



Underground Tank Technology Update

Vol. 18, No. 2 March/April 2004



uttu.engr.wisc.edu

Department of Engineering Professional Development

Underground Tank Technology Update is an electronic bimonthly publication of the University of Wisconsin-Madison, Department of Engineering Professional Development. UTTU supplies useful information to federal, state, and local officials working with groundwater technology and to other interested technical specialists.

UTTU is funded by the U.S. EPA under cooperative agreement No. 82933001 to the University of Wisconsin-Madison, which is responsible for its preparation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Comments and suggestions are welcome and may be directed to [John T. Quigley](mailto:quigley@epd.engr.wisc.edu) (quigley@epd.engr.wisc.edu), Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608-265-2083. To comment on an article, or to suggest topics for UTTU, please e-mail [Pat Dutt](mailto:pdutt@twcny.rr.com) (pdutt@twcny.rr.com) or call 607-272-3212.

Advisory Board

Gilberto Alvarez, Environmental Engineer
OUST, U.S. EPA, Region 5, Chicago, Illinois

Bruce Bauman, Research Coordinator
Soil/Groundwater, API, Washington D.C.

Lynn DePont, Grants Project Officer, OUST, U.S. EPA,
Washington D.C.

Louis Fournier, Ph.D., Chemist and President
STAR Environmental, Inc., Chadds Ford, Pennsylvania

Jeff Kuhn, DEQ, Petroleum Section, Helena, Montana

Joseph Odencrantz, Principal
Tri-S Environmental, Costa Mesa, California







Phil O'Leary, Professor, Department of Engineering Professional
Development, UW-Madison

Gerald W. Phillips, U.S. EPA, Region 5, Chicago, Illinois

Staff

John T. Quigley	Project Director
Pat Dutt	Geologist/Writer
Darrell Petska	Copy Editor
Debbie Benell	Program Assistant

Brief article summaries

-  **Characteristics of bioremedial compounds**2
Remediators often select biological techniques for treating contaminated soil because of the techniques' low cost and the contaminant's permanent removal. The authors discuss specific contaminant characteristics essential to ensure successful bioremediation.
-  **Modeling LNAPL**.....5
This article describes the dissolution and volatilization of subsurface LNAPL pools. The properties under discussion include contaminant density, viscosity, interfacial tensions and vapor pressure.
-  **UST testing, part III**6
UST testing, parts I and II described pre-installation tests, holiday tests, testing piping, cathodic protection systems, tank-hole liners, line-leak detectors/indicators, electronic monitors and overflow protection devices, precision testing and temperature issues. This final section describes the importance of tank deflections, vapor/volatile liquid impact, post-installation testing and precision testing of double-wall FRP tanks.
-  **Portable device for tightness testing**7
This article examines a portable device, the UST 2000/P, used for tightness testing in Israel. The authors outline a strategy for improved application and periodic inspection of the UST 2000/P.
-  **Research notes**.....8
Research notes include articles on MTBE biodegradation, estimating natural attenuation, and carbon isotope fractionation.
-  **Information sources**..... 10
Information sources list Web sites of recently published material

Free Subscription To receive this electronic newsletter, e-mail [Debbie Benell](mailto:benell@epd.engr.wisc.edu) (benell@epd.engr.wisc.edu) or call 608-263-7428. There is no cost to subscribers.



Characteristics of bioremedial compounds

Remediators often select biological techniques for treatment of contaminated soil/sediments because of the techniques' low cost and the contaminant's permanent removal. Bressler and Gray (2003) discuss specific contaminant and microbial characteristics essential to ensure successful bioremediation.

Transport and solubility limitations

Biological agents, such as microbes, can transform or mineralize contaminants. "Unfortunately, for a microbial cell to metabolize a compound, the cell's enzymes must gain direct access to the compound. With the exception of some extracellular enzymes from fungi, this access requires that the compound must either cross the cell membrane of the bacterial cells, or at least directly contact membrane-bound enzymes." Generally, "the compound must be in a solubilized state in an aqueous environment" (Bressler and Gray, 2003). Transfer will be dependent on the following:

- compound availability, particularly where the contaminant may be sorbed to natural organic matter
- presence of multiple phases that control partitioning and release of contaminant
- crossing of the bacterial membrane itself, to the interior of the cell where many active enzymes for transformation or mineralization are located

To assess these factors, one must consider the contaminant's physical properties.

Contaminant physical properties

Two main characteristics influence a contaminant's potential bioremediation:

- solubility (aqueous solubility)
- adsorption

For instance, a polar compound is expected to have a high water solubility. (A polar compound is either ionic or has a large permanent dipole moment.) The octanol-water partition is a good estimate of compound polarity and gives a measure of contaminant solubility in biological membranes and lipids.

Contaminants with low polarities and low aqueous solubilities can be difficult to bioremediate. "If a contaminant has extremely low polarity, then the compound is relatively insoluble in an aqueous environment. Compounds of this nature also tend to have high adsorption rates to various solid matrices in the environment." Aqueous solubility correlates inversely with a contaminant's experimental soil adsorption (K_{oc}), while K_{ow} (octanol-water partition coefficient) correlates directly with experimental soil adsorption (K_{oc}). Listed in Table 1 are some experimental properties, such as soil adsorption, of some contaminants. When a compound sorbs strongly to soil organics, because of the variability of soil types, *extrapolations of biodegradation rates from one site to another can be impossible.*

Another factor of contaminant biodegradability is the contaminant's chemical structure, which determines its partitioning characteristics. Homologous series of compounds (they have the same functional groups), for instance, can behave very differently, thus lumping them together for kinetic analysis is not necessarily valid.

Data taken from biodegradation studies show that "the maximum rates of aerobic biodegradation are usually an order of magnitude greater than anaerobic rates." Thus, *anaerobic* degradation is much less likely to be subject to mass transfer limitations.

Compound biodegradability is also influenced by

- phase
- membrane crossing

Phase. If a contaminant is not dissolved in water, then it exists as a separate phase. In such cases, the contaminant's solubilization rate would determine mass transfer limitations.

Membrane crossing. If a contaminant is somewhat water soluble, then next it must access the cell's (bacterial cell's) enzymatic machinery. "Most bacterial systems for remediation of chemical contaminants rely on enzymes found within the bacterial cell. These enzymes most often rely on cell-associated cofactors as either part of the enzyme machinery or as sources of oxidizing

	Aerobic biodegradation rate, d-1	Anaerobic biodegradation rate, d-1	Log K_{ow}	Maximum log K_{oc}	Water solubility (mg/l)
Toluene	42.5	3.36	2.73	2.57	526
Naphthalene	3.36	0.0057	3.3	4.43	31.9
Benzene	3.3	0.071	2.13	1.99	1750
Benzo(a)pyrene	0.057	Not available	5.97	6.70	0.0016
Methyl Ethyl Ketone	1.4	Not available	0.29	0.72	223,000

Table 1. Experimental properties of toluene, naphthalene, benzene, benzo(a)pyrene and methyl ethyl ketone (modified from Bressler and Gray, 2003).

or reduction potential. There are a few examples of membrane-bound enzymes, which are usually bound to the inner side of the cell membrane; therefore, most bacterial mineralization pathways rely on at least one intracellular enzyme that is separated from the surrounding environment by cell walls and outer membranes" (Bressler and Gray, 2003).

Next, the contaminant must gain entry into the microbial cell and pass through the cell membrane and other cell-wall obstacles, which can be significant. "The cell membrane is composed of a lipid bilayer, which can be characterized as having three unique polarity domains. The outside regions of both sides of the membrane are considered fairly polar due to the presence of polar head groups on the phospholipids that compose the majority of the membrane. The center region of the bilayer is nonpolar... In addition to the polarity obstacles of the cell membrane, there are often other membrane-associated proteins, peptidoglycan, and even outer membranes that must be crossed..."

After the contaminant has passed the cell barriers, it must gain access to the cell's insides... "It must either be selectively taken into the cell or have the right combination of polarity, size, and functional groups to allow it to get across the cell membranes...there appears to be a "window" in the range of $\log K_{ow}$ coefficients that allows optimal biodegradation under aerobic conditions." Above this optimal value, the "limitation is usually attributed to the poor aqueous solubilities and adsorption properties of these compounds, but the repulsion of these very nonpolar compounds by the polar regions of the cell membranes also plays a significant role. Interestingly, values below 1 also demonstrate reduced rates of biodegradation. This could be attributed to a reduced ability of these extremely polar compounds to diffuse across the nonpolar regions of the cell membranes of typical microorganisms" (Bressler and Gray, 2003).

Data suggest that the "broad trends of maximum possible bioremediation rate can be correlated with an estimate of membrane flux, as calculated from the physicochemical properties of contaminants." Some biodegradation rates are limited by membrane flux, while some compounds are transported by mechanisms other than diffusion across the lipid bilayer. Enzymatic conversion and soil desorption also play a role.

Three compounds with high aerobic degradation rates, toluene, naphthalene and phenol, "suggest more selective uptake, possibly by active transport against the concentration gradient. Many nutrients are actively transported into the cells using energy-requiring protein pumps. Some of these protein pumps are active against a wide range of compounds, while others can have very selective target compounds. These pumps have specific rates and could play a role in concentrating contaminants intracellularly, against the concentration gradient... membrane-bound pumps often pump contaminants out of the cell as a detoxification mechanism, even though the cell can biodegrade the contaminant. Protein pumps that pump out from the cell interior are also active in some bacteria for removing toluene and antibiotics, but no pumps for entry of hydrophobic compounds into cells have been identified. In many cases as a hydrophobic compound is concentrated inside the cell, it is stored in the form of an inclusion body, which can be a hydrophobic phase within the cell surrounded by a single phospholipid layer. The uptake of n-alkane hydrocarbons, for example, is selective to specific components and is likely active against the local concentration gradient. Such pumping and inclusions have not been identified for aromatic compounds, but this mechanism has the potential for the use of bacterial cells as concentration agents to reduce the aqueous concentration of contaminants" (Bressler and Gray, 2003)

"Extremes in combination of size, polarity, or charged groups ensure that simple diffusion alone could not

allow significant biodegradation rates for some compounds. For example, there are numerous reports of biodegradation and mineralization for two-, three- and even four-ringed polyaromatic hydrocarbons, but only select polyaromatic hydrocarbons with five rings have been shown to be subject to biotransformation. Biodegradation of larger compounds by bacterial systems has not been reported... It is possible that there is a finite physical size of a compound which is able to cross the bacterial membrane at a rate that allows detectable conversion" (Bressler and Gray, 2003).

Biological limitations

Limitations to biodegradation include the following:

- metabolic limitations
- growth limitations
- other biological factors

Metabolic limitations. Significant biological factors can influence biodegradation kinetics and mineralization. Limitations can include the organism's enzymatic properties related to substrate recognition and the substrate's steric hindrance. Growth limitations include all other factors that affect the growth and proliferation of the biocatalytic population.

If a compound is large in molecular size "...the structure may be too large to gain access and interact with the enzyme's active site. This type of steric hindrance would be expected to increase with increasing compound size. The principle may explain the relative recalcitrance of large molecular weight polycyclic aromatic hydrocarbons" (Bressler and Gray, 2003).

Another bioremediation limitation can be compound heterogeneity, which results in reduced biodegradation efficiency and can be "attributed to steric hindrance of the enzyme-substrate interaction. Bulky side groups are thought to prevent the compounds from efficiently entering the biocatalytic enzyme active sites, thus blocking

metabolism. Substitution at specific sites on the compound may also change compound properties such that the activation energy required for specific bond cleavage may increase, prohibiting further metabolism... In general, the more severe the substitution, the greater the inhibition to metabolism" (Bressler and Gray, 2003).

In the environment, contaminants are usually found as complex mixtures, not as pure compounds. "It is not uncommon to find catabolic repression in which one component of a contaminant mixture represses the activity of the biocatalyst toward a compound it would otherwise biodegrade as a sole carbon source. It is even possible for metabolites of biodegradation pathways to suppress induction of essential degradative enzymes. In some cases, mutation and genetic engineering can often be used to help alleviate this metabolic repression. Unfortunately, once these biocatalysts are released to the environment, there is selective pressure against these modified microorganisms" (Bressler and Gray, 2003). Some biodegradative pathways may also require inducers.

Xenobiotics can also have an effect on biodegradation. "Synthetic substituents such as halogens, sulfur bridges, and nitrogen functionalities offer further complications. Due to the fact that halogenated compounds are relatively uncommon in the environment, the enzymatic ability to remove the substituent may be rare or even nonexistent, even though steric hindrance may not be a problem... The danger presented by these xenobiotic compounds is that they often cause toxic effects at all levels of the trophic food chain." Furthermore, "if a compound does not fit into an existing pathway developed over the course of natural evolution, or can be converted to an intermediate in these pathways, then any transformation reactions would be fortuitous and random" (Bressler and Gray, 2003).

Growth limitations. Growth limitations depend on biocatalytic systems. Biocatalysts are biochemical catalysts, such as enzymes. "Microbial cell-based biocatalytic systems generally follow one of two scenarios. The first is inoculation of a relatively small number of biocatalytic systems into a contaminated system. Whether they are able to proliferate through the metabolism of the contaminant alone or require additional supplements, the cells can be considered to be for the most part in an exponential growth phase... the culture is self-sustaining and requires substantially less in terms of cultivation requirements. In the second type of system, a large culture of bioremediation agent is grown separately and then inoculated into a contaminated system. This augmentation approach often incorporates strains or populations that do not grow on the selected contaminant and tend to display more biotransformation than mineralization. These inoculations tend to be much more limited in application and relatively more expensive" (Bressler and Gray, 2003).

Environmental conditions can limit cell growth. For instance, where temperatures are too high, "cells are killed mainly due to protein and enzyme denaturation and membrane damage. At temperatures that are too low, the metabolic activity of the cells can be reduced drastically due to decreased kinetic rates, and membrane gelling results in decreased transport across cell membranes... At temperatures below freezing, ice crystal formation can destroy cellular structure and cohesion, causing cell death" (Bressler and Gray, 2003).

Other environmental conditions of concern include osmotic strength (salinity), oxygenation levels, soil compaction and moisture content, salinity and oxygen content.

Toxicity can limit growth. "Often a biocatalyst is able to utilize and detoxify a contaminant if the concentration is below the toxic threshold, but at higher concentrations the growth and viability of the biocatalyst are altered...

To utilize biodegradation in this scenario, Remediators usually have to extract and dilute the contaminant prior to biodegradation, resulting in a much greater expense. A second potential toxicity problem involves biodegradation that produces metabolites with increased toxicity" (Bressler and Gray, 2003).

In addition, "early oxidative biotransformations can produce metabolites with increased polarities and water solubilities. Consequently, these biotransformed compounds, if not further degraded, have the potential to have greater water and soil mobility and thus expand the area contaminated" (Bressler and Gray, 2003).

Remediators need to be aware of the potential reactivity of biodegradation metabolites. Reactive intermediates produced "may undergo side reactions producing terminal products that may be recalcitrant or have increased toxicity and genotoxicity."

"To grow and propagate, microbes require energy from the conversion of carbon sources to more oxidized forms, whether by aerobic growth with oxygen as the terminal electron acceptor or by anaerobic growth with electron acceptors such as sulfate or nitrate. The lower the flux of a contaminant, the lower the available energy from that compound... The minimum flux to cell survival, without cell division or growth, is the flux required to maintain the basal metabolism. If the cells cannot obtain this minimum amount of energy, then they cannot grow... Attempts to stimulate degradation by adding more readily available compounds can merely give growth and degradation of the added material, rather than general enhancement of activity against target contaminants" (Bressler and Gray, 2003).

Other biological factors. Additional factors that can increase or decrease bioremediation include biofilm formation. "Propagation of attached bacteria to give a biofilm can inhibit the mass transfer into the aqueous phase so that the overall rate of biodegradation

is reduced" (Bressler and Gray, 2003). Another factor involved surface-active compounds. According to the authors, "...the literature is replete with contradictory findings on surfactant use, due partly to the complex physical and biological impact of changing the interfacial compositions in a bioremediation environment... In some cases, addition of surfactants can reduce the rate of bioremediation."

Conclusions

Factors that can affect overall bioremediation of contaminated sites include aqueous solubility, soil adsorption and phase partitioning. Processes involved with cellular transport still require investigation as to their importance to the bioremediation process.

Reference

Bressler, D.C. and M.R. Gray, "Transport and Reaction Processes in Bioremediation of Organic Contaminants. 1. Review of Bacterial Degradation and Transport," *International Journal of Chemical Reactor Engineering*, Vol. 1, 2003; <http://www.bepress.com/ijcre/vol1/R3>.

UTTU thanks Dr. Murray Gray, murray.gray@ualberta.ca, for his help on this article.



Modeling LNAPL

This article describes the dissolution and volatilization of subsurface LNAPL pools.

Gasoline and jet fuels are LNAPLs, light nonaqueous-phase liquids, and are lighter than water. To describe LNAPL movement first requires a description of NAPL movement. NAPL properties important in terms of NAPL transport and contamination prediction include density, viscosity, interfacial tensions and vapor pressure.

"When a LNAPL leaks above an unconfined aquifer,

the NAPL migrates through the unsaturated zone as a separate phase under the dominant influence of gravity, leaving residual droplets in the unsaturated zone. Once it reaches the water table, the LNAPL forms a free-product mound floating on the water table. Then the LNAPL spreads laterally and moves in the direction of the decreasing hydraulic gradient, leaving residual LNAPL droplets. The LNAPL mound is always in contact with both soil gas and groundwater. Thus, a LNAPL migrating on the groundwater table is subject to both volatilization and dissolution. Volatilization is the primary direct mechanism by which contaminants partition from the NAPL phase to the soil gas phase. Once contaminants have partitioned into the soil gas phase, the volatilized contaminants move through the vadose zone by diffusion and advection. By dissolution, contaminants partition from the NAPL phase to the water phase in the unsaturated zone, then to the groundwater. The extent to which contaminants volatilize and dissolve is limited, in part, by vapor pressure and solubility, respectively" (Kim and Corapcioglu, 2003).

The authors studied the effects of LNAPL dissolution and volatilization and modeled its migration. The mathematical models normally used to investigate LNAPLs include:

- sharp-interface models
- immiscible-phase flow models with capillarity
- compositional models

Each model has assumptions and limitations. Kim and Corapcioglu developed their own two-dimensional model to account for "residual NAPL captured by capillary forces, dissolution at the interface between LNAPL and groundwater, and volatilization at the interface between LNAPL and soil gas. The NAPL transport model is coupled with the contaminant transport models to predict soil gas and groundwater contamination by migrating LNAPL."

For a more complete description of the model, see the authors' paper. Results of the model's simulations are described below.

Simulation results

Researchers modeled NAPL and found it was sensitive to ground surface boundary conditions. They conducted simulations with and without volatilization. "Case 1 represents maximum flux conditions from the unsaturated zone to the atmosphere via diffusion (i.e., a permeable ground surface), while case 2 represents negligible volatilization conditions (i.e., an impermeable ground surface). A volume of 10 m³ (corresponding to 8,700 kg) of benzene, one of the most soluble constituents of oil spills, is introduced through a cross-sectional area of 25 m² from a leaking tank. Because the infiltration process is not considered, the source shape is assumed unchanged during NAPL percolation downward from the water table."

Simulations showed that the LNAPL pool spreads or migrates (because of capillary forces) and leaves a trail of immobilized residual NAPL. "The immobilization process slows over time as the spreading of the pool diminishes. The residual mass in the unsaturated zone could be transported to the saturated zone by recharge events, water table fluctuations or diffusion."

Researchers used cases 1 and 2 to examine effects of the capillary fringe thickness and unsaturated zone depth with respect to pool size. They found that "The cumulative fraction of volatilized fractions with different depths at later times is not as different as at earlier times, because in all cases, the volatilized fractions are much greater than the dissolved fractions." Some LNAPL will also evaporate to the atmosphere; evaporative rate depends on ground surface conditions, contaminant vapor pressure, porosity, water content and unsaturated zone depth.

Conclusions

Kim and Corapcioglu (2003) modeled a pure benzene LNAPL and found that the LNAPL migration was chiefly affected by volatilization. "The generation and movement of the dissolved plume were affected by site geology and the free-product plume. Most of the spilled mass remained as a free LNAPL phase 20 years after the spill."

Reference

Kim, J. and M.Y. Corapcioglu, "Modeling Dissolution and Volatilization of LNAPL Sources Migrating on the Groundwater Table," *Journal of Contaminant Hydrology*, Vol. 65, 2003; <http://www.elsevier.com/locate/jconhyd>



UST testing, part III

By John Hartmann

UST testing, parts I and II, described pre-installation tests, holiday tests, testing piping, cathodic protection systems, tank-hole liners, line-leak detectors/indicators, electronic monitors and overflow protection devices, precision testing and temperature issues. This final section will describe tank deflections, vapor/volatile liquid impact, post-installation testing and precision testing of double-wall FRP tanks.

Tank deflections

Precision tests typically require the tested tank to be filled with product to a level above grade. A graduated standpipe is usually attached to the fill opening to accomplish this; product is then delivered to the tank until it is filled to the very top. Additional product is then added, bringing the liquid level up to a point in the standpipe two or three feet above grade level. Liquid level changes can then be noted in the standpipe.

Such deliberate overfilling can produce further variations that add to the difficulty of identifying a leak. In a 6-foot-diameter tank, a normal full load of gasoline creates a pressure of 0.98 pounds per square inch (psi) on the tank ends, or head. If the tank is buried three feet below grade and the fill tube and standpipe are filled to three feet above grade, the weight of this additional product increases the pressure on the head to 2.95 psi. This difference of approximately 1.97 psi adds another 14,000 pounds (or 7 tons) of pressure against the head, increasing deflection.

Most steel tanks are made of one-fourth-inch steel plate. Under pressure, this plate will deflect outward. In aboveground tanks, it is possible to accurately calculate the deflection changes that result from the weight of additional product. But support for underground tanks varies because of different soil types and varying types and thicknesses of backfill, making accurate deflection projections for such tanks extremely difficult.

Studies show that tank-end deflection will almost always be significant enough to influence precision test results; the amount of deflection must be factored out of the test calculations. After a tank is overfilled for a test, however, tank-end deflection takes several hours to stabilize.

Fiberglass tanks usually have oval or spherical-shaped ends. Tank ends of this type are not subject to the same degrees of deflection that occur in the flat ends of the steel tanks. However, when additional product is introduced into a fiberglass tank, expansion from pressure will manifest itself on the sides of the tank, between the ribs.

Measurements after installation should be taken to compare the tank deflection of the installed tank with the measurements taken before installation. Tank-end deflection is one of the greatest sources of error in any required future precision test. A 1/6 inch deflection in the center of a tank end of a 48-inch-diameter tank

looks like an apparent loss of 0.49 gallons to a tank tightness test. A one-inch deflection in a 120-inch-diameter tank looks like 49 gallons.

Vapor/volatile liquid impact

Trapped vapor is another important potential source of error. A pocket of vapor and air is subject to the same changes in temperature and pressure as liquid product. Expansion or contraction of trapped vapor will cause error in tests unless accounted for. With highly volatile liquids, evaporation of liquid product into the atmosphere is also a problem. Test methods must be able to show the effects of evaporation loss or be able to compensate for it.

Vapor pockets, or voids, may be created within a tank that is not set level in the ground, even if it is filled completely to the top. Unless compensated for, such voids can influence the accuracy of leak tests. The difficulties identified here and routinely encountered in precision tests are not intended to suggest test unreliability. Industry experience suggests the following:

- precision testing of storage tank integrity is a demanding exercise and must be performed by experienced specialists
- testing equipment and procedures that do not account for such variables as temperature stratification and tank-end deflection cannot be expected to give reliable test results

Post-installation testing

Various types of testing are necessary throughout the life of the tank installation. Precision tests are required at certain intervals by many regulatory authorities and by new federal legislation. It is good business practice to perform precision testing of tanks and piping when ownership is transferred.

If continuous water monitoring is not used, the tank

should be checked on a regular basis with a water-finding paste on a gauge stick. This can be done during deliveries and inventory checks. The presence of water does not necessarily indicate a leak. Check the fill cap, the fill cap seal and other connections to be sure they are not letting in water.

Unaccountable increases in water, especially after heavy rains, may indicate leaks, and a precision test may be necessary.

Precision testing of double-wall FRP tanks

The leading manufacturers of FRP tanks, Xerxes Corporation and O/C Tanks, have developed simple techniques for testing the integrity of both inner and outer walls of their double-wall tanks. The results produced by both tests exceed the performance criteria for precision tests as originally outlined in NFPA 329. (Editor's note: O/C Tanks no longer sells fiberglass tanks.)

Tanks produced by Xerxes and O/C contain brine in the interstice. To test the tank's integrity, simply check the liquid level of the brine. If either the inner or outer tank develops a leak, the brine level is immediately affected. The Xerxes test uses a calibrated dipstick. The O/C test provides for continuous monitoring of a brine reservoir near the tank top. Both techniques are simple and reliable.

Documentation

The tank installer must carefully document tests and inspections. An installer may experience a personal sense of pride if an air test run on the piping prior to final backfilling shows that the piping system is absolutely tight. This personal feeling will be of little value a year later, however, if an allegation is made in litigation that the piping system is leaking and has been leaking since it was installed. To protect against future claims, record

and retain test results. Make photographs showing tests while they were in progress. Have the supervisor in charge of each test sign off on the results.

In many jurisdictions, local authorities are responsible for certifying the system tightness and proving the proper functioning of all monitoring and detection systems. Include documentation of this certification in the installer's files. If a particular individual, say, an inspector with the office of the state fire marshal, has checked and approved an installation, include that person's name and position in the job records.

The results of a precision test should be permanently kept on the premises by the tank owner/operator, and records should be kept at least three years (API RP 1615).

Test planning

Because the testing requirements vary from job to job, good practice includes an advance plan for testing. The project manager, in reviewing specifications, should note which tests will be required and the sequence in which they will occur. Prepare checklists. Plan test procedures. If special equipment will be required, or if outside specialists will be needed for certain tests, make arrangements well in advance.

References

Hartmann, J. "Testing," Section 5 in *Underground and Aboveground Storage Tank Inspection*, April 21-23, 2003, Ft. Gordon, Georgia, given by the University of Wisconsin-Madison, <http://epdweb.engr.wisc.edu>
API, <http://api-ep.api.org/>

UTTU thanks John Hartmann, publisher of *Petroleum Equipment & Technology Magazine* Archive (www.pe-t.com), for allowing us to reprint this article. John Hartmann & Associates may be reached at Jhartmann@pe-t.com or 847-382-4010.



Portable device for tightness testing

This article describes a portable device, the UST 2000/P, used for UST tightness testing in Israel. Michlin and Pistiner (2003) assessed the device, considered means for improving its application and outlined a strategy for periodic inspection.

At present in Israel, there is no independent agency for checking test equipment under field conditions or ensuring qualifications and training of equipment operators. In addition, "statistical reliability of the decisions as to the serviceability of a device [for tank testing] is conditional on a large number of repetitions, which may prove economically prohibitive. This number can be reduced by recourse to sequential testing."

The UST 2000/P

The UST 2000/P operation relies on observation "of liquid level changes in the tank over a given time interval, with readings corrected for the temperature fluctuations on the basis of the established thermal-expansion coefficient of the liquid and its volume."

Testing the UST 2000/P

Researchers examined the results of checks on a population of 830 tanks. They found that 36 percent of the tanks could not be declared tight. Because this was an improbably high number, they designated the tanks as "rejected" rather than as "not tight." Researchers discovered that 46 percent of the rejected tanks contained 95 gasoline. (Gasolines were 95, 96 and 98, the numbers referring to the corresponding octane.) The distinctive feature of 95 gasoline is that about one-half of it is imported and the other half locally produced, while all the others are exclusively local and their composition shows less fluctuation.

A close correlation exists between a fuel's density and its thermal expansion coefficient. Researchers found that an excessive standard deviation in density for the 95 gasoline "is attributable to the already-mentioned circumstance that approximately half of it is imported with a density somewhat lower (on the average) than that of the local product. The standard deviation of the fuel density and the percentage of rejected tanks are linked, with a correlation coefficient of 0.82. Thus, the tanks of this fuel have a flattened distribution of the measured rate of volume change and an especially high percentage of rejections."

Michlin and Pistiner (2003) note that there is a "disparity between the scatter of data obtained with the UST 2000/P under field conditions on the one hand, and the characteristics obtained under standard test conditions on the other," confirming a need for "periodic checking of the device under field conditions."

Researchers also performed some fairly rigorous statistical analyses on the data. For a detailed description of their analyses, see their text.

Conclusions

Authors concluded the following:

- the statistics obtained through use of VTTT (volumetric tightness testing of underground storage tanks) permitted estimation of equipment accuracy under field conditions and enabled outlining of control techniques
- results from this study show that the "standard error of the leakage measurements was larger than the accuracy level prescribed by national standards, and much larger than that claimed by the manufacturer"
- "the distribution pattern of the measured leaks is characterized by three peaks, attributable to errors in thermal expansion coefficient of the fuel and to

choice of the measurement time interval; the device readings are affected by the properties of the fuel: the standard deviation of the fuel density and the percentage of tanks characterized as 'not tight' are correlated, with a correlation coefficient of 0.82"

- VTT (volumetric tank testing) devices should be periodically checked under field conditions, and at low rates of artificial change of fuel volume
- the number of necessary measurements to obtain an accurate hypothesis (of leak rate) may be economically prohibitive, therefore, researchers developed a modified algorithm with a criterion for early termination of the procedure

Authors recommend

- a modified plan for sequential testing of devices; this plan would reduce the necessary number of measurements and give a criterion for early termination of the procedure
- that checks for VTT devices be "carried out under the closest possible approximation of the actual field conditions and include control of the proficiency of the equipment operators"
- an optimal milieu for checks: "active filling stations, where the procedure can be applied on groups of five tanks and more... Tanks chosen for this purpose must be leak-free and their fuel content must be changed at the prescribed rates—e.g. with the aid of peristaltic pumps"
- "to ensure statistical independence of the tests and minimize the effect of uncontrolled factors, repeat tests should be run at other stations, or even at the same one but after a time interval long enough to necessitate topping up of the tanks"
- statistical analysis of the tank inspections should be performed along with the actual testing of the VTTT

Reference

Michlin, Y. and A. Pistiner, "Evaluation of a Portable Device for Volumetric UST Tightness Testing," *Advances in Environmental Research*, Vol. 7, 2003; <http://www.elsevier.com/locate/aer>

UTTU thank Yefim Michlin, yefim@techunix.technion.ac.il, for his help on this article.



Research notes

Aerobic Biodegradation of Methyl Tert-Butyl Ether in Gasoline-Contaminated Aquifer Sediments

Zoeckler, J.R., Widdowson, M.A. and J.T. Novak, *Journal of Environment Engineering*, July 2003; <http://scitation.aip.org/eoo/>

Researchers collected samples from a source area, then upgradient and downgradient of a gasoline-contaminated aquifer, and used the samples to create microcosms. The microcosms, which survived about 130 days, were analyzed for BTEX and MTBE biodegradation. Researchers found the following:

- "naturally occurring microorganisms previously exposed to MTBE were capable of biodegrading MTBE in the presence of oxygen with a relatively minor acclimation period and reducing MTBE concentrations from starting levels between 2.7 and 5.5 mg/l to below detection limit (0.05 mg/l)"
- results from microcosms constructed using aquifer sediments with little or no prior exposure to MTBE were less conclusive; "MTBE biodegradation rates for the MTBE-exposed microcosms were higher and statistically different from the rates observed in microcosms prepared with lightly contaminated aquifer sediments"

- "Samples with no known prior exposure to MTBE or BTEX compounds showed no evidence of MTBE biodegradation during the period of investigation"
- "BTEX compounds and petroleum hydrocarbon had a minor effect on the lag period prior to MTBE degradation, but it was unclear if MTBE degradation rate was impacted"
- "Microcosms present in the less contaminated sediment rapidly biodegraded certain petroleum hydrocarbon compounds during the 12-day lag period preceding MTBE degradation. These observations suggest that MTBE-degrading microorganisms preferentially utilize readily biodegradable petroleum hydrocarbons as growth substrates during which MTBE biodegradation is limited or inactive."
- MTBE biodegradation will occur with oxygen and in the absence of more readily biodegradable petroleum hydrocarbon compounds, which suggests that "a robust mathematical model for aerobic biodegradation of petroleum hydrocarbon compounds is warranted for application to MTBE fate and transport in groundwater."

Finally, researchers assert: "The results of this study suggest that only limited intrinsic MTBE bioremediation in oxygenated groundwater would be expected in the presence of more readily biodegradable petroleum hydrocarbon compounds. Natural attenuation of plumes derived from gasoline spills may be limited to those areas where oxygenated recharge waters mix with the periphery of the plume where MTBE has transported farther than other compounds."

Microbial In-situ Degradation of Aromatic Hydrocarbons in a Contaminated Aquifer Monitored by Carbon Isotope Fractionation

Richnow, H.H., Annweiler, E., Michaelis, W. and R.U. Mackenstock, *Journal of Contaminant Hydrology*, Vol. 65, 2003; <http://www.elsevier.com/locate/jconhyd>

Researchers used carbon isotope fractionation to estimate degree of in-situ biodegradation of toluene and o-xylene in a plume. "Several biochemical reactions result in carbon isotope fractionation while molecules containing the lighter ^{12}C -isotope are used preferentially. Consequently, the $^{13}\text{C}/^{12}\text{C}$ isotope ratio of the substrate's residual fraction is enriched in ^{13}C . For example, isotope fractionation is a well-accepted indicator of anaerobic and aerobic microbial methane oxidation in sediments" (Richnow and others, 2003). Researchers used a laboratory-derived carbon isotope fraction factor (α_{C}) calculated from the Rayleigh equation to describe in-situ biodegradation of aromatic hydrocarbons.

Field studies determined that dissolved electron acceptors such as nitrate, iron and sulfate were depleted in contaminated areas of the aquifer, indicating they functioned as electron acceptors. Anaerobic degradation was the predominant degradation mode.

Contaminant concentrations in the groundwater examined could be affected by:

- mixing with pristine groundwater
- adsorption to the aquifer matrix
- evaporation

Evaporation is thought not to be significant while "sorption and dilution may influence the contaminant concentration but did not affect the isotope composition to a significant extent." However, "calculations based on isotope fractionation could not quantitatively distinguish between dilution, adsorption and biodegradation; the

results describe the extent of biodegradation in different zones of the aquifer."

Remediators also need to consider the redox environment. "Aerobic and anaerobic bacteria use different biochemical reactions for degradation, and thus, isotope fractionation factors might differ. In this aquifer, the microbial community used nitrate, ferric iron, and sulfate as terminal electron acceptors, as indicated by their depletion along groundwater flow and the absence of molecular oxygen" (Richnow and others, 2003).

A term used in their analysis, percentage of biodegradation, refers to the hydrocarbon fraction available to the microorganism. "This fraction might have been reduced by dilution and adsorption before this fraction becomes bioavailable to the organisms, and therefore the percentage of biodegradation is not quantitative in terms of absolute concentration."

This value can be influenced by groundwater sampling that covers the aquifer's whole water column. "Water from different preferential flow paths may be mixed in the wells. In a worst-case situation, contaminants are almost completely degraded in one flow path, whereas no degradation occurs in the other flow path. After both water bodies are mixed in the well, the contaminant's isotope ratios show the initial isotopic composition of the source because the substrate from the flow path that does not exhibit biodegradation has a much higher concentration and influences the isotope ratio of the mixed sample to a higher extent. Thus, although significant amounts of substrate have been degraded, the calculation will only indicate minor biodegradation, underestimating its true extent. However, presuming that biochemical degradation conditions such as temperature, redox and electron acceptors are similar in different parts of the contaminated aquifer and that an appropriate isotope fractionation factor is accessible, the calculation will not overestimate the extent of biodegradation

regardless of mixing processes in the aquifer or sorption to the aquifer's matrix" (Richnow and others, 2003).

"Thus, the percentage of biodegradation may be a useful index in risk assessment studies concerning groundwater contamination and represent the first step toward a quantification of the in-situ biodegradation in aquifers." The authors also suggest that "In the future, combining the isotope fraction concept with groundwater modeling and tracer studies could certainly improve the quality and reliability of the data and lead to better interpretations by taking dilution effects into account."

Rate Parameters for Methyl Tert-Butyl Ether Biodegradation via a Radial Diffusion Model

Basagaoglu, H., Chung, E.E., Gandhi, D., Scow, K.M., McCoy, B.J. and T.R. Ginn, *Journal of Environmental Engineering*, June 2003; <http://scitation.aip.org/eeo/> Researchers developed "a mathematical model with simplified reaction kinetics and diffusive transport phenomena to describe MTBE biodegradation in soils." The model considered MTBE degradation kinetics and radial diffusion-limited mass transfer of MTBE between the extra- and intra-particulate aqueous phases."

Researchers applied "a dimensionless radial pore diffusion model to calculate the first-order biodegradation rate of MTBE by aerobic in-situ microorganisms at a laboratory scale under different oxygen and temperature treatments." Under these treatments, MTBE first-order biodegradation rates varied from 0.0015 (100 percent oxygen) to 0.0165 (20 percent oxygen) per hour. As temperature varied from 288° K to 303° K, the biodegradation rate varied from 0.005 to 0.03 per hour.



Information sources

U.S. EPA publications and information

Publications that can be downloaded from <http://clu-in.org/techpubs.htm> include

- A Review of Emerging Sensor Technologies for Facilitating Long-Term Ground Water Monitoring of Volatile Organic Compounds (EPA 542-R-03-007)
- Measurement of Fugitive Emissions at a Region I Landfill (EPA 600-R-04-001)
- National Emission Standards for Hazardous Air Pollutants (NESHAP) from Site Remediations
- Technology News and Trends

U.S. EPA Internet seminars

Seminars available at <http://clu-in.org/studio> (there are at least 40) include

- Facilitating Reuse at RCRA Sites: Innovative Technologies for Groundwater Characterization and Cleanup
- Initial Site Screening Using a Dynamic Field Activity: Callaway Drum Recycling Site
- ITRC Phytotechnologies

Other EPA publications and sites

- Capstone Report on the Application, Monitoring and Performance of Permeable Reactive Barriers for Groundwater Remediation: Volume I, Performance Evaluations at Two Sites (EPA 600-R03-045b), <http://www.epa.gov/ada/pubs/reports.html>
- Environmental Technology Opportunities Portal (ETOP), Web portal for environmental technologies, <http://www.epa.gov/etop/index.html>
- EPA Science Inventory Database, <http://cfpub.epa.gov/si/>

- EPA SITE Program Reports, <http://www.epa.gov/ORD/SITE/reports.html>
- Guidance for Developing Ecological Soil Screening Levels (OSWER Directive 9285.7-55), <http://www.epa.gov/superfund/programs/risk/ecorisk/ecossl.pdf>
- Report on Bioavailability of Chemical Wastes with Respect to the Potential for Soil Bioremediation (EPA 600-R-03-076), <http://es.epa.gov/ncer/publications/>
- Treatment Technologies for Site Cleanup: Annual Status Report, <http://cfpub.epa.gov/asr>

Other documents, Web sites and listserv

- ESTCP Cost and Performance Report: Application of Flow and Transport Optimization Codes to Groundwater Pump-and-Treat Systems (CU-0010), <http://www.estcp.org/documents/techdocs/>
- ETVoice, a listserv that highlights upcoming technology demonstrations, <http://www.epa.gov/etv/etvoice/subscribe.html>
- ITRC Quarterly Update, <http://www.itrcweb.org/ITRC0903Update.pdf>
- NICOLE News, a periodic newsletter from The Network for Industrially Contaminated Land in Europe, <http://www.nicole.org/>
- Vapor Intrusion Issues at Brownfield Sites, <http://www.itrcweb.org/BRNFLD-1.pdf>

UTTU obtained many of these sites from Tech-Direct (<http://clu-in.com/techdrct>) and Ground Water Monitoring and Remediation (<http://www.ngwa.org>). We thank the editors and writers for allowing us to reprint this material.