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Task 3 - Pyrolysis of Plastic Waste

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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 ion-exchange 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 will yield 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

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

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 will be 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.

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). 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.

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 objective of the proposed effort 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

With the auger reactor system described in the previous (April–September 1996) semiannual report and shown in Figure 1, a series of three thermal decomposition volume reduction tests was performed using cesium-loaded ion-exchange resin from GTS-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.

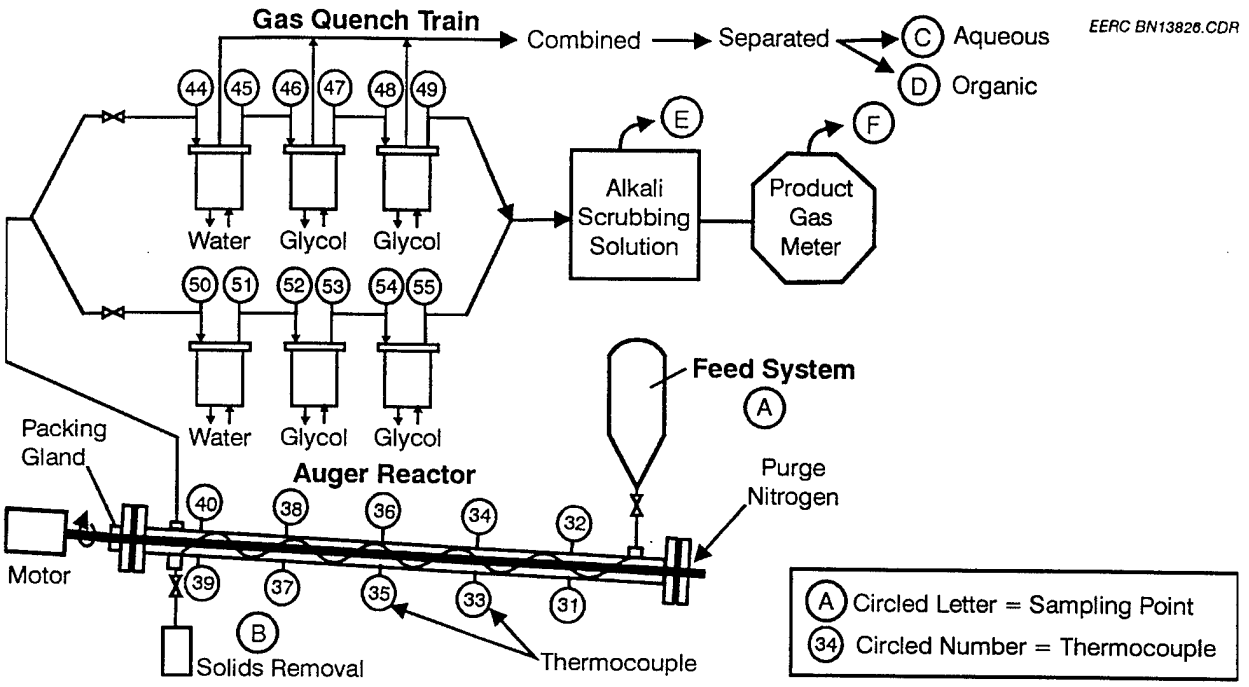

Figure 1. EERC auger reactor system.

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 1. The tests were performed over a 2-day period of 24-hour operation and were observed by Dr. Stan Finger of 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 (further downstream) components of the condensation train. The temperature of the gas exiting the third and final condensation pot was maintained between about 10° to 20°C throughout all reactor operation periods.

TABLE 1

Test M556 - Description and Results
Thermal Decomposition of Duratek-Supplied Cesium-Loaded Ion-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 μg/liter
Cesium Content of Total Offgas, without sweep gas	85.3 μg/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	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	About 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 g/cm^3 (48 lb/ft^3)
Moisture Content	27.3 wt%
Cesium Content	1960 μg/g
Sulfur Content	5.4 wt%
Solids Residual Characterization	
Density	0.70 g/cm^3 (44 lb/ft^3)
Cesium Content	9720 μg/g
Sulfur Content	2.3 wt%
Moisture Content	0.5 wt%

A small amount of the sticky material was recovered and analyzed using Fourier transform infrared 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.

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.

The fluid-bed option has been demonstrated with ion-exchange resins at the bench scale and has been demonstrated with postconsumer plastics at near commercial scale. The viability of the auger reactor in processing ion-exchange resin is being evaluated. The primary objective of the current EERC program is to determine whether the auger reactor will perform better than the fluid-bed reactor, as measured by the ability of the auger-based process to 1) achieve an 8-to-1 volume reduction, 2) concentrate at least 99.99% of the feedstock cesium in the solids residual, and 3) yield a solids residual with a sulfur content of less than 1% and a minimal carbon content. Longer-term objectives include 1) development of economic systems for monitoring and ensuring against radionuclide emissions, 2) development of an economic system for controlling sulfur emissions, and 3) development of an economic system for preprocess resin drying to ensure continuous feeding.

Based on the favorable auger system test results and Dr. Finger's impression of the EERC organization and facilities, plans were made for an EERC visit to Duratek headquarters in Columbia, Maryland, to discuss collaborative arrangements for commercial development of the ion-exchange resin volume reduction technology and other waste treatment technologies. Four EERC personnel visited Duratek on January 31 and met with about 10 Duratek personnel. Although collaboration on ion-exchange resin process development for U.S. markets looks less promising in light of a recent business arrangement between Duratek and Scientific Ecology Group, Incorporated (SEG) of Oak Ridge, Tennessee, other promising collaboration options were discussed including 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 WORK PLANNED FOR THE NEXT SIX MONTHS

Plans are being finalized for a Duratek visit to the EERC in May 1997. Duratek personnel will tour EERC facilities and discuss collaborative process development options. The discussion results will help shape work plans for commercial development of organic waste volume reduction thermal treatment technologies.

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