



# Underground Tank Technology Update

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## MTBE field pilot test using HRC™

Researchers used hydrogen release compound, HRC™, at a dissolved MTBE plume site in the Upper Glacial aquifer in Long Island, New York. The organizations involved in this field application were the New York State Department of Environmental Conservation (NYDEC), the U.S. EPA, Environmental Assessment & Remediations (EAR), Regenesis and Microseeps, Inc. HRC™ is a polylactate ester that slowly releases biodegradation stimulants into an aquifer. Some studies (McLoughlin in Haas and Trego, 2001) have shown that HRC™ fosters methanogenic conditions and can be conducive to MTBE biodegradation (Haas and Trego, 2001).

### MTBE vs. BTEX

Laboratory studies have elicited some well-known facts about MTBE and BTEX:

- pure MTBE is about 30 times more soluble in water than pure benzene, with a concentration approaching 5 percent by volume (i.e., 48,000 mg/L)
- MTBE is three times more volatile than benzene, resulting in an increased probability of soil vapor emissions
- MTBE is 10 times harder to remove from water via aeration because its Henry's law constant is 10 times less than benzene
- MTBE does not sorb to aquifer material as readily nor is it as readily biodegraded as BTEX
- MTBE moves farther and faster than BTEX, and MTBE may occur deeper in aquifers than BTEX

Because of these differences, techniques designed to remediate BTEX often fail when applied to MTBE; in

addition, MTBE is often found with TBA (tert-butyl alcohol).

### Study area

Remediators were drawn to the Upper Glacial aquifer of Long Island because it had been extensively characterized. In addition, the NYDEC identified the aquifer to be susceptible to contamination. Aquifer characteristics include

- high hydraulic conductivity
- high average pore velocities
- low organic carbon
- high recharge rates (22 inches/year)

The aquifer's unconsolidated sediments are glacial outwash sediments "comprised of uniform, poorly sorted, fine to coarse sands with some randomly dispersed fine gravel and occasional discontinuous clay layers and clay lenses" (Haas and Trego, 2001). Effective porosity is 0.25–0.30. Groundwater here

- occurs at a depth of 3 to 10 feet, depending on location and seasonal conditions
- can occur in glacial outwash that is as thick as 75 feet, but a 60-foot saturated aquifer thickness is assumed
- has a gradient of 0.0024 ft/ft, generally to the south
- has a velocity of 1.86 ft/d

"A comparative evaluation of several three-dimensionally characterized MTBE plumes in the Upper Glacial aquifer of Long Island indicated that the hydrogeologic conditions on Long Island and within the water table aquifer...have contributed to the formation of extensive, long, narrow and three-dimensional dissolved MTBE plumes that plunge into the aquifer in response to recharge. The characteristics of MTBE plumes in the

Upper Glacial aquifer, in combination with abundant sensitive receptors (mainly drinking water supply wells), often render monitored natural attenuation (MNA) plume management strategies inappropriate, resulting in the need for plume control, frequently via pumping and treating" (Haas and Trego, 2001). Because a previous study (by John Wilson, USEPA, 2000c in Haas and Trego, 2001) had documented natural attenuation of subsurface MTBE under methanogenic conditions, remediators were encouraged to try using HRC™ at the New York site: HRC™ would ideally create methanogenic conditions conducive to MTBE biodegradation.

The spill source here is an active gasoline retail station, located in a residential zone surrounded by commercial areas. The nearest house is approximately 100 feet south of the source while a surface water canal is 4,100 feet downgradient from the source. The site investigation was initiated when someone reported gasoline vapor emissions from the nearby house in May 1998.

### Site investigation

Investigators initially installed 13 1-inch monitoring wells (using a direct push technology) to delineate the NAPL plume. The plume had trace amounts to a few millimeters NAPL. For the next four months, investigators conducted an accelerated site assessment program (ASAP) in which they acquired 316 groundwater samples. These samples were

- taken from 119 locations
- analyzed on site using a gas chromatograph with a photoionization detector
- used to make real-time decisions
- instrumental in adjusting future sampling point locations

- used to identify locations of permanent multilevel wells that would provide information on concentration, vertical gradient and plume movement

Duplicate groundwater samples from each location were sent to laboratories to confirm field analyses. New well locations were restricted by well access (homes were in the way); thus, locating the MTBE centerline involved estimation. Investigators also installed 17 dual-level monitoring wells. "Each dual-level monitoring well contained two individual sampling points set at total depths of 15 and 25 feet. These 1-inch diameter wells were installed in the study zone using direct push technology" (Haas and Trego, 2001).

### HRC™ characteristics and injection

"HRC™ is a form of polylactate ester that, when hydrolyzed, results in the release of biodegradation-stimulating constituents, including lactic acid, into an aquifer. Anaerobic microbes can metabolize the lactic acid, producing consistent, low concentrations of dissolved hydrogen. Other studies have shown that these constituents foster methanogenic conditions that advance the (biological) reductive dechlorination of perchloroethene (PCE) and trichloroethene (TCE). Numerous reports discuss the biodegradation of MTBE under aerobic conditions as well as microcosm studies in which MTBE biodegradation was observed under anaerobic conditions. However, limited reports document the natural anaerobic biodegradation of dissolved MTBE. Despite this, it has been observed that MTBE transport often occurs under anoxic conditions resulting from the biodegradation of other fuel constituents, such as BTEX, which deplete the available dissolved oxygen as well as other terminal electron acceptors. Therefore, an anaerobic biodegradation strategy is attractive due to its synergy with the existing geochemical conditions. Consequently, the study was conceived and designed

to test the ability of HRC™ to foster the anaerobic biodegradation of dissolved MTBE as the sole contaminant under methanogenic conditions" (Haas and Trego, 2001).

Investigators injected approximately 2,700 pounds of HRC™, approximately 27 pounds per location, close to the estimated MTBE plume centerline. "The targeted zone of the HRC™ injection was 11 feet to 29 feet below grade (BG), which encompassed the known thickness of the MTBE plume in this area. The HRC™ was injected using direct push technology (Geoprobe) and a high-pressure grout pump. Due to its viscous nature, the HRC™ was heated prior to injection to reduce the viscosity, but it was not diluted" (Haas and Trego, 2001).

### Tracer study

Field workers installed six 1-inch wells east of the plume centerline to act as injection points for a tracer study. Over a 6-hour period, workers injected 3,100 gallons of a 600 mg/L (Cl<sup>-</sup>) NaCl solution into the control portion of the MTBE plume. They then took hourly conductivity readings from key monitoring points, and weekly ones from other monitoring locations. Peak tracer travel time (26 days) was consistent with the predicted value (24.8 days).

### Sampling

After the ASAP investigations and installation of the three-dimensional monitoring network, sample round one, which included sampling of all points, occurred in the fall of 1998. Round two in the winter of 1999 "included most of the available monitoring points throughout the site, yet excluded some monitoring points that were outside of the known extent of the BTEX and MTBE plumes...the samples were field screened for pH, temperature and terminal electron acceptors. The

terminal electron acceptors (dissolved oxygen, manganese, nitrate, sulfate, ferrous iron and total iron) were analyzed in the field using test kits from the Hach Company. Temperature and pH were obtained using field instruments" (Haas and Trego, 2001).

Additional samples were taken in May 1999 prior to HRC™ injection and analyzed for MTBE and TBA, terminal electron acceptors (sulfate, nitrate, ferrous iron, total iron, and manganese), alkalinity, dissolved organic carbon, organic acids (lactic, pyruvic, acetic and propionic) and dissolved gases (oxygen, carbon dioxide, methane, ethane, propane, normal and isobutane, and hydrogen) and phospholipid and fatty acid (PLFA) and deoxyribonucleic acid.

A third major groundwater sampling and analysis event occurred within the HRC™ study area in the summers of 1999 and 2000. Only VOCs were sampled.

After HRC™ injection, 35 monitoring points were sampled in the fall of 1999 for VOCs, organic acids, and dissolved gases. In addition, field workers used a flow-thru cell to obtain oxidation reduction potential (ORP) measurements, and dissolved oxygen. To understand ongoing geochemical changes caused by the HRC™, researchers again took samples (VOCs, organic acids and dissolved gases) in December of 1999. They also obtained oxidation reduction potential (ORP) measurements.

A fourth major round of groundwater sampling occurred in the winter of 2000, when samples were analyzed for VOCs, terminal electron acceptors and organic acids. Field workers used a flow-thru cell to obtain ORP measurements.

### Results

Data analysis indicated the presence of an anoxic plume with MTBE remaining at the leading edge. Three of the four major sampling rounds indicated:

- depleted oxygen levels (< 1 mg/L)
- depleted nitrate levels
- presence of dissolved ferrous iron
- presence of dissolved manganese

The presence of manganese only in the areas of the contaminant plume is evidence "that aerobic biodegradation in this area has occurred, has progressed from the aerobic stage to the anaerobic stage, and has also progressed through nitrate reduction, ferric iron reduction and manganese reduction. Although sulfate levels fluctuated, there does not appear to be a pattern that would indicate sulfate reduction throughout the entire site" (Haas and Trego, 2001).

In the HRC™ zone, prior to injection:

- dissolved oxygen levels were depleted
- carbon dioxide levels were elevated
- background levels of soluble organic carbon were low
- low levels of acetic and propionic acid, the natural products of biodegradation, existed

In the HRC™ zone, after injection:

- no dissolved BTEX remained
- considerable levels of MTBE remained
- dissolved nitrate levels were low, and trends mirrored those of dissolved oxygen
- ferrous iron and manganese levels increased, but only in the treated part of the plume
- small decreases of sulfate and increases of methane were noticed but not deemed to be significant
- dissolved hydrogen concentrations suggested sulfate reduction conditions may have been achieved, but were not high enough to indicate methanogenic conditions at the time of sampling

- bacterial cell concentrations increased an average of 10-fold
- PLFA analysis indicated significant diversification of the microbial population, with increases in organic-matter-degrading bacteria and anaerobic metal-reducing bacteria
- ORP readings showed a decrease
- The vertical extent of the MTBE plume ranged from 15 ft bgs (below grade surface) to approximately 40 ft bgs; highest concentrations were found 25 ft bgs (in the HRC area) and 30 ft bgs (current MTBE plume location)

Haas and Trego (2001) stated that "over the course of the study, MTBE concentrations near the study zone fluctuated greatly. Due to these fluctuations, it is possible that small effects of the HRC™ in reducing MTBE concentrations may have been hidden." Researchers concluded that application of HRC™

- resulted in the formation of a large area of enhanced reducing conditions in the plume vicinity and downgradient
- failed to induce methanogenic conditions required for anaerobic biodegradation of MTBE
  - the high hydraulic conductivity and high average pore velocity were likely responsible for this failure, and may have diluted levels of lactic acid slowly released by HRC™ hydration
  - the high hydraulic conductivity and high average pore velocity could have impeded microbial evolution by prematurely washing contaminants/microbes out of the reduced zone, preventing sufficient time for the bacteria to acclimate to changing geochemical conditions

In addition, followup MTBE and TBA analysis suggest that TBA concentrations originally reported may have been a result of the acid preservation of the samples as

opposed to indicating MTBE biodegradation to TBA. Several months ago workers installed a pump-and-treat system (P&T) that has collected 2,547 lbs of MTBE and 788 lbs of BTEX. Wells near the source area collected 396 gallons of LNAPL (light non-aqueous phase liquid). An installed vapor abatement system (VAS) has collected approximately 19 lbs of MTBE and 191 lbs of BTEX. The VAS and P&T were part of an interim remedial measure, designed to prevent further impact to nearby residences. Recently workers installed a downgradient P&T and Sparge and Vent system to further mitigate the MTBE plume whose downgradient concentrations approach 30,000 mg/L (Haas, February 2002 and Trego, May 2002).

## Recommendations

Researchers suggest that future field studies consider using an HRC™ primer prior to HRC™ injection. They also suggest that a more frequent geochemical analysis would be helpful in identifying small HRC™-induced effects. In addition, others might consider using HRC™ at sites with lower groundwater velocities or at sites that show the propensity for methanogenic (reductive) conditions.

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## Applying the precautionary principle to gasoline additives

By Arturo Keller and Linda Fernandez

It has often been said that if gasoline had recently been invented, it could not obtain approval for today's marketplace, given its toxicological properties. Most human beings will be exposed to significant amounts of gasoline in their lifetime. Gasoline contains benzene and other aromatic compounds, and should be classified as a carcinogenic substance. In addition, given that the intended use is to combust gasoline for fuel, there should be significant concern with the known generation of hundreds of products of incomplete combustion, including aldehydes, carbon monoxide and many other potentially toxic organic compounds, as well as nitrogen oxides. After more than 100 years of use, gasoline continues to generate significant controversy, as the recent experience with MTBE indicates.

In addition to the toxicity of some gasoline components, the introduction of gasoline additives to improve the performance of the internal combustion engine continues to present challenges. Adding compounds to gasoline to improve performance dates back almost 80 years, starting with the introduction of tetraethyl lead (TEL) to gasoline to reduce engine "knock" by improving the octane rating. As early as the 1920s, public health experts, government officials and others were acutely aware of the dangers posed by leaded gasoline, yet TEL was added for over 60 years in the US, and continues to be used in many other countries. In the early 1970s, gasoline producers felt pressure to find substitutes for TEL. Industry studies as early as the 1950s indicated that several ethers, including MTBE and Ethyl

tert-Butyl Ether (ETBE), could improve gasoline's octane rating. MTBE could be produced from isobutylene, a refining byproduct. As TEL was phased out, MTBE began to be widely used at 2 to 3% by volume. Studies by the automobile and oil industry indicated that the use of these ethers could significantly improve gasoline combustion, reducing carbon monoxide emissions. Preliminary results from these studies led to the incorporation of an "oxygen content" mandate in the 1990 Clean Air Act Amendments (CAAA), for reformulated gasoline sold in areas where air quality standards were not being met. A number of other specific requirements were imposed on the new gasoline formulations; rather than specify performance requirements, legislators decided to dictate the way gasoline should be produced. For the most part, gasoline producers decided to use MTBE since it provided the required oxygen content and was in general easier to blend with gasoline than ethanol. In addition, MTBE was cheaper than ethanol in most regions. In some Midwestern states, gasoline was blended with ethanol to produce "gasohol."

At this time, MTBE's toxicological information was incomplete. Fate and transport data indicated that these compounds from LUSTs could travel far because of their fairly high water solubility. Little information on biodegradability potential existed. The concern was air quality; potential impacts on water resources was not an issue. Once again, economic considerations came first, without a full consideration of the oxygenates' life cycle.

MTBE began to make headlines when UST releases in the City of Santa Monica, California, resulted in the shutdown of several drinking water supply wells. The potential liability incurred was in the millions of dollars. Once it became accepted protocol to analyze for MTBE near USTs, as well as surface water reservoirs

where motor boats are allowed, it became clear that MTBE contamination was much more widespread than regulators had foreseen. In a very short time, MTBE began to be detected in hundreds and then thousands of wells around the country, wherever MTBE had been used since the phaseout of TEL (CAL-DHS, 1998).

Several alternative blending components have been identified for MTBE, including ethanol, toluene and alkylates. We are at a crossroads where important decisions will be made on chemicals that will be widely used, and it would seem that using the precautionary principle is appropriate. This article presents a review of the most relevant considerations regarding these various gasoline formulations and discusses the issues that should be evaluated before another costly mistake is made. We limit our scope to gasoline formulations, but clearly the precautionary principle could be applied more generally to the use of gasoline.

### Precautionary principle

The precautionary principle was first applied internationally in the context of marine pollution control, through the 1987 Declaration of the Third Ministerial Conference on the North Sea, as "action to avoid potentially damaging impacts of substances that are persistent, toxic and liable to bioaccumulate". Behind every major environmental policy decision is an element of scientific uncertainty. The 1987 Bergen Declaration clearly states that policymaking should not be postponed due to incomplete information where sufficient reason indicates that preventive action might diminish environmental impacts. One preventive measure that should be taken immediately is a full cross-media assessment of environmental impacts, and a determination of scientific uncertainties. Research to reduce these uncertainties should be an integral component of any new legislation involving substances produced in large quantities that

are persistent and toxic and can bioaccumulate. Any substance added to gasoline in a significant amount should be fully characterized with respect to its persistence, toxicity and bioaccumulation, since it is a given that it will be produced and distributed in large amounts. Failure on any count should be a reason to search for alternatives.

On practical terms, it is not feasible to demand that companies demonstrate that every substance is absolutely harmless. However, a framework for evaluating new compounds should be established based on sound scientific methods that relate chemical structure to activity (e.g. hydrophobicity, biodegradability, toxicity). Good science involves raising a yellow flag when it is probable that a new substance is likely to produce a bad outcome, and this should be followed by an aggressive research effort to ensure that all the environmental impacts have been assessed. The increasing liability issues raised by these substances should lead firms to apply the precautionary principle as part of a "best management practice."

### Analysis costs and benefits of gasoline formulations

The following study of the costs and benefits of three gasoline formulations that meet California's Phase II reformulated gasoline (CaRFG2) requirements was conducted in 1998, after CaRFG2 with MTBE had been in the California market for more than two years. The study included CaRFG2 with ethanol and non-oxygenated CaRFG2. An important component of our analysis was keeping track of our uncertainties, and to make sure that the final answers (net cost or net benefit) reflected such uncertainty. Thus, if a proposed alternative results in a net cost, even when all the uncertainties are considered, the precautionary principle indicates that research to reduce the uncertainties should be

started immediately, and the implementation of the alternative should be contingent on a new outcome (i.e., a net benefit).

The study, which was focused on California due to the funding source, can be easily generalized to all those areas (United States or around the world) where MTBE is being used or is under consideration. There will be some differences, given the diversity of opinions on the level at which water contaminated with MTBE should be treated (which significantly impacts treatment costs). In addition, the air quality benefits may differ, depending on the level of air pollution. Also, the uncertainties regarding cost of blending components (MTBE, ethanol, toluene, alkylates) will become greater in the short term if many regions switch to these compounds. Clearly the replacement of TEL by MTBE has produced major health benefits, although it is probably true that the same benefits would have been realized with alternative formulations that would not adversely affect water quality.

All costs and benefits for the different gasoline formulations evaluated are estimated relative to conventional gasoline, the typical gasoline formulation sold before the implementation of the 1990 CAAA. To simplify the analysis, we assume that each gasoline alternative is used 100% in California.

### Air quality benefits

In evaluating air quality benefits, we considered reduction in benzene and other toxic concentrations in the atmosphere, as well as the projected decrease in carbon monoxide and ozone concentrations from cleaner-burning reformulated gasoline. The health benefits are essentially the same across all three formulations; studies have shown that all formulations, within statistical significance, achieve essentially the same carbon monoxide and ozone precursor emissions

reductions. To derive a value of air quality benefits associated with reduced morbidity effects from decreases in carbon monoxide and ozone, we used the cost-of-illness approach, which sums medical expenditures and lost wages associated with morbidity. The total value of benefits from avoiding morbidity due to carbon monoxide is the sum of hospital and restricted days avoided, or \$9.6 million. The total value of benefits from avoiding morbidity due to ozone is the sum of hospital days and restricted days avoided, or \$8.8 million. Ambient concentrations may vary widely, spatially and temporally, even within an air basin. To simplify our analysis, we assumed that the one-hour average ozone concentration was uniformly distributed, which may result in an overestimate of benefits, since a smaller subset of the population is experiencing the higher concentrations.

As air quality improves, the impact (measured in absolute terms) of reformulated gasoline such as CaRFG2 on ambient air quality will decrease. As an example, for the year 2000, the decrease in benzene concentrations was estimated to be only 0.03 to 0.08 ppb; the reduction in cancer risk will be much smaller than at the introduction of CaRFG2. We therefore expect the human health benefits of CaRFG2 to decrease over the next few years. Decreases in human health benefits of MTBE or oxygenates will occur due to changes in the emissions control technology of the vehicle fleet. Thus, the benefits of adding oxygenates to gasoline formulations are relatively small and decrease with time. Oxygenates may drive up health costs because of their production of combustion byproducts such as formaldehyde.

### Air quality costs

MTBE combustion, because it is incomplete, causes a slight increase in formaldehyde concentration. Ethanol

combustion produces increases in acetaldehyde. Both of these aldehydes are known carcinogens. While air quality costs for MTBE may range from \$0 to \$27 million, the uncertainty in the magnitude of acetaldehyde emissions from ethanol combustion produces a cost estimate of \$3 million to \$200 million. This uncertainty could be reduced by collecting data in the Midwest and Brazil, where ethanol/gasoline has been sold for years.

Combustion of additional toluene or alkylates has not been shown to significantly increase the emissions of air toxics, but existing studies are limited, and additional work is needed.

### Water quality costs

The annualized cost (i.e., total cost divided by the number of years considered for treatment) of treating MTBE-contaminated surface and groundwater in California was estimated in 1998 to be \$340 million to \$1.48 billion per year (Fernandez and Keller, 2000). Cost of LUST cleanup incurred if conventional gasoline without MTBE had been used would have ranged from \$327 million to \$1.4 billion. If the UST technology and workmanship could deliver 100 percent leakproof tanks, the savings and reduced environmental impact would be considerable. (Unit water treatment costs were prepared based on experimental studies.) Groundwater remediation costs include the legacy of older leaking USTs in California that stored gasoline with MTBE, which will cost from \$320 million to \$1.03 billion per year to remediate. The projected cost of future leaks of MTBE from upgraded USTs is between \$7 million and \$370 million, with a large uncertainty concerning upgraded tank effectiveness.

Since ethanol biodegrades fairly rapidly, it would appear that the cost of using ethanol, in terms of risk to the water supplies, is low. Recent studies indicate that

the rapid biodegradation of ethanol at the leading edge of a groundwater plume would deplete dissolved oxygen. This can result in an extension of the BTEX plume of up to 30 percent, which might result in a larger number of BTEX plumes reaching drinking water wells. (Reviewer's comment: Alvarez found 60 percent). The organoleptic properties of water with low concentrations of ethanol have not been identified; some might not detect ethanol at low concentrations, and others might find it unacceptable in their drinking water. Such uncertainties have not been included in our analysis but should be, if ethanol is considered as an MTBE replacement.

For non-oxygenated gasoline, the differential cost of remediation and/or water treatment relative to conventional gasoline is small. The increased volumetric fraction of toluene in non-oxygenated CaRFG2 will result in higher initial toluene concentrations, but toluene is easily biodegraded by the intrinsic microbial communities. Treatment technologies are well developed. If isooctane is used instead of MTBE, it has a very low solubility in water and is readily biodegraded along with other components of conventional gasoline. Natural attenuation will likely be applicable at the same rates as for conventional gasoline. Aboveground treatment costs may increase at most 10 percent (relative to treating water contaminated by conventional gasoline), which translates to an annualized cost increase of \$600,000 to \$10 million.

### Direct costs

Blending MTBE with gasoline at 11 percent by volume results in an increase of 1 to 5 cents/gallon. The extra cost of using MTBE to meet CaRFG2 requirements, considering an annual consumption of 13.5 billion gallons, is \$135 million to \$675 million. Although small, the price increase is significant.

A California Energy Commission study indicated that the cost of using MTBE alternatives (including ethanol) ranged from 1.9 to 6.7 cents per gallon. This estimate includes transportation, blending equipment, and ethanol costs (the latter obtained from the Midwestern and Brazilian producers). The additional cost of producing a non-oxygenated gasoline is estimated to range from 0.9 to 8.8 cents per gallon or from \$141 million to \$1.3 billion per year.

Another component of the overall direct price is the effect of the blending components on fuel consumption. Gasoline consumption increases when oxygenates are added to conventional gasoline, due to the gasoline's reduced energy content. The opposite occurs for the non-oxygenated gasoline formulations, where the energy content increases by about 0.8 to 1.2 percent, depending on the amount of toluene or alkylate used.

A number of additional costs were identified in our analysis, including the damages to ecosystems, the economic cost of restricting motorboats at multi-use drinking water reservoirs, and legal costs.

### Conclusions

Clearly, reformulated gasoline with MTBE was an expensive solution to air quality problems. Once a thorough analysis of the costs and benefits is performed, spending \$1 billion to \$3 billion a year in California certainly seems unjustified. The major uncertainties we identified were MTBE biodegradation rate, toxicity and organoleptic properties. Existing fate and transport data indicated a possibility that any gasoline component, used in large quantities, could contaminate the environment and cause more damage than benefits. The belief that the upgraded USTs would eliminate all spills was perhaps a factor in the decision-making process of oil companies. Granted, a decade ago the information needed to make this analysis was not available, but the

cost of such a research program would have been low and could have been implemented and completed before the large-scale introduction of MTBE. Remarkably, even today, there has been no coordinated effort by national or international authorities to reduce the uncertainties associated with MTBE.

We realize that some of the costs for CaRFG2-MTBE overlap, and therefore the net costs represent an upper bound. For example, if water treatment costs are incurred to clean up a water supply, the costs for alternative water supply will not be incurred, except for the immediate supply of water prior to treatment being completed.

Our study considered MTBE replacements to begin the process of evaluating options. It would be unacceptable to find out, a few years from now, that we have a new problem with ethanol, toluene or alkylates. We have evaluated the existing information, and in our opinion the non-oxygenated option appears to create less risks than MTBE or ethanol. There are some clear benefits of using ethanol. Ethanol can be produced from biomass, a renewable resource. Using ethanol would reduce carbon dioxide emissions, a major greenhouse gas. The potential air quality damages need to be assessed, however, and the effect on the price of gasoline should be considered relative to other alternatives. We should evaluate the biomass source: if we can use current agricultural waste products (e.g. corn stalks, rice straw), then this will be a beneficial shift in the source of fuel supply. If significant deforestation, however, is necessary to produce enough ethanol, then other options should be explored.

Thus, we need to apply the precautionary principle to any gasoline blending component and insist on a thorough lifecycle evaluation of the implications of such a decision. We must be much more certain of the toxicity, persistence and bioaccumulation of gasoline

blending components: it is a given that these chemicals will be used in large amounts throughout the world.

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The views expressed in this article are those of the authors. *UTTU thanks Dr. Arturo Keller, [keller@bren.ucsb.edu](mailto:keller@bren.ucsb.edu), for helping UTTU with this article.*



## Controlling galvanic corrosion in soil, part 2

By Jane M. Turner

Part one of "Controlling galvanic corrosion in soil" appeared in *UTTU* Vol. 16, No. 3. This article, part two, describes impressed current systems and anodes, galvanic anodes, monitoring, backfill material, lead wire insulation, rectifiers, and groundbed geometry.

### Impressed current systems for piping systems in soils

Selecting an impressed current cathodic protection system leads us to consider a number of questions:

- What type of anode material should be used?
- How long should the anode material last?
- What type of lead wire connection should be used?
- Should the anodes be prepackaged or bare?
- Is special insulation required for the lead wire?
- What type of rectifier should be used?
- What type of groundbed geometry should be used? (distributed, remote, conventional, or deep?)
- Where should the groundbed be located?
- Is there sufficient right-of-way?
- Does the possibility of stray current interference exist?
- What type of test points and monitoring devices are needed?

### Impressed current anodes

Several types of impressed current anodes are available to the designer. Anode selection must be based on the system's desired life and the manner in which the anode is installed. The most common impressed current anodes are graphite and high silicon cast iron. The anodes come in a variety of sizes. The graphite anodes can be treated or untreated and the lead wire can be connected to the longitudinal center. The anode lead wire connection is a critical factor when determining the useful anode life.

More recent entries into the impressed current anode list are the precious metal oxide coated rod and wire. These anodes are specified and purchased according to the desired current output and life of the anodes.

When selecting anodes, the designer needs to consider the following items:

- anode material
- anode size (dimensions and weight)

- type of lead wire connection and encapsulation
- type of packaging and canister size

### Lead wire insulation

All lead wire used to connect the anode to the rectifier must be installed to prevent damage to the insulation. Any nick in the cable insulation that exposes the wire core will allow current to discharge from the cable, thus causing premature failure of the cable. Once the cable is severed, one or more anodes (depending on where the insulation damage occurred) will no longer be a part of the system. This has some rather obvious ramifications.

The typical wire and cable insulation specified for cathodic protection installations is a high molecular weight polyethylene (HMWPE) made to ASTM Standard D 1248, Specification for Polyethylene Plastics Molding and Extrusion Materials. In severe environments insulations such as polyvinylidene fluorides or fluoropolymers may be necessary.

### Backfill

Special backfill material is used around impressed current anodes placed in soil. This material is low resistivity, in the range of 50.0-0.1 ohm-cm, and consists of metallurgical or calcined petroleum coke. The particle size can range from dust to 3/4 inch and larger. The backfill material lowers the anode-to-earth resistance and provides a homogeneous environment for the anode. This permits uniform current distribution from the anode surface. The ionic energy transfer between an impressed current anode and earth theoretically takes place at the anode backfill-earth interface and thus extends the anode life.

Impressed current anodes can be purchased in pre-packaged canisters. The canister is fabricated from steel of sufficient length and diameter to contain the anode

and required amount of coke backfill. The ends of the canister are sealed with wooden or plastic plugs. The anode lead wire is extended through the plug at one end for connection to the rectifier or a header cable. If the installation procedures do not specify a prepackaged anode, the backfill material must be purchased separately and installed around the anode at the job site.

### Rectifiers

Every impressed current cathodic protection system requires an external direct current power source to force current to flow from the anodes to the structure being protected. This direct current power source is provided by a rectifier.

Rectifiers are typically powered by ac (some installations require solar power sources, wind generators, thermoelectric units, etc., due to unavailability of an ac power source.) The alternating current is rectified to direct current by diodes that allow current to flow in only one direction.

Rectifiers can be purchased to meet a multitude of design parameters. They can be ordered with automatic potential control, constant voltage, constant current, solid state with no tap settings or standard tap setting to adjust the output.

These can also be supplied with a variety of optional features, such as lightning protection for the ac input and/or dc output, indicator lights, efficiency filters and slide-out racks. Rectifiers can be air cooled, oil cooled, oil cooled-explosion proof, fan air cooled, or forced oil cooled. Transformers, ac input and the type of cabinet to house the rectifier must also be selected.

Because of the wide range of available components, rectifiers are normally custom built.

### Groundbed geometry

A groundbed in cathodic protection jargon refers to the anode(s) when they are placed in the earth relative to the structure being protected. Anodes can be distributed (Figure 1), concentrated (Figure 2), or a point source

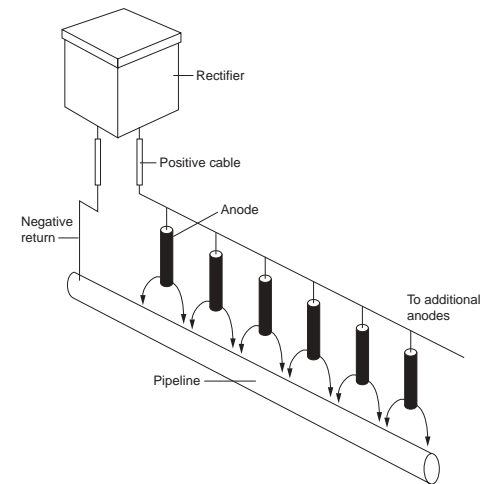


Figure 1  
Distributed Anode System

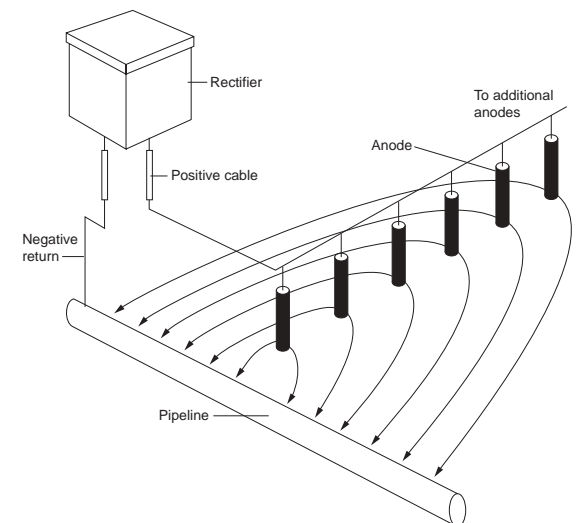


Figure 2  
Concentrated Anode System

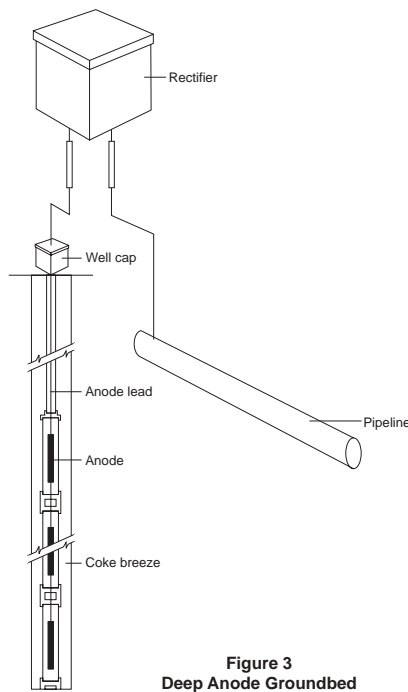


Figure 3  
Deep Anode Groundbed

(Figure 3). A point source is often termed a deep anode system. Each of the three systems has advantages and disadvantages, but the geometry selected is often dictated by existing conditions.

A distributed anode system is most useful when protecting large surface areas, which are either poorly coated or bare, where shielding due to congestion may be a problem, or where sufficient right-of-way is not available to accommodate a concentrated groundbed. A distributed system is more difficult to maintain when installed in areas where future construction could damage the anode collector cable. The collector cable, sometimes referred to as a header cable, is used to connect the anode lead wires to a main cable, which is then terminated at the rectifier positive connection.

A concentrated groundbed is most useful on well-coated structures regardless of the amount of surface area requiring protection. The cost of installing this type of system is generally less than the equivalent distributed system. Damage resulting from future construction would be minimized since the anode header cable would be remote from the structure.

A point source or deep anode groundbed has many advantages over either the distributed or conventional groundbed designs. The system can be installed in areas where open trenches and excavations must be kept to a minimum and right-of-way is restricted. The location of the system can be close to the structure being protected, when minimizing the probability of future damage is desirable. One disadvantage of this system is its higher installation cost when compared to concentrated groundbeds.

### Galvanic anode systems

A variety of galvanic anodes are available to the engineer for use in a galvanic anode cathodic protection system. Selection will depend on the following concerns:

- What type of anode material should be used?
- What size anode will give the desired system life?
- What electrical isolation is required to assure a properly functioning design?
- What types of monitoring devices and test points are necessary?

### Galvanic anode material

For steel and iron structures, the choices for galvanic anodes are more limited than for the impressed anodes. There are three types of galvanic anodes: magnesium, zinc, and aluminum. Magnesium anodes are by far the most widely used galvanic anode in soil. Zinc is used in

low-resistivity soils and in sea water, whereas aluminum is used primarily in sea water or brackish water.

Magnesium anodes are available in several grades, but those typically used are the high potential and the H-1 alloy. One of the significant differences between the two anodes is their solution potential. The potentials as compared to a copper/copper sulfate reference electrode are approximately  $-1.7$  volts and  $-1.5$  volts respectively. The difference in potential between the structure being protected and the anode, plus the soil resistivity adjacent to the anode, determines the amount of current available from the anode for protection.

Zinc anodes are more efficient than those made of magnesium; however, zinc's driving voltage is  $1/3$  that of the high potential magnesium. Because of this, zinc is primarily used in low-resistivity soils.

Aluminum anodes will passivate if buried in soil. Therefore, they are used only in sea water and brackish environments.

### Geometry

Galvanic anodes are either individually connected to the pipe being protected or placed on a collector (header) cable, which is then connected directly to the pipe or through a test station. The lead wire insulation on a galvanic anode system does not require the strength and durability of the impressed current anodes. This is because any nick in the galvanic anode lead wire insulation will normally be protected by the anode, provided that the protective current reaches the exposed conductor. In practice, care should still be taken to preserve the integrity of the insulation.

### Monitoring

Regardless of the type of protection system selected, it is important to provide a means for measuring performance. This is accomplished by installing test stations. A

test station can be used to monitor several facets of a cathodic protection system. Some examples where test stations prove beneficial are as follows:

- to monitor the actual current output of a galvanic anode and to provide means for interrupting output during testing of the system effectiveness
- to monitor the potential of the structure in an area that is not accessible to a portable reference electrode
- at crossings between pipelines protected by different cathodic protection systems
- to provide periodic connections to a structure, so that potential measurements can be made without needing to use hundreds or thousands of feet of wire
- at buried insulators

Test stations come in many sizes and shapes. The type of test station specified will need to endure the environment in which it is placed.

In part three (to follow in *UTTU* Vol. 16, No. 5), we will discuss installation procedures, impressed current anodes, inspection and maintenance.

## Reference

Turner, J.M., "Controlling Galvanic Corrosion in Soil with Cathodic Protection," 1988, Technical Paper Library, CP-17, Corpro Companies Inc., Chicago, Illinois.

*UTTU* thanks J.T. Lary, Corpro Companies, <http://www.corpro.com>, for his help on this article.



## Research notes

### Monitoring Biodegradation of Methyl tert-Butyl Ether (MTBE) Using Compound-Specific Carbon Isotope Analysis

Hunkeler, D., Butler, B.J., Aravena, R. and J.F. Barker, *Environmental Science & Technology*, Vol. 35, No. 4, 2001; <http://www.pubs.acs.org/>

A potential tool for monitoring in-situ MTBE biodegradation is carbon isotope analysis. Researchers recently developed a carbon isotope method for analysis of MTBE and TBA, which gives biodegradation and partitioning data (partitioning among the organic, aqueous and gas phases). Biodegradation studies included

- microcosms amended with MTBE
- microcosms amended with MTBE and 3-methylpentane (as a co-substrate)

According to Hunkeler and others (2001), "The method relies on the occurrence of a kinetic isotope effect during biodegradation of inorganic or organic compounds, whereby molecules with light isotopes react faster than molecules of the same compound with heavy isotopes. As a result, a characteristic difference in the isotope ratio between precursor and product occurs (isotope fractionation), and the precursor becomes increasingly enriched in the heavy isotopes as degradation proceeds. Large shifts in the carbon isotope composition of the remaining contaminant have been observed during reductive dechlorination of chlorinated ethenes, aerobic oxidation of dichloromethane, and aerobic oxidation of 1,2-dichloroethane. In contrast, smaller shifts occurred during biodegradation of

aromatic hydrocarbons. One of the reasons for this difference is that the kinetic isotope effect mainly occurs with respect to the atoms of the bond that is formed or broken in the initial transformation step, while the measurement yields the average isotope ratio of all atoms of an element in the compounds. Therefore, an enrichment of heavy isotopes is more likely to be detectable for small molecules. Given that MTBE and TBA contain only 5 and 4 carbon atoms, respectively, it is reasonable to expect detectable carbon isotope fractionation during their degradation."

Stable isotope analysis can potentially be used for biodegradation analysis if

- a kinetic isotope effect occurs during biodegradation
- the magnitude of the potential isotope fractionation associated with biodegradation is much larger than the isotope fractionation associated with physical processes

The physical processes of concern include dissolution of MTBE from gasoline, and advective and dispersive transport; sorption and volatilization would not be significant. In addition, advection and dispersion are not expected to significantly alter isotope ratios of dissolved components. Researchers found from their laboratory experiments that "dissolution of MTBE from an organic phase is not accompanied by significant carbon isotope fractionation, at least not under equilibrium conditions. Thus, physical processes are not expected to lead to significant changes of the  $\delta^{13}\text{C}$  of dissolved MTBE. In contrast, biodegradation of MTBE and TBA is accompanied by a systematic shift of the  $\delta^{13}\text{C}$  values. For MTBE, a significant shift (two times the uncertainty of measurement) occurs after 33% degradation, and for TBA after 13% degradation...The analytical method developed in this study makes it possible to determine compound-specific  $\delta^{13}\text{C}$  values of MTBE to concentra-

tions below the EPA advisory level. It is therefore well-suited for practical applications" (Hunkeler and others, 2001).

### Electrokinetic Barrier to Prevent Subsurface Contaminant Migration: Theoretical Model Development and Validation

Narasimhan, B. and R. Sri Ranjan, *Journal of Contaminant Hydrology*, Vol. 42, 2000; <http://www.elsevier.com/locate/jconhyd>

Electrokinetic remediation has proved effective in removing heavy metal contaminants like lead, copper, cadmium, nickel and zinc and other contaminants such as hydrocarbons. "The idea underlying the electrokinetic barrier to prevent contaminant migration is simple. A counter-gradient opposite in direction to that of the groundwater gradient is created by the continuous or periodic application of an electrical potential difference between the electrodes. This will halt the movement of water within that region and prevent contaminant migration. The contaminant migration is mitigated by the combined effects of electro-osmosis and effective ionic mobility of the contaminant in the soil under the influence of an imposed electric field. However, applying the electric current continuously over a long period of time results in several complications. These complications arise from the development of a sharp acid-base front causing the voltage and hydraulic gradient to become highly non-linear which, in turn, decreases the electro-osmotic flow rate. Modeling these changes and the contaminant transport under the coupled electrical, hydraulic and chemical gradients will be helpful for the successful application of this technique in preventing contaminant migration" (Narasimhan and Sri Ranjan, 2000).

Researchers developed a model to simulate contaminant migration in soil under coupled hydraulic, electrical and chemical gradients. The model can also predict changes in the soil such as pore water pressure, pH and voltage gradient as a function of time and distance from an electrode. This model was validated in the lab by monitoring contaminant transport through a compact clay.

### Articles of additional interest include the following:

"Analytical Model for Removal of a Uniformly Distributed Single-Component NAPL Under Nonequilibrium Conditions," Brouwers, H.J.H. and D.C.M. Augustijn, *Ground Water Monitoring and Remediation*, Summer 2001; <http://www.ngwa.org>.

"Enhancements of Nonpoint Source Monitoring of Volatile Organic Compounds in Ground Water," Lapham, W.W., Moran, M.J. and J.S. Zogorski, *American Water Resources Association*, Vol. 36, No. 6, December 2000; <http://www.awra.org/>.

"Fate of Treated and Weathered Hydrocarbons in Soil: Long-Term Changes," Loehr, R.C., Webster, M.T. and J.R. Smith, *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, April 2000, Vol. 4, No. 2; ASCE, 1801 Alexander Bell Drive, Reston, Virginia 20191-4400.

"Feasibility of Electrokinetic Soil Remediation in Horizontal Lasagna™ Cells," Roulier, M., Kemper, M., Al-Abed, S., Murdoch, L., Cluxton, P., Chem, J.L. and W. Davis-Hoover, *Journal of Hazardous Materials*, B77, 2000; <http://www.elsevier.nl/locate/jhazmat>.

"Hydraulic Tomography: Development of a New Aquifer Test Method," Yeh, T.C.J. and S. Liu, *Water Resources Research*, Vol. 36, No. 8, August 2000; <http://www.agu.org/wrr/>.

"Inferring the Relation Between Seismic Slowness and Hydraulic Conductivity in Heterogeneous Aquifers," Hyndman, D.W., Harris, J.M. and S.M. Gorelick, *Water Resources Research*, Vol. 36, No. 8, 2000; <http://www.agu.org/wrr/>.

"Soil Gas Transport Above a Jet Fuel/Solvent Spill at Plattsburg Air Force Base," Ostendorf, D.W., Hinlein, E.S., Lutenegger, A.J. and S.P. Kelley, *Water Resources Research*, Vol. 36, No. 9, September 2000; <http://www.agu.org/wrr/>.

"Solute Transport Through Unsaturated Soil Due to Evaporation," Mohamed, A.A., Sasaki, T., and K. Watanabe, *Journal of Environmental Engineering*, September 2000; <http://ojps.aip.org/eeo>.

"Summary of Workshop on Biodegradation of MTBE," U.S. EPA and API, February 1-3, 2001, U.S. EPA Office of Research and Development, EPA/625/R-01/001A, Washington, D.C. 20460.

"Volatile Organic Compounds in New Automobiles: Screening Assessment," Grabbs, J.S., Corsi, R.L. and V.M. Torres, *Journal of Environmental Engineering*, October 2000; <http://ojps.aip.org/eeo>.



## Information sources

### U.S. EPA publications and information

One of numerous publications that can be downloaded from <http://clu-in.org/techpubs.htm> includes

- NATO/CCMS Pilot Study Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III), 2001 Annual Report (EPA 542-R-02-001)

## U.S. EPA Web sites

BASINS, Better Assessment Science Integrating Point and Nonpoint Sources software, <http://www.epa.gov/ost/basins>

Central Data Exchange, which contains data on vastly different environmental programs, <http://www.epa.gov/cdx>

Introduction to Environmental Geophysics, <http://clu-in.org/studio>

Literature on Open-Path Monitoring Technologies, <http://clu-in.org/21m2>

MTBE Treatment Profiles Web Site, <http://clu-in.org/products/mtbe>

Pay-for-Performance Toolbox, <http://www.epa.gov/oust/pfp/toolbox.htm>

Performance Comparison: Direct-Push Wells vs. Drilled Wells (TR-2120-ENV), <http://clu-in.org/techpubs.htm>

Workshop on Monitoring Oxidation-Reduction Processes for Ground Water Restoration (EPA 600-R02-002), <http://www.epa.gov/ada/pubs/reports.html>

## Other Web sites

The Bureau of Land Management and USDA Forest Service have launched the GeoCommunicator Web site, <http://www.geocommunicator.gov>, providing geographic location and access information.

ITRC Diffusion Sampler Information Center, <http://diffusionsampler.itrcweb.org/common/default.asp>

Technology Evaluation Report: Permeable Reactive Barriers: A Case Study Review (TE-01-01), <http://www.gwrtac.org/pdf/prbtm.pdf>

Technology Evaluation Report: Phytoremediation of Soil and Groundwater (TE-02-01), [http://www.gwrtac.org/pdf/phyto\\_e\\_2002.pdf](http://www.gwrtac.org/pdf/phyto_e_2002.pdf)

Technology Status Report: A Catalogue of the Horizontal Environmental Wells in the United States (TS-02-01), <http://www.gwrtac.org/pdf/hor-wells.pdf>

The journal *Ground Water Monitoring and Review*, <http://www.ngwa.org>, offers the following information online:

- Afghanistan water summary
- testimony on terrorism threat to water infrastructure
- information on how to join an Ezine and a Newszine

## Other information

The editors of *The Encyclopedia of Water* are seeking written contributions for their encyclopedia; see <http://www.WileyWater.com> for details.

*Living with Karst, a Fragile Foundation*, is available from the American Geological Institute. Call 703-379-2480 or e-mail [pubs@agiweb.org](mailto:pubs@agiweb.org).

For information on U.S. environmental markets: 2001-2004, visit the Web site, <http://www.zweigwhite.com/store/inenv>

UTTU obtained this information from *Ground Water Monitoring and Review* (<http://www.ngwa.org>) and *TechDirect* (<http://clu-in.org/techpubs.htm>).

UTTU thanks the editors and writers for allowing us to reprint this information.