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AN INTERNATIONAL WORKSHOP ON SOLVENT SUBSTITUTION

Mediated Electrochemical Oxidation of Organics

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Introduction

Replacement of halogenated with nonhalogenated and toxic with nontoxic solvents is a worthy goal being sought within the DOE and DOD complexes. Today however, the substitutions that would be suitable are not all identified. Consequently, there is continuing production of both hazardous waste and mixed (hazardous-radioactive) waste. Furthermore, existing backlog inventories of halogenated solvents at many sites must be addressed, probably through some kind of destruction technology. Commercial technology exists for destruction of very dilute solutions of halocarbons in water. We are seeking nonincineration technologies suitable for destroying concentrated streams of various toxic organics.

Operating Principles

Some metal ions, when dissolved in nitric or some other mineral acid, can have their valence state raised at the anode of an electrochemical cell. One such metal ion is Ag^+ which can be raised to Ag^{++} without significant oxidation of water at the anode. This is particularly true if the anode is made of a material that exhibits a reasonably high oxygen bubble overpotential, such as Au or Pt. Other examples of metal ions that may be raised to higher valence states and used as chemical mediators are Ce^{+++} and Fe^{+++}. Of these, silver is the most thoroughly studied.(1)

The Ag^{++} formed at the anode almost immediately forms a complex with a nitrate ion, $AgNO_3^+$ which is very strongly absorbing spectroscopically through a broad range of the visible spectrum. Formation of the complex does not significantly reduce the oxidizing power of the Ag^{++}. The complex readily attacks water to form OH free radicals and H^+, at which time the silver is reduced to its original state, Ag^+. A constant replenishment of Ag^{++} ions is accomplished by continuously circulating the electrolyte past the anode. Hydroxyl free radicals are themselves powerful oxidizers, particularly with respect to hydrocarbon molecules. In the case of ethylene glycol, the major component of antifreeze, $(CH_2OH)_2$ reacts with both $AgNO_3^+$ and OH (from water) to form CO_2, H^+, NO_3^-, and Ag^+.

On the cathode side of the electrochemical cell, NO_2 and water are produced by reduction of nitrate ion. If the NO_2 is regenerated with oxygen in a separate reactor to produce nitrate ion (which is recycled to the cell), then the overall reaction is for ethylene glycol to be converted to CO_2 and H_2O. Since the only chemical added is the O_2 used to regenerate nitrate ion, the stoichiometry is identical to combustion, i.e. $2(CH_2OH)_2 + 5O_2 = 4CO_2 + 6H_2O$.

The differences between the process just described and combustion are obvious. One is done in an aqueous electrolyte and requires an electrochemical cell that operates near ambient conditions. Normal combustion operates near ambient pressure but at very high temperatures. Residence times in combustion are quite short. That gives some people concern about stack gas emissions, whereas the residence time in this aqueous system is quite long, and complete destruction of the starting material can be verified before anything is discharged to the environment.

Lab Scale Experiments

The principles described above have been checked in many small experiments. They have been used to develop several different parts of the demonstration bench-scale system that was eventually built. For example, at the anode of the electrolytic cell, it is easy to evolve molecular oxygen if the anode potential is raised too high. Scanning voltammetry using a computer controlled potentiostat allowed us to determine the maximum anode potential that could be used to produce Ag^{++} but avoid oxygen evolution, a process inefficiency. Using rotating disc electrode methods, diffusion coefficients for Ag^{+} in the electrolyte were determined so the demonstration cell could be optimized with regard to Ag^{++} production. The reaction between $AgNO_3^{+}$ and water to form OH and eventually O_2 was followed spectrophotometrically. This helped determine the way that OH attacked hydrocarbon molecules. It also provided important information that was incorporated into the numerical model of the system. Kinetics of destruction of ethylene glycol were measured and a proposed mechanism was developed.(2) It should be applicable to ketones, aldehydes, alcohols, organic acids, and the starting parent hydrocarbon such as octane. This is shown in Figure 1. Various other organic compounds also were destroyed, such as tetraphenylborate and benzene.

Modeling

Numerical models were developed for the developmental scale electrochemical cell. It is an annular design with a porous ceramic separator between the gold anode and the stainless steel cathode. Because we had measured or otherwise obtained the physical properties of the electrolyte and had measured the reaction kinetics of Ag^{++} with both water and ethylene glycol, the model was able to predict how fast a given amount of glycol could be destroyed as functions of cell dimensions, electrolyte temperature and concentrations, electrolyte flow rate, and potential. A schematic diagram is shown in Figure 2. Parametric runs were done on a small computer to calculate both the optimum cell design as well as predict the system's ability to destroy antifreeze.

Demonstration

The demonstration hardware, which included not only the electrochemical cell but other items as well, was installed in a gloved enclosure ventilated with untreated room air. This is shown in Figure 3. The other hardware items included a demister for each side of the electrochemical cell. The cathode side allowed NO_2 to be removed without entraining liquid droplets as the gas vented to the stack. Similarly, the anode side had a comparable unit to vent the CO_2 produced and any O_2 that may have been produced. Temperature was held at about 70°C using electrical heaters immersed in the electrolyte. Each side of the cell, of course, had its

own circulation pump. We chose a magnetically coupled centrifugal design, with wetted surfaces made entirely of polyvinylidene fluoride. Piping and values were of the same material or else either teflon or titanium.

The results of the demonstration were very gratifying. We had determined from the numerical model that we could destroy 0.5L ethylene glycol in 22 hours. The destruction rate would be limited by the rate at which the electrochemical cell could produce Ag^{++}. During the run, CO_2, CO, and O_2 were monitored on-line in the off-gas from the anode loop. The first two used infrared detectors and O_2 used an electrochemical method. Only CO_2 and O_2 were detected. This was later confirmed by grab samples of gas analyzed by mass spectroscopy. We also monitored $AgNO_3^+$ on-line in the anolyte. This was done by absorption spectroscopy using fiberoptics to connect the probe to the spectrophotometer. At 20 hours, based on negligible CO_2 evolution, increased O_2 evolution, and a high concentration of $AgNO_3^+$ being maintained in the anolyte, the run was terminated. Using off-line total organic carbon analysis, it was determined that we had destroyed more than 99.9% of the ethylene glycol in the anolyte. The numerical model had predicted the time for destruction within 10% of the actual time, which is excellent agreement for this kind of developmental work.

Summary and Future Directions

The demonstration of the technology on this scale gives us confidence in both our ability to predict the systems performance, and also gives us some confidence in the destruction mechanism at work in the electrolyte. Other classes of organic compounds are under study, such as halogenated species. Also, destroying 0.5L in 20 hours is a scale far too small to be of practical value. A new system is being designed and constructed that has a capacity expandable to about 120 times larger than our initial demonstration system.

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Figure Captions

Figure 1: Proposed steps in the destruction of ethylene glycol and related hydrocarbons.

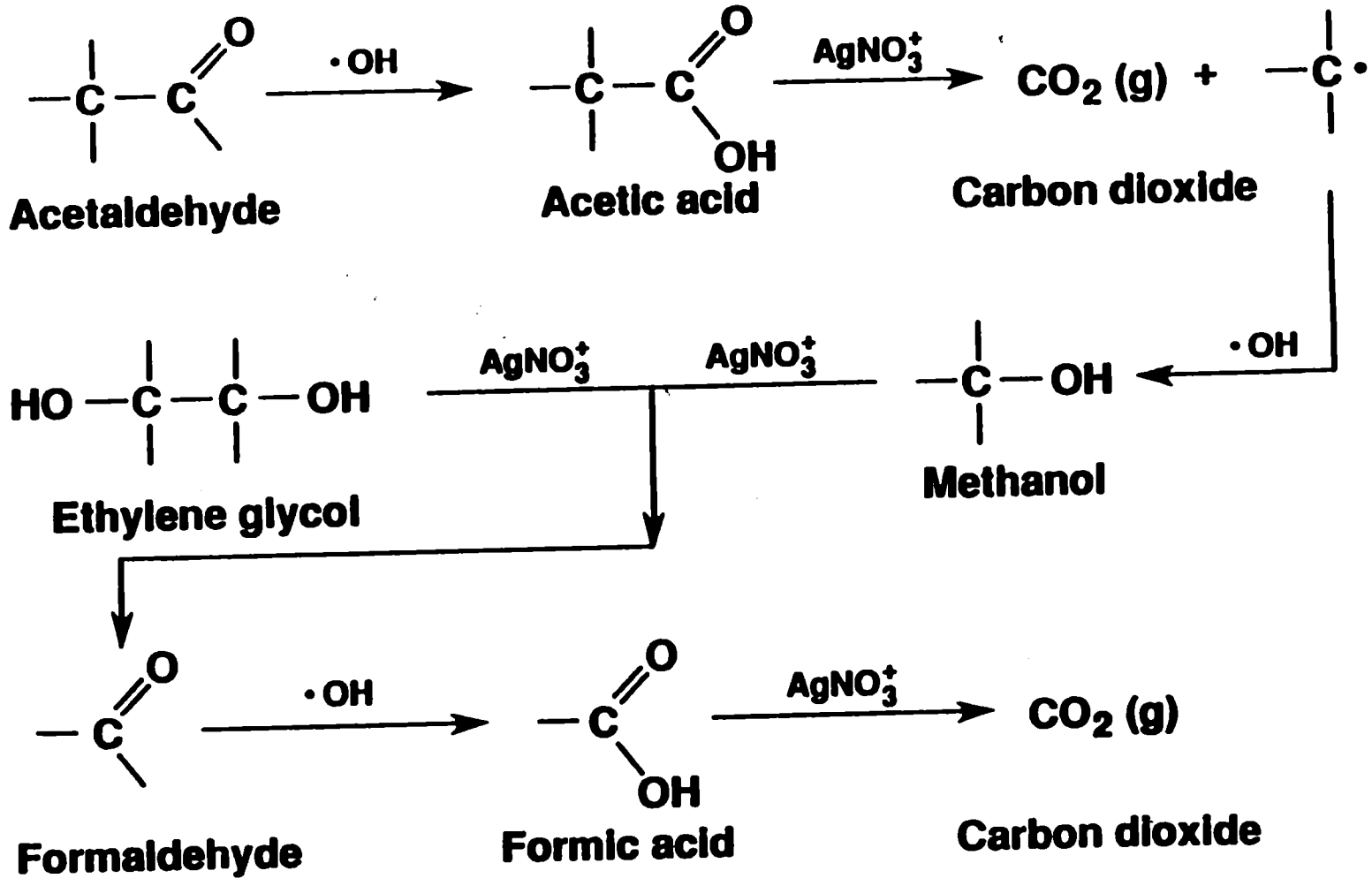
Figure 2: Schematic drawing of the electrochemical cell for which the numerical model was developed.

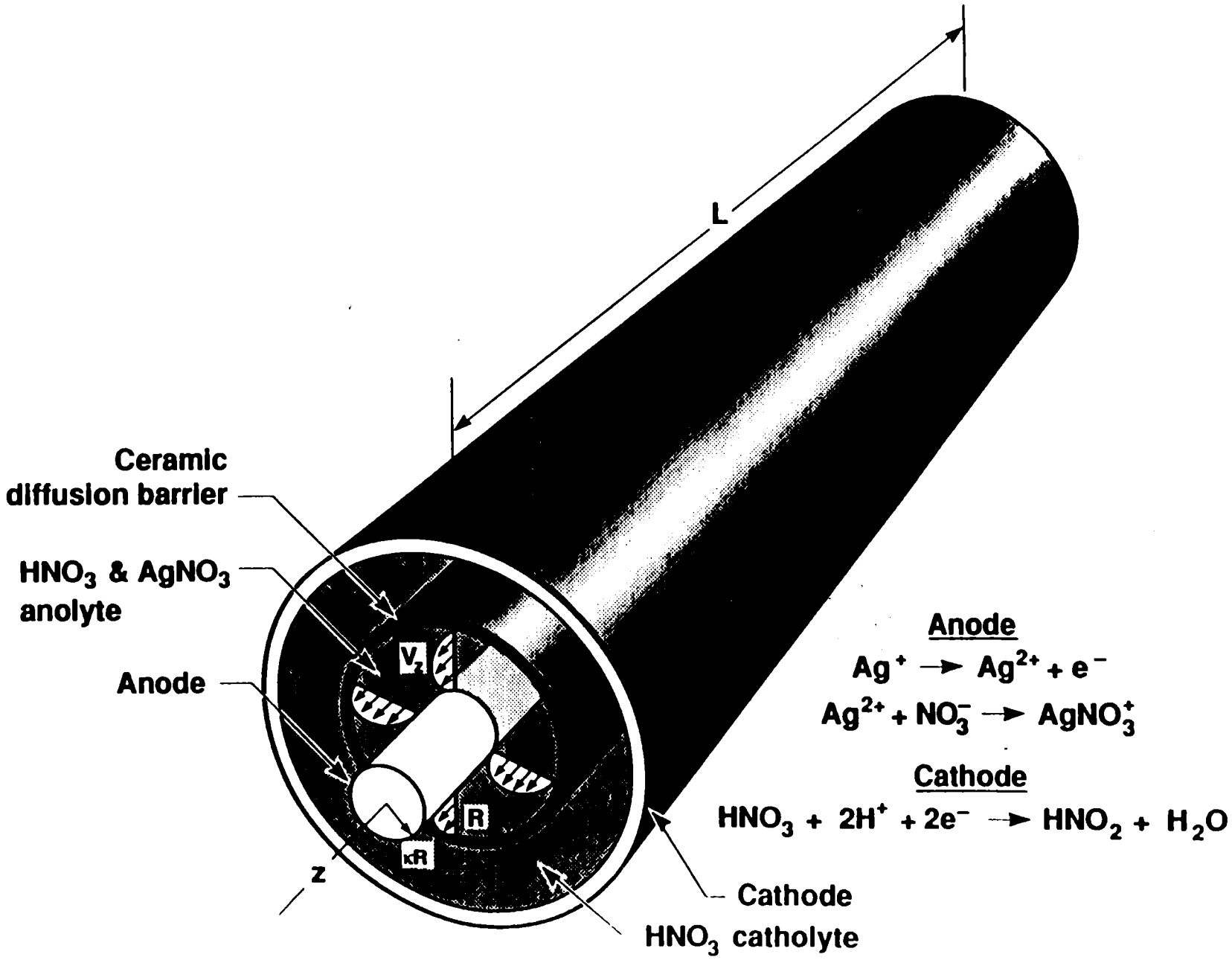
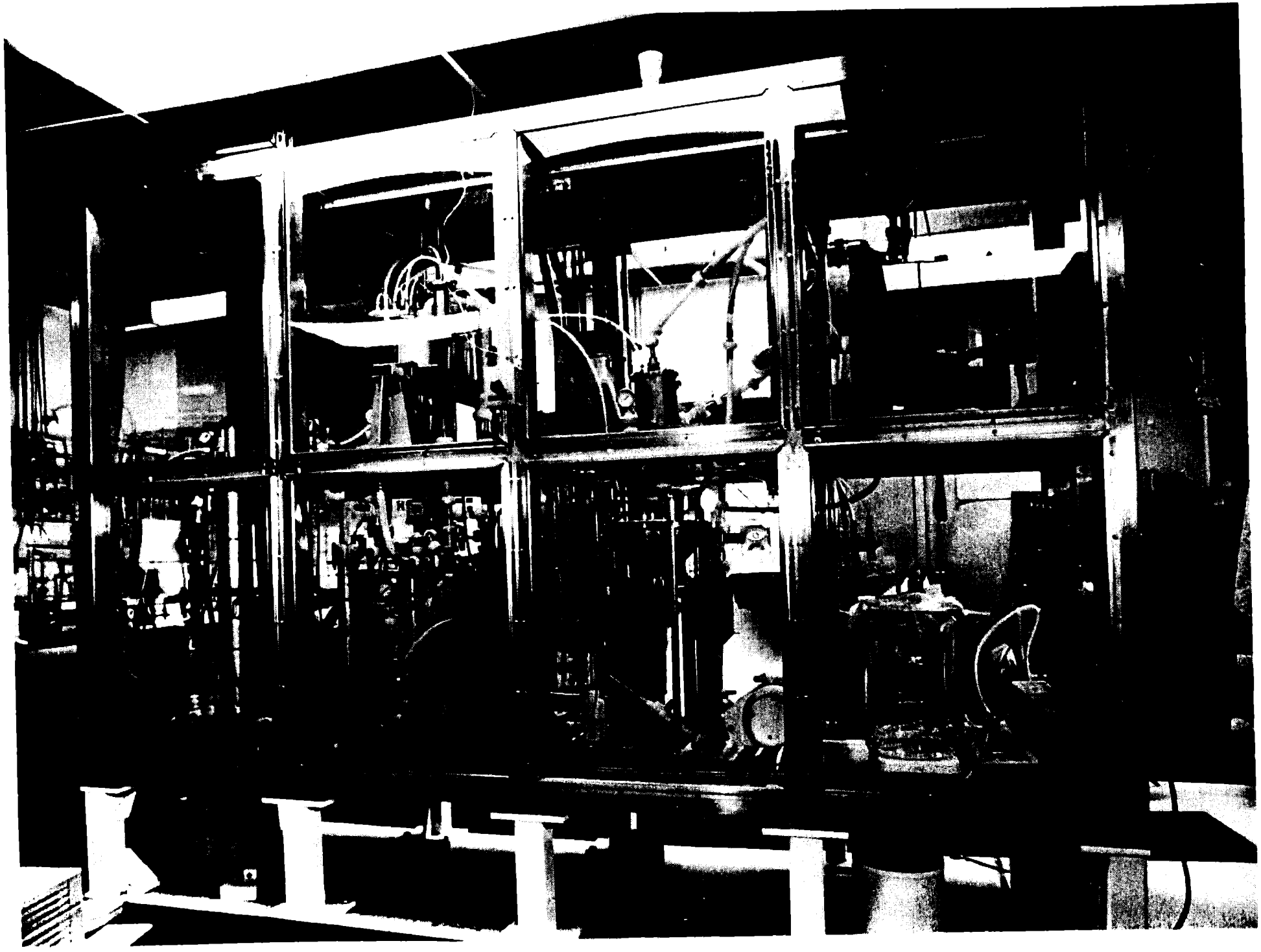
Figure 3: Photograph of bench-scale organic destruction system.

References

1. D. Steele, "Electrochemical destruction of toxic organic industrial waste," Plat. Met. Rev., 34 10 (1990).

2. J. Farmer, et.al., "Initial study of the complete mediated electrochemical oxidation of ethylene glycol", Lawrence Livermore National Laboratory, Livermore, CA. Report No. UCRL-106479 (March, 1991).


Acetaldehyde
•OH
Acetic acid
$AgNO_3^+$
CO_2 (g) +
Carbon dioxide
•OH
Methanol
$AgNO_3^+$
$AgNO_3^+$
Ethylene glycol
Formaldehyde
•OH
Formic acid
$AgNO_3^+$
CO_2 (g)
Carbon dioxide


L
Ceramic diffusion barrier
HNO_3 & $AgNO_3$ anolyte
Anode
V_z
R
kR
z
Cathode
HNO_3 catholyte
Anode
$Ag^+ \rightarrow Ag^{2+} + e^-$
$Ag^{2+} + NO_3^- \rightarrow AgNO_3^+$
Cathode
$HNO_3 + 2H^+ + 2e^- \rightarrow HNO_2 + H_2O$