*Microwave Fluidized-Bed Detoxification
of Hazardous Waste*

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ANNUAL REPORT

MICROWAVE FLUIDIZED-BED DETOXIFICATION OF HAZARDOUS WASTE

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EXECUTIVE SUMMARY

The purpose of the previous and the current research and development (R&D) work has been to demonstrate the technical feasibility of total detoxification (4 9's DREs) of halocarbon vapor, liquid, solid, slurry, or sludge waste forms by use of microwave energy through oxidation/degradation in an air-stream over a microwave heated/activated SiC fluidized/packed bed under mild ($<600^{\circ}\text{C}$) conditions. The objectives relating to detoxification of halocarbon vapor and liquid waste forms only have been achieved.

Extensive R&D work completed by this investigator, through his direct participation and leadership (as the principal investigator and project leader), over a period of 4.5 years (3 years of DOE-HAZWRAP-sponsored R&D work [1985-87] at ANL; 1 year of EPRI-sponsored exploratory research [1989-90] at SRI International; and 6 months of DOE/OTD-DOE/AL-sponsored R&D work [1990 to present] at Los Alamos National Laboratory) suggests the advantages of using microwave energy to activate/heat the SiC-particulate/vapor (or even liquid) interfaces to facilitate total detoxification of TCEs (trichloroethane [TCE-A], trichloroethylene [TCE-E], tetrachloroethylene, carbon tetrachloride, etc.) in an air-stream over such SiC-particulate fluidized/packed beds under mild ($<600^{\circ}\text{C}$) conditions. This situation may be attributed to higher reaction rates at lower temperatures for the case of microwave effect compared with conventional thermal effect.

Enhanced single-pass detoxification ($>99\%$) of TCE-A, when a mixed stream of TCE-A and air is passed through a microwave heated/activated silicon carbide particulate fluidized-bed (1-in.-diam $\times$ 8-in. MFB) reactor under mild (500° to 580°C bed temperatures) conditions, has been validated by the R&D work completed by this author at ANL. Microwave-assisted reactions were observed to proceed at higher rates and at lower temperatures in comparison with thermal runs.

The aforesaid conclusions were further supported by the R&D work conducted on microwave-assisted detoxification of TCE-E at SRI International. Using a 2.45-GHz, 1.2-kW microwave source to heat/activate a silicon carbide particulate fixed bed in a single-mode cavity, a total detoxification of TCE-E in an air-stream was observed at 540°C bed temperature. It was also shown by the study that the product gas stream, in the case of microwave-assisted reaction, was free from toxic contaminants or PICs (such as COCl_2 , Cl_2 , CCl_4). However, in the case of thermal heating of the silicon carbide particulate bed, total detoxification of TCE-E under equivalent conditions (TCE-E/air ratio, gas flow rate, bed characteristics) was observed only at higher bed-temperatures ($\geq 600^{\circ}\text{C}$), and the product effluents contained traces of toxic (PIC) contaminants. We have also established that mixing the silicon carbide bed with the natural sorbent mineral nahacolite (NaHCO_3) can result in total in-bed scavenging of HCl gas produced in detoxification runs.

The work just completed at Los Alamos National Laboratory has elaborated on energy needs of the aforesaid microwave process. It is suggested that for a TCE-A load or throughput of 24 kg/h detoxified, the microwave power required is only 9.4 kW. Even with a cost penalty because of losses incurred in electricity to microwave conversion, the microwave-assisted processes of the kind described above appear to be extremely cost effective.

A 0.915-GHz, 30-kW microwave system (with a single-mode cavity applicator) incorporating a SiC-particulate MFB reactor has been designed and procured and will be set up very soon.

The Los Alamos team is ready to demonstrate the MFB technology for total detoxification of halocarbon waste streams at DOE-DP sites such as Savannah River, Rocky Flats, etc.

MICROWAVE FLUIDIZED-BED DETOXIFICATION OF HAZARDOUS WASTE

by

Ravi Varma

ABSTRACT

Our ongoing research and development (R&D) work focuses on demonstrating the technical feasibility of total detoxification of "CIHC" hazardous waste by using microwave energy. In addition, we investigated the capability of nahacolite for in-bed scavenging of HCl and found it to be very effective. So far, detoxification of halocarbon vapor and liquid waste forms has been achieved. Microwave energy heats and activates the particulates of silicon carbide (SiC) and promotes chemical interactions, facilitating total detoxification of chlorinated hydrocarbons (TCEs) in an air-stream over SiC-fluidized beds under mild ($<600^{\circ}$) conditions. The SiC promotes surface-enhanced reactions and also is a heat transfer medium. These microwave-assisted processes appear to be extremely energy efficient. The Los Alamos National Laboratory (LANL) team can demonstrate the microwave fluidized bed (MFB) technology for total detoxification of halocarbon waste streams. The technology is applicable for treatment of hazardous waste at DOE sites.

1.0 OBJECTIVE

The purpose of the proposed work has been to demonstrate the technology for total detoxification (4 9's or better DREs) of vapor, liquid, solid, slurry, or sludge halocarbon waste streams (10% of DOE-DP wastes¹ that contain contaminants such as trichloroethane [TCE-A], trichloroethylene [TCE-E], tetrachloroethylene, carbon tetrachloride, PCBs, etc.) by air-oxidation in microwave-fluidized bed (MFB) reactors under mild (400° to 600°) conditions with in-bed scavenging of HCl gas. The target is to develop technologies for detoxification of mixed hazardous waste.

2.0 TECHNICAL PROGRESS

Extensive research and development (R&D) work completed by this investigator over a period of 4.5 years (3 years of DOE-HAZWRAP-sponsored R&D work [1985–87] at ANL; one year of EPRI-sponsored exploratory research [1989–90] at SRI International; and 6 months of R&D work [1990–present] at Los Alamos

National Laboratory) has shown the advantages of using microwave energy for total and complete detoxification of TCEs over a SiC-fluidized/packed particulate bed at moderate (500° to 600°C) temperatures as well as the concomitant use of an in-bed HCl scavenger. Chlorinated hydrocarbons constitute a significant component of mixed waste¹ at DOE field sites. The major breakthroughs in research are itemized below.

2.1 R&D Work Completed (1985–87) at ANL

Enhanced microwave-assisted single-pass detoxification ($>99\%$) of TCE-A, when a mixed TCE-A and air stream is passed through a microwave-heated/activated SiC-particulate fluidized-bed (1-in.-diam. $\times$ 8-in. MFB resting on a fritted disc in a fused silica tube) under mild (500° to 580°C) conditions, has been validated (see Fig. 1) by the work completed. Microwave-assisted reactions² were observed to proceed at lower temperatures in comparison with thermal runs. A 2.45-GHz, 0- to 6-kW microwave source was used to irradiate/heat MFB reactors located in a 2' $\times$ 2' $\times$ 4' multimode cavity.

Fig. 1. Detoxification Efficiency as a Function of SiC Fluidized/Packed Bed Temperature.

2.2 Exploratory Research Completed (1989-90) at SRI International

The conclusions derived from the aforesaid studies (conducted at ANL by this author) were further verified

by research³ conducted on microwave-assisted detoxification of TCE-E at SRI International. Using a 2.45-GHz, 1.2-kW microwave source to heat/activate a silicon carbide particulate fixed-bed in a single-mode cavity (see Fig. 2), a total detoxification³ of TCE-E in an air-stream was observed at 540°C bed temperatures. It was also shown by the study that the exit product gas stream in the case of the microwave run was almost free from toxic contaminants (or PICs) such as COCl_2 , Cl_2 , and CCl_4 . However, in the case of thermal heating of the silicon carbide particulate fixed-bed, the detoxification reactions³ of TCE-E under equivalent conditions (TCE-E/air ratio, gas flow rate, bed characteristics) were observed only at a higher ($\geq 600^\circ\text{C}$) bed temperature. Even then, the effluent product stream was not free of PICs (COCl_2 , Cl_2 , CCl_4).

The results obtained from the aforesaid microwave and thermal runs are plotted in Figs. 3 and 4 respectively.

We also investigated the effectiveness of a natural sorbent rock-material nahacolate (NaHCO_3) for in-bed scavenging of HCl. It was established that mixing approximately 9 wt % nahacolate pellets with a silicon carbide particulate bed can result in almost total (>90%) scavenging of HCl produced in the detoxification reactions.

The results^{4,5} obtained in analogous research, "microwave-enhanced catalysis" completed at SRI, also provide support for our concepts.

Fig. 2. Microwave Single-mode Cavity Reactor System.

Fig. 3. Product Distribution in the Effluent from a 2.5-cm SiC Bed during Microwave Oxidation of TCE-E in an Air-Stream.

Fig. 4. Product Distribution in the Effluent from a 2.5-cm SiC Bed during Thermal Oxidation of TCE-E in an Air-Stream.

2.3 R&D Work Completed at LANL

A 0.915-GHz, 30-kW microwave reactor system equipped with a single-mode cavity applicator is being readied. The facility will be ready for execution of the proposed work in late 1991. The microwave reactor system consisting of the following has been procured:

1. 0.915-GHz, 30-kW magnetron.
2. WR 975 wave-guide sections, E- and H-bends.
3. Two microwave circulators, two dummy water loads (one modified with a manually operated stub to provide reflected power for low wattage through mismatch).
4. Dual directional couplers for forward and reflected power monitoring.
5. Triple stub tuner.
6. A single-probe slotted line and sliding short for cavity load-tuning.
7. WR 975 resonant cavity applicator for heating and plasma in a 2-in.-i.d. fused silica tube-reactor running centro-symmetric to broad wave-guide face in a vertical direction.
8. Automated HP gas chromatograph.
9. Gas-vapor, liquid/slurry feed lines, and product output lines.

10. IRCON model 6000 series, low-temperature 250° to 600°C pyrometer, Acufiber fiber optic temperature probes.

A mobile truck-mounted MFB reactor setup (consisting of three strings of four MFB reactors in series) in a 4' × 4' × 8' multimode cavity and a SiC-stirred 18-in.-diam × 6-ft reactor, energized by a 0.915-GHz, 60-kW microwave source have been conceptually designed. Schematics are shown in Fig. 5.

Energy and Materials Balance:

Complete energy and materials balance sheets were prepared for use by DOE-AL/DOE-HQ. The conclusions provide clear "energy justification" for the development of microwave technology for detoxification of hazardous waste. This may provide an extremely optimistic outlook. For example, TCE-A detoxification (24 kg/h throughput) requires only 9.43 kW of microwave power, whereas for a 12-kg/h throughput of TCE-E, 31.1 kW of microwave power are needed. The energy balance in both cases will become extremely attractive if reactor tubes are properly insulated and convection losses minimized. The details follow in the appendix.

Truck-mounted Mobile Unit

Fig. 5. Multiple-Pass Fluidized Bed Reactor System Schematic.

3.0 ACKNOWLEDGMENTS

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APPENDIX

MICROWAVE FLUIDIZED-BED DETOXIFICATION OF HAZARDOUS WASTE: MATERIALS AND ENERGY BALANCE

INTRODUCTION

Materials and energy balances for oxidative detoxification to 4 9's DRE, of trichloroethane (TCE-A) and trichloroethylene (TCE-E) over a silicon carbide fluidized-bed in an air-stream using microwave activation/heating of the bed are estimated for waste throughputs of 24 kg/h of TCE-A and 12 kg/h of TCE-E treated, i.e., converted into CO₂ and HCl and CO + CO₂ + HCl, respectively, in SiC fluidized-beds using multiple passes to achieve the required DREs.

RESULTS

A. TCE-A Detoxification of 4 9's DREs: Materials and Energy Balance

A 24 kg/h throughput of TCE-A in a dry air-stream is converted to CO₂ and HCl products over a silicon carbide (60 × 80 mesh) fluidized-bed. The reactor system is organized into three strings of multiple-pass fluidized-bed reactors, with each string consisting of four 6-in.-diam fluidized-bed reactors to provide the 4 9's DREs.

Data Base

Single-pass conversion efficiencies for a 1.6 mole % TCE-A in a dry-air stream passed at 100 cc/min over a silicon carbide (60 × 80 mesh) fluidized-bed heated with microwaves to moderate (500° to 580°C) temperatures are at 500°C ~96%, at 540°C ~98%, and at 580° ~99%.

Using the above data base and up-scaling, a 24 kg/h throughput is divided into the three strings of multiple-pass fluidized-bed reactors (12 in all) for total detoxification. The material balance and energy balance are calculated for 500°C, 540°C, and 580°C. The schematic of the microwave fluid-bed reactors (MFBs) energized by a 30- or a 60-kW, 0.915-GHz magnetron is shown in Figure 5; the inset figure outlines the conceptual design of the prototype mobile truck-mounted unit.

The reaction is

Material balance implies mass transport of 1.00 mole TCE-A/min, 3.00 mole HCl/min, and 2.00 mole CO₂/min.

$$\begin{aligned} 8 \text{ kg TCE/h} &= 1 \text{ mole TCE/min} \\ \text{Scale-up factor} &= 1.5 (10^4) \end{aligned}$$

Reaction being O₂-limited, dry air flow required (based on our data base) is given as follows:

$$100 \times 1.5(10^4) \times 1.3/8.1 \text{ cc/min} = 241 \text{ L/min}$$

Fluidization Conditions

Onset velocity for fluidization of 60 × 80 mesh SiC particulates (size = 100 μm, D = 3.21) at 540°C in a 6-in.-diam reactor tube is ~4 cm/s; the elution velocity is ~170 cm/s. An average practical air velocity of ~23 cm/s, quite consistent with a state-of-the-art fluid-bed, will provide an air throughput of 241 L/min.

Reactant

$$\begin{aligned} \text{TCE-A} &= 24 \text{ kg/h} \\ \text{Dry Air} &= 1532 \text{ ft}^3/\text{h} \end{aligned}$$

Note: O₂ supply is ~6.2 times that needed by stoichiometry demand.

Products

$$\begin{aligned} \text{CO}_2 &= 15.8 \text{ kg/h} \\ \text{HCl} &= 19.6 \text{ kg/h} \\ \text{Na}_2\text{CO}_3 &= 28.6 \text{ kg/h} \\ \text{NaCl} &= 31.6 \text{ kg/h} \end{aligned}$$

Energy Balance

Trichloroethane, TCE-A detoxification at 500°C, 540°C, and 580°C. Reaction is

The energy balance in watts given for 24 kg/h is given in Table I.

Table I. Energy Balance in Watts for 24 kg/h TCE-A Detoxification Using Three Strings with 6-in.-diam × 8-in. Fluidized-beds in Four Reactor Tubes (see Fig. 5).

Temperature of Fluidized-bed Reactor	500°C	540°C	580°C
Heat Loss			
Convection*(-)	2.72(10 ⁴)	2.99(10 ⁴)	3.31(10 ⁴)
Radiation*(-)	1.79(10 ⁴)	2.20(10 ⁴)	2.72(10 ⁴)
Conduction*(-)	0.75(10 ³)	0.83(10 ³)	0.90(10 ³)
Sensible Heat (-)	1.62(10 ³)	1.7(10 ³)	1.9(10 ³)
Total (kW)(-)	47.47	54.43	63.1
Heat Generated			
Chemical Reaction (+)	4.5(10 ⁴)	4.5(10 ⁴)	4.5(10 ⁴)
Total Energy in kW (+)	45	45	45
(-) Net Energy in kW	2.47	9.43	18.1
*Upper Bound Values			
*Convection can be considerably reduced by use of insulator jacket.			

B. TCE-E DETOXIFICATION TO 4.9'S DRE: MATERIALS AND ENERGY BALANCE

The arrangement of MFBs is exactly the same; in this case, a smaller throughput of 12 kg/h of TCE-E is considered. Three strings of MFBs handle a throughput of 12 kg/h, 4 kg/h in each string.

The detoxification reaction is given below:

Data Base

A 1.6 mole % TCE-E in a moist-air stream at 100 cc/min over a 1-in.-diam silicon carbide bed heated to 540°C (or greater) gets detoxified to ~98% in a single pass. In fact, in the temperature range 500° to 580°C, the conversion efficiencies are in the range of 96° to 99.9°C.

The continued cycling of residual "ClHC" and the concomitant gas cleanup provide the total detoxification of 12 kg/h throughput using the MFB system shown in Fig. 5.

Materials Balance

Reactants:

TCE-E = 12 kg/h
Air (~150°C) = 783 ft³/h
H₂O (~150°C) = 1.6 kg/h

Products:

CO₂ = 7.92 kg/h
HCl = 9.86 kg/h
Na₂CO₃ = 14.31 kg/h
NaCl = 15.80 kg/h

Fluidizing Condition

The TCE-E + air + H₂O flow of 370L/min is divided into three strings of 6-in.-diam × 8-in. 60 × 80 mesh SiC fluidized beds; thus, 124 L/min throughput of gaseous stream in each MFB of the three strings can be maintained with space velocity of air at ~18 cm/s.

Reaction is given by Equation (2).

Energy Balance

Energy balance is calculated in the manner given before. For detoxification of 12 kg/h using string of 4-MFBs in series, the energy balance is given in Table II.

Table II. Energy Balance in Watts for 12 kg/h TCE-E Detoxification Using Two Strings of Four MFBs in Series with 6-in.-diam × 8-in. Fluidized-Beds of 60 × 80 Mesh Silicon Carbide.

Temperature of Fluidized-Bed			
Heat Loss			
Convection (-)	2.72(10 ⁴)	2.99(10 ⁴)	3.31(10 ⁴)
Radiation (-)	1.79(10 ⁴)	2.20(10 ⁴)	2.72(10 ⁴)
Conduction (-)	0.75(10 ³)	0.83(10 ³)	0.90(10 ³)
Sensible Heat (-)	0.81(10 ³)	0.85(10 ³)	0.95(10 ³)
Total kW (-)	46.7	53.6	62.1
Heat Generated			
Chemical Reaction (+)	2.25(10 ⁴)	2.25(10 ⁴)	2.25(10 ⁴)
Net (12 kg/h)			
Energy Needed in kW (-)	24.2	31.1	39.6

SUMMARY

The schematic of the MFB system proposed for DT & E pilot-scale work is shown in Fig. 5. It consists of three strings of multiple-pass fluidized-bed reactors (MFBs), each string in turn containing four MFBs. Each MFB is a 6-in.-diam fused silica tube-reactor with a fluidized-bed of 6-in.-diam and 8 in. high. Both trichloroethene (TCE-A) and trichloroethylene (TCE-E) are detoxified completely to 49's DREs. The products in each case are CO_2 that can be vented and HCl that can be scrubbed easily.

Two cases have been considered: a throughput of (i) TCE-A at 24 kg/h and (ii) TCE-E at 12 kg/h.

Examining the energy balance Tables I and II, it appears that at a higher throughput of TCE-A (i.e., 24 kg/h), the need is only for 2.43 kW of microwave at 540°C, whereas at a throughput of 12 kg/h for TCE-E, a need of 31.1 kW of microwave power is shown at the same temperature. The energy balance in both cases becomes extremely attractive if the reactor tubes are insulated properly, thus eliminating convection heat loss.

The results are indeed encouraging for using microwave energy in detoxification of "CIHC" hazardous waste. Perhaps the surface-enhanced effects on chemical reactions play a dominant role in the oxidation of TCEs.

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