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Task 3 - Pyrolysis of Plastic Waste

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TASK 3 – PYROLYSIS OF PLASTIC WASTE

Work for the period is summarized in the final report for the project, which is attached.

1

TASK 3 – PYROLYSIS OF PLASTIC WASTE

Final Report

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LIST	of fig	URES i
LIST	OF TAI	ii ii
EXE	CUTIVE	SUMMARY iii
1.0	INTRO	DUCTION/BACKGROUND 1
2.0	OBJEC	TIVES
3.0	ACCON 3.1 Pi 3. 3.2 M 3.3 3.2 M 3.3 3.3 3.3 3.3 In 3.4 Pi 3. 3.3 3.3 3.3 3.3 3.3 3.3 3.3	IPLISHMENTS/WORK PERFORMED4ocess Commercialization Requirements41.1 Process Applicability/Market Niche41.2 Development Needs41.3 Marketing/Commercialization Needs5arket Assessment52.1 Waste Volume52.2 Waste Composition62.3 Radionuclide Surrogate Selection7itial Concept Evaluation Tests – High Detection Limits134.1 Establishment of Minimum Detection Limits134.2 CFBR Process Optimization Testing134.3 Initial Ion-Exchange Resin Tests164.3.1 Fluid-Bed Reactor Test164.3.2 Auger Reactor Construction and Shakedown17
10	3.	4.4 Auger Reactor Ion-Exchange Resin Tests
4.0 5.0	REFER	$ENCES \dots \dots$

TABLE OF CONTENTS

LIST OF FIGURES

1	EERC CFBR system process flow schematic	3
2	Auger reactor system process flow schematic	8
3	EERC Auger reactor system	18

LIST OF TABLES

K,

1	Radioactive Waste Generation Volumes	6
2	Radionuclide Surrogates for Investigation of Pyrolysis Reactivity Effects	7
3	Surrogates to Represent Nuclear Defense-Related Radionuclides - Actinides	7
4	Surrogates to Represent Nuclear Reactor-Based Radionuclides	8
5	As-Weighed Compositions of Total Feedstock Mixtures	10
6	Surrogate Concentrations in Thermal Decomposition Products – General Reactivity Effects	11
7	Surrogate Concentrations in Thermal Decomposition Products – Actinide Simulation	11
8	Surrogate Concentrations in Thermal Decomposition Products – Reactor Waste Simulation	12
9	Thermal Decomposition of Surrogate-Spiked Mixed Wastes: Yield Data	12
10	Radionuclide Surrogate Detection Limits	13
11	Postconsumer Plastics-Based Reactant Mixture Compositions	14
12	Radionuclide Surrogate Concentrations in Reactant Mixtures D, E, and F	14
13	Postconsumer/Surrogate Test Reaction Parameters and Sample Procedures	14
14	Surrogate Concentrations in Test M549 (450°C) Products	15
15	Surrogate Concentrations in Test M550 (450°C) Products	16
16	Cesium Separation from Ion-Exchange Resin – M553 CFBR Test Results	17
17	Test M556 – Description and Results	19
18	Process Commercialization Criteria	21

ii

PYROLYSIS OF PLASTIC WASTE

EXECUTIVE SUMMARY

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The Energy & Environmental Research Center (EERC) has developed a low-temperature thermal decomposition process for volume reduction of high-organic-content wastes from activities associated with nuclear defense and power generation, energy and manufacturing industries, medical practices, and biological research. The process evolved from work on thermal depolymerization of mixed-waste postconsumer plastics for production of fuel and chemical feedstocks sponsored by the U.S. Department of Energy (DOE), the American Plastics Council, 3M Company, Amoco Chemical Company, and the U.S. Environmental Protection Agency (EPA). Motivation for commercial application of the process to radioactive waste volume reduction is provided by the cost of Class A nuclear waste landfill disposal, which is about \$400 per cubic foot.

Primary project objectives were to optimize the thermal decomposition process for application to volume reduction of 1) high-organic-content radioactive mixed wastes and 2) spent (radioactive) ion-exchange resins from nuclear power facilities. Stone & Webster Environmental Technology & Services, Boston, was retained by the EERC to provide data and information regarding nuclear industry waste generation and waste-processing needs. Using radionuclide surrogates selected with assistance from Los Alamos National Laboratory, we performed tests using the EERC's lab-scale (1- to 4-pounds per hour [lb/hr]) continuous fluid-bed reactor system. Tests were also performed using the EERC's lab-scale Auger reactor system to evaluate the effect of a lower purge gas flow rate (versus a higher fluidization gas flow rate) on particulate entrainment and postreactor gas treatment requirements. Test feedstocks included surrogate-spiked mixtures of postconsumer plastics and cesium-loaded commercial-grade ion-exchange resin. The resin was supplied by GTS-Duratek, a commercial nuclear waste-processing company headquartered in Columbia, Maryland, with an interest in commercial application of the EERC polymer decomposition process. Throughout the project, Duratek consulted with and provided information to the EERC regarding desired process throughput and related work on resin processing.

Test results demonstrated that the EERC process concentrated radionuclide surrogates in a solids residual and yielded a nearly surrogate-free offgas (or condensate) product. Control of sulfur and chlorine emissions was also demonstrated with the use of a temperature-controlled postreactor packed-bed filter containing alkaline material. In fluid-bed tests with feedstock mixtures of waste plastics and nine surrogate species (added in concentrations of about 1000 to 3000 micrograms per gram [μ g/g]), product analyses indicated that with the exception of tin (which has a boiling point of about 232°C), all surrogates were concentrated in the solids residual. However, small amounts of particulate carryover were observed in some tests. In all cases, the small quantities of surrogates observed in the fluid-bed offgas streams were removable by filtration, which indicated particulate carryover due to fluidization gas stream entrainment. In tests with an Auger reactor, which enabled the use of a lower gas flow rate (since fluidization was not required), surrogate carryover was significantly reduced. In an Auger reactor test conducted at about 550°C with an ion-exchange resin loaded with 1960 μ g/g of cesium, the following key results were achieved:

Volume reduction (without crushing or compaction)79%Cesium content of total offgas $29.9 \ \mu g/L$

Portion of cesium recovered in solids residual	96.8%
Portion of cesium recovered in offgas	2.1%
Cesium closure (based on calculated mass balance)	98.9%

Based on the work performed in this and prior projects, it appears that the Auger reactor configuration has significantly higher commercial potential for applications in which quantitative separation and recovery of radionuclides and/or heavy metals (both inorganically and organically associated) is important. Based on discussions with Duratek and other industry personnel regarding application of the EERC process to commercial and defense industry radioactive waste streams, key viability criteria include:

- Achievement of an approximate 8-to-1 waste volume reduction
- Concentration of 99.9% to 99.99% of feedstock-contained radionuclides in a solids residual
- Generation of a solids residual with a sulfur content of about 1% and a minimal carbon content
- Demonstration of an economic system for monitoring and ensuring against radionuclide emissions
- Demonstration of adequate sulfur emission control
- Development and demonstration of an economic system for preprocess feedstock drying that enables continuous feeding

Over the course of the project, the EERC and Duratek personnel have visited each other's facilities to discuss collaborative arrangements for commercial development of a variety of waste treatment technologies including volume reduction of radioactive ion-exchange resins, decontamination of high-organic-content mixed waste at several nuclear material processing sites, and disposal and stabilization technologies for wastes containing sulfur and chlorine.

PYROLYSIS OF PLASTIC WASTE

1.0 INTRODUCTION/BACKGROUND

> Over the last 50 years, the U.S. Department of Energy (DOE) has produced a wide variety of radioactive wastes from activities associated with nuclear defense and nuclear power generation. These wastes include low-level radioactive solid wastes, mixed wastes, and transuranic (TRU) wastes. A portion of these wastes consists of high-organic-content materials, such as resins, plastics, and other polymers; synthetic and natural rubbers; cellulosic-based materials; and oils, organic solvents, and chlorinated organic solvents. Many of these wastes contain hazardous and/or pyrophoric materials in addition to radioactive species. Physical forms of the waste include ionexchange resins used to remove radioactive elements from nuclear reactor cooling water, lab equipment and tools (e.g., measurement and containment vessels, hoses, wrappings, equipment coverings and components, and countertops), oil products (e.g., vacuum pump and lubrication oils), bags and other storage containers (for liquids, solids, and gases), solvents, gloves, lab coats and anticontamination clothing, and other items. Major polymer and chemical groups found in high-organic-content radioactive wastes include polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), Teflon[™], polystyrene (PS), nylon, latex, polyethylene terephthalate (PET), vinyl, high-density polyethylene (HDPE), polycarbonate, nitriles, Tygon[®], butyl, and Tyvec[®].

> Costs associated with the accumulation, storage, and disposal of high-organic-content radioactive wastes are high because of irregularities in shape, volume, and composition. Storage of combinations of these contaminated materials in sealed barrels and other containers can cause degradation reactions that yield a wide range of radioactive products (many of which have some degree of volatility and/or environmental mobility) and other hazardous materials, including hydrogen gas. Options for dealing with high-organic-content radioactive waste include volume reduction and storage. Large quantities of these wastes are currently being stored in barrels and casks. One waste reduction option involves separating wastes into combustibles and noncombustibles and then incinerating the combustibles to yield ash and gas. The radioactive component of the waste is reduced in volume and can be stored more easily. Difficulties associated with this approach include the potential for entrainment of radioactive species in the product gas stream and volatilization of radioactive species during the high-temperature combustion process. On-line and full-stream gas analysis systems are being developed to monitor emissions more accurately, but controlling volatile emissions is limited by physical constraints and statistical probabilities.

The University of North Dakota Energy & Environmental Research Center (EERC) is developing a process for efficient, complete separation of radionuclides from high-organic-content radioactive waste. The process is a low-temperature thermal decomposition-separation technology that yields a small volume of particulate solids product containing radioactive species, a nonradioactive organic condensable gas product, and a nonradioactive hydrocarbon-rich gas product. By controlling process conditions, the yield of condensable gas product can be varied from 20 to 80 wt% of the feed material, with the remaining organic content of the feed material converted to gas. Processing at a low reactor temperature (600°C or below) ensures against

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radionuclide volatilization and results in a high condensable versus a high noncondensable gas yield.

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The EERC thermal decomposition-separation process for radionuclide separation is not a combustion process. The process will accomplish the following:

- Decompose, volatilize, and recover (for disposal) the condensable organic content of a waste
- Volatilize and capture chlorine (which may be present in the waste as either organic or inorganic materials)
- Concentrate radionuclide species in a dry particulate solids product

The process is applicable to the separation of radionuclides from the following waste streams:

- Low-level radioactive solid waste, defined as solid radioactive waste that is not classified as high-level waste, TRU waste, or spent nuclear fuel as defined in DOE Order 5820.2A. This category is generally used to refer to wastes that are radioactive but do not contain components classified as hazardous.
- Mixed wastes, defined as wastes that contain both radioactive and hazardous components as defined by the Atomic Energy Act and the Resource Conservation and Recovery Act (RCRA), including solvents, pyrophoric substances, and other chemically contaminated items. Wastes under this category are of special importance 1) because no current plan for their treatment has been accepted and 2) because of their chemical diversity, these wastes could react during containment to yield a wide variety of products, many of which may be volatile, reactive, ignitable, toxic, or otherwise hazardous.
- TRU waste, defined as waste that has a radioactivity greater than 100 nanocuries per gram (nCi/g) and is contaminated with alpha-emitting radionuclides that have an atomic number greater than 92 and a half-life of greater than 20 years.

New processes are being developed to thermally depolymerize and decompose plastic wastes to monomers and/or oils. Most of these processes are extremely limited in terms of type and combination of acceptable feedstocks (1–12). Many processes are applicable only to single- or dual-component feedstocks, which requires expensive preprocess sorting. Through projects sponsored by DOE, the American Plastics Council, 3M Company, Amoco Chemical Company, and the U.S Environmental Protection Agency (EPA), the EERC has developed technologies capable of accommodating the wide variety of plastic materials found in postconsumer and postindustrial waste streams (13–17). Figure 1 is a process schematic that illustrates process flow, components, and reactions in the EERC continuous fluid-bed reactor (CFBR). Application of the process to the separation of radionuclides from high-organic-content waste streams was pursued in tests with feedstock mixtures of mixed-waste plastics and radionuclide surrogate species. The primary technical objectives of the tests were maximum solids volume reduction and complete recovery of all surrogates in a solids residual comprising an overflow stream from the reactor and particulate removed from the postreactor gas stream via the cyclone.



Figure 1. EERC CFBR system process flow schematic.

2.0 OBJECTIVES

The EERC is developing a technology for the thermal decomposition of high-organic-content, radionuclide-contaminated mixed wastes and spent (radioactive) ion-exchange resins from the nuclear power industry that will enable the separation and concentration of radionuclides as dry particulate solids and the generation of nonradioactive condensable and noncondensable gas products. Successful application of the technology will enable a significant volume reduction of radioactive waste and the production of an inexpensively disposable nonradioactive organic product. The project objective is to develop and demonstrate the commercial viability of a continuous thermal decomposition process that can fulfill the following requirements:

- Separate radionuclides from radioactive waste streams containing a variety of types and levels of polymers, chlorinated species, and other organics, including rubber, oils, resins, and cellulosic-based materials.
- Concentrate radionuclides in a homogeneous, dry particulate product that can be recovered, handled, and disposed of efficiently and safely.

- Separate and recover any chlorine present (as PVC, chlorinated solvents, or inorganic chlorine) in the contaminated mixed-waste stream.
- Yield a nonradioactive, low-chlorine-content, condensable organic product that can be economically disposed.

As a result of ongoing discussions with personnel at commercial nuclear waste-processing facilities and Stone & Webster Engineering Corporation (subcontracted by the EERC to provide guidance on process optimization and radioactive waste stream targeting), the EERC decided to target application of the thermal decomposition process to volume reduction of spent (radioactive) ion-exchange resin. Commercial application of the technology to spent ion-exchange resin, which accounts for about 50,000 to 200,000 cubic feet per year of the total annual U.S. nuclear waste volume of 500,000 to 700,000 cubic feet, would establish the viability of the process and help in its application to other less homogeneous waste streams. Economic motivation is provided by the cost of landfill disposal, which is about \$400 per cubic foot, since contaminated resin is categorized as a Class A nuclear waste. A primary project objective is to effectively reduce this cost to \$200 per cubic foot by economic optimization of the volume reduction process.

3.0 ACCOMPLISHMENTS/WORK PERFORMED

11

3.1 Process Commercialization Requirements

The EERC contracted Stone & Webster Environmental Technology & Services (S&W) to evaluate the commercial potential and assist in the development of the EERC waste plastics thermal decomposition process as applied to separation of radionuclides from high-organic-content nuclear industry wastes. Dr. Joe Cardito of S&W spent 2 days at the EERC inspecting facilities and equipment, reviewing technical information, and discussing process commercialization and marketing strategies. A summary of Dr. Cardito's assessments and recommendations is provided below.

3.1.1 Process Applicability/Market Niche

Efforts should be focused on application of the EERC process to spent (fully loaded) ionexchange resins used to remove radionuclides from aqueous solution at nuclear power facilities. Demonstration of process economics and technical viability with resins should facilitate its marketing to commercialization entities, either as a stand-alone technology or as a component of a larger process, and should enable further applications testing with more varied waste streams. Consideration should be given to developing and marketing a skid-mounted version of the process, which may provide significant economic advantage.

3.1.2 Development Needs

The following are development needs:

• A series of process demonstration tests should be performed at the EERC in which Amberlite IRN-150/nuclear-grade resin loaded with (nonradioactive) cesium is used as feedstock. The resin should be loaded with at least 0.64 grams of cesium per cubic foot of resin (a calculated maximum value for spent resin from operating nuclear power facilities) at the EERC prior to test performance. A primary test objective will be to demonstrate (to the extent possible without the use of radioactive material) that the process residual would qualify as a Class A waste, according to Department of Transportation and Nuclear Regulatory Commission Regulations in Title 49 and Title 10 of the Code of Federal Regulations.

- A series of process demonstration tests should be performed at the EERC in which a wellcharacterized postconsumer plastics mixture with added polymers (to represent nuclear facility organic waste materials) and several radionuclide surrogates is used as feedstock.
- A complete material balance should be performed around the EERC process as applied to 1) the cesium-loaded Amberlite resin and 2) the postconsumer plastics mixture, into which has been added several polymers representative of nuclear facility lab waste, including recycled Tyvec[®] and polycarbonate, virgin nylon and acrylonitrile butadiene styrene (ABS), and several radionuclide surrogates. The material balance data will be used to assess process economics.

3.1.3 Marketing/Commercialization Needs

- Work should be initiated on preparation of a "technology application analysis" for marketing the EERC process to commercialization entities.
- Contact should be made with representatives of nuclear waste-processing companies including Scientific Ecology Group, Inc. (Oak Ridge, Tennessee); M4 Environmental L.P. (Oak Ridge, Tennessee); and GTS-Duratek (Columbia, Maryland) to initiate discussions on possible commercial application of the EERC process and to set up site visits.

3.2 Market Assessment

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3.2.1 Waste Volume

Inventories of low-level, mixed, and TRU wastes accumulated throughout the United States as of 1993 have been compiled and are detailed in a report prepared by Oak Ridge National Laboratory entitled "Integrated Data Base Report – 1993: U.S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections, and Characteristics" (DOE/RW-0006, Rev. 10, December, 1994). Table 1 compares data from the report with data from Los Alamos National Laboratory (LANL) on radioactive waste generation through 1993 and with data for LANL radioactive waste generation in 1994. A significant portion of annually generated radioactive organic waste is made up of spent (radionuclide-loaded) ion-exchange resins from nuclear power facilities, and in addition to nuclear defense and power generation activities, large volumes of low-level radioactive wastes are generated by hospitals and medical research facilities. The EERC technology is being developed for application to these and other waste streams.

DOE Volume LANL Volume LANL Volume Image: Non-the logo Image: Non-the logo 1004					
waste Type	Inrough 1993	Inrough 1993	1994		
Low-Level	2,911,000	220,700	2963		
Low-Level/Mixed	173,900	665	76		
TRU	104,100	10,810	67		
TRU/Mixed	5187	619	17		

3.2.2 Waste Composition

In a recent investigation, LANL personnel used a near-infrared fiber optic spectroscopic technique to determine the types of organic materials present in 12 waste drums containing "TRUCON CODE 111/211" waste (combustibles). Major organic constituents included PVC, LDPE, PP, Teflon, and PS. Other components included nylon, latex, PET, vinyl, HDPE, polycarbonate, Tygon, and butyl. Major radionuclides identified included plutonium-239 (Pu-239) and americium-241 (Am-241).

In the early stage of the project, EERC personnel met with personnel at LANL and Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada, to discuss selection of a representative high-organic-content nuclear industry waste mixture for use in process application and optimization testing. Selection of a representative waste mixture was difficult because limited data are available on the compositional breakdown (e.g., plastics versus rubber and type of plastic and type of rubber) of mixed waste currently stored at and around Los Alamos and other sites, most of which is contained in sealed barrels and some of which has been stored for about 40 years. Based on the LANL and Lockheed discussions, the waste drum data provided above, and EERC reactor operation experience with mixed plastics feedstocks in process development work funded by the American Plastics Council and 3M Company, a decision was made to perform initial process evaluation tests with a polymer feedstock comprising a previously characterized postconsumer plastics waste stream. The postconsumer mixture had been used in prior depolymerization work at the EERC and was characterized by Southwest Research Institute (SRI) of San Antonio, Texas. According to SRI's analysis, the approximate composition, in wt%, of the polymer feedstock was as follows:

HDPE:	28.7
PET:	9.8
PP:	21.6
PS:	18.6
LDPE:	18.2
PVC:	3.1

3.2.3 Radionuclide Surrogate Selection

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EERC personnel met with personnel at LANL and Lockheed to discuss selection of suitable radionuclide surrogates for use in process application and optimization testing. Based on the discussions and ongoing communication with LANL, primary surrogate selection criteria were elemental oxidation state(s), electronic configuration, melting point, and reactivity with chlorine. Tables 2–4 provide information on the compounds selected as radionuclide surrogates.

Radionuclide	Surrogates for Invest	igation of Pyrolysis Rea	activity Effects
Surrogate	Chemical Formula	To Represent	To Investigate
Vanadium Pentoxide	V ₂ O ₅	Actinide oxides	Oxide reactivity and volatilization effects
Tin	Sn	Actinide and fission product metals	Reactivity—especially with Cl
Antimony	Sb	Actinide and fission product metals	Reactivity—especially with Cl
Copper	Cu	Actinide and fission product metals	Reactivity—especially with Cl
Titanium Trichloride	TiCl ₃	Actinide and fission product metals	Highly reactive materials effects

TABLE 2

TABLE 3

Surrogates to Represent Nuclear Defense-Related Radionuclides - Actinides

Surrogate	Chemical Formula	To Represent	To Investigate
Vanadium Pentoxide	V ₂ O ₅	Several oxidation states of U, Np, Pu	Oxide reactivity and volatilization effects
Neodymium Nitrate Hexahydrate	$Nd(NO_3)_3 \cdot 6H_2O$	Am	Nitrate reactivity and volatilization effects
Zirconium Tetrachloride	ZrCl_4	Th and +4 oxidation state of U, Np, Pu	Chloride reactivity and volatilization effects
Cerium Trichloride Heptahydrate	$CeCl_3 \cdot 7H_2O$	U	Chloride reactivity and volatilization effects

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Surrogate	Chemical Formula	To Represent	To Investigate
Cesium Chloride	CsCl	Radioactive Cs	Chloride reactivity and volatilization effects
Strontium Nitrate	Sr(NO ₃) ₂	Radioactive Sr	Nitrate reactivity and volatilization effects
Ruthenium Trichloride Hydrate	$RuCl_3 \cdot xH_2O$	Radioactive Ru	Chloride reactivity and volatilization effects
Rhenium Dioxide	ReO ₂	Radioactive Tc	Oxide reactivity and volatilization effects
Rhenium(VII) Oxide	Re ₂ O ₇	Radioactive Tc	Oxide reactivity and volatilization effects
Potassium Iodide	KI	Radioactive I	Reactivity and volatilization effects

Surrogates to Represent Nuclear Reactor-Based Radionuclides

3.3 Initial Concept Evaluation Tests – High Detection Limits

Separation of radionuclides can be performed with a fluid-bed reactor-based system (Figure 1) or an Auger reactor-based system (Figure 2) at a temperature of 450° - 600° C in the



Figure 2. Auger reactor system process flow schematic.

presence of an alkaline bed material. During processing, three general reactions occur in the reactor system. Addition polymers, such as polyethylene, PP, PS, and PVC are thermally decomposed to produce an oil with a boiling point range between that of No. 2 diesel fuel and JP-4 (commercial jet fuel). Condensation polymers like PET hydrolyze to form terephthalic or benzoic acid. Chlorine species that evolve during processing because of the presence of PVC or chlorinated solvents are captured and removed from the process stream via reaction with the alkaline bed material or reaction with alkaline material in a temperature-controlled packed-bed filter system located downstream from the reactor.

11 14

An initial series of tests with the EERC CFBR was performed according to the following procedures. Feed mixtures of postconsumer plastics and radionuclide surrogates are placed in the feed hopper, metered, and fed through two augers into the bottom of the fluid bed. Unconverted and spent bed solids are drained from the top of the bed into a solids receiver. Fluidization gas is preheated and fed into the bottom of the reactor. The organic wastes decompose, vaporize, leave from the top of the reactor, pass through a hot cyclone (for particulate control), and are condensed in one of two identical condensation trains. As shown in the schematic, the reactor system can be configured so that the gas stream exiting the cyclone is routed through a controlled-temperature, packed (with alkaline sorbent)-bed filter for chlorine capture prior to entering one of the condensation trains. Each condensation train has three indirectly cooled (with chilled water or glycol) collection vessels. Gas exiting the condensation system can be routed through a caustic scrubber and then to a gas meter before discharge, or routed directly to the gas meter, depending on sampling and analytical requirements. Gas samples can be obtained at any desired point beyond the condensation train, and process gas can be routed through a Fourier transform infrared (FT-IR) analyzer for on-line analysis.

Nine CFBR tests were performed at a reactor feed rate of about 1 kg/hr of mixed polymers with added alkaline chlorine sorbent and selected radionuclide surrogates. The objective of these preliminary screening tests was to investigate the effectiveness of the EERC thermal decomposition process in concentrating radionuclide surrogates in a solid product while yielding surrogate-free condensate and gas products. Because these initial tests were performed for concept validation and to screen a fairly wide range of reaction parameters, extremely low analytical detection limits for the radionuclide surrogates were not required. To minimize analytical costs, detection limits for the surrogates in the condensate products were set at 5 parts per million (ppm). In later process optimization testing, detection limits were set significantly lower, as described in Section 4.4.1.

Three separate surrogate mixtures, representing the three surrogate groups described in Tables 2–4, were mixed with CaO and polymer feedstock to provide three total feedstock mixtures, each containing carefully weighed amounts of surrogates, polymer mix, and CaO. Table 5 shows the compositions of Mixes A, B, and C prepared for testing to investigate general reactivity effects, nuclear defense-related contaminant effects, and nuclear reactor-related contaminant effects, respectively. To help ensure adequate mixing, weighed amounts of each surrogate were added to a weighed amount of CaO, the resulting surrogate group-CaO mixture was added to a weighed amount of polymer mix, and the resulting total feedstock mixture was sealed (under nitrogen) in a plastic barrel and mixed for 2 hours using a barrel rotater (a machine for end-over-end barrel rotation).

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	Tis weighed compositions	of four feedstock mint	
	General Reactivity	Actinides	Reactor Waste
	Mix A	Mix B	Mix C
	Concentration, wt%	Concentration, wt%	Concentration, wt%
HDPE	26.7	26.4	26.7
PET	9.1	9.0	9.1
PP	20.1	19.9	20.1
PS	17.3	17.2	17.4
LDPE	16.9	16.7	16.9
PVC	2.8	2.7	2.8
CaO	4.9	4.9	5.1
	Concentration, $\mu g/g$	Concentration, $\mu g/g$	Concentration, $\mu g/g$
$V_{2}O_{5}$	4890	4850	4910
Sn	4890	4850	
Sb	4890	4850	
Cu	4890	4850	
TiCl ₃	3630		
$Nd(NO_3)_3 \cdot 6H_2O$		3590	
ZrCl ₄		4850	
$CeCl_3 \cdot 7H_2O$		4920	
CsCl			4910
$Sr(NO_3)_2$			3640
$RuCl_3 \cdot xH_2O$			910
ReO ₂			180
Re_2O_7			180
KI			4910

As-Weighed Compositions of Total Feedstock Mixtures

Each feedstock mixture was reacted at three different temperatures (450°, 500°, and 600°C), for a total of nine tests. For each test, feedstock mixture was fed into the reactor for about 2 hours (to ensure establishment of steady-state conditions), after which a 4-hour balance period commenced. All solid and condensable offgas (condensate) products generated during the course of the balance period are carefully recovered, weighed, and stored for analysis. Gas samples are collected at the halfway point and immediately before completion of the balance period. Data from analysis of each set of balance period samples are used for the evaluation of each of the nine test conditions (feedstock-temperature combinations).

Tables 6–8 provide data on the surrogate concentrations determined for the solids residuals and condensable offgas products of the three 600°C tests, and Table 9 shows calculated yields for eight of the nine tests. Each solid and condensate product referred to in the table was sampled and analyzed in duplicate, and each value shown in the table is an average of the two analyses. Following microwave digestion of each sample in a mixture of hydrochloric, nitric, and sulfuric acids, analyte quantitations were performed with inductively coupled argon plasma (ICAP) spectrometry according to EPA Method 200.7. For both solids and condensable product analysis, the quality assurance (QA) objective for analytical precision (per analyte basis) is $\leq 55\%$, calculated as relative percent difference (RPD) between laboratory duplicates.

Surrogate Conce	Surrogate Concentrations in Thermal Decomposition Products – General Reactivity Effects						
Test Number	M525	M525	M525	M525			
Temperature, °C	588	588	588	588			
Sample	Feed Material	Solids Residual	Unfiltered	Filtered			
			Condensate	Condensate			
Calcium, $\mu g/g$	35,000	275,600	<5	<5			
Vanadium, $\mu g/g$	2750	15,490	<6	<5			
Tin, $\mu g/g$	4890	10,020	<6	<5			
Antimony, $\mu g/g$	4890	25,160	<9	<5			
Copper, µg/g	4890	8120	<5	<5			
Titanium, $\mu g/g$	1630	2930	< 8	< 5			

Surrogate Concentrations in Thermal Decomposition Products – General Reactivity Effect	Surrogate C	Concentrations	in Therma	al Decomposition	Products – (General Reactiv	ity Effects ¹
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¹ All solids and condensate product concentration values are averages of duplicate analyses, and all surrogate detection limits are 5 ppm.

TABLE 7

Surrogate Concentrations in Thermal Decomposition Products – Actinide Simulation ¹					
Test Number	M529	M529	M529	M529	
Temperature, °C	602	602	602	602	
Sample	Feed Material	Solids Residual	Unfiltered	Filtered	
-			Condensate	Condensate	
Calcium, µg/g	35,000	194,800	11,240	<5	
Vanadium, $\mu g/g$	2720	17,670	540	<5	
Tin, μg/g	4850	22,640	1580	<5	
Antimony, $\mu g/g$	4850	28,340	2450	< 5	
Copper, $\mu g/g$	4850	12,060	110	<5	
Zirconium, $\mu g/g$	1890	8079	740	<5	
Cerium, µg/g	1850	7313	240	<5	
Neodymium, $\mu g/g$	1180	4289	100	< 5	

¹ All solids and condensate product concentration values are averages of duplicate analyses, and all surrogate detection limits are 5 ppm.

The data in Tables 6-8 show that even at a decomposition temperature of 600°C, the surrogates (even the highly reactive chlorides, nitrates, and vanadium pentoxide) do not react to form volatile species, but either react to yield nonvolatile solids or remain inert to enable their concentration and recovery as nonvolatile solids. The fact that all filtered (with an $8-\mu m$ filter) condensate surrogate concentrations were below detection limits (which, for these preliminary tests, were set at 5 μ g/g) indicates that the surrogates detected in the unfiltered liquids were not present as volatile species, but were probably present as a result of entrainment in the process gas stream and nonremoval by the less-than-adequate particulate control system. Resizing of the product gas stream cyclone will increase particulate removal effectiveness. The use of a postreactor sorbent bed (primarily for chlorine capture) would also reduce particulate carryover.

Surrogate Concentrations in Thermal Decomposition Products – Reactor Waste Simulation					
Test Number	M531	M531	M531	M531	
Temperature, °C	583	583	583	583	
Sample	Feed Material	Solids Residual	Unfiltered Condensate	Filtered Condensate	
Calcium, $\mu g/g$	36,400	244,400	<5	<5	
Vanadium, $\mu g/g$	2750	21,850	<5	< 5	
Cesium, $\mu g/g$	3880	22,240	<5	<5	
Ruthenium, $\mu g/g$	330	2400	<5	<5	
Rhenium, $\mu g/g$	300	1220	<5	< 5	
Strontium, $\mu g/g$	1510	10,990	<5	<5	

¹ All solids and condensate product concentration values are averages of duplicate analyses, and all surrogate detection limits are 5 ppm.

It is recognized that demonstration of "zero" radioactive emissions will be required of any technology being seriously evaluated for commercial-scale volume reduction of radioactive wastes. The preliminary tests reported in this section were technical feasibility studies and were not conducted to demonstrate zero radioactive emissions. To provide a better assessment of process effectiveness in partitioning radionuclides (surrogates) to solids residuals, surrogate detection limits were lowered significantly in more recent tests.

TABLE 9

Thermal Decomposition of Surrogate-Spiked Mixed Wastes: Yield Data					
Test		Average	Solids Yield,	Condensate	Gas Yield,
No.	Mix	Temp.,°C	<u>wt %</u>	Yield, wt%	wt %
M524	A	494	11.5	74.7	13.8
M525	Α	588	6.9	33.2	59.2
M526	Α	451	13.5	79.6	7.0
M527	В	451	11.5	79.1	9.3
M529	В	602	3.8	41.6	54.6
M530	C	497	7.2	77.7	15.1
M531	С	583	NA ¹	38.5	61.5
M532	С	447	13.0	74.2	12.7

¹ Not available.

3.4 Process Optimization Testing – Minimum Detection Limits

3.4.1 Establishment of Minimum Detection Limits

A series of investigations was performed to determine minimum analytical detection limits for radionuclide surrogates in plastics decomposition condensate products. While the first nine process evaluation tests (reported in Section 4.1) employed per surrogate detection limits of about $5 \mu g/g$, the objective for future tests is a per surrogate detection limit of 0.1 $\mu g/g$. Earlier detection limit estimates (as listed in the April–October 1995 semiannual project report) were based on the commercial availability of a more powerful detector for the EERC ICAP spectrometer. Because the detection limits through optimization of analytical procedures for use with the ICAP as currently configured. The investigations involved the addition of known quantities of surrogates to condensate products from prior work for use in analytical procedures optimization tests. The resulting optimized detection limits are listed in Table 10.

Radionuclide Surrogate Detection Limits				
Surrogate	Chemical Symbol	Detection Limit, $\mu g/g$		
Vanadium	V	2.0		
Tin	Sn	0.1		
Antimony	Sb	0.1		
Copper	Cu	5.0		
Titanium	Ti	0.1		
Strontium	Sr	0.3		
Cerium	Ce	5.0		
Zirconium	Zr	1.0		
Cesium	Cs	0.1		

TABLE 10

3.4.2 CFBR Process Optimization Testing

A series of CFBR tests was performed at a reactor feed rate of about 1 kg/hr of mixed-waste plastics with added calcium oxide (for catalytic activity and chlorine capture), virgin polymer resins (to more closely simulate potential organic radioactive waste streams), and radionuclide surrogates. Three reactant mixtures were prepared. Tables 11 and 12 provide composition data on the plastics-plus-calcium oxide portion and the radionuclide surrogate portion, respectively, of each reactant mixture. With each feedstock mix, three tests were performed at three different temperatures: 450°, 500°, and 600°C. Table 13 lists reaction parameters and sampling procedures for the nine-test series. In Table 11, "Addition Polymer" refers to the fact that Tyvec[®] and ABS are addition polymers, and "Condensation Polymer" refers to the fact that nylon and polycarbonate are condensation polymers. Water addition is often advantageous to reactor operation when processing reactant mixtures with high levels of condensation polymer, because the presence of water enables monomer formation through hydrolysis reactions. Without water, decomposing condensation polymers have a greater tendency to form reactor-plugging coke.

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Postconsumer Plastics-Based Reactant Mixture Compositions				
	Postconsumer	Addition	Condensation	
Reactant Mixture, wt%	(Mix D)	Polymer (Mix E)	Polymer (Mix F)	
Postcomsumer Plastics Content	95	85	85	
Calcium Oxide Content	5	5	5	
Tyvec [®] Content		5		
ABS Content		5		
Nylon Content			5	
Polycarbonate Content			5	

TABLE 12

Radionuclide Surrogate Concentrations in Reactant Mixtures D, E, and F				
		Surrogate-Only		
Radionuclide Surrogate	Added as:	Concentration, $\mu g/g$		
Cesium (Cs)	Cesium Chloride (CsCl)	2810		
Strontium (Sr)	Strontium Nitrate $(Sr[NO_3]_2)$	1810		
Zirconium (Zr)	Zirconium Chloride (ZrCl ₄)	1710		
Cerium (Ce)	Cerium Chloride Hydrate	1630		
Titanium (Ti)	Titanium Chloride (TiCl ₃)	740		
Vanadium (V)	Vanadium Pentoxide (V_2O_5)	2000		
Tin (Sn)	Sn	2740		
Antimony (Sb)	Sb	3580		
Copper (Cu)	Cu	2740		

TABLE 13

Postconsumer/Surrogate Test	Reaction	Parameters and Sample Procedures
Reaction Temperature		450°, 500°, and 600°C
Reaction Pressure		30 psig
Reactant Mixture Feed Rate	æ	1.0 kg/hr
Fluidization Gas Velocity		0.75 linear feet per second
Water Injection Rate		No water injection
Condenser Exit Temperature		25°-30°C
Postcondenser Gas Scrubber Solution		1.0 M potassium hydroxide
Pretest Stabilization Period Duration		2 hours
Balance Period Duration		4 hours
Solids Residual Sample Collection		Cumulative, sample collected over duration of balance period
Condensable Gas Sample Collection		Cumulative, sample collected over duration of balance period
Noncondensable Gas Sample Collection		Gas bag samples collected at midpoint and end of balance period

Following each test, each solids residual was weighed, ground (to ensure homogeneity), and sampled for ash and surrogate quantitation. Each condensable gas product was weighed, blended (to ensure homogeneity), and sampled for surrogate quantitation. Each noncondensable gas sample was analyzed for quantitation (mole percent basis) of hydrogen, methane, acetylene, C_2-C_4 paraffins and olefins, carbon monoxide, carbon hydroxide, oxygen, nitrogen, carbonyl sulfide, and hydrogen sulfide. Based on the mole percent data, an average molecular weight is calculated for each gas sample, which is used in conjunction with total balance period gas volume data to calculate a total weight of product gas generated during the balance period. The total balance period weights of solids residual, condensate, and product gas are used to calculate material balances for each test.

The objective of these tests was to investigate the effectiveness of the EERC thermal decomposition process in concentrating radionuclide surrogates in a solids residual while yielding a surrogate-free condensate product. Tables 14 and 15 show surrogate quantitation data for 450° C tests performed with Mix E (with added addition polymers) and Mix F (with added condensation polymers), respectively. The data indicate that, with the exception of tin (which has a boiling point of about 232°C), all of the surrogates were concentrated in the solids residual, but that some carryover occurred, as noted by the presence of detectable levels of antimony, titanium, and cesium. The problem of solids carryover and how it is being addressed are discussed in Section 4.5.

TABLE 14

Surrogate Concentrations in Test W349 (450 C) Troducts					
Surrogate	Feedstock	Solids Residual ²	Condensate	Postcondenser Scrubber Solution ³	
V	2000	9030	<2	NA ⁴	
Sn	2740	1410	6	NA	
Sb	3580	15,300	2	< 60 ⁵	
Cu	2740	21,800	<5	NA	
Ti	740	1400	6	NA	
Sr	1810	11,500	0.3	NA	
Ce	1630	5800	<5	NA	
Zr	1710	3520	<1	NA	
Cs	2810	9640	0.4	15	

Surrogate Concentrations in Test M549 (450°C) Products⁴

¹ All concentration values are averages of duplicate analyses, and unless otherwise noted, all values are in $\mu g/g$.

² Samples consist of all solids recovered from reactor overflow and the cyclone particulate removal system over the balance period; a portion of the solids generated during each balance period is unrecovered and remains as reactor bed material.

³ Concentration values given as micrograms per liter (μ g/L).

⁴ Not analyzed.

⁵ Higher detection limit due to caustic scrubber solution matrix effects.

Surrogate Concentrations in Test M550 (450°C) Products				
Surrogate	Feedstock	Solids Residual ²	Condensate	Postcondenser Scrubber Solution ³
V	2000	8500	<2	NA ⁴
Sn	2740	1270	12	NA
Sb	3580	23,500	1	< 60 ^s
Cu	2740	15,000	<5	NA
Ti	740	1460	6	NA
Sr	1810	17,300	< 0.3	NA
Ce	1630	6610	<5	NA
Zr	1710	4280	<1	NA
Cs	2810	13,800	0.4	50

All concentration values are averages of duplicate analyses, and unless otherwise noted, all values given are in $\mu g/g$.

² Samples consist of all solids recovered from reactor overflow and the cyclone particulate removal system over the balance period; a portion of the solids generated during each balance period is unrecovered and remains as reactor bed material.

³ Concentration values given as $\mu g/L$.

⁴ Not analyzed.

⁵ Higher detecton limit due to caustic scrubber solution matrix effects.

3.4.3 Initial Ion-Exchange Resin Tests

3.4.3.1 Fluid-Bed Reactor Test

A fluid-bed test was conducted using Rohm and Haas Amberlite[®] IRN-150 nuclear-grade resin, into which approximately 30 grams per cubic foot of cesium was ion-exchanged, according to procedures provided by Stone & Webster, as feedstock. The 1.0-kg/hr test was performed at a reactor temperature of 550°C and a pressure of 30 psig. Steady-state conditions were maintained for an approximate 2-hour balance period, during which solids residual and condensed vapor samples were accumulated. Product gas samples were collected at the midpoint and the end of the balance period. Analytical results from the resin test, provided in Table 16, show that the cesium level in the condensed, filtered (through a 0.45-micron filter) offgas material was less than the current EERC analytical detection limit of 400 nanograms per gram (ng/g). However, the cesium concentration in unfiltered condensate was determined to be about 4 to 20 μ g/g, which indicates that fine particulate material passed through the reactor cyclone. This finding led to consideration of reconfiguring the reactor to reduce the probability of reactor carryover.

In all tests with radionuclide surrogates, the small quantities of surrogates observed in product gas streams appeared to be present as particulates, since the surrogates were removable with filtration. While the small particulate loadings observed would be acceptable for most industries, the presence of radioactive species makes any amount of particulate emissions unacceptable. It should be noted that probably any system will produce a limited amount of reactor carryover and/or will require some form of emission control to provide protection against a system upset.

16

TABLE 16

Cesium Separation from Ion-Exchange Resin – M553 CFBR Test Results				
Feedstock Cesium Concentration, g/ft ³	25			
Overall Mass Balance, %	106			
Normalized Product Yields, wt%				
Solids	3			
Condensable Organic Vapors	60			
Noncondensable Gas	37			
Cesium Separation ¹				
Ion-Exchange Resin Volume Reduction, %	97			
Cesium Balance, wt%	78			
Calculated wt% of Cesium Recovered in				
Solids Residual	99.998			
Cesium Concentration in Condensed Offgas,	•			
ng/g	<400			
All accium analyzan manformed in dumlicate vaira	aid direction followed by			

All cesium analyses performed in duplicate using acid digestion followed by quantitation with atomic absorption spectroscopy.

3.4.3.2 Auger Reactor Construction and Shakedown

The EERC objective is to establish a reactor system configuration that provides the best radioactive volume reduction and the most safety at the least capital, operational, and maintenance costs. After analyzing the results of several fluid-bed resin tests that indicated the occurrence of low-level cesium carryover into the offgas product, a decision was made to evaluate the use of an Auger reactor in place of the fluid-bed reactor. This decision was based on performance and cost considerations. It is likely that capital and operational costs could be significantly reduced by reducing the required capacity of postreactor particulate and sulfur control devices, which is achievable provided that the amount and rate of gas flowing through the reactor are reduced. This would reduce the amount of gas requiring treatment, the velocity of product gas leaving the reactor, and the amount of particle entrainment. The Auger reactor was selected as an alternative to the fluid bed because it can be operated at a low-purge gas flow rate, since reactant fluidization is not required.

Based on the process schematic shown in Figure 2, an Auger reactor system was constructed using unit operation components of the CFBR. Throughout construction and installation of the Auger reactor, EERC staff maintained contact with personnel at Duratek. Duratek staff visited the EERC to observe the Auger reactor shakedown testing, and Duratek has supplied resin feedstocks to the EERC for demonstration testing and provided information regarding desired process throughput and related work on resin processing.

Although systems analysis indicates that the Auger reactor should be superior to the fluid bed in processing spent ion-exchange resin, it must be proven technically. EERC personnel are familiar with several projects in which rotary reactors for soil treatment, coal gasification, or tire pyrolysis have been modified to treat high-polymer-content streams. The success rate has been low to medium, primarily because of lack of knowledge regarding the effects of thermal depolymerization on specific polymers and polymer combinations. Over the last 2 years, the EERC has demonstrated with a variety of feedstocks and radionuclide surrogates that thermal decomposition is a viable approach to separating radioactive materials from an organic matrix. The next ongoing step is to optimize the process as applied to ion-exchange resin based on a performance evaluation and a cost/benefit analysis comparing an Auger reactor-based system with a fluid-bed-based system. Issues that need to be addressed include the following:

- Ensuring that the resin polymer does not form a sticky liquid that reduces heat-transfer capacity and plugs up the solids removal system
- Ensuring that feed material flows freely through the feed system
- Ensuring that liquids do not collect in the offgas-sampling system
- Deciding whether inert material should be added to the feedstock to enhance reactor performance
- Determining whether the process will generate a dioxin problem
- Ensuring process safety

3.4.4 Auger Reactor Ion-Exchange Resin Tests

With the Auger reactor system shown in Figure 3, a series of three thermal decomposition volume reduction tests was performed using cesium-loaded ion-exchange resin from Duratek as





feedstock. The 1-pound-per-hour tests were performed at reaction temperatures ranging from 540° to 600° C. Steady-state operation was achieved, and solids residual, condensable gas, and noncondensable gas samples were collected to enable calculation of overall material and cesium balances. The test results Duratek is most interested in are 1) cesium disposition, 2) resin volume reduction, and 3) sulfur disposition.

During the first two tests, problems with the condensation system resulted in early termination and insufficient data from which to calculate material balances. However, the condensation system problems were resolved, and the third test yielded excellent data for calculation of cesium, sulfur, and overall material balances, as shown in Table 17. The tests were performed over a 2-day period of 24-hour operation and were observed by Dr. Stan Finger of

TABLE 17

Test M556 – Description and Results

Therman Decomposition of Duratek-Supplied Ces	Juin-Loaded Join-Exchange Resin	
Summarized Results		
Volume Reduction Achieved, without crushing or		
compaction of solids residual	79%	
Cesium Content of Total Offgas, with sweep gas	29.9 μ g/liter	
Cesium Content of Total Offgas, without sweep gas	85.3 μ g/liter	
Portion of Cesium Recovered in Solids Residual 96.8%		
Portion of Cesium Recovered in Offgas 2.1%		
Cesium Closure	98.9%	
Sulfur Content of Solids Residual	2.3 wt%	
Sulfur Content of Total Offgas, with sweep gas	0.030 g/liter	
Sulfur Content of Total Offgas, without sweep gas	weep gas 0.087 g/liter	
Sulfur Closure	82.1%	
Overall Material Balance, weight total feed per		
weight total material recovered	91.2%	
Reaction Conditions and Parameters		
Reaction Temperature	550°C	
Reaction Pressure	Atmospheric	
Sweep Gas and Flow Rate	Nitrogen @ about 30 scfh	
Length of Balance Period 2 hours		
Reactant Feed Rate 0.5 kg/hr		
Reactant Characterization		
Density	$0.77 \text{ g/cm}^3 (48 \text{ lb/ft}^3)$	
Moisture Content	27.3 wt%	
Cesium Content	1960 μg/g	
Sulfur Content	5.4 wt%	
Solids Residual Characterization		
Density	$0.70 \text{ g/cm}^3 (44 \text{ lb/ft}^3)$	
Cesium Content	9720 μg/g	
Sulfur Content	2.3 wt%	
Moisture Content	0.5 wt%	

19

Duratek. A higher cesium recovery in the solids residual is anticipated with operation at a lower temperature and with a lower purge gas flow rate (which was set at a higher-than-needed velocity in this shakedown test to help ensure against plugging).

During Auger reactor system operation at temperatures ranging from about 550° to 600° C, small amounts of a translucent, yellow-tinted, sticky material were observed as thinly distributed coatings on surfaces throughout the condensation train. At the 600° C temperature, it appeared that the sticky material contributed to solids residual agglomeration (very slightly) and offgas line plugging. At the 550° C temperature, operational difficulties diminished significantly, but the material was still present in the condensation train. It is likely that this material is a generic problem with thermal decomposition processing of ion-exchange resin. The material was sticky like honey but significantly more viscous, almost imperceptibly flowable at room temperature, and essentially insoluble at room temperature in methylene chloride, hexane, tetrahydrofuran, and acetone. The material also appeared to contain a small concentration of a very fine brown particulate. Although the particulate was distributed throughout the condensation train, it appeared to be slightly more noticeable on surfaces of the lower-temperature (farther downstream) components of the condensation pot was maintained between about 10° to 20° C throughout all reactor operation periods.

A small amount of the sticky material was recovered and analyzed using FT-IR spectrometry. Based on this analysis, the material appears to be highly branched with many sulfonate and amine groups (which are also present in the unreacted resin) and does not appear to be the result of sulfur cross-linking (vulcanization-type) reactions. It is likely that the material has some solubility in acid or base due to the sulfonate and amine functionalities, but this theory has not yet been investigated. Regarding potential effects of the sticky material, most of the reactor system operational difficulties were eliminated by decreasing reactor temperature, which should also help decrease the amount of cesium carryover. Another approach to investigate would be to increase gas residence time (the amount of time required for a "plug" of gas to move through the reactor). In past work with thermally decomposing plastics, an increased gas residence time produced lighter organic vapor. More sampling and analysis of the sticky material will provide more complete data for use in evaluating operational effects and optimizing the overall process.

Four EERC personnel visited Duratek on January 31, 1997, and met with about ten Duratek personnel to discuss results of Auger reactor tests on ion-exchange resin volume reduction. Additional EERC-Duratek collaboration options discussed included 1) decontamination of high-organic-content mixed waste at Savannah and Idaho sites; 2) mercury sampling and control technologies; and 3) disposal and stabilization technologies for wastes containing mercury, sulfur, and chlorine.

4.0 ACHIEVEMENTS/RECOMMENDATIONS

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The effectiveness of the fluid-bed reactor configuration in separation of radionuclide surrogates from organics has been demonstrated at the bench scale with postconsumer plastics mixtures and ion-exchange resins, and the effectiveness of the Auger reactor configuration has been demonstrated at the bench scale with ion-exchange resins. In prior work, the fluid-bed configuration has been effectively employed in thermal decomposition of postconsumer plastics at the pilot scale (100 pounds per hour); however, this work was focused solely on optimization of depolymerization conditions, and separation of radionuclides was not an issue. Based on the work to date, it appears that the Auger reactor configuration has significantly higher commercial potential for applications in which quantitative separation and recovery of radionuclides and/or heavy metals (both inorganically and organically associated) are important. Project achievements include:

- Identification of process application markets in volume reduction of spent (radioactive) ion-exchange resins and postconsumer-type mixed-plastic wastes.
- Development of a radionuclide surrogate list for use in process concept validation tests.
- Development of process-specific analytical techniques.
- Process viability demonstration with a 98.9% cesium closure.

Discussions ongoing throughout the project are continuing with Duratek and other industry personnel regarding application of the EERC process to commercial and defense industry radioactive waste streams. Table 18 lists key commercialization criteria and compares commercialization targets with EERC achievements.

TABLE 18

Process Commercialization Criteria		
Criteria	Target for Commercialization	Achieved in Project
Waste Volume Reduction	8 to 1, or 88%	5 to 1, or 79%
Segregation of Radionuclides into Solids Residual	99.9% to 99.99%	96.8% (for cesium)
Solids Residual Sulfur Ccontent	1 wt%	2.3 wt%
Solids Residual Carbon Content	Minimal	89 wt%
Radionuclide Emissions Control	Demonstrate economic system for monitoring and prohibiting emissions	Outside of project scope
Sulfur Emissions Control	Demonstrate economic system for adequate control	Outside of project scope
Preprocess Feedstock Drying	Demonstrate economic system for continuous-process drying	Outside of project scope

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