LONG-TERM INVESTIGATION OF CAPPING REMEDIATION OF CONTAMINATED SEDIMENT

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ABSTRACT

The McCormick & Baxter site, located on the Willamette River in Portland, Oregon, is a former creosote wood treating facility. From 1945 to 1969, creosote-contaminated waste water and cooling water were discharged directly into the river. Creosote was identified up to 90 feet into the sediment and also found to be seeping into the river from upland source areas. In 1994, the site was placed on the federal Superfund list because of soil, groundwater, and sediment contamination. The sediment remedy consists of 23 acres of a 2- to 5-foot-thick sand cap with armoring including 600 tons of bulk granular organoclay placed over the active creosote seep areas and 25,000 square feet of organoclay Reactive Core Mats® (RCM) placed over nearshore areas with ebullition-induced creosote sheens. This paper reviews the investigation of the organoclay capped areas several years after the installation. Tests indicate that the organoclay has not been affected significantly by nonaqueous-phase liquid (NAPL) to date. The results from sorption capacity were essentially equivalent to that expected of water-saturated fresh organoclay. The permeability of the core samples and mat also was essentially equivalent to fresh organoclay (i.e., not significantly NAPL-affected), suggesting that NAPL can continue to penetrate and be sorbed by fresh organoclay. These results indicate that the placed organoclay, both bulk and mat, continue to perform as designed and their ability to contain NAPL has not been compromised by reduction in either capacity or permeability.

Keywords: Organoclay, RCM, sediment capping, sorption capacity, NAPL, creosote.

INTRODUCTION

The McCormick & Baxter Creosoting Company was founded in 1944 to produce treated wood products. The site is located along the Willamette River in Portland, Oregon (Figure 1).
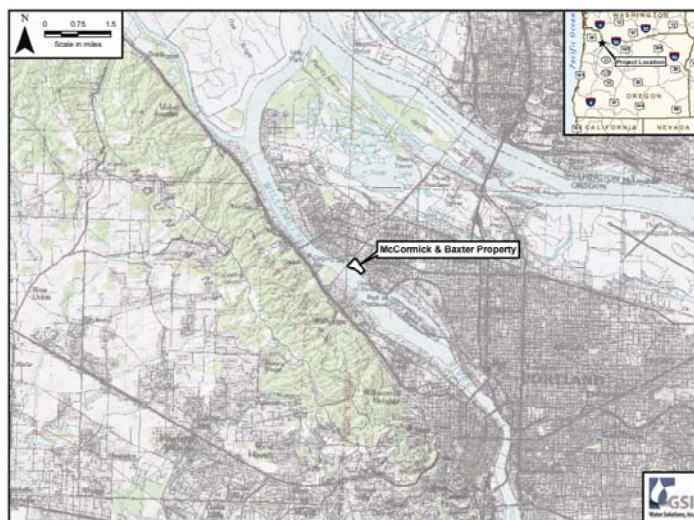

Figure 1. McCormick & Baxter location map.

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From 1945 to 1969, creosote-contaminated waste water and cooling water were discharged directly into the Willamette River. Creosote was identified in sediment at as much as 90 feet below the mudline and also found to be seeping into the river from upland source areas. The selected sediment remedy required capping areas that contain contaminant concentrations above human health and ecological risk-based protective levels, or that exhibit significant toxicity to biological organisms in the surface sediments. Surface water, groundwater, and transition zone water samples were collected in September 2002 and 2003 and crayfish tissue sampling was conducted in 2003. Results from these investigations and previous site investigation data were used to determine appropriate construction for the sediment cap as well as provide baseline conditions before cap installation. The 23 acre sediment cap was installed during the summer of 2004. Approximately 131,000 tons of sand were placed over contaminated sediment (2 to 5 feet) and 600 tons of bulk granular organoclay were placed over the creosote seep areas (1 foot) as an active capping material to prevent premature breakthrough of the creosote. Articulated concrete block armoring was placed over the shore and shallow water portions of the cap, and rock was used as armoring over the remaining portion of the cap. Figure 2 shows the location of the sediment cap and other remedial actions.
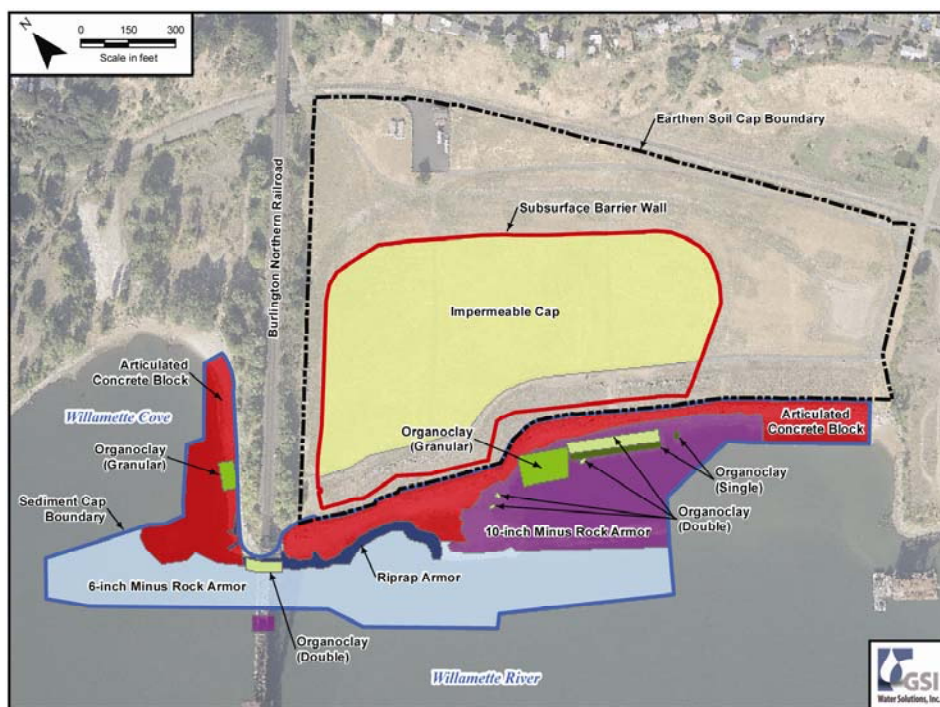

Figure 2. Site map.

As part of the groundwater remedy, a fully encompassing, impermeable subsurface barrier wall was installed in 2003 around the bulk of the upland contamination. It was designed to minimize nonaqueous-phase liquid (NAPL) discharges to the Willamette River. It was constrained in area by the presence of a high-pressure sewer line along the Burlington Northern Railroad (BNRR) right-of-way and the Willamette River. With respect to the Willamette River, the barrier wall was placed as close to the river as possible while not resulting in an aboveground bulkhead or overly steep bank treatment when grading and covering the riverbank to cover the barrier wall. In 2005, a Resource Conservation and Recovery Act (RCRA)-type impermeable cap was constructed over 15 of the 18 acres encircled by the subsurface barrier wall. The RCRA-type cap did not cover the remaining 3 acres of the barrier wall comprised of the riparian zone that borders the Willamette River. Capping of the riparian zone with an earthen cap was completed in 2004 during construction of the sediment cap. The barrier wall and impermeable cap are shown in Figure 2.

The project was conducted collaboratively with the U.S. Environmental Protection Agency (EPA), National Oceanic and Atmospheric Administration (NOAA), and local Indian tribes. Much of the work needed to be completed within a narrow federal Endangered Species Act-mandated fish in-water construction window. The design included considerations for enhancing fish habitat and protection.

EBULLITION-INDUCED SHEEN

Subsequent to emplacement of the sediment cap, ebullition-induced sheens were observed in the nearshore environment in locations where known residual NAPL was present in the sediments underlying the cap. Figure 3 shows the conceptual understanding of the generation of sheen resulting from ebullition.
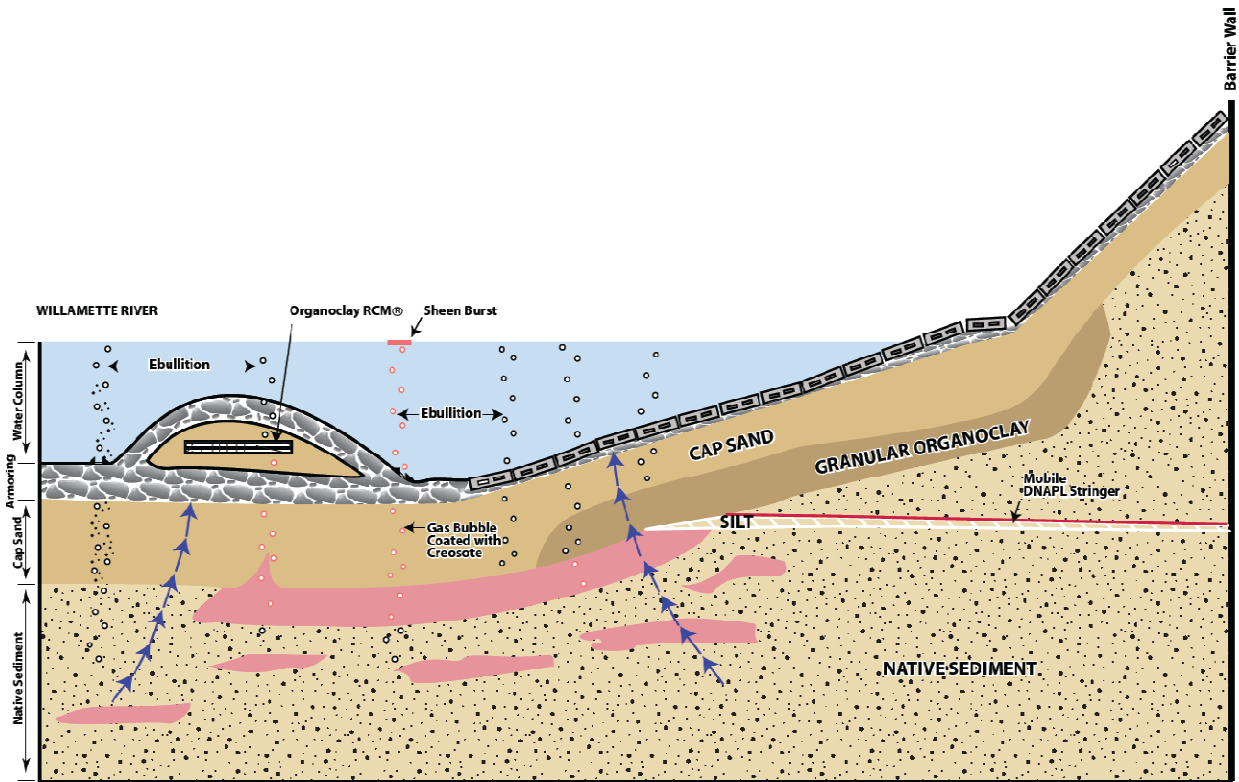

Figure 3. Ebullition-induced sheen conceptual model for McCormick & Baxter.

Historically, NAPL migrated from the upland and was also discharged directly into the river as a wastestream, resulting in the presence of residual NAPL in the sediment. When gas bubbles are produced beneath or within these areas of residual NAPL, NAPL coats the bubbles as they rise to the surface. In several locations where bulk granular organoclay was not placed and residual NAPL is present in the sediments, ebullition periodically has resulted in transport of NAPL to the overlying surface water, resulting in a sheen burst at the water's surface (Figure 4). Although ebullition has been prevalent overtop of the bulk granular organoclay footprint, no sheen has been observed associated with the ebullition. In most locations above the sediment cap footprint, there is no visual sign of contamination associated with the ebullition. However, in a few spatially discrete locations, sheen bursts were observed at the water surface in association with ebullition (Figure 4). The estimated volume of NAPL present in the ebullition-induced sheen is small; therefore, placement of organoclay-filled Reactive Core Mats® (RCM) in these select areas was determined to be the appropriate remedial action (see Figure 3).

Figure 4. Ebullition-induced sheen (left) and ebullition without sheen (right) (2005).

Significant quantities of gas are generated in the sediments as a result of the degradation of organic material present, including both the residual creosote and buried wood waste. Ebullition is most prolific in the nearshore environment during the late summer and fall when the Willamette River stage is low. The implications of gas generation and subsequent release of contaminants from sediments is not completely understood (Yuan et al. 2008).

Ebullition is prominent at the site, emanating from the sediment in the summer and fall months (Figure 5). Before installation of the sediment cap and barrier wall, ebullition was observed along the shoreline when the Willamette River stage was low. Since installation of the sediment cap and barrier wall, ebullition has increased significantly. Originally, the increase in ebullition was attributed to settlement of the sediment cap; however, the increase in ebullition has remained constant in the 4 years since sediment cap installation, discounting the possibility of being caused primarily due to sediment cap settling. The increase in ebullition may in part be attributed to the presence of the 88-foot subsurface upland barrier wall which significantly reduced the upland flow of shallow groundwater into the Willamette River along the shoreline where the barrier wall is present subsequently allowing the gas to accumulate in the sediments instead of being flushed out by groundwater discharge. The gas production is primarily the result of biodegradation of organics producing methane and carbon dioxide which was confirmed with the sampling of gas from flux chambers in 2008 where methane was found to comprise up to 100 percent of the gas produced from the bulk granular organoclay while a mixture of carbon dioxide and methane was observed from the flux chambers located within the sediment outside of the granular organoclay footprints.

Figure 5. Ebullition in the former Tank Farm Area (2006).

BULK GRANULAR ORGANOCLAY

In areas of potential creosote seeps from the upland, as part of the sediment cap, 1 foot of bulk granular organoclay (AquaTechnologies, ET-1) was placed directly overlying the contaminated sediments. One foot of sand followed by armoring was placed over the top of the organoclay. Placement of the bulk organoclay is difficult because the

organoclay retains air causing the organoclay to float. To reduce the amount of organoclay lost to the river, the organoclay was placed into the river in "Super Sacks", allowed to hydrate before divers cut the bags as shown in Figure 6.

Figure 6. Placement of granular organoclay (2004).

To determine whether a one foot thickness of bulk granular organoclay was adequate, the potential amount of NAPL that could migrate into the river was calculated using Darcy's law. The fully saturated NAPL hydraulic conductivity for each potential flowpath was calculated from the average calibrated hydraulic conductivity used in the site groundwater flow model for the flow path vicinity. The NAPL thickness along each flow path was the average of thickness measurements in wells and in cores showing saturations described as "moderate sheen" or greater. Free product mobility testing was conducted on cores from the site. The density and porosity were determined by API Method RP40 and measurement of initial oil and water saturations according to ASTM D425M with Dean-Stark extraction for oil, centrifuging at a force 1,000 times that of gravity for 1 hour to remove mobile liquid (air displacing oil and water) and measurement of residual oil and water saturations. Initial total liquid saturations on the cores were mostly 90 percent or higher. Bulk density varied from 1.2 to 1.6 grams/cubic centimeter (g/cm^3) for sand and 0.9 to 1.2 g/cm^3 for silt. Porosity varied from 38 to 52 percent for sand and 52 to 61 percent for silts. Initial total liquid saturations on the cores were mostly 90 percent or higher and the initial NAPL saturations ranged from 0.1 to 16 percent. Only one sample showed a lower NAPL saturation after centrifuging (15.8 percent initially to 7.3 percent after centrifuging) indicating mobile NAPL. Estimated residual NAPL saturation was 9 percent for the silt and varied from 7 to 12 percent for the sand. The core with mobile NAPL was described in the field as having "free product." Thus, using a visual description of "moderate sheen" to determine field thickness of potentially mobile NAPL is conservative.

Using the above information, two flow paths (Willamette Cove and the former Tank Farm Area [TFA]) were identified where NAPL potentially could migrate from outside the barrier wall to the river from the upland through seeps. In Willamette Cove, the light NAPL (LNAPL) elevation at its discharge point into the river versus distance from the LNAPL source outside the barrier wall shows a gradient of 0.024 foot/foot (ft/ft), which could support a NAPL-discharge rate of 0.07 gallon/year/square foot (gal/yr/ft^2) (GSI 2007). This calculated value, is about half of the discharge rate that was measured at low tide before the barrier wall construction (DEQ 2003). The amount of mobile NAPL was calculated to be 355 cubic feet (ft^3) resulting in a time for depletion of the NAPL to the river of 130 years. Using the calculated NAPL discharge rate, the cap life was calculated to be greater than 500 years for 1 foot of organoclay assuming a sorption capacity of 0.5 gram of NAPL for 1 gram of organoclay (g NAPL/g organoclay). The second potential NAPL flowpath to the river is located along the Willamette River side of the site. Boring data along the shoreline indicated the presence of dense NAPL (DNAPL) outside the barrier wall where it could continue to flow into the Willamette River. NAPL saturation predicted from soil and NAPL properties were above the measured residual saturations from mobility testing. A plot of DNAPL elevation versus distance from the barrier wall showed a DNAPL gradient of 0.003 ft/ft. This could support a DNAPL discharge rate of 0.5 gal/yr/ft^2. In this case, the depletion time for the available mobile NAPL (3,841 ft^3) was estimated to take 5 years while the estimated cap life at the calculated discharge rate was 7 years (GSI 2007).

In 2005, Dr. Reible, with the University of Texas at Austin, conducted a series of experiments to assess the sorption capacity, permeability, swelling characteristics, leachability, and strength of the two organoclays used at the McCormick & Baxter site (Aqua Technologies ET-1 as the granular organoclay and CETCO PM-200 as the organoclay in the RCM) when exposed to NAPL from the site (Reible 2005). Both organoclays were found to be effective sorbents for the site NAPL. In the batch study, the sorption capacity of PM-200 was found to be as high as 4.82 g NAPL/g organoclay and that of ET-1 was 1.39 g NAPL/g organoclay. As expected, the effective capacity in column tests was less because of the heterogeneity of flow and the time required to achieve maximum capacity. The sorption capacity measured from the column study was 0.6 g NAPL/g organoclay for ET-1 and 1.37 g NAPL/g organoclay for PM-200. Thus, the 0.5 g NAPL/g organoclay sorption capacity value was reasonable to use for estimating sediment cap life.

In 2006, cores were collected to determine the effectiveness of the granular organoclay cap placed in 2004 to contain potential mobile NAPL in Willamette Cove and the former TFA. The thickness of organoclay also was measured to determine whether the correct thickness (1 foot) was achieved during placement. Figure 7 shows a representative picture of organoclay from a core and NAPL that migrated to the surface through the open borehole after coring prior to abandonment. The organoclay was generally 1 foot thick, verifying that placement was according to design. The contact between the native contaminated sediment and the overlying cap sand was typically sharp. At the upper surface of the organoclay and within the bottommost portion of the overlying cap sand, there was evidence of biological or chemical activity: gas voids, discoloration to dark gray, and a strong odor.
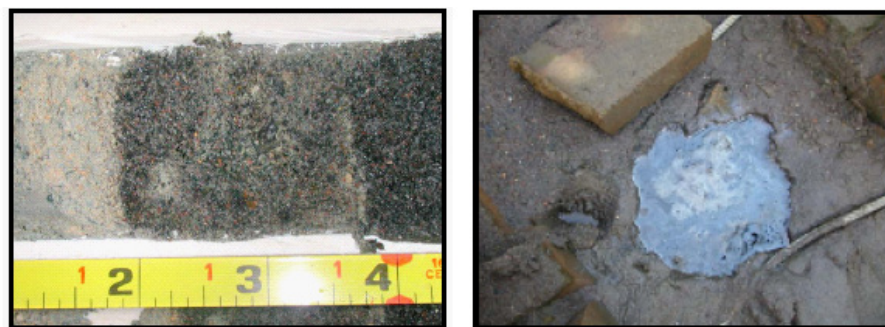

Figure 7. Bulk organoclay and native sediment in a core (left) and resulting NAPL in a core from penetrating the sediment cap after coring prior to abandonment (right) (2006).

Dr. Reible conducted a series of tests on the organoclay cores collected from the site in October 2006 to evaluate the performance of organoclay placed in 2004 (2 years) (Reible 2007). The following tests were conducted by Dr. Reible: available sorption capacity for NAPL, percent hexane extractable material (percent HEM), permeability, and water content. Available sorption capacity and percent HEM were designed to determine the extent to which the organoclay has absorbed NAPL and the potential for further NAPL retention. Permeability was used to assess the ability of NAPL to access available organoclay capacity. Water content influences NAPL capacity and assisted in interpretation of available capacity. The tests indicated that the organoclay has not been affected significantly by NAPL to date. The results of sorption capacity and percent HEM tests were essentially equivalent to that expected of water-saturated fresh organoclay. The permeability of the core samples also was essentially equivalent to fresh organoclay, suggesting the NAPL can continue to penetrate and be sorbed by fresh organoclay if any mobile NAPL exists.

As discussed above, there is significant gas production within the sediments at the site. Gas production overtop of the areas with granular organoclay was observed to be significantly greater than in the surrounding areas. In the summer of 2008, two ebullition surveys were conducted: in early summer, when the river stage was still relatively high; and in early fall, when the river stage was low. As shown in Figure 8, ebullition is prominent over the areas where granular organoclay was placed while absent from other areas when the river stage is still high. After the river stage dropped, ebullition continues to be prominent overtop of the organoclay footprint; however, it is also present within the embayment in the former TFA and outside and south of the sediment cap footprint.
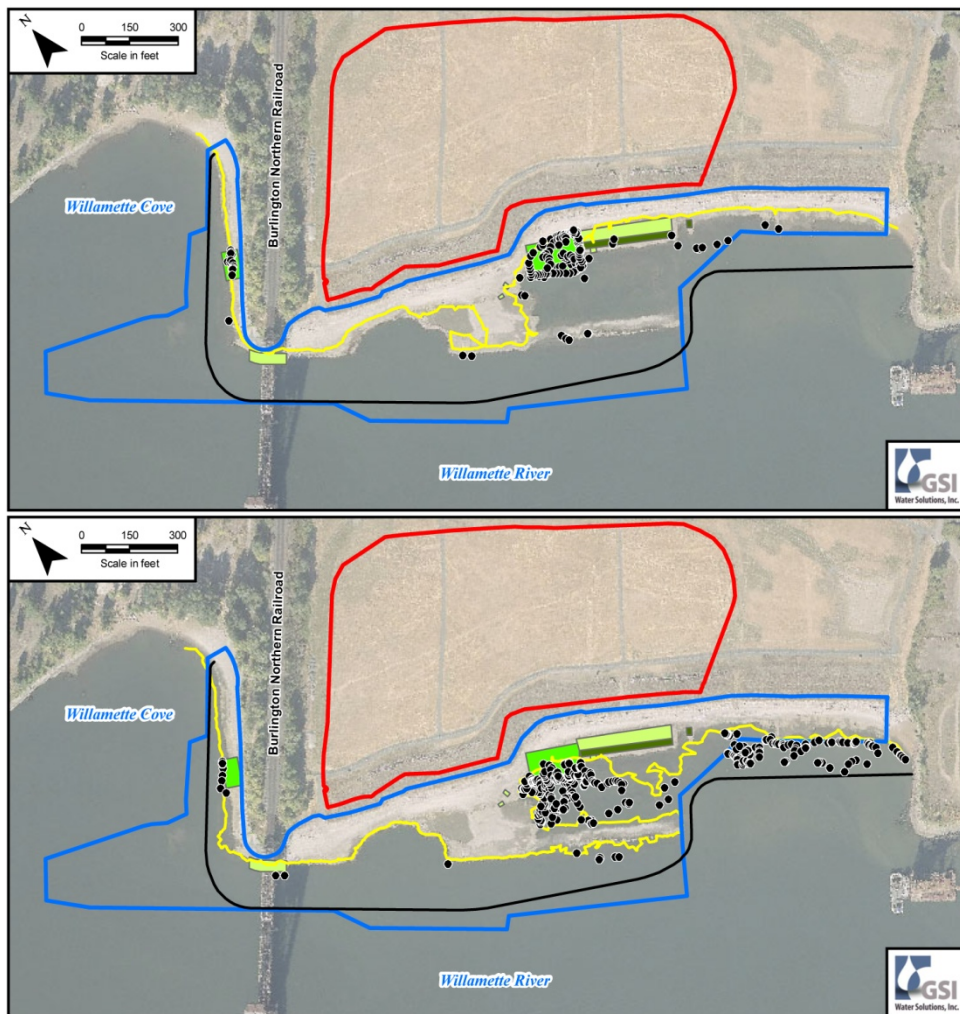
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Figure 8. Ebullition in late July 2008 (top) and ebullition in October 2008 (bottom) (yellow line is river stage elevation; black line is the area of survey, blue line is the sediment cap boundary, and red line is the barrier wall outline; black dots are ebullition locations).

Using flux chambers, the calculated rate of ebullition overtop the organoclay is 2.9 liters/m^2/day while the rate outside of the organoclay footprint where residual creosote is known to be present in the native sediment was calculated to be approximately 0.02 to 0.09 liters/m^2/day. Yuan and Reible (2009 in review) report ebullition rates ranging from $3 \times 10\text{-}4$ to 2.64 liters/m^2/day within differing site conditions. The ebullition rate within the organoclay footprint is slightly above the high end of that in Yuan and Reible (2009 in review). The higher gas production rate within the organoclay layer allows the gas to be released (ebullition to occur) at a lower drop in pressure (i.e., drop in the river level) while adjacent to the organoclay, where the gas production rate is slower, it takes a larger drop in river level before ebullition occurs.

Ten sets of flux chambers were placed in the sediment cap area (see Figure 9). Each set had one flux chamber placed overtop of an ebullition pathway and an adjacent flux chamber placed where no ebullition was observed. Porewater samples collected from flux chambers suggest that ebullition is a pathway for contaminant transport as indicated by consistently higher concentrations of polynuclear aromatic hydrocarbons (PAH) in the porewater from the flux chambers placed overtop of the ebullition pathways as compared to the adjacent flux chambers. However, the PAH concentrations measured from both ebullition and non-ebullition flux chambers were generally below risk-based ambient water quality standards.

Figure 9. Flux chamber set (2008).

In 2008, Dr. Reible collected additional cores for analysis. The test results are pending; however, he reported that the preliminary results are similar to the 2006 core analysis, suggesting that the organoclay continues to perform as designed and that its ability to contain NAPL has not been compromised by reduction in either capacity or permeability. This is important because it suggests that the increase in gas production within the organoclay layer is not adversely affecting the organoclay's capacity to sorb NAPL.

ORGANOCLAY REACTIVE CORE MATS®

In response to the ebullition-induced sheen observed following the 2004 sediment cap construction, approximately 25,000 ft^2 of organoclay (RCM) were installed in 2005. The first RCM (called the "test mat") was placed manually over a single ebullition pathway from which ebullition-induced sheen was observed. The 10- by 15-foot mat was centered over the gas bubble pathway. It was placed with the intent of being able to remove it after 1 year for field and analytical testing.

In addition to the test mat area, a 300-foot-long area (18,000 ft^2) along the shoreline upstream of the granular organoclay in the former TFA and a 115-foot-long stretch (6,000 ft^2) beneath the BNRR bridge were capped with primarily double layer organoclay mats (see Figure 2). Figure 10 shows the placement of the RCM beneath the BNRR bridge.

Figure 10. Organoclay Reactive Core Mat® placement under the BNRR bridge (2005).

The organoclay mats were covered with sand and rock armoring. In 2006, two additional small RCMs were placed over ebullition-induced sheen within the former TFA and another RCM was placed in 2007. No observations of ebullition-induced sheen were observed during the weekly shoreline surveys conducted in 2008.

In 2006, the test mat was exhumed for observation and sampling. No visual signs of NAPL staining were present on the mat. Portions of the mat were cut out and samples of sand were collected from beneath the cap and were analyzed by Dr. Reible under contract to the Oregon Department of Environmental Quality (ODEQ) (see Figure 11). The measured sorption capacity of the organoclay from the mat was 3.99 g NAPL/g organoclay, which is near the full sorption capacity of fresh CETCO PM-200 that was used in the RCM.

Figure 11. Exhumation of the "test" Reactive Core Mat® for sampling (2006).

In 2008, a corner of the large area with RCM located in the former TFA was removed for testing because it was uncertain whether gas was capable of passing through the mats. Significant ebullition was observed overtop of the bulk granular organoclay footprint, and also emanating from the northeast mat corner, while little ebullition was observed overtop of the organoclay mats. When the corner of the RCM was pulled back and inspected, the sand layer placed overtop of the original sediment cap armoring obviously had washed into the armoring, allowing gas to pass beneath and discharge through the high permeability armoring at the corner of the mat. This observation, in addition to the results of the ebullition survey (shown in Figure 8) support a conclusion that gas is not preferentially migrating to the edges of the organoclay mats. No sheens have been observed in association with the gas discharging from beneath the RCM. In addition, CETCO conducted sorption capacity testing and permeability testing on a piece of the removed mat. The oil sorption capacity of organoclay taken from the RCM was 0.54 pound/pound (lb/lb) organoclay, which still exceeded the manufacturer's certified property of 0.5 lb/lb organoclay for virgin organoclay. The permeability per ASTM D2434 of the organoclay RCM was 5.9×10^{-2} cm/s, which is characteristic of clean sand.

Porewater sampling shows that there is a significant reduction in concentrations through the organoclay RMC in the former TFA. A 2 order of magnitude reduction was observed between contaminants detected in porewater samples from below the organoclay RMC to overtop of the organoclay RMC. Porewater was collected using a Henry's sampler, which is a ¼-inch-diameter hollow stainless steel rod with a 1-inch screened interval at the tip. Total PAHs in the porewater sample beneath the mat were 2.354 micrograms per liter (µg/L) and 0.0274 µg/L directly above the mat. Porewater samples have been collected from the sand, armoring, and surface water overlying the organoclay RCM semi-annually since installation. PAHs from surface water or armoring have not been detected above the National Recommended Water Quality Criteria (NRWQC) published in August 2007 (E&E 2008). These data

support the performance of the organoclay RCMs used to prevent creosote migration associated with ebullition.

CONCLUSIONS

Based on extensive laboratory and field testing of water and sediment at the McCormick & Baxter site, it is clear that the bulk granular organoclay and organoclay RCM are performing as designed. Ebullition was not expected; however, does not appear to be significantly affecting the sediment cap performance. Organoclay as a reactive capping material is preventing the migration of NAPL and associated dissolved phase constituents above ambient water quality criteria into the river. The organoclays used at the site continue to have similar sorption capacity to water-saturated fresh organoclay in addition to retaining sufficient permeability to allow for groundwater transport through the sediment cap. The extensive methanogenesis occurring within the bulk granular organoclay is being studied further by Kiara Smith (Portland State University PhD student) under contract to ODEQ; however, testing indicated that the organoclay continues to maintain its sorptive capacity for NAPL. The organoclay RCMs have eliminated ebullition-induced sheen occurrences and provide the added benefit of reducing the concentrations of PAHs dissolved in water from reaching surface water.

ACKNOWLEDGEMENTS

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