Evaluation of Permeable Reactive Barriers to Treat Manufactured Gas Plant (MGP) Impacted Groundwater

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An evaluation of the feasibility of using oleophyllic materials to passively treat groundwater residuals (up to 10,000 ppb total VOCs, and PAHs) associated with Manufactured Gas Plant (MGP) operations was conducted. The key component of the evaluation is the performance of a formal Treatability Testing Program designed to identify and evaluate potential treatment media for use in passive treatment walls at two demonstration sites; one in Wisconsin and another in North Carolina.

The treatability-testing portion of the study consisted of three stages:

- Stage 1 -- Comparative Jar Tests
- Stage 2 -- Isotherm Jar Tests
- Stage 3 -- Column Tests

The jar tests were used for comparative purposes, to identify the most effective select media to be carried forward to the column test. The column tests were used to identify media performance under dynamic flow conditions that roughly mimic site and anticipated PRB design conditions. The conceptual site model and design concept identified site and design conditions including; the target constituents, treatment objectives, geochemistry, groundwater flow rates and design conditions. Treatability testing evaluated media effectiveness under those conditions, to the extent practicable.

Stage 1 and Stage 2

Two sets of batch tests were conducted to evaluate media effectiveness for the treatment of organic constituents. Initially, Stage 1 Comparative Jar Tests were conducted to compare the ability of nine different media to adsorb target constituents. The most effective media were identified and brought forward for Stage 2 Isotherm Jar Tests. The Stage 2 tests involved an in-depth evaluation of the most effective media. Batch tests for the Wisconsin site also included an evaluation of media for cyanide treatment. The batch tests were conducted by placing select media and site groundwater in zero headspace jars and agitating them for a specified time interval to obtain absorptive data for the target constituents.

Jar tests were conducted in sets of about six samples using the same water. An influent sample was collected to identify the concentration of target constituents in the water placed into the jars, and a control sample was collected to quantify any losses occurring during testing. The control jar was handled in exactly the same manner as the other jars. It was agitated over the same time frame and filtered. The control sample is used to confirm the overall results are not impacted by the way the samples were handled during testing.

The evaluation of media during the comparative jar tests focused on benzene and naphthalene removal. As the project focus narrowed to several select media, the parameters of interest were increased to include semivolatile organic compounds (SVOCs) and total organic carbon (TOC). SVOCs were evaluated for the Wisconsin site because several SVOC are present above regulatory criteria, and it was therefore important to confirm the effectiveness of the media for their treatment. TOC is of interest because it represents the total organic load the media would treat.

VOC samples were analyzed initially (Stage 1 Comparative Jar Tests) in-house using a gas chromatographic determination following Modified Method 8021A (SW-846, Third Edition, Update III, December 1996). The method was modified to capture naphthalene, and analysis focused on benzene and naphthalene. Later samples were analyzed at Great Lakes Analytical Laboratory, Oak Creek, Wisc., by Modified Method 8021, Method 8270, TOC and total cyanide.

In-house samples were analyzed on a Hewlett Packard Gas Chromatograph Model # 5890 Series II equipped with a PID/FID detector, using purge and trap with an OI 4560 concentrator.

The Stage 1 results for both the North Carolina and Wisconsin sites show a wide range of removal efficiencies for the different test media. Generally, activated carbon is the most effective, followed by the organically modified clays. Other media show some potential effectiveness, but are not considered viable candidates for a full-scale treatment system and are therefore dropped.

Results for cyanide testing indicate that an inorganic resin was the most effective and achieved up to 67% removal of cyanide. Water from different locations at the site produced different removal efficiencies. We believe this suggests that the media is only effective on certain types of cyanide (e.g., ferric cyanide).

Stage 3

Based on the Stage 1 and Stage 2 results, several media were selected for Stage 3 column tests. The select media include the most successful media from the Stage 1 and 2 jar tests. For the Wisconsin site, the selected test media include activated carbon, and organically modified clay. While less effective, the organically modified clay was brought forward for the Wisconsin site based on the anticipated effectiveness on free product removal should it become and issues during design. The media brought forward for the Wisconsin site included activated carbon.

Carbon adsorption appears to be capable of meeting the treatment objectives for removal of the target constituents to the regulatory criteria at both sites and had the most difficulty removing benzene to target criteria. Where benzene tends to control the design based on its low regulatory criteria and its typically lower removal efficiencies as compared to other constituents such as naphthalene.

The Column Studies for the North Carolina site were performed at URS's Treatability Testing facility in Milwaukee, Wisc. Column testing for the Wisconsin site was implemented on site. Analytical testing was performed, using EPA compliant methods, by Great Lakes Analytical, Oak Creek, Wisc.

Samples of groundwater from the North Carolina site that are representative of the distribution of groundwater contamination observed at the site were from October 2001 to April 2002. The site groundwater samples were stored and kept refrigerated at 40°C. Prior to start of the column studies, representative samples were obtained and analyzed to insure that the contaminants present are as consistent as possible with the concentrations measured in the field. Water for testing at the Wisconsin site was collected from an on site monitoring well and placed directly into the column test apparatus.

The column test conditions represent the worst-case scenario at the site for the permeable reactive barrier, and as such are conservative. The test conditions are based on the site model and a revised design concept consisting of a treatment window of about 50 square feet (sf) for each site. The design concept is an attempt to present a representative worst-case scenario that maintains a balance between feasibility and cost, while maintaining as much flexibility for design as possible.

The column test apparatus for the Wisconsin site consisted of one inch diameter glass columns, two inches in length. Four of the columns were placed in series, and connected by Teflon tubing. Two inches of activated carbon media were placed and tamped in each of the columns. The media was held in place with glass wool and fritted Teflon discs. The Teflon discs will distribute flow through the cross-sectional area of the columns. A total of five sample ports were placed in the apparatus. The sample ports consisted of a ball valve placed in the Teflon tubing. The sample ports allowed for the periodic collection of samples to monitor the breakthrough of the target constituents. Before starting the column tests, the media was saturated with DI water for 24-hours, and the flow rate was adjusted.

The column test apparatus for the Wisconsin site consisted of three 2-inch diameter glass columns. The first column was three inches in length, the second column was six inches in length, and the third column was nine inches in length. Cyanide was not tested. The three columns were placed in parallel, and connected by Teflon tubing. The columns were filled with activated carbon media, which was placed and tamped in 1/2-inch lifts in each column. The media was held in place with fritted Teflon discs. The Teflon discs distributed flow through the cross-sectional area of the columns.

A total of four sample points were placed in the apparatus. One sample port was placed at the influent to the columns. In addition, each column had an effluent sample point. The sample ports consist of a ball valve placed in the Teflon tubing and allowed for the periodic collection of samples to monitor the breakthrough of the target constituents. Before starting the column tests, the media was saturated for 24-hours with DI water, and the flow rate was adjusted.

The influent and effluent reservoir for the North Carolina columns consisted of 5-liter Tedlar bags. The purpose of the bags was to minimize losses as water passed through the columns. The site water was pumped from the influent reservoir using a peristaltic pump. The pump maintained a constant flow (+/- 5%) through the columns that was about the same as the flow identified in the design concept. Based on the design concept for the North Carolina site, the groundwater was pumped through the columns at a flow rate of about seven feet/day. Based on the design concept for the Wisconsin site, the site water was pumped at a flow rate of about 10 feet/day. The flow rate through the columns was checked periodically by measuring the weight of the effluent Tedlar bag and dividing it by the time interval over which the flow occurred. This confirmed the column flow rate over the column test period.

Samples were collected (at all sample ports) at a maximum of up to once a day. A subset of these samples that best represent column performance was selected based on ongoing analytical results.

Based on the target constituents identified in the conceptual site model, a select parameter list was analyzed. While the primary target constituents are benzene and naphthalene, additional samples were collected from the overall influent and effluent from the columns to demonstrate removal of secondary target constituents such as acenaphthene. The purpose of testing for the secondary constituents of concern is to demonstrate the removal of these constituents.

The analytes and their test method include:

- BTEX/Naphthalene (SW 846 Method 8021)
- VOCs (SW 846 Method 8021)
- PAHs (SW 846 Method 8310)
- Phenol (EPA 340.2)
- Metals (EPA Method 6010B -- Fe, Ca, and Mg. Will also do Cd, Cr, Pb, as necessary)

- Cyanide (EPA 9012A)
- TOC (ASTM Method 2874-87)
- Hardness (EPA Method 130.2).

The column tests were run until breakthrough was achieved. Data evaluation consisted of developing breakthrough curves from the data. Based on the breakthrough curves and isotherms developed previously, carbon utilization rates and pore volumes to breakthrough for the full-scale system were estimated. Analysis of the results focuses on benzene. As discussed previously, our experience has shown benzene typically controls the design of carbon treatment systems for removal of BTEX and PAHs from water. Benzene typically breaks through first, and requires more carbon to achieve its typically low regulatory criteria as compared to other BTEX and PAH constituents.

Breakthrough of benzene occurred after approximately 1,000 pore volumes for both the North Carolina and Wisconsin sites. These results are consistent with the batch test results and our experience with other sites.

A preliminary estimate of activated carbon consumption for the proposed PRB system at the demonstration sites can be calculated based on the batch and column tests. Based on this information, to achieve a roughly five year regeneration cycle at the North Carolina site, approximately nine tons of activated carbon would be required. At the Wisconsin site, about 18 tons of carbon would be required. However, due to actual site conditions (e.g., biological activity) carbon life will vary.

Based on this preliminary analysis, a reasonable amount of activated carbon would be required for a PRB system at both sites, and/or the frequency of carbon replacement is not expected to be excessive. Given an approximate cost of $1300/ton for activated carbon, it is expected to be about $11,700 for the North Carolina site and $23,400 for the Wisconsin site for the five year period. Based on the relatively low cost for the media, the PRB approach at both sites is considered viable.

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