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Plasma Technology for Treatment of Waste*

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ABSTRACT

Meeting goals for waste cleanup will require new technology with improved environmental attractiveness and reduced cost. Plasma technology appears promising because of the high degree of controllability; capability to process waste without the adverse effects of combustion; and a very wide temperature range of operation. At the Plasma Fusion Center at the Massachusetts Institute of Technology, we are investigating a range of plasma technologies. "Hot" thermal plasmas produced by DC arc technology are being investigated for treatment of solid waste. In conjunction with this activity, new diagnostics are being developed for monitoring arc furnace operating parameters and gaseous emissions. Electron-beam generated plasma technology is being investigated as a means of producing non-thermal "cold" plasmas for selective processing of dilute concentrations of gaseous waste.

INTRODUCTION

Plasma technology is showing promise for a variety of waste processing applications. Conventional approaches for high throughput waste processing have significant drawbacks. Landfilling raises concerns about release of hazardous materials to water, the ground, and air. There is also a shortage of acceptable space for landfilling in many areas of the world. Incineration raises concerns about undesirable air emissions and toxic ash. Plasma technology has the potential to remove these concerns and to reduce cost. The attractiveness of plasmas results from the capability to provide high temperatures, a high degree of controllability, and the use of electricity for heating rather than heat from combustion.

The temperature range of interest for plasma applications extends from approximately 10,000^0 C to room temperature. At MIT we are studying the use of high temperature (10,000^0 C range) arc plasmas for "hot plasma" treatment of solid waste and room-temperature range "cold" plasmas for treatment of gaseous waste.

HOT PLASMA VITRIFICATION OF WASTE

We have been investigating vitrification of solid waste using heating provided by a graphite electrode dc arc plasma furnace. The high temperature heating can melt almost any type of material and facilitate transformation into glass. The objective of the program, which is a joint effort with Battelle Pacific Northwest Laboratories, is to develop an improved means to treat mixed waste (radioactive and chemical) for U. S. Department of Energy needs.

The goal is to develop a process for a high throughput system to turn solid waste into stable non-leachable products which can be safely stored and to greatly reduce air pollution relative to incineration. Because the heating is electrical rather than combustion-powered, there is less off-gas, and there can be a significant reduction in entrained particulates. Moreover, because the atmosphere of the plasma furnace can be non-oxidizing, production of hazardous compounds such as dioxin can be greatly reduced or eliminated.

For radioactive waste, with treatment costs of over $1,000 per ton, the electricity cost for plasma processing (for example, $50 per ton assuming 1000 kWhr per ton and $.05 per kW hr) is not an important cost factor.

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Plasma vitrification could also be used for treatment of hazardous waste, medical waste, and incinerator ash. Costs for incineration and landfilling are typically in the $200-$1000 per ton range. In addition plasma vitrification has potential for economically competitive treatment of municipal waste. Generation of electricity using combustible gas produced by plasma processing would be used to reduce cost. The present relatively low cost for treatment of municipal waste ($30-$100/ton plus transportation cost) imposes demanding requirements on plasma vitrification costs.

The plasma in our furnace is created between a cylindrical electrode and waste material which is in a graphite crucible. The plasma is in thermal equilibrium with approximately equal electron, ion, and neutral temperatures. Typical central plasma temperatures are around 10,000° C. The material is typically heated to temperature in the 1500° C range. The plasmas are produced in atmospheric-pressure range nitrogen gas.

Graphite electrodes are used because of their ruggedness and capability for carrying high current. An important mode of operation that is facilitated by use of a graphite electrode is submerged operation where the plasma is formed in a cavity underneath the surface of the material to be processed. This mode of operation greatly reduces particulate emission. The material on top of the plasma acts as a "cold top" to prevent emissions.

A small graphite electrode dc arc plasma furnace, the Mark 1, has been used to melt a variety of simulated wastes of interest to the Department of Energy Cleanup Program. These wastes have consisted of mixtures of soils, metals, and combustibles. The furnace produced a black glass which is very stable and passed standard leaching tests[1]. The Mark 1 was batch-fed and typically operated at power levels of 30 kW.

A pilot-scale research furnace with continuous feed capability, the Mark 2 furnace, has undergone initial tests at the MIT Plasma Fusion Center. Figure 1 shows a schematic diagram of the Mark 2 pilot-scale research furnace. The furnace has been operated at power levels in the 250 kW range. It has processed waste material at a rate of about 200 pounds per hour.

A key future direction is to study the effect of various furnace conditions upon particulate and hazardous metals emission from the graphite electrode arc plasma furnace.

New monitoring technology is being developed to optimize furnace performance and to ensure that environmental quality goals are met. One diagnostic uses a microwave-generated plasma to make continuous sensitive measurements of off-gas metals emission[2]. The plasma is formed in a special robust waveguide inserted into the off-gas system. Material that passes through the plasma is vaporized, ionized, and electrically excited. Light emitted from the plasma is conducted by fiber optics to a spectrometer for analysis.

Figure 2 shows metals that have been measured in an initial test on simulated waste processed in the Mark 2 furnace. A determination of sensitivity for furnace use has not yet been made. Laboratory tests have indicated a sensitivity in the one to ten parts per billion range for a number of metals and this type of sensitivity should be possible in furnace operation.

The microwave plasma continuous emissions monitoring has also been used to make sensitive laboratory measurements of plutonium at Battelle Pacific Northwest Laboratories.

Another diagnostic is a millimeter wave pyrometer which determines the temperature of the material to be processed and the temperature of the walls of the furnace by measurement of millimeter wave radiation which is emitted from these hot bodies An important advantage of this approach relative to conventional infrared pyrometers is that millimeter radiation can be seen through the hostile smoky environment of the plasma furnace, and the system is very rugged [3].

The millimeter wave pyrometer, microwave plasma metals sensor, and other diagnostics will be used to study a wide range of dependences of particulates, metals, and organic gas emissions on various furnace operating parameters. Over the long term, this information may be used for feedback control of the waste treatment units.

COLD PLASMA WASTE TREATMENT

Cold plasmas with gas temperatures in the room temperature range are useful for treating hazardous gases with dilute concentrations of contaminants. The plasma is in a non-equilibrium condition where the electron temperature is much greater than the ion and neutral temperatures. The plasma electrons and radicals selectively attack the contaminant molecules. As a result, the process is highly efficient because, in contrast to thermal processes where every

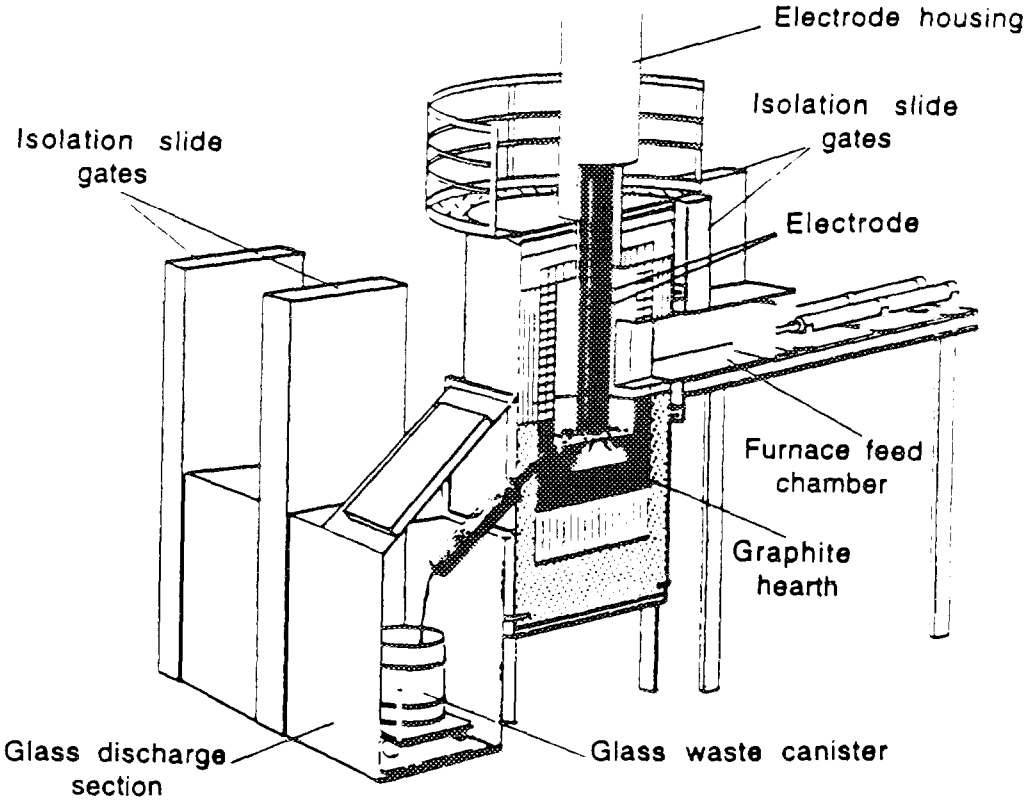

Figure 1 Mark 2 graphite electrode dc arc furnace.

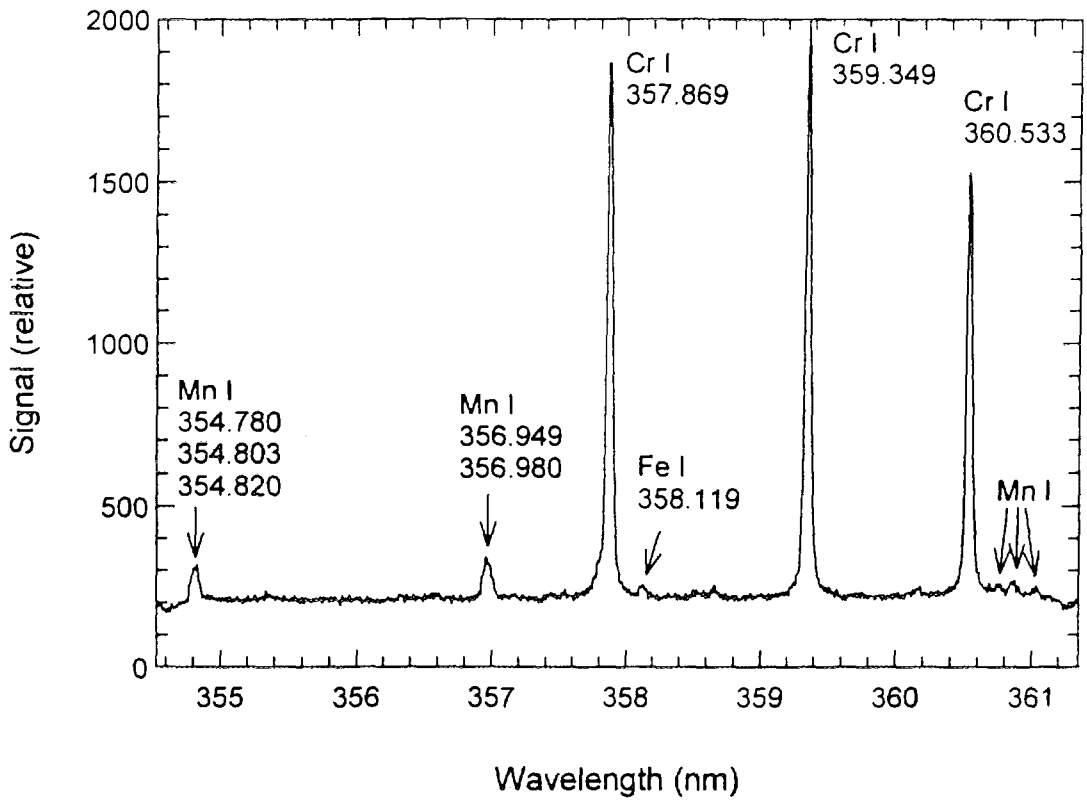

Figure 2 Mark 2 exhaust spectrum with high-resolution spectrometer just prior to start of soil loading. Waste material temperature 1410° C.

molecule in the gas stream must be heated up to temperatures needed for decomposition, the energy in the plasma is highly directed into the molecules that it is the goal to destroy.

In order to develop a practical high throughput system, it is desirable to operate at atmospheric pressures. The attainment of non-equilibrium conditions at atmospheric pressures requires special conditions because of the high collision rate among electrons, ions, and neutrals which tends to equilibrate their temperatures. At MIT, an electron beam is being used to generate the cold plasma. Electron beams are a very efficient way to generate low-energy electrons in a cold plasma. In contrast to standard plasma discharges, less energy is lost in the production of excited atomic and molecular states.

The electron-beam vacuum is separated from the gas to be processed by a thin foil. The electron beam energy is in the 150-300 keV range. Special external shielding is not needed for this range of energies, and highly reliable commercial systems are available.

We have used the electron-beam generated plasmas to decompose various chlorinated compounds in air streams. This work is motivated by the need for a system to provide low cost, environmentally attractive decomposition of solvents that are vacuum-extracted from the ground. The work has been supported by the Department of Energy.

For chlorinated compounds like carbon tetrachloride and trichloroethylene, the decomposition process appears to be electron-attachment-induced decomposition:
$e^- + CCl_4 \rightarrow CCl_4^{*-} \rightarrow CCl_3 + Cl^-$ where * indicates an activated unstable species. The decomposition initially breaks off a chlorine ion. The resulting product chlorine radical CCl_3 undergoes further decomposition. The final products are simple molecules such as chlorine which can be readily converted into benign products such as salt.

As shown in Figure 3, laboratory studies of carbon tetrachloride indicate that around 60 eV of energy is needed per molecule decomposed for 75 percent decomposition of CCl_4 in air streams with concentrations in the 300-600 ppm range. Decomposition measurements were made with a gas chromatograph and a mass spectrometer. The 60 eV requirement is consistent with a requirement of approximately 30 eV for electron-beam generation of an electron. Approximately 100 eV is needed for 95 percent decomposition due to competition for electrons from the decomposition products. Competition for electrons also leads to higher energy requirements for lower initial concentrations.

For trichloroethylene, which is perhaps the most widely encountered solvent in remediation activities, about 10 times less energy is required per decomposition relative to the amount required for the decomposition of CCl_4. The energy expense is typically 10 eV per molecule decomposed. It appears that the reason for this decrease in energy expense is due to the presence of a chain reaction where chlorine ions released in the decomposition in turn create more decompositions. The mechanism appears to be:

$$e^- + C_2HCl_3 \rightarrow C_2HCl_3^{*-} \rightarrow C_2HCl_2 + Cl^-$$
$$C_2HCl_3 + Cl \rightarrow C_2HCl_4 \rightarrow \text{products.}$$

TCE which has a double carbon bond is vulnerable to chlorine ion attack, whereas carbon tetrachloride is not vulnerable[4], [5].

The 10-eV energy requirement for decomposition of trichloroethylene is orders of magnitude less than the energy that would be required if a thermal process were used for 100-ppm range initial concentrations. Assuming approximately 0.2 eV required per molecule for thermal decomposition, the energy required per contaminant molecule is $0.2 \text{ eV}/10^{-4} = 2000$ eV. This amount of energy is 200 times that required for non-thermal decomposition. This increase in efficiency can more than compensate for the increased cost of an electron-beam generated plasma system relative to thermal treatment systems.

Laboratory studies have been made of the decomposition of a variety of other volatile organic compounds[5]. These compounds include toluene in addition to various chlorinated compounds.

Following a wide range of laboratory tests, an electron-beam generated cold plasma field unit was assembled in a trailer. Figure 4 shows the field test unit as assembled in a 43-foot trailer. The unit included a commercial electron beam and a conventional scrubber which converted the decomposition products, such as chlorine, into benign final products such as salt. The unit used infrared detectors to monitor inlet and outlet concentration levels. It was designed for automatic control without the presence of an operator. The unit was employed in

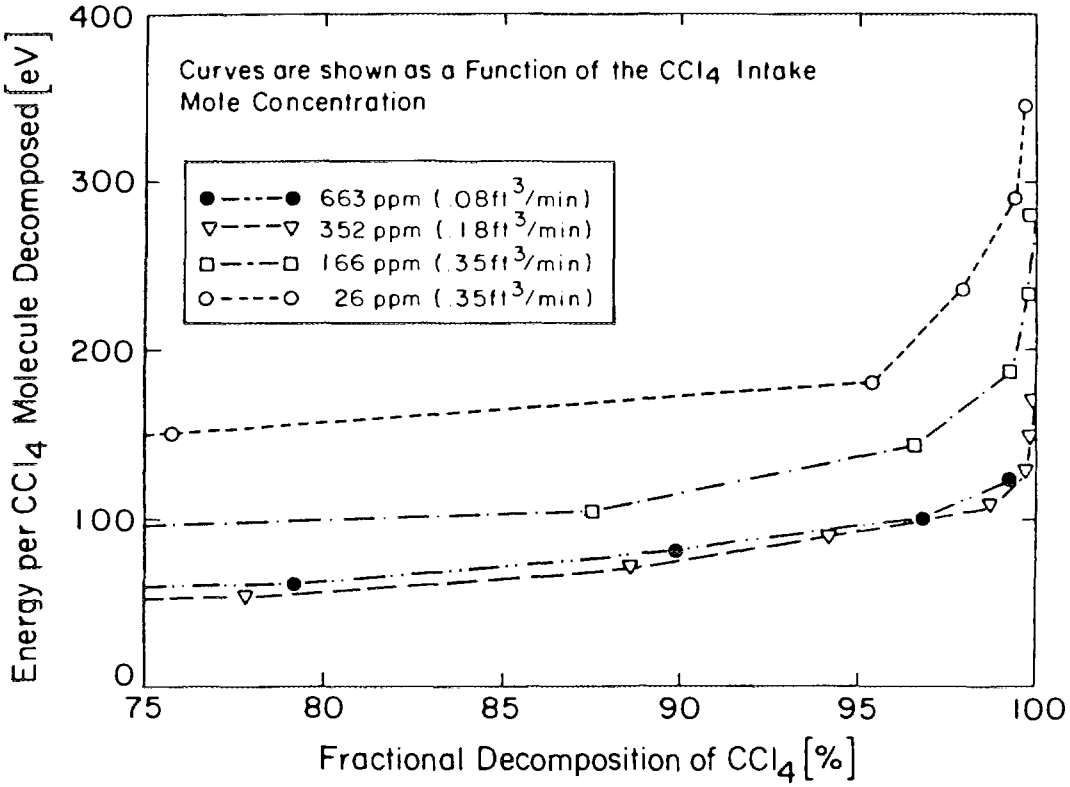

Figure 3 Energy requirement per CCl_4 molecule decomposed as a function of fractional decomposition.

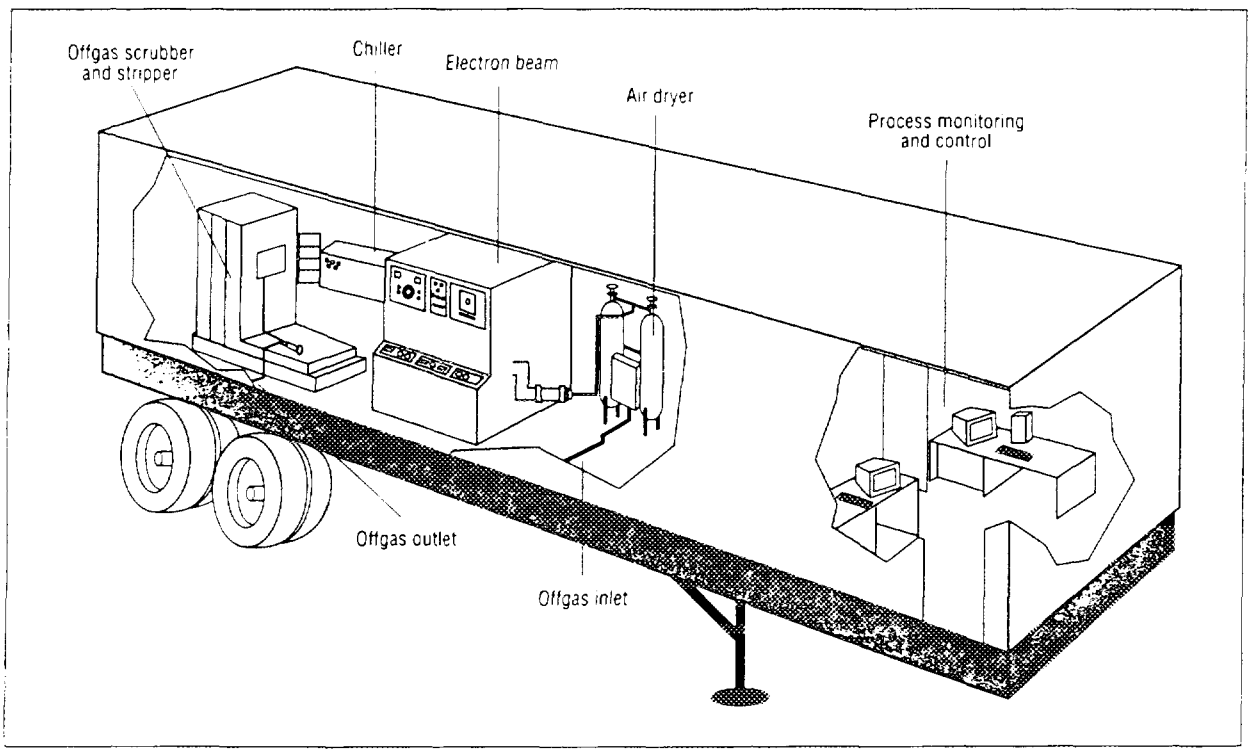

Figure 4 Field test unit as assembled in a 43-foot trailer.

initial field tests at the DOE Hanford site and operated successfully for 300 hours. It was used to decompose CCl_4 in the 300-ppm concentration range in vacuum-extracted air streams.

In addition to use for treating vacuum-extracted solvents, the cold plasma technology could also be used for treatment of contaminants which are air-stripped from contaminated water. Another potential area of research is the treatment of industrial process emissions.

SUMMARY

To date combustion heating has been virtually the only means used to create changes in states of matter for environmental applications. The wide temperature capability and controllability of plasma technology may add important new capability in applications to waste treatment. Significant practical applications are likely within this decade.

ACKNOWLEDGEMENTS

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