dismountable on the same work-day. The MFR consisted of a 5% (v/v) solution of H_2O_2 amended by selected activator/stabilizer mixture, while the Klozur SP reagent at a 1% (w/w) solution concentration. Significant pore-clogging occurred by gas bubbles of O_2 and VOC after MFR injection into the aquifer (especially at places of higher dissolved VOC concentrations), hindering the reagent discharge. To avoid this, Klozur SP was injected prior to MFR for several days, causing the oxidation of pollutant present within the immediate vicinity of the application well with no excessive gas generation. The subsequent injection of MFR followed without reagent uptake rate changes. Venting was used to extract and clean soil vapor with activated carbon filters eliminating potential health and safety risks

Figure 3. Spatial extent of benzene contamination: A, February 2015; B, September 2017.

Results

Figure 2 displays the development of benzene concentrations after almost two years of full-scale ISCO application. A considerable reduction of contaminant plume spatial extent is visible with two main residual contamination areas that correspond with the identified historical source zones: first, located at the northeast part of the area, outlined by the drain sewerage; and, the second at the center-south of the area.

Summary

This case-study provides an insight on the complexity of larger-scale ISCO applications within actively producing petrochemical facilities. Despite the strenuous site conditions, a combined remedy ISCO approach using the combination of MFR and Klozur SP proved to be a successful strategy.

The effectiveness and feasibility of remediation using ISCO in target site conditions was successfully verified and the technology was deployed in full scale. The tools for real time monitoring and process control were tested, optimized, and used daily. Due to detailed (partly automated) on site monitoring, the strict safety regulations of EX-1 zone were met with significant reduction in pollutant levels (by several orders of magnitude) and in contaminant plume area was achieved after approximately 2 years of monitoring.

References

1. Waska K., Beneš P., Kamas J., Vilhelm Z., Šnajdar O., Minařík M. (2017) Combined ISCO Treatment In Petrochemical Explosive Zone (Class-I): Application Control And Safety Management. Proceedings of 14th AquaConSoil Conference on Sustainable Use and Management of Soil, Sediment and Water Resources, Lyon (FRA).