## Carroll's Grocery Surfactant Flushing—In Situ Chemical Oxidation

Site Name: Carroll's Grocery Site Location: Golden, Oklahoma Technology Used:

- Surfactant Flushing
- In Situ Chemical Oxidation (ISCO) (Fenton's Reagent)

**Regulatory Program:** Oklahoma Corporation Commission (OCC). OCC Administers the State Underground Storage Tank Program.

**Remediation Scale:** Full

**Project Duration:** About six months of treatment and periodic rebound monitoring for 30 months.

**Site Information:** A rural grocery store with a gasoline pump station has been operating on the site for over 30 years. Gasoline-free product was found under and around the store. The original release was discovered in 1991. Efforts at the time to clean up the release failed. Groundwater monitoring wells at the site contained free product, and the water table was approximately 11 ft below ground surface (bgs). The treatment approach involved injection of surfactant to mobilize the non-aqueous phase liquids (NAPL) to extraction wells followed by an oxidant to meet benzene, toluene, ethylbenzene, and xylenes (BTEX) cleanup levels.

**Contaminants:** Monitoring wells at the site contained as much as 11 ft of free product. Soil cores indicated that a smear zone up to 3-ft thick existed over a 1.5-acre area. BTEX compounds were the dissolved contaminants of concern.

**Hydrogeology:** The site has a complex lithology (Figure 1). The surface layer is a 4 ft thick silt and sand unit. The surface layer is underlain by about 13 ft of interbedded clay and silty clay followed by a bed of cobbles with clay and silty clay that constitute the upper aquifer. The upper aquifer is bounded below by low-permeability clay that is about 2 ft thick. Below the clay aquitard, about 6 ft of silty sand form the lower aquifer. A clay layer beneath it acts as a second aquitard.

The groundwater piezometric surface is at about 11 ft bgs. Free product and residual light nonaqueous phase liquids (LNAPL) were located primarily at the interface of the cobble unit and the overlying clay silty-clay unit. A small amount of free product was also found at the interface of the aguitard and lower aguifer. This contamination was believed to have occurred as a result of penetration of the aquitard during a previous cleanup action. Benzene concentrations in the lower aquifer, which is a source of drinking water, ranged up to 3,000 µg/L. However, natural attenuation appeared to be reducing the concentrations of contaminants to safe levels before the contaminant plume reached any of the drinking water wells.



**Project Goals:** The regulatory agency desired complete removal of the free product from the subsurface, and if possible, achieve reduction of dissolved benzene concentrations to a level that would eliminate the possibility of benzene ever reaching the downgradient drinking water wells at a concentration above the maximum contaminant level (MCL) of 5  $\mu$ g/L.

**Cleanup Approach:** The chosen remedy involved removing the free product with surfactant

flushing. Because LNAPLs, such as fuels, are less dense than water, they are bounded by the water table and once they are mobilized, they are relatively easy to control with pumping. Treating the dissolved fraction and any remaining residuals requires a different technology. ISCO was selected for these phases to destroy the relatively low level concentrations in place.

One pore volume of surfactant solution was injected into the zone containing free-phase and residual-phase NAPL (Figure 2). This zone included the silty clay, which has a low permeability. Injection rates into this zone were low at 0.15 gallons per minute (0.57 L/minute) in 2inch (5 cm) wells.

The surfactant contained a mixture of a sodium mono and dialkyl diphenyloxide disulfonate blended with a sodium dialkylsufosuccinate. The total concentration of the two surfactants was under one percent by weight. Adjusting the ratio of the two surfactants and adjusting the concentration of sodium chloride added to the injected solution optimized the phase behavior of the system. No alcohol was required.

Approximately 190,000 gallons of the solution was injected by low-pressure pumping into the target area over 60 days. Thirty-three 2-inch (5 cm) vertical wells were used for injection of the surfactant and extraction of the mobilized free product. A horizontal injection well was installed under the store itself, with 2-inch extraction wells around the store perimeter. An additional 20 wells were placed around the perimeter of the free-product zone for fresh-water injection to maintain hydraulic control of the surfactant. Extraction wells used liquid-ring pumps.

Effluent was captured in a 500-gallon tank that allowed free product to separate from the solution. The surfactant solution was air stripped to remove volatiles (e.g., BTEX) and reinjected after surfactant makeup. This eliminated the need for offsite disposal of the surfactant. No surfactant was detected in monitoring wells around the site during or after the injection phase. Three months after the injection event, 22 of 25 wells had no evidence of free product. The remaining three had sheens. Further investigation revealed a small area of free product that had not been flushed and this area was addressed with a second surfactant flush. Benzene concentrations in the groundwater of the treatment zone were reduced by 70 to 99%. The highest level of benzene detected was  $350 \mu g/L$ .

Following the removal of free product and residual smear contamination, a polishing step using ISCO was employed to reduce the levels of dissolved BTEX in the groundwater. One pore volume of a solution containing 8 mg/L of Fenton's Reagent was injected into the lower and upper aquifers. After the injection, groundwater concentrations of benzene fell to levels near or below the MCL. No further treatment was carried out at that time, and the well field was closed but not abandoned.



**Project Results:** The periodic monitoring of the 25 monitoring wells showed some dissolved-phase rebound and occasional sheen in some wells, but concentrations of dissolved-phase contaminants remained below site goals. The state required no further action at the site.

The Carroll's Grocery site demonstrates that mass removal leads to reductions in groundwater concentrations of contaminants. Even before the chemical oxidation flush, groundwater concentrations were reduced 70-90% after the injection system had been shut down for three months.

Total project cost was \$715,000, including flushing for a full pore volume with 8 mg/L of Fenton's Reagent. The soil volume treated (smear zone only) was  $15,500 \text{ yd}^3$  at a unit cost of \$46/yd<sup>3</sup> (\$60/m<sup>3</sup>). Soil volume was based on total aquifer volume (1.5 acres to a depth of 12 ft) was 27,000 yd<sup>3</sup> for a unit cost of \$26/yd<sup>3</sup>.

## Sources:

Surfactant-Flushing Followed by Chemical Oxidation: The Carroll's Grocery Case Study Golden, Oklahoma, Surbec Environmental, LLC.

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