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MTBE odor study

This article summarizes the results of the first MTBE odor study using consumers as panelists. Several odor studies have been undertaken because the U.S. EPA has not yet set drinking water standards for MTBE; however, an advisory issued in December 1997 recommended that "keeping the concentration in the range of 20 to 40 $\mu\text{g/L}$ or below will likely avert unpleasant taste and odor effects" (U.S. EPA, 1997, in Stocking and others, 2001).

Expert vs. untrained (consumer) panelists

To date, five taste and odor tests have been completed in an effort to define taste and odor thresholds for MTBE in drinking water. Each study used trained, expert panelists; expert panelists have an increased sensitivity to odor. Expert panelists can also characterize odors but generally do not guess whether a taste or an odor exists. This present study used an untrained consumer panel, "a group that was believed to reflect public sensitivities more accurately" (Stocking and others, 2001). Group members were chosen from a broad range of society in terms of age, gender and ethnicity. Such a group determines whether "multiple samples are different, and is often required to guess which sample is different, even if the individual cannot detect a taste or odor." Therefore, the untrained panelists incur a higher risk of false positives than do expert panelists. Ultimately the untrained panelists help define the detection threshold, "the threshold at which a consumer can detect a difference but cannot identify or characterize that difference."

Most odor studies use expert panelists because

- they are familiar with the taste/odor protocol
- fewer panelists are required to identify a threshold

ASTM's Standard Methods (ASTM, 1995, in Stocking and others, 2001) recommend that expert panelists consist of more than five people, and preferably 10 or more. "...statistical analysis of the results from taste and odor studies is a complex issue, and it is particularly dependent on panel size and composition. Typically, threshold standards for various chemicals are determined using the geometric mean of the taste and odor thresholds from the panelists' results, in which case a panel of 8 to 10 trained panelists is usually sufficient" (Stocking and others, 2001).

When using untrained panelists, additional panelists are required because these panelists may not be as sensitive to taste and smell concerns as expert panelists. To circumvent this problem, the untrained panelists chosen are usually sensitive to the chemicals of concern, and they typically identify a lower threshold value.

Previous taste/odor studies

The five MTBE taste and/or odor studies produced to date have used

- expert panelists to describe odors
- descriptors such as "sweet solvent", "estery, vanilla, and sweet"
- descriptor solvents (frequently) at concentrations greater than 20 $\mu\text{g/L}$
- protocols that deviated from published protocols (some problems are described in the text)

Two studies identified detection thresholds of 39-48 $\mu\text{g/L}$ and 95-140 $\mu\text{g/L}$, and two studies determined recognition thresholds of 44-65 $\mu\text{g/L}$ and 174-212 $\mu\text{g/L}$.

The "difference between a detection and a recognition threshold is significant because, on the basis of regulatory experience, consumers will not complain about the quality of their drinking water until the recognition threshold is exceeded: that is, the point when they can describe the offending taste and/or odor" (Stocking and others, 2001).

Consumer panel study and created protocol

To address the problems and discrepancies in the previous studies, a consulting company performed another MTBE odor study using untrained consumer panelists. "This consumer study was designed to complement previous studies and to correct the limitations of those studies, namely the size and makeup of their panels. Considerable effort was made to incorporate the experiences of the previous studies through discussions with some of the principal investigators of those studies" (Stocking and others, 2001).

The final protocol of the consumer panel study had these features:

- it was based on a consensus of ideas from individuals familiar with MTBE studies
- an odor study was conducted; such studies are thought to result in lower thresholds than taste studies; furthermore, laboratories would not accept the liability of performing a taste study without an established MCL (maximum contaminant level)
- the forced-choice triangle method was used; this requires a panelist to guess which of three samples is strongest in odor
- eight samples were presented to panelists with increasing concentration (2 $\mu\text{g/L}$, 3.5 $\mu\text{g/L}$, 6 $\mu\text{g/L}$, 10 $\mu\text{g/L}$, 18 $\mu\text{g/L}$, 30 $\mu\text{g/L}$, 60 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$)

- panelists were subjected to a maximum of eight trials to avoid olfactory fatigue
- bottled water with less than 500 mg/L total dissolved solids was used rather than deionized or distilled water, to avoid masking/enhancing MTBE odor
- room temperature (19.8-23.1°C; 67.7-73.4°F) was selected as operating temperature to ensure conformity with other studies; this is also the temperature at which the public most often consumes drinking water
- samples of four ounces each were given to panelists in 7-ounce plastic cups that were odor-free
- spiked and blank samples were covered with a clean watch glass
- panelists lifted each sample, swirled it several times, lifted the watch glass and smelled the sample
- trial repetitions were allowed if requested by a panelist
- panelists indicated on a card which sample smelled different from the other two; if panelists did not know, they were instructed to guess

Formation of panel and testing conditions

The panel was selected from a database of more than 10,000 consumers. Many of the panelists had participated in previous sensory testing. Pregnant women, asthmatics and smokers were eliminated. The final panel of 57 participants became familiarized with the triangle testing technique by participating in an activity that requested them to grade various types of sandpaper. Five sessions were held over two days, each session involving 9 to 14 odor testers. Fans were used between the sessions to dispel odors.

Results

"Once collected, data were analyzed according to ASTM Method E679-91. This method calculates individual threshold concentrations by taking the geometric mean of the last concentration missed and the first concentration detected, given that all higher concentrations were successfully detected. If a panelist could detect all the concentrations presented, the threshold concentration for that panelist was the geometric mean of 2 µg/L and the next lowest theoretical concentration (1 µg/L). If a panelist did not detect the highest concentration (100 µg/L), it was assumed that the panelist would have detected the next highest theoretical concentration and the threshold was calculated to be 132 µg/L (the geometric mean of 100 and 175 µg/L)" (Stocking and others, 2001).

Testing indicated that panelists determined thresholds ranging from 1.4 µg/L (10 of the 57 panelists) to 132 µg/L (13 of the 57 panelists).

Implications for setting a secondary maximum contaminant level (SMCL)

According to Stocking and others (2001) "...the purpose of SMCLs is to prevent 'a substantial number of the persons...to discontinue [public water system] use'" (USEPA, 1996 in Stocking and others, 2001). "There is no indication of whether the term 'substantial' should represent 50, 75 or even 95 percent of the population."

The authors point out that odor-free water was used in the testing. "In practice, consumers would be exposed to MTBE in a natural water matrix that may enhance or mask the odor of MTBE...field data suggest that a consumer threshold concentration for MTBE in a natural water matrix will be greater than such a threshold in odor-free water" (Stocking and others, 2001).

Results from this MTBE odor study suggest that 15 µg/L is a conservative, approximate MTBE odor threshold,

representing the lower range of the taste and odor threshold values reported in the five studies done previously. Stocking and others (2001) also suggest that the methodology used in this study could be used for establishing SMCLs for other organic chemicals. "...the authors believe that 15 µg/L is the only scientifically defensible value when the establishment of an SMCL for MTBE is under consideration. Although setting the SMCL below 15 µg/L would be even more restrictive because even fewer consumers could detect MTBE, an SMCL set at such a level would have to be a public policy decision. Currently, there is no precedent for setting SMCLs that are protective of all consumers, an approach that would likely apply an increased burden on the regulated water utilities" (Stocking and others, 2001).

Reference

Stocking, A.J., Suffet, I.H., McGuire, M.J. and M.C. Kavanaugh, "Implications of an MTBE Odor Study for Setting Drinking Water Standards," *AWWA Journal*, March 2001; <http://www.awwa.org>.



MNA considerations

Monitored natural attenuation (MNA) is a practice used to help monitor the processes governing plume movement. This article describes MNA criteria such as site characterization elements, factors that affect monitoring data, and modeling considerations.

Site characterization criteria to examine

Characterization of contaminant concentration and distribution, soil geochemistry, aquifer material and hydrogeology can help establish background concentrations that can be compared to existing plume conditions. To accomplish this, Azadpour-Keeley and

others (2001) advocate measuring the following:

- dissolved oxygen, nitrate, Fe(II), Mn(IV), sulfate and sulfide at the plume axis and transverse to the plume; with this information, biological activity with respect to redox state can be estimated
- rate of change of geochemical parameters (listed in bullet above) to be used in predictive models; these parameters can give information on principal electron acceptors and oxygen, nitrate and sulfate concentrations, and also allow one to estimate length of natural attenuation viability
- H₂ for TEAP (terminal electron acceptor process)
- dissolved methane, which is produced after other TEAs (terminal electron acceptors)
- dissolved organic carbon, and the presence of macro- and micronutrients and TEAs to describe a site's microbial activities

Factors that affect monitoring data

Factors other than natural attenuation that impact on monitoring data include

- infiltrating precipitation
- monitoring well problems
- influence of pumping wells

Infiltrating precipitation. High precipitation rates may lower the apparent concentration of contaminants. There are "two time periods after a precipitation event when dilution may have an effect on monitoring. The first is a few hours after a precipitation event where flow is through macropores or 'wormholes' to the water table, and the second is a few days after with flow through the vadose zone. The time required for both of these processes to occur will be a function of the number and size of the macropores, overall permeability of the unsaturated zone, and water table depth. Monitoring during these events can result in an appar-

ent decrease in the concentration of contaminants by dilution, or if contaminants are present in the vadose zone, an increase in concentrations due to their infiltration" (Azadpour-Keeley and others, 2001).

Monitoring well problems. Water from an uncontaminated part of the aquifer may be drawn into a monitoring well's cone of depression. Or if a well is pumped for an extended period prior to sampling, "the amount of clean water coming into the well will result in an apparent decrease" in contaminant concentration. Conditions that exacerbate the problem include well screens that are larger than 2 m, inconsistent screened intervals, and inappropriate sampling methods.

Influence of pumping wells. Wells in an interdiction field, and water supply or irrigation wells, can affect plume movement depending on well design and construction and on how wells are pumped.

The authors caution practitioners of MNA to consider the above factors when designing monitoring programs. In addition, placement of monitoring wells will depend on knowledge of

- water table depth
- hydraulic conductivity
- hydraulic gradient (and if it is affected seasonally)
- groundwater flow direction
- storage coefficient/specific yield
- vertical and horizontal conductivity distribution
- plume movement direction
- effects of manmade or natural influences (e.g., lagoons/seeps)

Another concern is appropriate sentinel screen depth and length. Short screens, for instance, minimize water quality differences and are thus preferable to long screens.

Monitoring well design

The monitoring well design should be based on

- plume size
- site complexity
- source strength
- groundwater/subsurface water interactions
- distance to receptors
- confidence limits

Authors recommend that "The wells should be capable of monitoring singular flowpaths within a plume's course and subsequent movement of contaminants along these flow paths." To identify natural attenuation, field workers could sample water "at one location and sample the same volume of water for the same parameters at some distance downgradient. It is generally impractical to monitor flowpaths within a plume, with the exception of the plume axis, which is the only flow line that can be located with any reasonable level of certainty" (Azadpour-Keeley and others, 2001). The flow lines, however, may change with time. (*Reviewer's comment: this is usually not an issue if sampling is more or less simultaneous along a flowpath of wells.*)

Authors suggest that another strategy for monitoring natural attenuation is to assume that the plume is in equilibrium, even though plumes are never in complete hydraulic or geochemical equilibrium. "Monitoring wells even a few feet apart differ significantly in observed concentrations of contaminants" (Azadpour-Keeley and others, 2001). Tracers such as trimethylbenzene (TMB) can be used, but in anaerobic conditions, TMB degrades and produces aromatic acid intermediates.

Data validity

"The number of sampling points and sampling rounds are often insufficient to establish statistically valid trends given the natural variability in groundwater quality, and

the variability due to pumping and sampling and differences between analytical laboratories" (Azadpour-Keeley and others, 2001). Authors recommend that natural attenuation programs be based on a detailed statistical evaluation of pertinent data and that sufficient high-quality data be sampled with enough frequency over a protracted period to perform a meaningful statistical evaluation.

Degradation and rate constants

"Precision and accuracy in estimation of rate constants are essential to conclude how quickly the groundwater plume will be cleaned up following the source control" (Azadpour-Keeley and others, 2001). Biodegradation rate constants should be calculated at the points of compliance, and those rates should be compared to those in the literature. "Although microcosms are used as an effective tool to determine the biodegradation potentials, the use of the microbiological laboratory data for calculation of rate constants may be inappropriate since they are not always representative of the biodegradation rate(s) under the field conditions. (Reviewer's comment: these rate constants are rarely or never representative of field condition rates.) Results from laboratory studies may significantly over- or underestimate biodegradation rates if laboratory environmental conditions differ from field conditions...Although useful in evaluating the biodegradation potential, microcosms can disrupt the normal structure of ecosystems and prevent the direct extrapolation of microcosm-determined biodegradation rates to field scale."

Two methods to approximate first-order rate constants are

- using a conservative tracer that is biologically recalcitrant and found in the dissolved plume

- using Buscheck's and Alcantar's (1995) interpretation of a steady-state contaminant plume (Reviewer's note: this procedure assumes the plume is at steady-state, which, under most conditions, is not a valid assumption.)

Modeling

Monitoring natural attenuation requires identification of a conceptual model, which must be verified with further data. Next, a fate and transport model can be chosen for the site. The model is calibrated with site data, then used to predict future extent and concentration of dissolved contaminant plume by simulating processes such as advection, dispersion, sorption and biodegradation. The authors caution practitioners that "When using a model that incorporates a biodegradation term, care should be taken to verify that assumptions made about degradation rates and the amount and activity of biomass are valid for the site in question. Degradation rates are sensitive to a wide array of field conditions that have been discussed. Extrapolation of laboratory-derived rates to a site can also lead to significant errors. Likewise, using models to derive degradation rates from limited field data where abiotic variables are not well defined can be misleading...Kinetic constants derived from laboratory microcosms or other sites are generally not useful on a wide scale to predict overall removal rates. Site-specific degradation rates should be developed and incorporated into a model" (Azadpour-Keeley and others, 2001).

Conclusions

The authors define four basic conditions that must be present to confirm effectiveness of natural attenuation:

- sampling points must be on the flow lines; increasing the number of sampling points and sampling frequency can increase confidence level

- contaminant mass or concentration reduction must occur in excess of that caused by dilution
- contaminant reduction conditions, with respect to mineral nutrients, electron acceptors, the state of redox, temperature and pH, must be appropriate
- claims of intrinsic or natural biodegradation must be supported by data – for instance, the relationship between mass loss and loss of oxygen; natural biodegradation processes will often result in the creation of byproducts such as dissolved Fe(II), Mn(II), HCO_3^- , and CO_3^{2-}

Factors that can limit application of natural attenuation include

- long time frames required to reach the desired goals
- site characterization investigations that may be more costly and extensive than proactive remedial techniques
- added responsibility of long-term monitoring and costs
- byproduct toxicity
- potential for continued contaminant migration (especially near a production well)
- required alternatives if natural attenuation fails to meet established goals
- lack of significant biodegradation processes

Heterogeneity concerns at MNA sites

Hurt and others (2001) offer the following perspective with respect to MNA at heterogeneous sites:

- "it is likely that many 'simple' sites would be determined to be complex if they were inspected more closely"
- due to economic constraints, "professionals are compelled to gather a less than desirable amount of information...and at some sites this may yield

perfectly accepted results if the limited amount of data is taken in the locations needed to accurately define the site...conversely, some sites will have less than optimal results if significant heterogeneities are missed"

- "it is unlikely that anyone truly knows when enough data has been collected because professional judgment or 'gut feelings' are typically used to make the determination"
- "outliers may define important aspects of the site, i.e., unknown hydrogeologic or contaminant heterogeneity"

Hurt and others (2001) examined a 1-acre, closed gasification site to determine if site heterogeneity was of a complexity to invalidate MNA. Field workers took direct-push (DP) samples near conventional wells. "Both conventional wells and DP sampling points were sampled by low-flow methods using peristaltic pumps. All samples were acquired within a 48-hour time span...relative hydraulic conductivity tests were conducted at each DP sampling interval by a DP field method."

Sampling results and BTEX analyses indicated that "dramatic differences in contaminant concentration were evident over relatively short lateral distances". Researchers also found that "hydraulic conductivity varied by *three orders of magnitude* over vertical distances as little as 1.5 feet". That both methods "detected alternatively higher or lower concentrations of contaminants in a given vicinity demonstrates the extreme variability of subsurface environments and the crudeness of conventional sampling techniques with respect to accurately detecting heterogeneities." (Reviewer's comments: the difference on contaminant concentration is probably entirely due to subsurface heterogeneity.)

Extreme variability in the vertical distribution of relative hydraulic conductivity also "illustrates the need to consider very limited, high permeability zones at potential remediation sites. Bulk aquifer testing would almost surely not yield groundwater velocities in the range detected in the discrete zones. The effect of this would be an overestimation of travel time between site and potential receptor that could possibly yield deleterious results if contaminants were allowed to migrate unimpeded."

Hurt and others (2001) suggest that at sites with a high degree of temporal heterogeneity, sampling frequency may not accurately characterize a site to meet the requirements of MNA assessments. The leading edge of the plume should be given extra consideration to determine that MNA is performing in a way to protect receptors.

Other sampling considerations

Nyer and Fierro (2001) give an example of what a soil core represents. If a core sample is taken every 100 feet, then a sample "represents a volume of 100 feet by 100 feet by 10 feet depth. Let's assume we are using a 3-inch core with a 2-foot length...we are basically sampling a 100,000-cubic-foot area and trying to represent it with a 1-cubic-foot sample. This is a .0001 percent sample volume of a nonmixed media" (Nyer and Fierro, 2001), which is not a representative sample. Authors caution those who work on remediation sites to understand that numbers gleaned from samples are approximations and may not truly represent a site.

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UTU thanks Kelly Hurt for his help on this article.



Plume management using barriers and MNA

A new approach for managing plumes at contaminated sites uses barriers in combination with the principles of monitored natural attenuation (MNA). Barrier-controlled monitored natural attenuation (BCMNA) integrates ideas of

- source containment
- monitored natural attenuation
- engineered source reduction (an optional component)

"In BCMNA, a vertical barrier with low hydraulic

conductivity is constructed around a source of contaminated groundwater. By applying hydraulic control inside the contaminated region, the contaminant can be metered out of the source area at a rate that takes maximum advantage of the natural attenuation capacity of the surrounding aquifer to reduce contaminant concentrations to safe levels at a downgradient point of compliance" (Filz and others, 2001).

"Vertical barriers can be formed by grouting, deep soil mixing with additives, steel sheet piles with interlock seals, polymer membranes and excavated trenches or panels that are backfilled with mixtures of soil, cement, slag and/or flyash. For contaminant containment, trenches backfilled with mixtures of soil and bentonite clay are most widely used in the United States. Construction of a soil-bentonite barrier typically involves mixing bentonite and water with trench excavation spoils to create a low hydraulic conductivity barrier. Costs for soil-bentonite barriers range from \$20 to \$80 per square meter (1995 dollars). With good construction practices and good quality control and quality assurance programs, the hydraulic conductivity of vertical barriers can be controlled" (Filz and others, 2001). Typically, barriers are constructed to entirely surround the contaminant.

Benefits of BCMNA include

- risk reduction because the barrier coupled with groundwater adjustment inside the contained area provides a greater degree of process control than is available with MNA alone
- cost savings
 - the vertical barrier decreases the need for monitoring wells, because the plume length is decreased in comparison to the plume for MNA alone

- the most cost-effective amount of active source reduction can be applied within the contained area

Remediation duration

Researchers developed a one-dimensional analytical model with several simplifying assumptions for screening purposes and preliminary barrier design, and for estimating remediation duration. Assumptions and model characteristics include

- no advective-dispersive transport in the direction transverse to groundwater movement
- first-order decay
- spatial distribution is not considered, e.g., redox state is not included
- transient contaminant transport within the barrier or aquifer prior to reaching steady state is not accounted for
- reduced reliability near the barrier (as opposed to areas downgradient)

Other considerations and limitations include the following:

- prior to implementation, sorption tests are recommended using site-specific barrier and aquifer materials
- feasible depth is limited by construction technologies and cost; as depth increases, cost increases
- cost effectiveness and risk reduction will be limited by absence of naturally occurring aquitard
- hard ground formations can interfere with barrier construction
- aquifer heterogeneity may limit MNA effectiveness downgradient from the barrier

Researchers recommend that 2-D and 3-D modeling be performed to address lateral dispersion. They suggest

applying this modeling "to a range of case studies to investigate the feasibility of BCMNA at real sites. This would permit assessment of the impact of aquifer heterogeneity (instead of the simplified 1-D representation) as well as consideration of transient phenomena instead of considering a steady-state plume" (Filz and others, 2001).

Reductive whey and oxidative ORC barriers

Barcelona and Xie (2001) installed a reductive whey and an oxidative ORC barrier at an MTBE research site. The aquifer here consisted of an uncontaminated, unconsolidated medium- to fine-grained sand and gravel (60-feet thick) underlain by lacustrine silts and clays (several hundred feet thick). The groundwater table is 3 to 6 m below ground surface.

Researchers performed tracer tests using Br, SF₆, MTBE and BTEX; they were able to "calculate oxidizing or reducing equivalents, develop mathematical models with knowledge of the flow field, and estimate their reactivity and lifetimes" (Barcelona and Xie, 2001). The information they acquired ultimately enabled them to estimate the following:

- barrier loading
- reactivity
- barrier reactive lifetime and assessment of remediation strategies

The test was conducted in the following three phases:

- first, field workers installed the whey barrier, which was used to "simulate the impact of the release of degradable constituents of fuels, which later results in the creation of an anoxic source zone"
- the second phase involved injecting a solution containing MTBE and BTEX

- the last phase involved installing a downgradient oxidizing barrier (ORC barrier) and evaluating MTBE degradation

The whey barrier is a "continuous source of reductive redox capacity, which depleted the available oxidants in the system. The change of the reduction capacity in the whey barrier was tracked by measuring the upgradient and downgradient O₂ concentrations." Researchers estimated that the in-situ lifetime of the whey barrier was from 1,631 to 2,031 days.

The ORC barrier

"The ORC mixture initially has a low permeability and forms a cement structure after reaction with water. Oxygen released from ORC must diffuse to the annular groundwater. In a relatively poorly mixed system such as a groundwater system, the reaction of MgO₂ with H₂O is expected to be fast enough for oxygen release to be controlled by the difference between the field saturation and local actual oxygen concentrations. The difference is the driving force for further release of oxygen. The release process, like the whey dissolution process, is likely subject to the effects exerted by the complicated mass transfer processes in the aquifer system" (Barcelona and Xie, 2001).

The total quantity of MgO₂ injected to create the ORC barrier was 109 kg, and the O₂ release rate was calculated at 63.2 g O₂/day, which gives an O₂ maximum concentration of 25.1 mg/L in the ORC. By plotting O₂ depletion vs. time, researchers estimated the lifetime of the ORC barrier at 482 days. They also suggest that high salinity and biological activity can accelerate the oxygen release rate from ORC.

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UTTU thanks Dr. Michael Barcelona, University of Michigan, for his help on this article.



Controlling galvanic corrosion in soil, part 1

By Jane M. Turner

Corrosion is a natural phenomenon that can often be controlled, once it is understood. Energy cannot be created or destroyed; it may be transformed from one form into another, but the total amount of energy never changes. Therefore, energy added to iron ores during processing into finished steel products is released when the finished metal product is placed back in the earth. The release of this energy is called corrosion. The relative positions of some metals in terms of the energy required to convert an ore to the metallic state are listed below in order of most to least energy required:

- potassium
- magnesium
- aluminum
- zinc
- chromium
- iron

- nickel
- tin
- copper
- silver
- platinum
- gold

For the corrosion process to occur, four items must be present:

- an anode
- a cathode
- an electrolyte
- a metallic path connecting the anode and cathode

ASTM G-15 defines an anode as "the electrode of an electrolytic cell at which oxidation is the principal reaction. Electrons flow away from the anode in the metallic path or external circuit. It is the electrode where corrosion occurs and metal ions enter solution." Cathode is defined as "the electrode of an electrolytic cell at which reduction is the principal reaction. Electrons flow toward the cathode in the [metallic path or] external circuit." An electrolyte is an ionic conducting substance in which the anode and cathode are immersed, and the metallic path is the external circuit that connects an anode to the cathode and permits the flow of electrons between the two. In general, if all four items are present, the metal requiring the most energy to produce (from an ore) will corrode at a faster rate than one that requires less energy.

One galvanic series of metals lists the potential of several metals and alloys in sea water with reference to a saturated calomel half-cell reference electrode. Another practical galvanic series (Table 1, pg. 9) lists metal potentials normally observed in water and neutral soils with reference to a copper/copper sulfate reference electrode. If a metallic path is installed

between any two metals listed in the series and the two metals are placed in the same electrolyte, the metal with the more negative potential will be anodic and corrode more rapidly, whereas the less negative metal will be cathodic and corrosion will be reduced or eliminated. For a corrosion reaction to occur, the reaction must be thermodynamically possible. The reaction will be spontaneous if the change in energy is from a higher state to a lower state as expressed by Gibb's free energy equation:

$$G = -nFE$$

where G = the change in Gibb's free energy

n = the number of equivalents

F = Faraday's constant

E = cell EMF in volts

The spontaneity of the reaction can be determined by the following:

G	E	Cell reaction
-	+	Spontaneous
+	-	Non-spontaneous
0	0	At equilibrium

The cell EMF is determined using the Nernst equation; however, the metal ion concentration is difficult to determine in practical situations, especially when surface oxide films form. The Nernst equation states:

$$E = E_o + rT/nF \ln Q$$

where E_o = EMF under standard conditions

r = universal gas constant

n = number of equivalents

F = Faraday's constant

Q = quotient of metal ion concentrations

T = temperature in °K

The practical galvanic series is useful when selecting materials for new construction and repairing an existing structure. A typical example is the repair of an old ferrous metal pipe by installing a new ferrous metal pipe section. A metallic connection between the buried new and old pipes creates a galvanic corrosion cell in which the new pipe will be the corroding anode, the old pipe will be the protected cathode, the metallic path is the pipe itself, and the electrolyte is in the soil. Galvanic corrosion of the new pipe will proceed. A more obvious problem is created when copper pipe or tubing is directly connected to steel. The steel will corrode to protect the copper (Table 1).

Practical Galvanic Series

Metal	Volts
Commercially pure magnesium	-1.75
Magnesium alloy (6% Al, 3% Zn, 0.15% Mn)	-1.6
Zinc	-1.1
Aluminum alloy (5% Zn)	-1.05
Commercially pure aluminum	-0.8
Mild steel (clean and shiny)	-0.5 to -0.8
Mild steel (rusted)	-0.2 to -0.5
Cast iron (not graphitized)	-0.5
Lead	-0.5
Mild steel in concrete	-0.2
Copper, brass, bronze	-0.2
High silicon cast iron	-0.2
Mill scale on steel	-0.2
Carbon, graphite, coke	+0.3

Table 1. Potentials normally observed in neutral soils and water, measured with respect to copper/copper sulfate reference electrode (Turner, 1987).

In addition to bimetallic couples and the connection of old ferrous pipe to new ferrous pipe, corrosion cells can also be caused by dissimilar soil conditions. These dissimilar conditions could be created by mixtures of different soils, differences in oxygen concentrations, soil pH, or partial encasement in concrete. Galvanic corrosion will also occur any time that a refined metal is placed in an electrolyte. Time to corrosion failure will vary according to the metal and the environment. These facts have been established and are recognized by the engineering community.

Federal law requires that USTs:

- must prevent releases resulting from corrosion or structural failure for the life of the tank
- must be cathodically protected against corrosion, constructed of non-corrosive material, and steel clad with non-corrosive materials
- have the tanks/liners made of materials compatible with the stored substances

Galvanic corrosion of buried steel tanks will, with time, result in perforation of the tank wall. Once perforated, the stored product is free to leak into the surrounding environment, polluting groundwater and soil. Corrosion failure is costly, and the public liability risks are even greater. These leaks can be virtually eliminated if a properly designed cathodic protection system is installed and maintained.

Design considerations

If corrosion will have a detrimental impact on the environment, resulting in increased or unacceptable maintenance/repair costs or reduced structural stability, the question becomes, "How do we prevent corrosion from occurring or at least slow it down to an acceptable rate?" A properly designed and maintained cathodic protection system can extend indefinitely the

life of a facility. When designing a cathodic protection system, the designer should ask several questions:

- What are the soil characteristics? (resistivity, pH, chemistry, moisture content, etc.)
- What is the intended life of the structure and the desired life of the cathodic protection system?
- What other facilities are in the area? Are the other facilities cathodically protected? If so, what type of system is being used?
- Is the structure coated with a high-quality coating?
- How much current is required to achieve cathodic protection?
- What type of system should be installed: galvanic or impressed?
- If an impressed current system is required, is ac power readily available?
- What time of year will construction take place?
- What would be the environmental impact of a corrosion failure?
- How was the existing structure installed?
- Is the structure electrically continuous?
- What provisions should be made to facilitate future testing?

Designing cathodic protection systems

Whether designing a cathodic protection system for new or existing structures, the designer must conduct certain tests. The results of these tests will determine which system, impressed or galvanic, is the best engineering choice. If the system is being designed for an existing structure, the first test will be to determine the amount of dc current required to achieve protection. This test is commonly called a current requirement test. Conducting the test requires the following items:

- temporary anode
- direct current (dc) source
- current interrupter
- shunts
- high impedance voltmeter
- reference electrode
- wire reel
- cable

The intent of the test is to actually install a temporary impressed current cathodic protection system, interrupt the current and record the structure-to-electrolyte potential at each test point when the current is on and off. This will provide information pertaining to electrical continuity and discontinuity and approximate current distribution. Polarization tests are run to determine how readily the structure can be polarized and to determine how much current will be required to achieve cathodic protection. The results of the polarization tests and past experience with similar structures will provide the designer with the information necessary to design an appropriate protection system.

If the system is being designed for a new structure, several items in addition to those already stated must be known:

- dimensions of the structure to be protected
- coating type
- structure location with reference to other structures

This information will assist the designer in determining the approximate current required.

Soil resistivity

Soil resistivity is typically measured according to ASTM Standard G57, Standard Method for Field Measurement of Soil Resistivity Using the Werner Four-Electrode Method.

Soil resistivity is a determining factor when calculating the current output of a galvanic anode or the voltage required for an impressed current cathodic protection system. After the anode type, size and shape are selected, the resistance of the anode-to-earth is calculated. If the resistance is too high, another size and shape anode may be required.

To determine the current output of a single anode installed vertically, the designer can use Dwight's equation to calculate the anode resistance-to-earth:

$$R_v = [(0.00521) (SR)/L] [(2.3 \log 8L-d)]$$

R_v = resistance of vertical anode to earth in ohms

SR = resistivity of electrolyte (or earth) in ohm-cm

L = length of anode in feet

d = diameter of anode in feet

Similar calculations are used for determining the resistance of multiple anodes and anodes installed horizontally.

For galvanic anode systems, the theoretical current output for each individual anode will be:

$I = \text{open circuit anode potential-expected polarized potential/anode-to-structure resistance (ohms)}$

The total resistance is derived by adding together total anode-to-earth resistance, wire resistance, resistance to earth of the pipeline and back voltage between the anodes and pipe. The current required is determined by conducting current requirement tests or polarization tests, or by calculating the total exposed surface area. The theoretical voltage required is calculated using Ohm's law ($E = IR$).

Soil chemistry

The design life of a cathodic protection system is dependent on the amount of current driven from the anode, the anode size, and composition of the anode.

As a structure polarizes, less current is required from the anode to maintain the polarized potentials so the anode life will be increased. Electrolyte chemistry will often determine the ease with which a structure can be polarized. For this reason, analyses for substances such as chloride and sulfides, and for moisture content, pH and soil moisture hardness are often suggested.

Electrolyte chemistry will also dictate which anode material to use. Zinc anodes are often used in low-resistivity soils and marine environments. Aluminum anodes are used in seawater, but do not operate well in soil. Magnesium anodes are used in both high- and low-resistivity soils. No anode is suitable for all applications. The sacrificial anode must be chosen with regard to its performance characteristics in a particular environment.

Part II of this article, to appear in *UTTU* Vol. 16, No. 4, will describe impressed current systems and galvanic anode systems.

Reference

Turner, J.M., "Controlling Galvanic Corrosion in Soil with Cathodic Protection," Corpro Companies, Inc., Chicago, Illinois.

UTTU thanks James T. Lary, Corpro Companies, Inc. (<http://www.corpro.com>), Medina, Ohio, for contributing this article.



Research notes

Bioremediation Kinetics of Crude Oil at 5°C

Gibb, A., Chu, A., Wong, C.K. and Goodman, R.H., *Journal of Environmental Engineering*, September 2001; <http://ojs.aip.org/eeo>.

Researchers recently have demonstrated that bioremediation of petroleum can occur at low temperatures and at rates close to those of bioremediation in more moderate environments. Gibb and others (2001) assert that "...there exists in nature microbes that have the ability to grow well at extreme temperatures. Indigenous microorganisms in cold climates often have adapted to the extreme conditions of the environment in which they live. It has been found that by providing these microbes with nutrients and O₂, which are frequently limiting, significant biodegradation rates can be maintained."

Researchers set up 14 experimental columns that contained 1,300 cm³ of soil: a poorly graded sand with an acceptable microbial concentration and an organic content of 0.73 percent. Soil bulk density and dry density were approximately 1.83 g/cm³ and 1.55 g/cm³. The soil was obtained from the greenhouse grounds on the University of Calgary campus. Conditions of the experiment included the following:

- air was injected into each column top at a rate of 4 ml/min
- test columns were kept at 5°C and ambient temperatures of 21°C
- a 2 percent oil concentration by dry weight of soil (i.e., 2 g of oil/100 g of dry soil) was used; this concentration was below the irreducible oil saturation level
- nutrients were added, with C:N:P in a ratio of 100:1.53:0.31
- nutrient-rich water was injected to prevent nutrient limitations
- daily analysis of off-gas was performed using a gas chromatograph
- microbial enumerations were performed at the beginning, middle, and end of the experiment

Mechanisms that can contribute to crude oil loss include volatilization, sorption, abiotic and biotic processes. Abiotic loss was not considered in these short-term experiments as such processes usually occur over years. To evaluate crude oil losses, researchers used the following methods:

- CO₂ production rates calculated from daily measurements of CO₂ concentrations in the column off-gas by GC
- cumulative ascarite II adsorption of CO₂
- volatile solids reduction
- total extractable hydrocarbon loss from soxhlet extraction

"Because crude oil in soil may inhibit, stimulate, or have no effect on degradation of soil organic matter, the CO₂ measured, therefore, represents the cumulative CO₂ evolved from crude oil and soil organic matter mineralization" (Gibb and others, 2001). The presence of oil would have no effect on soil organic matter degradation. "Therefore, the amount of CO₂ produced from the soil columns controls that were not contaminated with crude oil will be assumed to represent the amount of CO₂ produced from the degradation of soil organic matter in the contaminated soil columns" (Gibb and others, 2001).

Researchers found that after 105 days, CO₂ production rates in columns at 5°C and 21°C were essentially the same, implying that once bioremediation is in the stationary phase, temperature has no effect on hydrocarbon degradation rate. In the initial stage (growth stage, before the 105-day mark is reached), CO₂ production rates differed. Researchers noted that "From a biodegradability perspective, it appears that temperature only has an effect on the mineralization rate of the readily degradable hydrocarbon fraction (during the

initial growth phase). Temperature does not seem to affect the degradation rate of slowly degradable hydrocarbons."

Assuming that crude oil had no effect on soil organic matter degradation, researchers estimated the following degradation rates:

- 100 mg hydrocarbon/kg dry soil/day at 21°C during the growth phase
- 64 mg hydrocarbon/kg dry soil/day at 5°C during the growth phase
- 11 mg hydrocarbon/kg dry soil/day during the stationary phase

Researchers thus concluded that significant mineralization of crude oils can occur at cold temperatures.

Evidence for Simultaneous Abiotic-Biotic Oxidations in a Microbial-Fenton's System

Howsawkung, J., Watts, R.J., Washington, D.L., Teel, A.L., Hess, T.F. and R.L. Crawford, *Environmental Science and Technology*, Vol. 35, No. 14, 2001; <http://www.pubs.acs.org>.

Remediators can inject H₂O₂ into the subsurface, supplying oxygen to microorganisms to help degrade organic contaminants. Howsawkung and others (2001) report that H₂O₂ may also be important in the in-situ chemical oxidation of organic contaminants by Fenton-like reactions. "Although the presence of OH• can be measured both directly and indirectly, and procedures for quantifying microbial metabolisms are well established, evaluating the simultaneous activity of OH• and aerobic microbial metabolism is difficult because both are oxidative processes. Many compounds that are metabolized by aerobic heterotrophic metabolism (e.g., aliphatic and aromatic hydrocarbons) also react rapidly with OH•, making the two processes difficult to distinguish" (Howsawkung and others, 2001). This

paper describes the process researchers undertook to distinguish between OH•-mediated oxidation and heterotrophic aerobic metabolism to evaluate coexisting OH• oxidations and heterotrophic aerobic metabolism.

High Levels of Monoaromatic Compounds Limit the Use of Solid-Phase Microextraction of Methyl tert-Butyl Ether and tert-Butyl Alcohol

Black, L. and D. Fine, *Environmental Science and Technology*, Vol. 35, No. 15, 2001; <http://www.pubs.acs.org>.

Solid-phase micro-extraction (SPME) has been used to identify trace levels of MTBE and TBA (tert-butyl alcohol) in water. Researchers used this technique to analyze water samples containing high levels of BTEX compounds and trimethylbenzenes (TMBs). Results were poor if total aromatic compounds were above 1 ppm. This happens because the matrix effect of a high aromatic content causes an unacceptable decrease in the internal standard peak area. Compensating for this matrix effect by using a static headspace method, researchers successfully analyzed groundwater from 670 monitoring wells at 74 service stations. Thirty percent of the wells contained BTEX and TMBs above 1 ppm. Researchers concluded: "Both static headspace GC/MS and purge-and-trap GC/MS methods are good alternatives to the SPME method when samples containing high TPH or high aromatic content are suspected."

Additional papers of interest include the following:

"An Evaluation of Physicochemical Treatment Technologies for Water Contaminated with MTBE," Keller, A.A., Sandall, O.C., Rinker, R.G., Mitani, M.M., Bierwagen, B. and M.J. Snodgrass, *Ground Water Monitoring and Remediation*, Fall 2000; <http://www.ngwa.org>.

"Applications of Ultrasound in NAPL Remediation: Sonochemical Degradation of TCE in Aqueous Surfactant Solutions," Destailats, H., Alderson II, T.W. and M.R. Hoffmann, *Environmental Science and Technology*, Vol. 35, No. 14, 2001; <http://www.pubs.acs.org>.

"A Water Extraction, Static Headspace Sampling, Gas Chromatographic Method to Determine MTBE in Heating Oil and Diesel Fuel," Cummins, T.M., Robbins, G.A., Henebry, B.J., Goad, C.R., Gilbert, E.J., Miller, M.E. and J.D. Stuart, *Environmental Science and Technology*, preprint, April 2001; <http://www.pubs.acs.org>.

"Contaminant Vapor Adsorption at the Gas-Water Interface in Soils," Costanza, M.S. and M.L. Brusseau, *Environmental Science and Technology*, Vol. 34, No. 1, 2000; <http://www.pubs.acs.org>.

"Laboratory and Numerical Investigations of Air Sparging Using MTBE as a Tracer," Mortensen, A.P., Jensen, K.H., Sonnenborg, T.O. and E. Arvin, *Ground Water Monitoring and Remediation*, Fall 2000; <http://www.ngwa.org>.