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ABSTRACT

A growing number of environmental remediation technologies (e.g., drying, melting, or sintering) utilize microwave radiation as an integral part of the process. An increasing number of novel applications, such as sustaining low-temperature plasmas or enhancing chemical reactivity, are also being developed. An overview of such technologies being developed by the Department of Energy is presented. A specific example being developed at Argonne National Laboratory, microwave-induced plasma reactors for the destruction of volatile organic compounds, is discussed in more detail.

INTRODUCTION

The Office of Environmental Restoration and Waste Management (EM) within the Department of Energy (DOE) is responsible for conducting the largest environmental remediation program in the history of our country[1], the cleanup of the DOE Nuclear Weapons Complex which encompasses 112 sites in 33 states. In 1989, then-Secretary of Energy Watkins gave EM the goal to clean up these sites by the year 2019.

The environmental problems confronting EM are vast and diverse. For example, the Hanford site has 177 storage tanks containing an estimated 106 million gallons of radioactive process waste[2] and an estimated 250 metric tons of CCl_4 in the soil.[3] Oak Ridge has an estimated 20 million square feet of uranium-contaminated concrete at its K-25 Gaseous Diffusion Facilities[4].

The DOE laboratories are currently developing a variety of technologies that use microwave radiation as an integral part of their process to address such problems. The applications of microwave radiation in these technologies range from more conventional applications such as sintering and heating to novel applications such as promoting chemical reactions and sustaining plasmas. This article will review five technologies: (1) the microwave spaller for concrete decontamination at Oak Ridge National Laboratory, (2) the microwave solidification process at the EG&G Rocky Flats Plant, (3) the microwave vitrification of radioactive waste at Savannah River National Laboratory, (4) the microwave fluidized bed reactor at Los Alamos National Laboratory, and (5) the microwave plasma reactor at Argonne National Laboratory.

A. MICROWAVE SPALLER FOR CONCRETE DECONTAMINATION

Concrete contamination is a major problem at many DOE facilities, including K-25 at Oak Ridge. Research has indicated that the major portion of the contamination, primarily ^{235}U and ^{238}U, lies within the top few millimeters of the exposed surface. DOE is currently investigating a number of decontamination technologies to remove this layer and thus significantly decrease the cost of decommissioning these facilities.

Present decontamination technologies generally use mechanical techniques (e.g., impact breaking, mechanical chisels, high-pressure water sprayers, or steel shot blasters), which utilize high-energy blasting of the surface. While these technologies can very rapidly remove contaminated surface layers, they produce large amounts of dust particles that must be contained and removed. Water, used either for blasting or for suppressing dust generation and entrainment, produces a secondary waste stream that will require subsequent treatment. Water can also solubilize some contaminants driving them deeper into the concrete.

The microwave spaller currently being developed at Oak Ridge[5a-b] is a dry technique that generates little airborn dust. It uses microwaves to heat absorbed water within the concrete matrix and create pressure-induced mechanical stresses. These stresses cause the surface to burst, yielding small particles in the 1- to 10-mm range. A vacuum cleaner collects the dust particles generated.

The microwave spaller uses microwave radiation, either 2.45 or 10.6 GHz, directed at the concrete surface by a waveguide. The dimensions of the waveguide depend on the frequency, 7.21 cm x 3.4 cm for 2.45 GHz and 2.29

cm x 1.01 cm for 10.6 GHz.

Both static and dynamic tests have been conducted. In static testing at 2.45 GHz, a 3.1-cm^3 crater 6.4 mm depth was removed in about 59 s at a power level of 6 kW. Not all attempts at 2.45 GHz to remove concrete were successful. In static testing at 10.6 GHz, an average 2.6 cm^3 crater with a 1.7 mm depth was removed with 4.8 kW in 15 s. Concrete was removed in all attempts at 10.6 GHz.

In dynamic testing, using the 7.21 cm x 3.4 cm waveguide, trenches of 38 cm x 7 cm x 0.56 cm and 35.5 cm x 7 cm x 0.52 cm were removed at 2.45 and 10.6 GHz, respectively, at a slab speed of 5 mm/s. Continuous concrete removal rates of 1.07 cm^3/s with 5.2 kW at 2.45 GHz and 2.11 cm^3/s with 3.6 kW at 10.6 GHz have been measured. The particle size distribution indicated that most particles were 1-10 mm. Less than 1% of the particles were <1 mm; therefore, airborne contamination should not posse a significant hazard.

Based on these experiments, researchers concluded that at the higher frequency (1) heating is faster and more efficient, and, consequently, the surface removal would be more reliable and (2) the power density is higher for the same applicator size and power level. Factors effecting the overall removal efficiency include (1) the microwave frequency and power, (2) the translation speed, and (3) the distribution of microwave power over the area being heated.

Future work involves the optimizing and scaling the equipment and developing a mobile unit for an actual decommissioning demonstration.

B. MICROWAVE SOLIDIFICATION PROCESS

At Rocky Flats, plutonium and other heavy metals are recovered from aqueous waste streams by hydroxide precipitation[6a-d]. The resultant slurry is filtered through a rotary drum vacuum filter that is precoated with diatomaceous earth to remove solids from the waste stream. A thin filter cake is continuously cut from the drum filter yielding a wet sludge. Because free liquids may not be present for acceptance at the Waste Isolation Pilot Plant (WIPP), a portland cement/diatomite mixture is added, followed by microwave solidification to remove all free liquids.

The microwave solidification unit uses a 60-kW, 915-MHz microwave generator connected to a 40-inch, cubic applicator cavity by a WR975 waveguide. The system is contained in a glovebox. The waste material is

mixed with a silica source/matrix modifier to produce a waste loading of 60 to 70%. The mixture is pelletized using an extrusion pelletizer and dried using a multiple-tray direct dryer prior to microwave solidification. Initially, 10 kilograms of dried pellets are loaded into a 30-gallon stainless steel drum. The drum is connected to the applicator cavity by a lifting turntable which compresses it against a rotary choke, allowing the interior of the drum to become part of the resonance cavity. Microwave heating raises the temperature of the material inside the drum to approximately 1000°C, causing it to melt. After the initial charge becomes molten, waste material is continuously loaded using a vibrating feeder that penetrates the wall of the applicator cavity. The process continues until 160 kilograms of waste have been accumulated. At that point, the process is interrupted while the drum is transferred to a cool-down inspection station and a new cycle begins.

The advantages of the microwave treatment process include the following: (1) Waste loadings of up to 70% and product densities of 3.0 g/cm^3 result in volume reductions of up to 80% compared to current cement-based grouting processes. (2) Selective heating of the waste form eliminates thermal cycling which could lead to stress-related failure of the process equipment. (3) The "in-drum" process eliminates the need to transfer of the final waste form. (4) The equipment is inexpensive and easily maintained.

This technology has been under development since 1986. Both laboratory-scale tests on actual and surrogate wastes and pilot-scale tests on surrogate wastes have been performed. A full-scale, cold demonstration system has been in operation since 1991. Future work will focus on integrating of ancillary equipment required for the system, including a bagless posting to allow efficient transfer of the drum in and out of the glovebox.

C. MICROWAVE VITRIFICATION OF RADIOACTIVE WASTE

The current plan for storaging of high-level nuclear waste within DOE is to stabilize and contain in glass-like logs formed by vitrification processes. At Savannah River, the high-level wastes will be vitrified in borosilicated glasses and poured into stainless steel cannisters[6a-b]. Ultimately, the cannisters will be deposited in a geological repository.

The vitrification process requires well-controlled temperatures in the range of 1150-1250°C to prevent the melt from foaming and devitrifing the glass. Conditions must be slightly reducing for maximum glass performance, but not reducing enough to precipitate metals. Scoping experiments have been

performed to compare conventional thermal and microwave vitrification of slurry-mix evaporator/melt feed tank surrogates. The microwave vitrification tests were conducted using a model CEM MDS-205 furnace (1000 w output) with a ceramic susceptor block in which the crucible was placed. The results of these tests demonstrated that microwave fusion required a shorter process time, 10-15 minutes, and produced a more homogenous glass phase than conventional thermal processing, which required 4 hours. The improved homogeneity observed for microwave vitrification was attributed to rapid thermal convection currents. In addition, using redox measurements based on the Fe^{+2}/Fe^{+3} ratio indicated that the microwave vitrification may yield more representative measures of glass redox than conventional melting.

D. MICROWAVE FLUIDIZED BED REACTOR

Chlorinated hydrocarbons, such as trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and tetrachloroethylene (PCE), are the most frequently identified nonmetal contaminant in soil and groundwater waste sites at DOE facilities[8]. The remediation of chlorinated hydrocarbon-contaminated soils and groundwater has become a major focus of EM. For instance, 260,000 pounds of trichloroethylene have been extracted from the soil/groundwater at Savannah River by a variety of technology demonstrations, such as vacuum extraction, since 1983[9]. However, extraction technologies only transferred the contaminant from one medium, soil/groundwater, to another medium, air streams. Ultimately, these chlorinated hydrocarbons must be chemically converted to more environmentally benign compounds. Incineration is the current EPA-approved method; however, incineration of air streams containing low concentrations of these compounds are generally not practical.

The microwave fluidized bed reactor[10a-d] under development at Los Alamos National Laboratory uses microwave radiation, either 0.915 or 2.45 GHz , to promote chemical oxidation reactions. In this process, the microwave radiation selectively heats the surface of silicon carbide particles to a relatively high temperature, approximately 500-600°C, without heating the reactor walls. The microwave radiation also activates the silicon carbide surface to enhance surface oxidation reactions. Silicon carbide is used because of its relatively high dielectric loss factor. Tests performed on trichloroethane-air mixtures have demonstrated 92-98% conversion of TCA in single-pass experiments, as follows:

$$C_2H_3Cl_3 + 2O_2 \rightarrow 2CO_2 + 3HCl \qquad (2)$$

There is no evidence for the formation of products of incomplete combustion, such as $COCl_2$ or Cl_2. Under comparable temperature (500-600°C) generated thermally in the absence of microwave radiation, conversions of only 27-36% were observed.

The major advantages of microwave heating over conventional thermal treatment include (1) rapid, uniform *in situ* heating, (2) selective heating of only the bed material, and (3) enhancing chemical reactivity.

E. MICROWAVE-INDUCED PLASMA REACTOR

Plasma processing for environmental remediation applications is a rapidly developing technology. The primary reasons its ability to generate higher temperatures and greater concentrations of free-radical reaction initiators than thermal (combustion) processes. The major application of plasma technology has been the plasma arc reactor, due its the ability to generate extremely high temperatures, often in excess of 10,000°C. Recently, there has been interest in the applications of low temperature plasmas (<5000°C), of one which is the microwave-induced plasma reactor currently under development at Argonne National Laboratory[11a-b].

The microwave-induced plasma utilizes microwave radiation at 2.45 GHz and a forward power ranging from 200-1000 w to sustain either an argon, oxygen-argon, or air-argon plasma at atmospheric pressure. Microwave radiation is transferred to the reactor by a TE_{10} waveguide. The reactor, a 1-inch quartz reactor tube, bisects the waveguide at a 90° angle. A tunable "short" causes the portion of the waveguide containing the reactor to act as a resonance cavity.

TCA or TCE , in concentrations ranging from approximately 100-10,000 ppm, along with reactants such as oxygen, water vapor, or an oxygen-water mixture are feed by a manifold system into the plasma. Free electrons and radicals generated in the plasma initiate reactions which destroy the TCE or TCA. The product selectivities depends on the reactant mixture and relative ratio of the various feed components. For example, the reaction of TCA or TCE with water vapor (2.45% by volume) yields a mixture of CO_2, CO, H_2, and HCl. The ratio of CO_2/CO is dependent on the initial ratio of TCA or TCE ratio ranging from 0.905 for a TCE/H_2O feed ratio of 173 to 0.528 for a H_2O/TCE feed ratio of 10.3. By utilizing a water vapor-oxygen mixture (2.45% water vapor, 20% oxygen, balance argon) all carbon is converted to CO_2 . TCE and TCA conversions in excess of 99.9% have been observed for single-pass,

nonoptimized experiments. This is no evidence of the formation of products of incomplete combustion.

Future work will focus on the issues of reactor scale-up, use of air plasmas, and multicomponent mixtures, such as aromatic and aliphatic chlorinated compounds.

CONCLUSIONS

The ability of microwave radiation to induce a wide variety of physical and chemical phenomena, coupled with the maturity of microwave generators, will play an increasingly significant role in the development of new and existing technologies to meet the challenges facing DOE in its remediation of the Nuclear Weapon Complex.

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