environmental MANAGEMENT

Electrolytic respirometry taps bioremediation's potential for site cleanup

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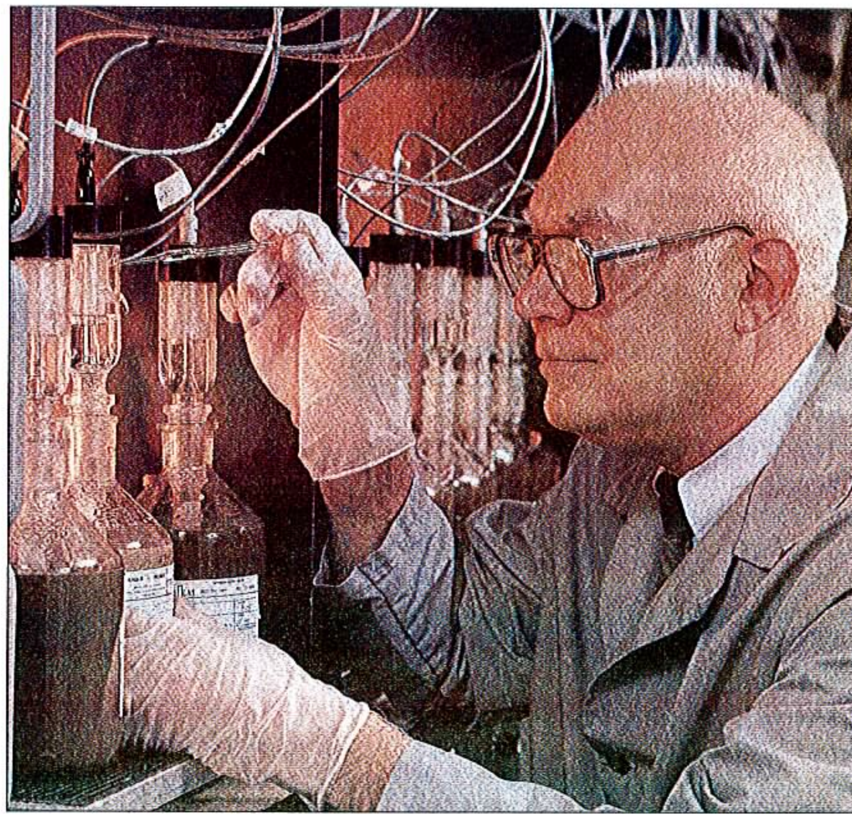

OHM REMEDIATION SERVICES CORP.

ELECTROLYTIC RESPIROMETRY SINCE 1980 has been the workhorse of biological wastewater treatment monitoring and research. Electrolytic respirometers measure microbial populations' oxygen uptake in treatment vessels where oxygen is generated by electrolysis in a closed system. Oxygen uptake under these conditions is a direct, continuous measurement of the amount of biodegradation that occurs.

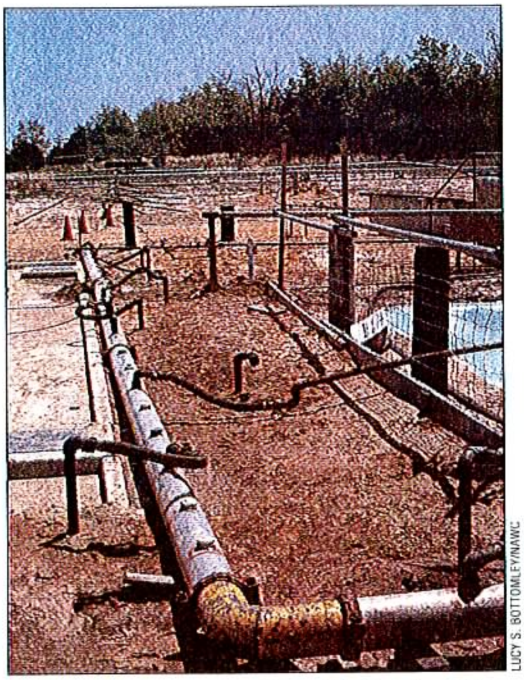
Electrolytic respirometry is used for toxicity testing, determining biodegradability, process monitoring and other analyses to determine the effects of various substrates on biological activity. It also is used in conjunction with biokinetic software packages to design and control biological processes in such applications as activated sludge treatment and groundwater remediation. Using appropriate treatment vessels, respirometry also can determine the biodegradation potential of contaminants in soils and sludges.

Electrolytic respirometry was commercialized in the 1970s to automate and expand the capacity of earlier manometric devices, which were air-fed, labor-intensive and limited in oxygen-transfer capacity. In today's electrolytic respirometer treatment vessels, microorganisms assimilate oxygen and emit carbon dioxide, which is removed by a scrubber, lowering the pressure within the closed vessel. When the pressure is lowered sufficiently, it causes an electrolyte to make contact with a trigger electrode. Platinum electrodes then generate oxygen by electrolysis of water. Oxygen is generated and resupplied until demand within the vessel is satisfied, and electrolysis then is terminated. The electric current required to supply make-up oxygen to treatment vessels is converted mathematically into biochemical oxygen demand data and reported as a concentration in parts per million. The operation is highly accurate and reproducible.

Special treatment vessels have been developed to evaluate high- and low-strength wastes for cases in which the rates of oxygen transfer or carbon dioxide removal limit the applicability of standard, 1-liter treatment vessels (Figure 1).

Groundwater treatability study. In one of its first uses of electrolytic respirometry, OHM Remediation Services Corp. of Findlay, Ohio, performed a treatability study of groundwater contaminated with ethylene glycol. A break had occurred in a lined storage lagoon containing about 4,000 gallons of cooling water (25 percent volume/volume ethylene glycol) at the Naval Air Warfare Center in Lakehurst, N.J. Groundwater at the site was contaminated at an average concentration of 1,440 ppm.

Ethylene glycol was known to be degradable under aerobic and anaerobic conditions. However, because site-specific conditions can affect biodegradation rates, a treatability study was required to assess whether an environment was present that was toxic or inhibitory to microbial growth, and to evaluate techniques that would enhance natural biodegradation.



Electrolytic respirometry studies verified that *in situ* biological treatment was a viable option for remediating ethylene glycol-contaminated groundwater.

Table 1

Experimental design for treatments in electrolytic respirometer vessels used to establish biodegradation potential of ethylene glycol in a composite groundwater sample.

Vessel number	Treatment
	Natural bacterial flora
1	Groundwater + basal salts + TCMP
	Toxicity/inhibition control
2	Groundwater + basal salts + TCMP + glucose
3	Laboratory-grade water + basal salts + TCMP + glucose + inoculum of indigenous bacteria
	Abiotic control
4	Groundwater + basal salts + TCMP + poisons

Figure 1. Treatment vessel for use with ER-100 or BI-1000 electrolytic respirometer.

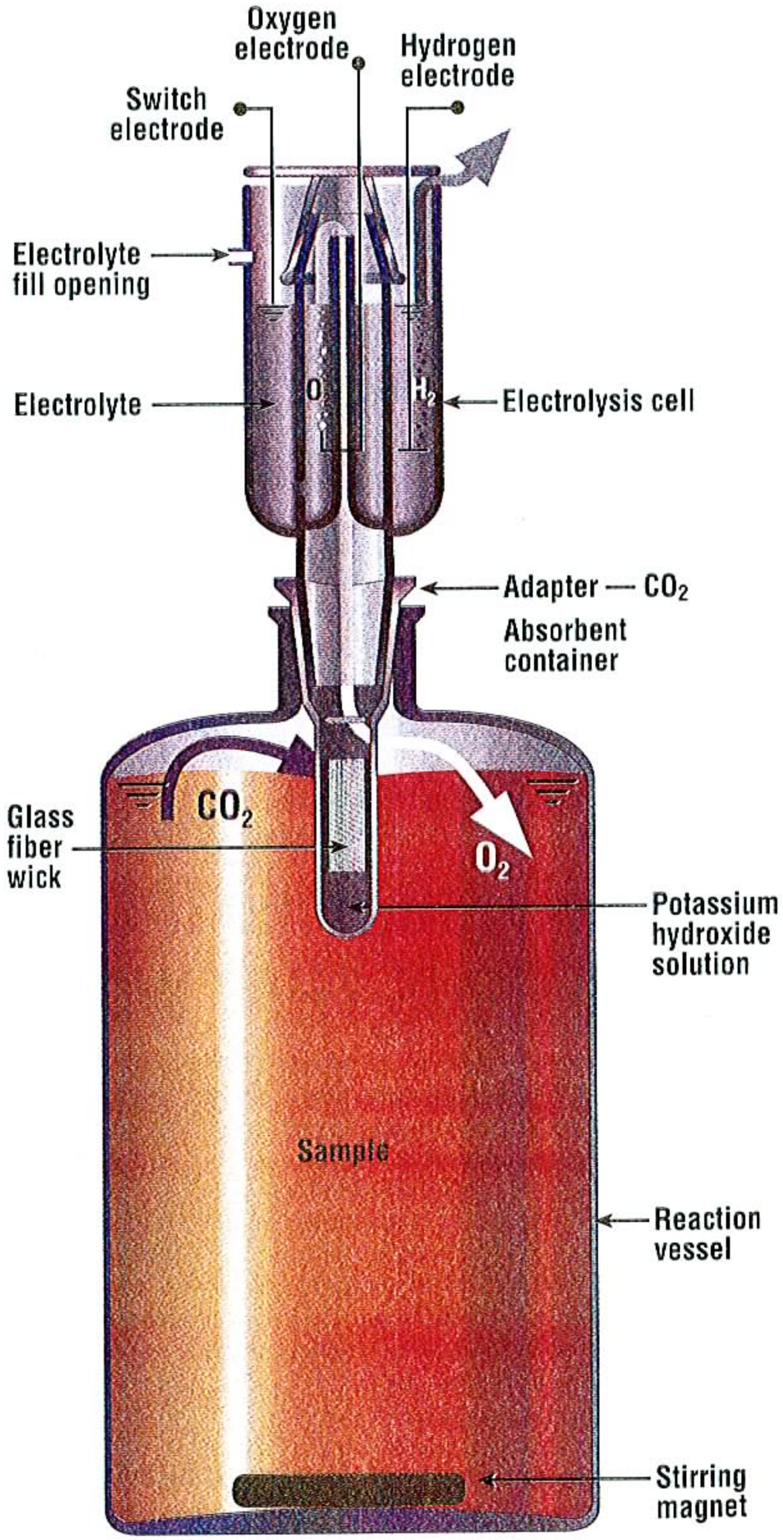


Table 1 presents the experimental design for the treatability study. Vessel 1 demonstrated the biodegradation potential of ethylene glycol for naturally occurring or indigenous microflora already present in site groundwater. Comparison of oxygen uptake rates in vessels 2 and 3 was used to determine whether significant quantities of toxic or inhibitory substances were present in the site matrix groundwater. Vessel 4 was an abiotic control to quantify nonbiological loss of ethylene glycol.

To supply the inorganic nitrogen required for bacterial growth, ammonium nitrate was added to each 1-liter treatment vessel to a final concentration of 1 gram per liter. Nitrification was inhibited by adding 10 milligrams of 2-chloro-6-(trichloromethyl) pyridine, so that oxygen uptake would be the result of only carbonaceous demand. Sodium dihydrogen phosphate (monohydrate) neutralized to a pH of 7.2 with potassium hydroxide served as a buffer and a source of available phosphorus to support enhanced bacterial growth on ethylene glycol. Glucose was added to a final concentration of 1 gram per liter in the toxicity/inhibition control (vessels 2 and 3), while the abiotic control received the microbial poisons mercuric chloride, potassium cyanide and sodium azide to final concentrations of 100, 320 and 320 ppm, respectively.

Figure 2 shows oxygen uptake data for the composite groundwater sample in vessel 1. No loss of ethylene glycol was observed in the abiotic control. These results and the calculation of theoretical vs. ultimate BOD (BOD_u) suggested that ethylene glycol was completely oxidized to carbon dioxide and water without the accumulation of incomplete oxidation products. With a calculated BOD_u of 1,700 ppm, an estimated 170 ppm ammonium-nitrogen and 17 ppm phosphate-phosphorous would be required in the groundwater to prevent nitrogen and phosphorus from limiting microbial growth during biological treatment.

The lack of significant lag periods in oxygen uptake and ethylene glycol degradation indicated that indigenous microflora were adapted to ethylene glycol. The groundwater appeared to be slightly stimulatory to bacterial growth, as evidenced by the slightly higher rate of oxygen uptake in the composite sample compared to the glucose-basal salts control (Figure 3).

Treatability study results showed that *in situ* biological treatment was a viable option for remediating the ethylene glycol-contaminated groundwater. The management approach for the project was to enhance the natural biodegradation rate by adjusting the

Figure 2

Biodegradation of ethylene glycol in an electrolytic respirometer treatment vessel containing the composite groundwater sample (vessel 1).

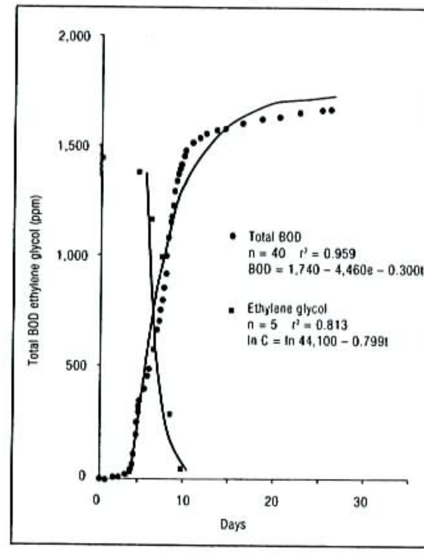
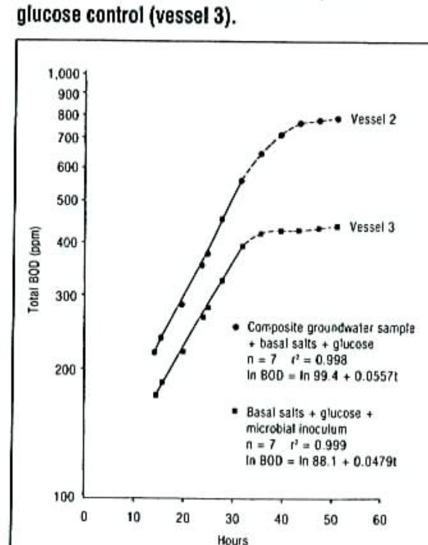


Figure 3

Oxygen uptake in the composite groundwater sample containing glucose (vessel 2) and in a glucose control (vessel 3).



pH of the groundwater and adding mineral nutrients. This was accomplished by treating extracted groundwater in an aboveground reactor and re-injecting the treatment-system effluent into the vadose zone, creating a closed-loop system in which biodegradation occurred in the soil and groundwater environment, as well as in the aboveground reactor. Between 85 percent and 93 percent of the ethylene glycol was removed from the groundwater environment within the first 26 days of treatment. At the end of a six-month maintenance phase, the ethylene glycol was reduced to a level below the analytical limit of detection in all production wells at the site.

Dichloromethane bioremediation. The ease of using electrolytic respirometry led to another project in which the technique was used to determine the potential for remediating groundwater contaminated with dichloromethane. Bioremediation was considered for residual cleanup after air stripping of recovered groundwater had reduced dichloromethane contamination from 9,300 ppm to 300 ppm, with an 11 day half-life for removal.

Biodegradation of dichloromethane under aerobic conditions in the laboratory is well documented in the literature. However, it is necessary to determine biodegradation potential by indigenous microflora in the groundwater before onsite biological treatment can be performed. This is because unknown compounds in a site matrix may — independently or synergistically — inhibit microbial growth. Dichloromethane loss and chloride release resulting from biodegrading dichloromethane in electrolytic respirometer treatment vessels were used as the test parameters; groundwater recovered from the site was used for the treatability study. Treatment vessels were inoculated with sludge collected from one of the plant's industrial wastewater treatment basins. Sludge from the basin reportedly was exposed to low levels of dichloromethane over the years and was thought to contain populations of bacteria acclimated to dichloromethane.

Table 2

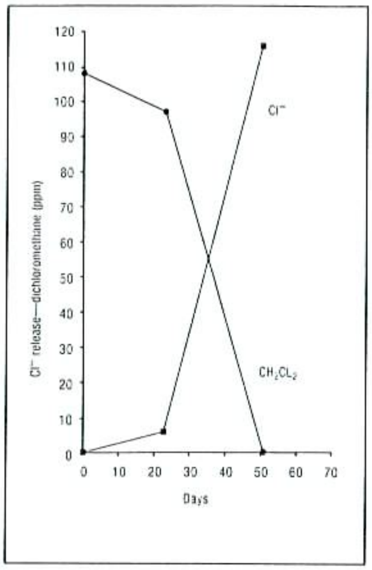
Experimental design for treatments in electrolytic respirometer vessels used to establish biodegradation potential of dichloromethane (DCM) in a composite groundwater sample.

Vessel number	Treatment
	Natural bacterial flora
1, 2	Groundwater + DCM + basal salts + sludge inoculum
	Abiotic control
3, 4	Groundwater + DCM + basal salts + sludge inoculum+ poisons

Table 2 shows the treatability study's experimental design. Dichloromethane was added to all respirometer treatment vessels to a final concentration of 100 ppm, approximating the average concentration remaining in groundwater at the site. Vessels 1 and 2 were replicates that demonstrated the potential of indigenous microflora to degrade

Figure 4

Biodegradation of DCM with chloride release in an electrolytic respirometer treatment vessel containing a representative groundwater sample.



dichloromethane. Vessels 3 and 4, the abiotic control, were designed to quantify any nonbiological loss of dichloromethane. Mineral nutrients were added to treatment vessels to support microbial growth. Aliquots were removed from treatment vessels periodically and analyzed for dichloromethane and chloride. The aliquots also were analyzed for pH and concentrations of mineral nutrients, such as ammonium-nitrogen and phosphate-phosphorous.

Neither dichloromethane loss nor chloride release by indigenous microflora was observed in the abiotic control (Figure 4). Bacterial acclimation to dichloromethane occurred within one day. Bacteria from the plant's wastewater treatment system used in the treatability study later were used to start an aboveground biological reactor for treating recovered groundwater before reinjecting it into the contaminated soil and groundwater environment. Before the sludge inoculum was used, microflora in soil collected near the ruptured pipeline had been used to inoculate the treatment vessels. Dichloromethane biodegradation was not observed during two weeks of observation while using those organisms.

Based on treatability study results, biological treatment at the site was begun using a batch reactor seeded with bacteria from the plant's wastewater treatment system. Continuous treatment of dichloromethane was initiated after two weeks. Removal of dichloromethane from the groundwater environment was rapid. Interrupted by freezing weather, biological treatment continued later, reducing the dichloromethane concentration to less than 1 part per billion, representing more than a 500,000-fold reduction in concentration following the pipeline rupture. Biological treatment far exceeded the ability of physical treatment alone to remediate this groundwater environment.

Using electrolytic respirometry in preliminary site studies provides remediation contractors with a cost-effective tool for assessing bioremediation's potential for cleaning a site. Besides determining biodegradation rate, molecular oxygen and mineral nutrient requirements, the method allows comparison of treatments for enhancing site contaminants' natural biodegradation rate. The results electrolytic respirometry produces are readily transferable to full-scale biological treatment, and the method's predictability allows confident use of its parameters in process design. □

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