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Long-term Verification of Cover Systems Using Perfluorocarbon Tracers

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ABSTRACT

The expanded use of caps and cover systems is an important aspect of the U.S. Department of Energy Environmental Management's (DOE EM) strategy for restoration and long-term stewardship of sites throughout the complex. However, very little is available in terms of long-term monitoring of covers other than downstream groundwater or surface water monitoring. A novel methodology for verifying and monitoring subsurface barriers and cover systems has been developed. Gaseous perfluorocarbon tracers (PFTs) are injected on one side of the barrier and searched for on the opposite side of the barrier. The capability for leak detection in subsurface barriers using PFTs has been proven at multiple demonstrations. Adaptation of this concept to covers is a necessary step prior to full-scale demonstration. This paper discusses the PFT technology and a successful proof-of-principle test of the PFT technology as a leak detection tool for cover verification and monitoring.

INTRODUCTION

Caps and cover systems (covers) provide an essential tool to the waste management community. All wastefill sites have within their design some form of a cover overlying the waste. The basic functionality of the cover is to minimize, to an acceptable level, water infiltration into the waste site thereby minimizing or eliminating mobilization of contaminants. With the exception of evapotranspiration designs, covers provide a physical barrier to water percolation and precipitation is redirected away from the waste. [Evapotranspiration covers preclude water from the waste by having sufficient water storage capacity and high enough evaporation rates, such that transpiration

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rates are greater than percolation rates.] If the physical barrier is compromised, either locally or globally, by a hole, breach, or flaw then the ability of that cover to successfully preclude water and contain the contaminants may be diminished beyond acceptable levels.

The Department of Energy Environmental Management (DOE EM) has committed itself to an accelerated cleanup of its national facilities. With the increased focus on accelerated cleanup, there has been considerable concern about long-term stewardship issues in general, and verification and long-term monitoring of covers, in particular. Covers are vital remedial options that are being extensively used in meeting cleanup goals. Every buried waste site within the DOE complex will require some form of cover system. These covers are expected to last from 100 to 1000 years or more. The stakeholders can be expected to focus on system durability and sustained performance.

Covers are subject to subsidence, erosion, desiccation, animal intrusion, plant root infiltration, etc., all of which will affect the overall performance of the cover. A cover cannot be considered sustainable if the long-term monitoring and stewardship concerns cannot be addressed. This is likely the biggest obstacle to closure many DOE sites will have. There are many waste treatment technologies and cover system designs available for final disposition of waste streams, but very little available technology to address long-term performance, monitoring and stewardship issues. Currently, containment system failures are detected by monitoring wells downstream of the waste site. Clearly this approach is inefficient, as this can only indicate that failure of the cover system has already occurred and that contaminants have been transported away from the site. Methods that indicate early cover failure (prior to contaminant release) or predict impending cover failure are needed.

A novel methodology for determining the gaseous transport pathways through a cover has been developed. The technology uses gaseous perfluorocarbon tracers (PFTs) to determine flaws (e.g., holes or cracks) and high permeability areas in the cover. This verification/monitoring technology was originally developed for subsurface containment barriers (Sullivan et. al. 1998, Heiser and Dwyer 1997); cover verification and monitoring is a natural extension for the system. For covers, the difficulty (compared to subsurface barriers) lies in the close proximity to the surface atmosphere. For example, barometric pumping and dilution effects are negligible for subsurface barriers but can be significant phenomena for covers.

In this method, the tracers are injected underneath the cover and searched for on the topside of the barrier (see Fig. 1). The sampling grid, concentration, and time of arrival of the tracer(s) on the opposite side are used to determine the size and location of flaws and effective diffusion coefficient through the barrier. In addition, there are multiple tracers available, which allow different tracers to be injected in different quadrants of the cover or between different layers in a multi-layer cover. This yields additional information on transport phenomena through the barrier.

As a barrier verification tool, the PFT technology has proven to be more capable than competing systems (Heiser and Sullivan 2002). The capability for leak detection in subsurface barriers using PFTs has been proven at multiple demonstrations (Sullivan et. al., 1998, Sullivan, et. al., 2000, Heiser, et. al., 2001). Adaptation of this concept to covers is a necessary step prior to full-scale demonstration.

This paper discusses the PFT technology, a small proof-of-concept test conducted at the Savannah River Site (SRS), and presents some of the engineering concepts that when fully developed will make the PFT technology a valuable resource for long-term cover verification and monitoring.

BACKGROUND

A tracer is any substance that can be easily or clearly monitored (traced) in the study media. Tracers for soil studies can be radioactive or non-radioactive liquids, gases, or solids. Tracer technologies can be used in transport/dispersion studies, leak detection studies, and defining material location. Leak detection studies use tracers to locate and estimate leak rates under various conditions. These can be as simple as colored dyes used to visually locate cracks and holes in tanks or as complex as mass spectroscopy detection of helium to find leaks in vacuum systems.

Rapid and sensitive analytical methods for a host of perfluorocarbon tracers have been developed. These tracers were originally utilized in atmospheric and oceanographic studies and have since been applied to a great variety of applications including detecting leaks in buried natural gas pipelines and locating radon ingress pathways in residential basements (D'Ottavio and Dietz 1987, Horn et. al. 1991). It was the application to residential basements that lead to the use of PFTs for subsurface barrier verification. The basements can be visualized as miniature "barriers" with vertical concrete walls and a horizontal concrete floor and the radon ingress simulates contaminant egress. Thus, it seemed clear that the PFT tracer technology should be directly applicable to finding leaks in barrier systems.

The Tracer Technology

PFT technology consists of the tracers themselves, injection techniques, samplers, and analyzers. PFTs have the following advantages over conventional gaseous tracers:

a) There are negligible background concentrations of PFTs in the environment. Consequently, only small quantities are needed.

b) As stated on the Chemical Safety Data Sheet for each PFT, they are nontoxic, nonreactive, nonflammable, no effect when in contact with skin or eyes and have no assigned health and safety exposure limit. In addition, they do not contain chlorine and are commercially available.

c) PFT technology is the most sensitive of all non-radioactive tracer technologies and concentrations in the range of 10 parts per quadrillion (10^{15}) of air can be routinely measured (Dietz et. al., 1986); and

d) The PFT technology is a multi-tracer technology permitting up to six unique PFTs (Table 1) to be simultaneously deployed, sampled, and analyzed with the same instrumentation. This results in a lower cost and flexibility in experimental design and data interpretation. All six PFTs can be analyzed in fifteen minutes on a laboratory-based gas chromatograph (Dietz and Dabberdt 1983).

Typically, the PFTs are sampled using a capillary adsorbent tracer sampler (CATS) which is a small cigarette-sized glass tube containing a carbonaceous adsorbent specific for the PFTs. This sampler can be used dynamically (flowing a sample through the CATS) or passively (opening only one end so as to allow the CATS to sample by diffusion). The passive mode allows a time integrated PFT concentration to be measured in a simple manner. The CATS are shipped back to the laboratory for PFT analysis.

PFTs have regulatory acceptance and are used commercially (e.g. detecting leaks in underground power cable systems) (Dietz, et.al., 1986, D;Ottavio and Dietz, 1987, Horn et. al., , 1991, Sullivan, et. al., 2000). PFTs can be detected at extremely low levels and this allows detection of faults in a barrier on the order of fractions of an inch. Typically, the source injection zone concentration is on the order of 0.1 to 1.0 ppm and leak/fault zone concentrations range from 0.1 to 100 ppb (Sullivan et. al. 2000, Heiser et. al. 2001). The tracers (see Table I) used have already been approved for use in atmospheric, oceanographic, and leak detection (for buried gas lines and fluid-filled dielectric cables). They were also approved for subsurface barrier testing by state regulators at the Waldo New Mexico Subsurface Barrier Test site (Sullivan et. al. 2000). The materials are environmentally benign and no PFT-specific safety and health concerns have been encountered. In summary, the tracers pose no real threat in the low amounts used in each test. Flow rates for subsurface tests are generally run around 15 to 50 cc/min at 100 to 400 ppm and flow is continued for 3 to 7 days (Sullivan et. al. 2000, Heiser and Sullivan 2001, Heiser et. al. 2001). The total mass of PFT injected over the duration of such an experiment is typically a few grams. Analysis of the PFTs is by gas chromatograph, either a laboratory unit or a field-deployed unit, which is slightly less accurate but very rugged.

Detecting Leaks and Flaws

Leaks (or areas of reduced performance) are located by injecting a series of tracers on one side of a barrier wall and then monitoring for those tracers on the other side (Fig. 1). The injection and monitoring of the tracers is accomplished using conventional, low-cost monitoring methods. The amount, type of tracer (speciation), and arrival times can all be used to characterize the size and location of a breach. It is easy to see that the larger the opening in a barrier the greater the amount of tracer that is transported across the barrier. Locating the breach requires more sophistication in the tracer methodology including triangulation methods or using multiple tracers. Injecting multiple tracer types at different points along the barrier, in both vertical and horizontal directions, allows investigation of the spectra of tracers coming through a breach. This, in turn, gives information about the flaw location relative to the various tracer injection points. Arrival times of the different tracers can also be measured to obtain a more detailed analysis. Having multiple tracers also allows for confirmation of holes and differentiation between holes and spill over.

Tracer Distribution and Sampling

As mentioned earlier, the tracers must be distributed on one side of the cover (or individual layer within a multi-layer system) and sampled on the other side. How this is accomplished depends on the cover type and whether the cover is pre-existing or a new construction. To date the technology has only been deployed at pre-existing sites and injection and sampling lines have been retrofitted to the sites. We will first discuss the retrofit design and then discuss several installation designs that can be incorporated into the design of a new cover.

For pre-existing covers a simplistic approach has been used to install monitoring ports. The boreholes were placed using a Geoprobe® Model 54 LT continuous push soil-probing unit. This unit is a hydraulically driven penetrometer that can push a 19-mm to 54-mm O.D. steel rod into the subsurface. A rod is pushed into the soil to the desired depth (no closer than 15cm from the cover to preclude disturbing the cover). The rod was then withdrawn and the resultant hole used for installation of the monitoring ports. The ports themselves are of simple design (see Fig. 2); a sintered glass filter (to prevent plugging) is attached to a length of 3 mm polypropylene tubing. The port is then lowered into the borehole until it reaches the desired depth. Once the filter is in place, the hole is backfilled with a blended-sand mix. The sand is used to prevent advective currents in the borehole. Backfilling is completed by slowly pouring sand down the hole. The sand firmly holds the port in place and keeps it at the desired depth. The ends of the monitoring port access tubes (attached to the filters) extend to the surface to allow sampling of the soil gases. The polypropylene tubing is protected using short lengths of poly-vinyl chloride (PVC) pipe to cover the exposed end. The pipe is placed over the tubing and into the top of the borehole as the last foot of borehole is backfilled.

The layout of the monitoring ports is determined by the thickness of the soil layer overlying the cover and the resolution required for leak/flaw size and location. Most covers have a layer of soil (for vegetation and erosion control) that is between 1 and 2 meters thick. The PFT "escapes" through the cover at the soil/cover interface. The tracer then diffuses radially away from the breach. The concentration of the tracer decreases uniformly with distance unless there is an interfering phenomenon. For covers, the shallow soil layer allows barometric pumping to affect the tracer concentration within the first meter of overburden (Nilson et. al. 1991, Neeper 2001). The effects are greatest in the upper one-third of this zone. Therefore, port depth is such that no ports are placed closer than 0.3 meters to the surface. Port separation (horizontal spacing) is determined by the resolution required for both locating a hole, the size of the hole/flaw of interest, overburden thickness and the measurement time allowed. If tight spacing is used the time to complete a measurement is minimized as the tracer does not have to diffuse far to reach a sampling port. [As a rough estimate, the tracer diffuses approximately one meter per day in sands.] Tighter spacing also allows a simple concentration contour to be used to locate a flaw. If ports are placed at greater distances more sophisticated modeling based on diffusion transport rates, geometry, and injection source rates is required to "triangulate" a flaw. In addition, wider spacing between ports causes the test time to increase, as the tracer must travel further to reach the ports.

Injection of the tracers is accomplished through one to several injection ports placed below the cover. An injection port is installed in a manner similar to the monitoring port. If the injection port is installed vertically (through the cover) the borehole must first be partially backfilled with sand (to allow free flow of soil gases) and then the upper portion of the borehole is filled with a low permeability backfill such as cement grout or bentonite grout. The injection port can also be placed in a horizontal (or near horizontal) manner. In this case a small rod (< 5 cm in diameter), is pushed into the soil using a GeoProbe at an obtuse angle starting outside the perimeter of the cover. The rod is pushed horizontally, but with some vertical component (up to 45 degrees) until it reaches the desired point under the cover layer(s). Backfilling is more difficult due to the obtuse angle of the borehole. Sand may have to be air blown into the hole via a tremé tube followed by a flowable grout. One or only a few injection ports are used and the tracer is allowed to diffuse throughout the soil beneath the cover. This may take several days to a week before a consistent concentration profile is achieved.

For new construction the injection and sampling ports can be integrated into the system design. Plumbing for the tracer injection can be placed prior to installation of the cover layer(s). Upon completion of the cover, the sampling ports can be placed before the final soil layer is placed over the cover. For a multi-layer cover system (e.g., the Hanford barrier), injection and sample ports can be placed in between each layer, thereby allowing independent verification of each layer.

One simple and rapid method to install the injection and sampling ports is to attach them to the geomembranes/geotextiles prior to installation. A sampling method that uses long (>300 meters) sampling lines with multiple sample/injections ports on each line (i.e., every one or two feet) has been developed. Composite samples can be taken to determine if any leakage is occurring. In addition, time-of-flight information can be used to locate the flaw. Such sampling lines (made of polypropylene, polyethylene or some other plastic that is compatible with the geotextiles used) can be attached to the geotextiles used to line the cover. When the liner(s) are laid down the sampling and injection ports will be placed at the same time. The lines are attached in a criss-cross fashion to give complete coverage of the site and also allow accurate triangulation. The technology exists to attach these sample lines to the geotextiles after manufacture or to co-extrude the sample lines with the geotextile. However, full-scale demonstration of co-extrusion for this application has not been attempted.

For multilayer covers a unique tracer can be injected into each layer. Monitoring of the various layers could be used to track the potential flow pathways through each layer. This would provide a more complete and accurate understanding of barrier performance.

PROOF-OF-CONCEPT TESTING AT SAVANNAH RIVER

The PFT technology had been proven as a leak detection system for subsurface barriers but still needs to be demonstrated, at a proof-of-principle level, that the technology was capable of being utilized for cover verification and monitoring. A test facility at the Savannah River Site (SRS) was available for demonstration of the PFT technology. The facility consisted of several experimental test pads and is described below. This facility provided a very conservative test (aggressive test of the PFT technology) as the Bentomat Test pad only has ~ 0.6 meters of cover soil. This means that barometric pumping and dilution effects could be important. However, the clay soil cover will reduce barometric pumping as compared to a sandy soil. The tracers diffuse to the surface after only 0.6 meters of travel making horizontal travel minimal past the 0.6 meters boundary.

The main objective of this program was to demonstrate that PFTs could be used to accurately and quickly locate flaws in a cover system. To this end, PFTs were used to verify the integrity of the part of the geosynthetic/geomembrame composite layer of the Bentomat Test Pad at SRS. Our approach was to install tracer injection lines below the composite layer and monitor for the tracers in the soils above the layer.

A secondary objective was to demonstrate a field-deployable PFT detection system. The system consisted of a dual-trap gas chromatograph and a compositing sampling approach (multiple soil-gas samples were combined and sampled as one composite).

The Site

The Bentonite Mat Demonstration was established to provide data on alternative cover systems at the SRS (Serrato, 1994). The test facility pads consisted of (bottom to top) a 1.3 meters loose sand layer, 0.3 meters separation layer (silty soil), 0.6 meters of compacted sandy clay layer (local soils), a composite geosynthetic clay liner/geomembrane layer (except the control pad), and a 0.3 to 0.6 meters cover soil layer. Four test pads were constructed: a Control Test Pad and three test pads with geosynthetic clay liners (Gundseal®, Claymax®, and Bentomat®). The three geosynthetic liner test pads were also covered by a 1mm (40 mil) Gundline® HD smooth High Density Polyethylene (HDPE) geomembrane. Each pad was covered with a final layer of clay soil. The demonstration facility was also used to study effects of induced subsidence on the performance of the cover systems. The Bentomat®Test Pad was chosen for the PFT verification study and had large areas of induced subsidence as well as having large voids in the sand layer beneath the geosynthetic liner. Test pad dimensions were nominally 15 meters x 42 meters x 2.5 meters. A full description of the test pads and materials properties (e.g., clay content, grain size) can be found in "Bentonite Mat Demonstration Final Report" (Serrato, 1994). The Bentomat® Test pad (Fig 3) used a 6.4mm thick, Bentomat® layer consisting of a layer of sodium bentonite clay encapsulated between a woven polypropylene geotextile (upper side) and an unwoven polypropylene geotextile (bottom side). The hydraulic conductivity of this layer is reported as 5×10^{-9} cm/sec. Overlying the Bentomat® layer was a 1 mm thick (40 mil) HDPE flexible membrane liner from Gundle Lining Systems. The reported hydraulic conductivity of the HDPE liner was 2.7×10^{-13} cm/s (via ASTM E96). The geosynthetic materials also required seaming and these areas represented "areas of concern" for possible leakage.

Each test pad had a series of access pipes embedded into the sand layer to allow excavation of some of the sand for the induced subsidence testing. The Bentomat® pad had six clusters of five nominally one foot diameter pipes embedded on each side (long axis) of the cover. The pipes were stated to be 3.3 meters long (conversation with site manager/principal investigator). The depth into the sand layer was extended during the induced subsidence activities (sand removal). The penetration length, as measured during the field activities for the PFT trials, was nominally 8 meters for all of the 6 clusters measured (the southern most 3 on the east slope and the southern most 3 on the west slope). These penetrations were used as the injection points for the tracers.

SITE PREPARATION

The proof-of-concept test of the PFT technology utilized 60% of the top surface of the test pad (Fig. 4). The remaining portion of the pad was left undisturbed for future evaluation of the pad. Three tracers were used in the study and each tracer was injection into a given zone from both the east and west sides of the cover. The two-sided injection scheme was used to obtain a more uniform tracer concentration under the cover and to minimize injection times.

The PFT injection ports consisted of 6 mm copper tubing inserted into the excavation pipe clusters. An injection tube was inserted 8 meters into the six southern most clusters. The tubing extended through a PVC cap that sealed off the open end of the excavation pipe. The remaining 4 pipes of each cluster were sealed with polyethylene end caps.

Monitoring ports were installed on top of the cover. Gas sampling ports were constructed from sintered glass filters attached to 3 mm polypropylene tubing. A 30 mm diameter rod was driven 30cm to 45 cm into the ground and removed. This left a hole that the glass filter and tubing were lowered into. Once the sample port was lowered to the desired depth, the hole was backfilled with sand to minimize advection. The sampling port was placed just above the HDPE geomembrane (~ 15 cm). The end of the polypropylene tubing extended out of the soil and was attached to a pump to perform soil gas sampling. Ports were placed every 1.5 meters (5 feet) north to south and east to west, resulting in a total of 84 sampling points. Columns were designated A - G with 12 ports in each column (Fig. 5).

EXPERIMENTAL

On August 7th the injection port installation and excavation pipe sealing was completed and tracer gas flows were turned on. Three tracers were used in the study. This allowed confirmatory data and also gave information on the interconnectivity of the subsurface below the composite layer (cavities did in fact interconnect and a fair degree of tracer mixing occurred). Three distinct regions of tracers were set up. In the southern most region PMCH tracer was injected at a rate of 12 mL/min at a source concentration of 1600 ppm. The mid section had PMCP injected at 44 mL/min with a source concentration of 400 ppm. The northern most region of the test region was injected with ocPDCH at a flow of 53 mL/min and 95-ppm source concentration. The injection rates were set such that the internal concentrations beneath the hydraulic barrier would be between 1 and 10 ppm after 5 to 7 days of injection. The injection spacing was approximately 4.6 m (15 feet) between tracers. Tracer injection continued until August 16th.

The initial tracer injections were allowed to continue for six days prior to starting soil gas sampling. This allowed the volume below the cover to build up to ppm levels of the PFTs. On August 13th soil gas sampling was initiated. All 84 sample ports were sampled on August 13th and 14th. Sampling was accomplished using battery powered gas-sampling pumps. The inlet side of the pump was connected to the sample port tubing. The pump was turned on and purged for 15 seconds. The outlet side of the pump was then connected to the inlet of a Tedlar gas-sampling bag. The valve to the bag was opened and sampling began. Approximately 500 ml of sample was collected over 30 seconds. When the desired sample was collected, the sample bag valve was closed, the bag disconnected from the pump, and the pump turned off. The bags were brought to a portable gas chromatograph for analysis.

On August 15th, samples of the internal tracer concentrations were also taken. Air samples were taken from the pipe adjacent to the injection pipe in a given pipe cluster. A 50 mL syringe with a needle attached was used to capture the sample. The needle was pushed through the polyethylene cover sealing the pipe and an air sample was withdrawn into the syringe. The sample was transferred to a gas-sampling bag for storage and later analysis.

Samples were analyzed using a field-deployable gas chromatograph (GC) which was customized for detecting PFTs. The instrument had dual traps for capturing the PFTs. This allowed individual sample analysis every four minutes. Each day prior to sample analysis, a standard gas tracer was run on each trap of the GC. Blanks and background checks were also performed each day prior to sample analysis. The standard was run twice each day, background checks and duplicates were performed every twenty analyses and blanks were performed every ten samples. In addition, samples were also sent back to BNL to be verified on a laboratory GC.

The GC has two parallel gas circuits running to the detector. Each of these loops has an absorption trap. Gas flows through both traps at all times. One trap leads to a vent while the other trap is analyzed. While the trap is vented, the air sample(s) is injected into the trap. The PFTs (and some other impurities) absorb onto the trap and are held in place. During the analysis mode the trap is heated which causes the PFTs to desorb and eventually travel through the detector. Several air samples can be loaded on the trap while it is in the vent mode. This allows compositing of samples and a rapid screening of many bags at once. If a composite came up hot (detectable tracer concentrations) then each bag would be sampled individually to find the hot sample(s).

The procedure was to inject gas samples from six bags. This was one half of a column (A-G) in the sample grid. As an example, samples A1, A2, A3, A4, A5, and A6 were all analyzed together. Five mL subsamples were taken from each bag and injected into the same trap of the GC. The samples had to be injected on to one trap while the second trap was being analyzed. Logistically six was the maximum number of samples that could be comfortably injected during the four-minute cycle time.

The sample size of 5 mL allowed us to easily detect 0.01 ppb of the tracers. As the internal concentration goal was 1 ppm this allowed for 5 orders of magnitude dilution across the geosynthetic liner/geomembrane and the ~ 0.3m of cover soil below the sample ports. From past experience, even small leaks from a flaw with a radius on the order of 15 mm would be expected to have much less than three orders of magnitude dilution over this travel distance.

After the first two days of sampling and analysis, the data showed that the hydraulic barrier was intact (discussed later in results). At this point, three induced flaws were engineered into the cover. The flaws were placed in the front half of the grid (Fig 6) to leave as much of the original cover "intact" as was reasonable. The flaws were introduced by simply driving a 3 cm (1.25 inch) diameter pipe into the subsurface a distance of 1.25 m (4 feet). The pipe was removed and the resulting hole was backfilled with a fine sand. In two of the holes, sampling ports were also installed both above and below the geosynthetic liner. In one hole, CH-E, a subsidence cavity extending two feet below the Bentomat layer was found. These ports would give confirmation of internal tracer concentrations in areas well removed from the injection point.

On August 15th and 16th samples were taken at the sample ports surrounding the flaw locations. The four nearest neighbors to the flaws were sampled resulting in twelve samples taken each day. In addition, the internal concentrations were measured at the access pipes on August 15th and at the port locations installed in the flaws on both days. Tracer injection was discontinued on August 16th at 2 PM. With the low number of samples taken and the expected higher tracer concentrations, no compositing was performed. All samples were analyzed individually. On August 15th, samples were taken at random locations away from the flaws to provide confirmation that leaks were not present in other locations.

RESULTS

All samples from August 13th and 14th were non-detects. Composite air sampling showed all locations to have less than 0.01 ppb of any of the 3 tracers. The data was entered into a modeling software package, C-Tech Corporation's Environmental Visualization Systems. Figure 7 shows the plan and side views (side view has a vertical exaggeration of 5X for clarity) of the cover test grid with a color-coded mapping of tracer concentrations on August 13th. The side view includes tracer concentrations for both internals and externals. Blue areas represent low (<0.01ppb) tracer concentrations while pink areas are high concentrations (~1.0 ppm). Data visualizations for August 14th were identical. While the internal volume of the cover clearly has high concentrations of PFTs, the tracers are not reaching the external ports that are approximately six inches above the bentomat liner. The composite hydraulic barrier, provided by the geosynthetic clay liner and HDPE membrane, remained intact and leak free.

Modeling of diffusion of the gas through the Bentomat/HDPE layer was performed by solving the diffusion equation in one-dimension for the geometry of the site. Below the liner, the initial concentration was set to 1. Above the liner, it was set to 0. A range of effective diffusion coefficients from 10^{-6} – 10^{-12} cm^2/s was used in the analysis to determine the minimum value of the effective diffusion coefficient through the liner that would allow measurable PFT concentrations to occur in the monitoring points above the liner. The results indicated that the PFT effective diffusion coefficient through the liner was less than 10^{-8} cm^2/s. Higher diffusion coefficient values would have led to detection of PFTs at concentrations greater than 0.01 ppb. The low value for the diffusion coefficient is consistent with the low hydraulic conductivity of the liner Based on previous work, the diffusion coefficient of PFTs in sandy soils is approximately 10^{-2} cm^2/s (Sullivan et. al. 1998), at least 6 orders of magnitude greater than through the Bentomat/HDPE liner. This further supports the contention that the cover was not leaking.

On August 15th, after introduction of the flaws, all cavity hole concentrations were around 1 ppm. This confirmed that tracer was at high concentrations beneath the Bentomat liner. Mixing between PMCH and PMCP was evidenced and shows that transport (diffusion) is occurring beneath the liner. The flaws near sample locations B3 and G4 were readily seen by the monitoring network at the nearest port location within three hours of formation of the flaw. The flaw near location D4 was not observed within three hours of its formation. This was attributed to the slightly lower concentration observed in this flaw as compared to the other two flaws and the short time between creating the flaw and taking the measurement.

On August 16th tracer levels beneath the Bentomat layer remained near 1 ppm. Analysis of the data showed all three flaws with the nearest sample locations showing ppb levels of tracers (see Fig.8). Near two flaws, CH-E and CH-W in Figure 8, two monitoring locations approximately 1.6 m from the flaws had PFT levels around 0.1 ppb. All other locations were non-detects. The ratio of PMCH/PMCP in the cavity hole (introduced flaw) is similar to that seen in the monitoring network. Detection of PMCH and PMCP at the ports near the flaw gave confirmatory data that a leak existed. The data for the two tracers correlated well.

Overall the concentration difference from internal (beneath the Bentomat liner) to external (above the Bentomat liner) was greater than seen in previous subsurface barrier testing and other deep, below-grade tracer studies. This is attributed to the low diffusion rate through the Bentomat/HDPE liner, barometric pumping, and higher diffusion coefficient in the sand backfilled flaw as compared to the native clay soil. A loss of between 3 and 4 orders of magnitude in concentration was seen between the 3 cm diameter flaw and the monitoring ports located approximately 0.3 to 0.4 meters from the flaw. One-dimensional modeling of PFT diffusion from the flaw through the clay topsoil indicates the diffusion coefficient of the clay soil is in the range of 0.002 – 0.0002 cm^2/s. This is one to two orders of magnitude lower than in sandy soils (Sullivan et. al. 1998). Thus, although the distance from the flaw to the monitoring port (~ 0.3 meters) is less than the distance from the flaw to the surface (~0.6 meters), the higher diffusion coefficient of the backfilled sand makes transport faster along this pathway. Coupling this with barometric pumping in which the backfilled sand region acts as a chimney, it is clear that concentrations away from a flaw will be low and sensitive measurement techniques are needed. As this is the most difficult cover system expected, in terms of the thickness of the surface cover, these data provide confidence that small flaws can be readily detected.

PRACTICAL IMPLICATIONS

The PFT technology has been shown to be capable of detecting flaws as small as 3 cm in diameter at the Savannah River Test facility. Other tests (Sullivan, 1998, Sullivan, 2000, Heiser, 2000, Heiser, 2001) have also successfully detected small flaws in subsurface systems. The field tests performed to date have covered small areas and have not required integration of PFT injection and monitoring equipment as part of the cover design. For cover system assessment, the PFT technology requires some additional development in order that it can be considered fully functional, fully developed (all capabilities utilized), and commercially viable. Development needs include:

- The development of the PFT technology for cover/capping integrity verification requires additional theoretical modeling to examine the impacts of barometric pumping and channeling on the movement and distribution of PFT's which impacts on defining the location of the flaw.
- Consistent protocols for the installation of the PFT technology as part of existing and new cover/capping systems need to be developed.
- A cost estimate and life-cycle assessment needs to be developed.

CONCLUSIONS

The proof-of-concept testing at SRS was successful. Initially, there were no flaws in the Bentomat liner. Concentrations beneath the liner were on the order of 1 ppm while concentrations ~0.3 meters above the liner were less than 10^{-5} ppm. Three small (3 cm) flaws were introduced in the cover system. Two flaws were seen within three hours of their creation, while all three flaws were detectable within one day of introduction of the flaw. The results were repeatable day to day and were confirmed by two separate tracers. The Bentomat test pad represented a worst-case scenario for tracer verification of covers. The cover has a very thin soil layer overlying the hydraulic barrier, less than two feet of soil covered the HDPE membrane in most areas. This allows barometric pumping, wind effects, and atmospheric dilution effects to be maximized.

In addition, the use of the field-deployable gas chromatograph PFT detector was successfully demonstrated. This unit was able to analyze samples on a four-minute cycle down to levels of a few parts per trillion. This provided almost six orders of magnitude span between the concentrations beneath the liner (ppm) and non-detectable levels. This is more than sufficient to accurately determine the presence of a leak. Up to six sampling locations were composited to speed analysis time when examining for leaks.

Small flaws were detected without having to increase the internal concentrations of PFTs over normally used values (based on barrier verification). If the dilution effects had been greater, the flow rate of the tracers could have been increased or higher tracer concentration source tanks could have been used. The internal concentrations could be raised from 1-10 ppm to 1000 ppm or greater if needed. This provides an increase of several orders of magnitude sensitivity to leak detection. It also increases the cost of the technology slightly (increased tracer cost), makes analysis a little more complicated as one needs to watch out for "swamping" the GC detector (lost time waiting for detector to clean out), and increases PFT gas releases to the environment.

The existing low, internal concentration requirements allow for greater design flexibility. For example, very fine tubing can be used to deliver the small amount of tracer required. The smaller diameter tubing can be fitted to the geotextiles prior to installation at the cover site. Low tracer concentration requirements also allow different methods of tracer introduction (i.e., slow release permeation cells implanted under the cover). There are many advantages to remaining at the lower PFT concentration beneath the liner.

The multiple tracers available with PFTs (and not with competing systems) allow greater flexibility in experimental/installation design, yields redundant (re: confirmatory) data, and gives information on internal transport pathways not available from single tracer systems. This advantage is magnified when the PFT technology is applied to multi-layer cover systems. With multiple layers there may be convoluted leak pathways. Flaws in two layers may not be aligned and the transport pathway may have a horizontal aspect. In this case single tracer technology would see only the exit hole. Multiple tracers allow different tracers to be injected between layers. With monitoring ports placed within each layer it is easy to tell flaw location for each layer. Even having only monitoring ports above the final layer, the spectrum of tracers coming from an exit hole can be used to determine which layers are faulted and the concentrations can be used to estimate how convoluted the travel pathway is.

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Table I. Tracers Available for the Cover Verification/Monitoring Technology

Chemical Acronym	**Chemical Name**	**Chemical Formula**
PDCB	Perfluorodimethylcyclobutane	C_6F_{12}
PMCP	Perfluoromethylcyclopentane	C_6F_{12}
PMCH	Perfluoromethylcyclohexane	C_7F_{14}
pt-PDCH	Perfluorotrans 1,4 dimethylcyclohexane	C_8F_{16}
oc-PDCH	ortho-cis-perfluorodimethylcyclohexane	C_8F_{16}
PTCH	Perfluorotrimethylcyclohexane	C_9F_{18}

Figure 1

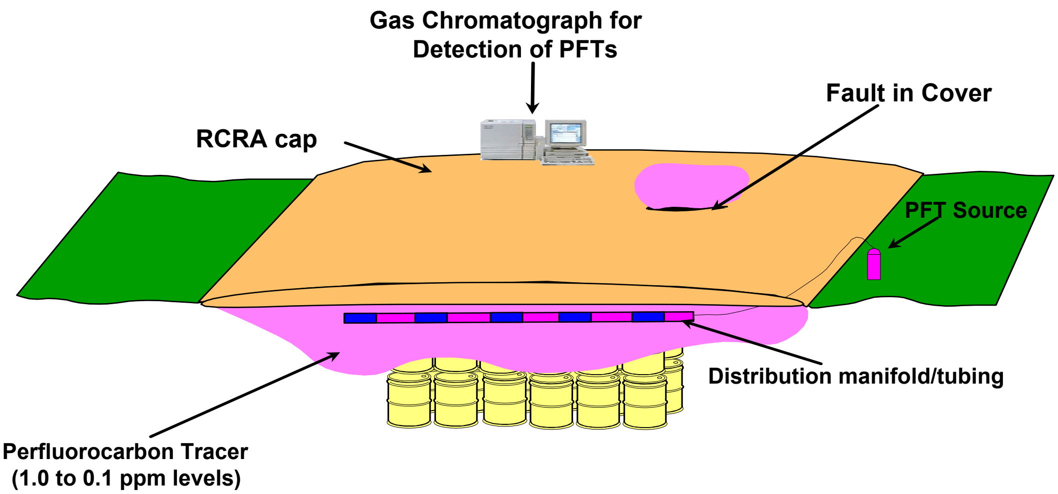

Gas Chromatograph for Detection of PFTs
Fault in Cover
RCRA cap
PFT Source
Distribution manifold/tubing
Perfluorocarbon Tracer
(1.0 to 0.1 ppm levels)

Figure 2

6 inches

Figure 3

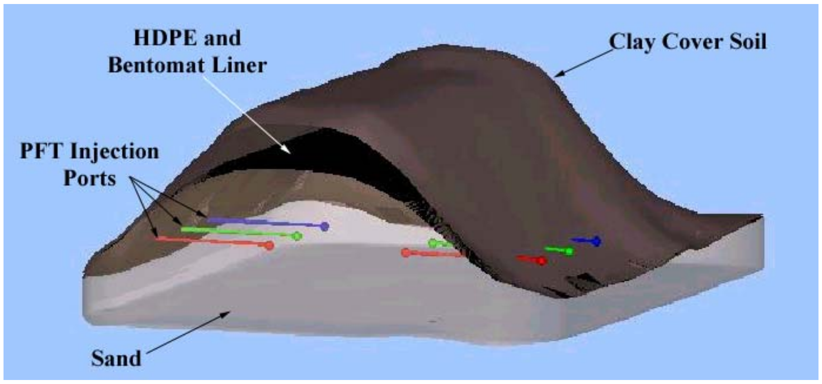

HDPE and
Bentomat Liner
Clay Cover Soil
PFT Injection
Ports
Sand

Figure 4

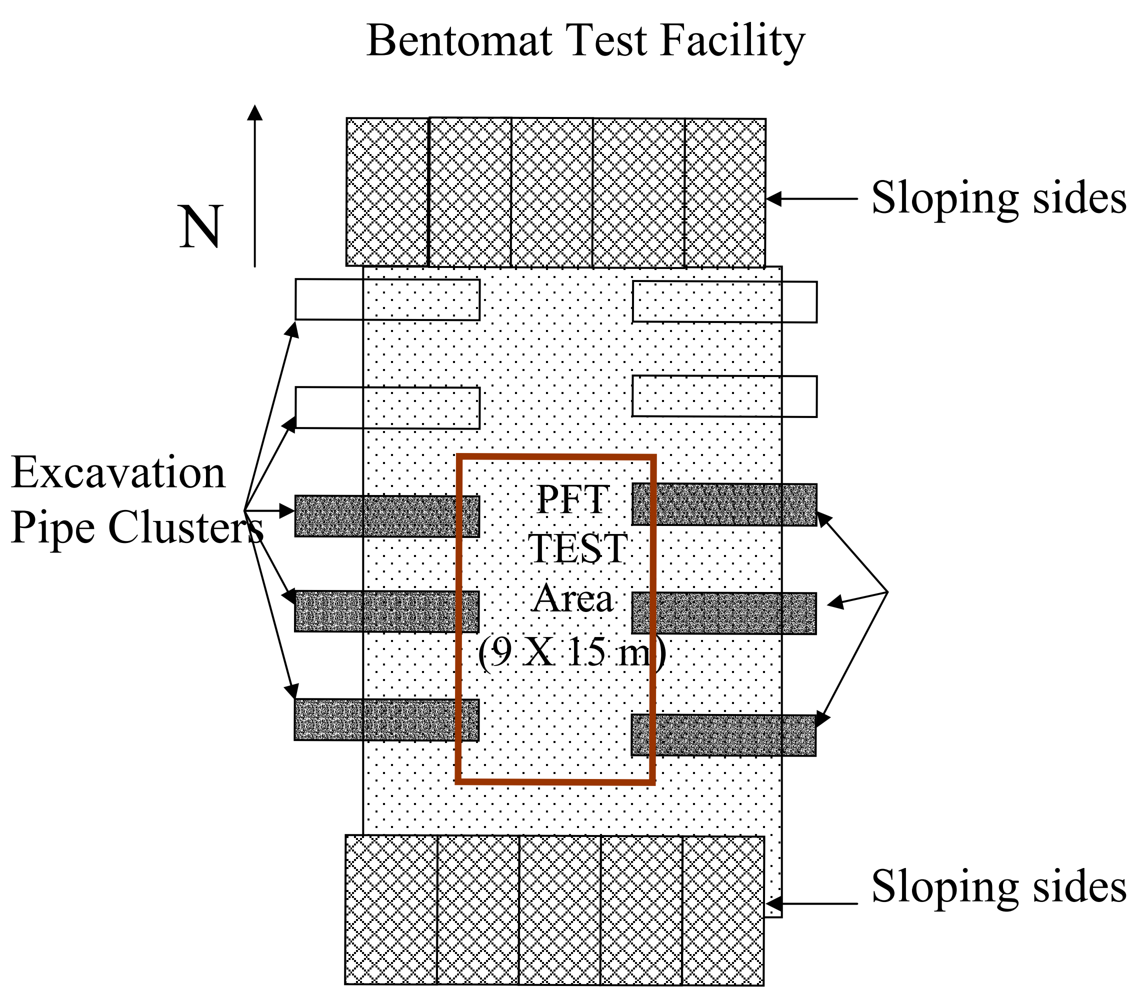

Bentomat Test Facility
N
Sloping sides
Excavation
Pipe Clusters
PFT
TEST
Area
(9 X 15 m)
Sloping sides

Figure 5

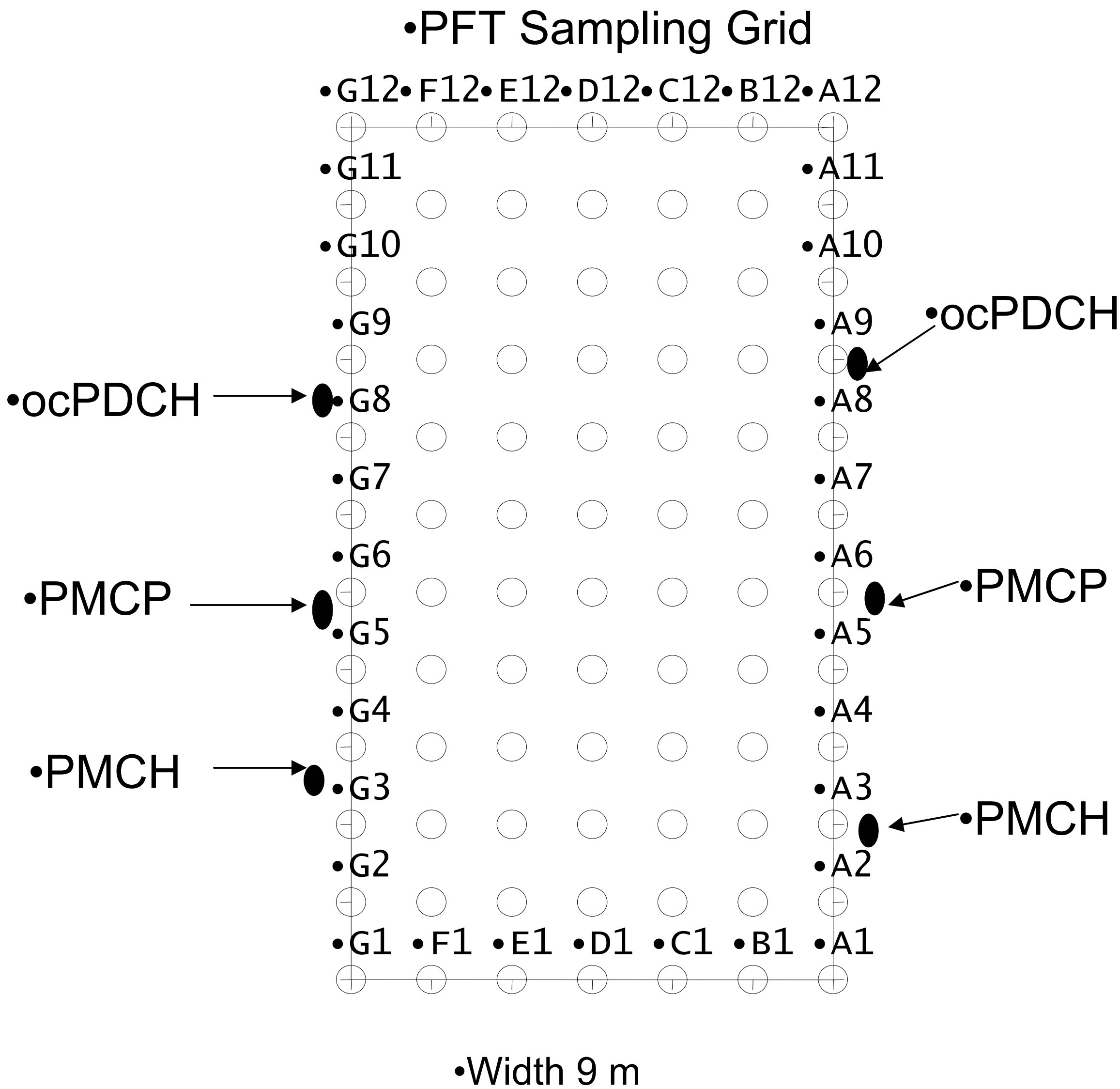

•PFT Sampling Grid
•G12 •F12 •E12 •D12 •C12 •B12 •A12
•G11
•A11
•G10
•A10
•G9
•A9
•ocPDCH
•ocPDCH
•G8
•A8
•G7
•A7
•G6
•A6
•PMCP
•PMCP
•G5
•A5
•G4
•A4
•PMCH
•G3
•A3
•PMCH
•G2
•A2
•G1 •F1 •E1 •D1 •C1 •B1 •A1
•Width 9 m

Figure 6

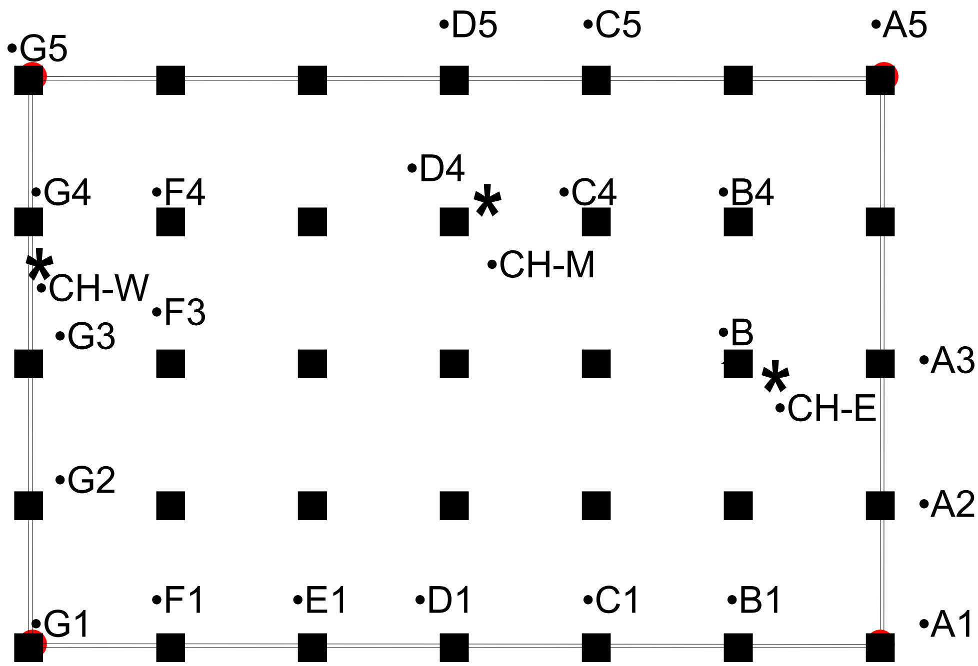

•G5
•D5
•C5
•A5
•G4
•F4
•D4
•C4
•B4
•CH-M
•CH-W
•F3
•G3
•B
•A3
•CH-E
•G2
•A2
•F1
•E1
•D1
•C1
•B1
•G1
•A1

Figure 7

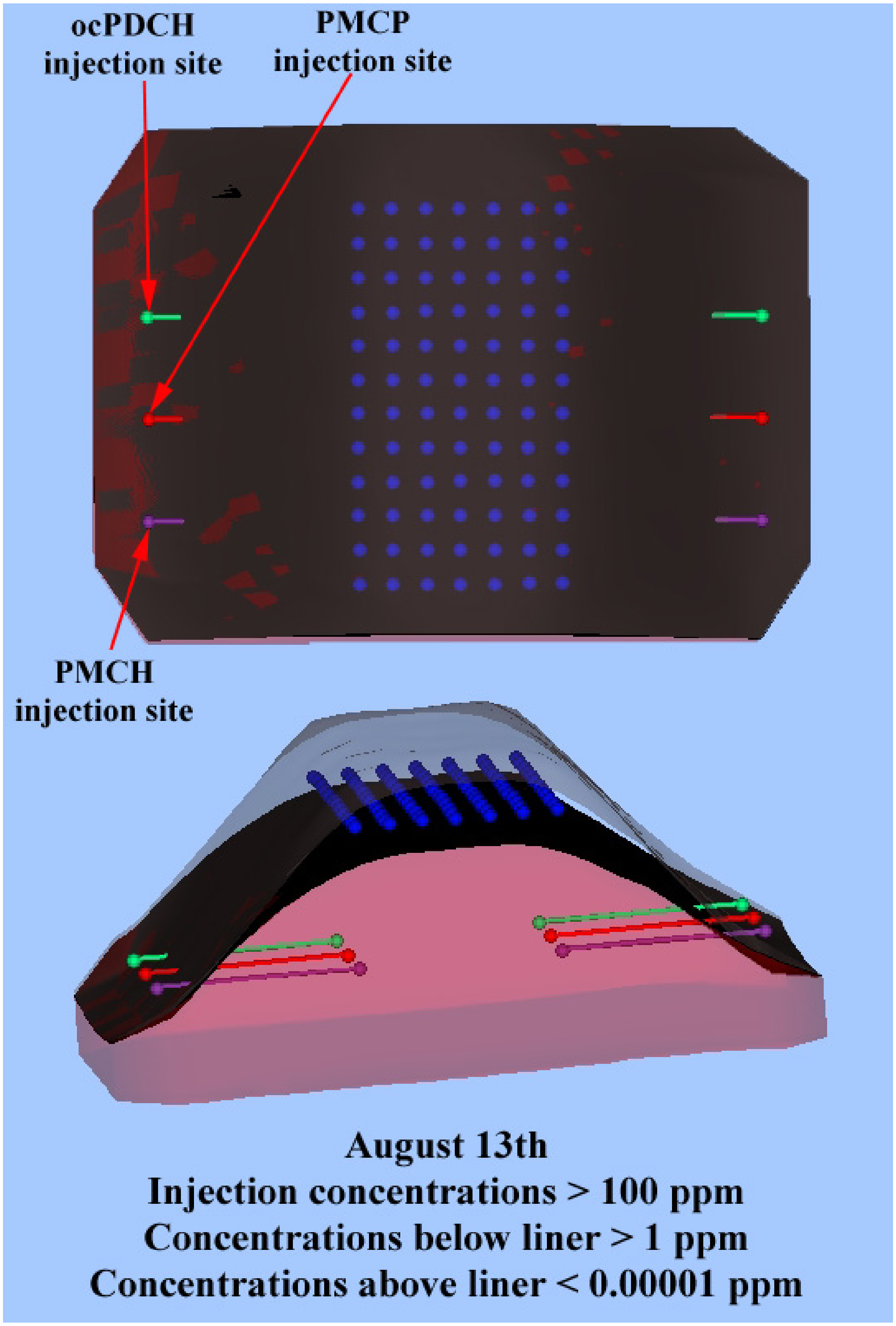
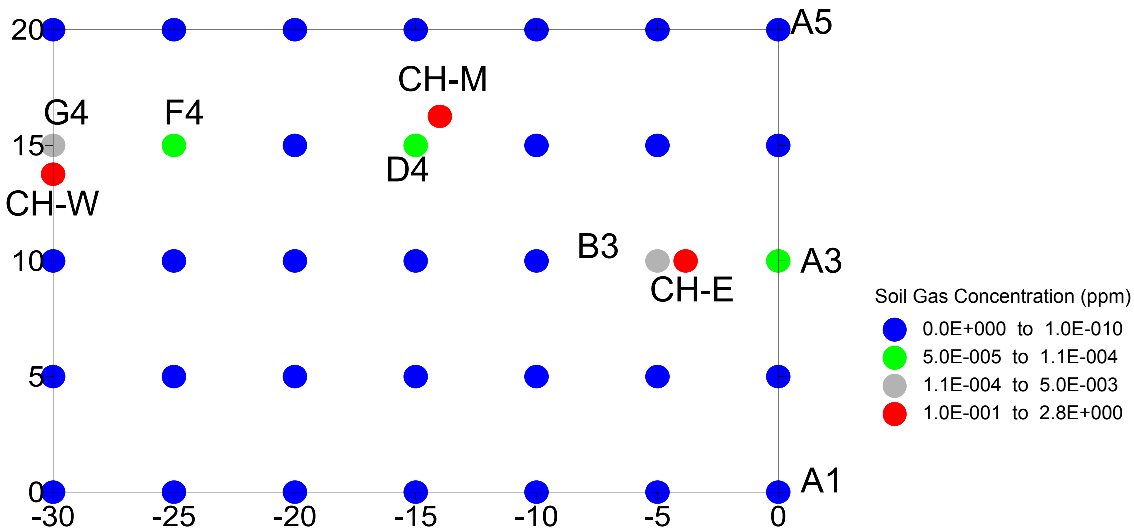

ocPDCH
injection site
PMCP
injection site
PMCH
injection site
August 13th
Injection concentrations > 100 ppm
Concentrations below liner > 1 ppm
Concentrations above liner < 0.00001 ppm

Figure 8



A5
CH-M
G4
F4
D4
CH-W
B3
A3
CH-E
A1
20
15
10
5
0
-30
-25
-20
-15
-10
-5
0
Soil Gas Concentration (ppm)
0.0E+000 to 1.0E-010
5.0E-005 to 1.1E-004
1.1E-004 to 5.0E-003
1.0E-001 to 2.8E+000

Figures

Figure 1 Perfluorocarbon Tracer System for verification and monitoring of caps and cover systems

Figure 2 Bundle of sample ports showing the sintered glass filters attached to polypropylene tubing.

Figure 3 Schematic of test pad (vertically expanded 5x for clarity) Different color injection lines represent different PFTs.

Figure 4 Aerial view of Bentomat test pad with verification test area highlighted (Redraw, photo does not add anything.

Figure 5 Port locations for PFT verification tests

Figure 6 Flaw locations in relation to sample port grid points are separated by 1.5 m.

Figure 7 Results of perfluorocarbon tracer gas (tracer = PMCH) evaluation of the Bentomat Cover for August 13th. Plan view is the upper figure, cross-sectional side-view is the lower figure. Blue circles above the cover indicate no tracer release. Purple, red, and green below the cover represent the different tracers and their injection locations. Gray shaded contour above the data points is the ground surface.

Figure 8 Results of perfluorocarbon tracer gas (tracer = PMCH) evaluation of the Bentomat Cover for August 16th. Introduced flaws labeled CH-E, CH--M, CH-W show concentrations above 0.1 ppm. Adjacent monitoring points range from 0.00005 to 0.005 ppm. All other locations were non-detects.