DEVELOPMENT OF THE FLUIDIZED BED THERMAL TREATMENT PROCESS FOR TREATING MIXED WASTE

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ABSTRACT
A fluidized bed system is being developed at Rocky Flats for the treatment of mixed waste (a mixture of radioactive and chemically hazardous waste). The current program builds on experience gained in the 1970's and 1980's in tests with bench-scale, pilot-scale, and demonstration-scale fluidized bed systems. The system operates at low temperatures (~525-600 °C) which eliminates many of the disadvantages associated with high temperature thermal treatment processes. The process has shown the ability to destroy polychlorinated biphenyls (PCB's) with 99.9999% ("six-nines") destruction efficiency in tests monitored by the Environmental Protection Agency (EPA). The bed makes use of *in situ* neutralization of acidic off-gases by incorporating sodium carbonate (Na_2CO_3) in the bed media. This eliminates using wet scrubbers to treat the off-gas; these produce a high volume of secondary waste. Once in operation, it is expected that the fluidized bed process will yield up to a 40:1 reduction in the volume of the waste.

DESCRIPTION OF THE FBU

The Fluidized Bed Unit (FBU) under development at Rocky Flats is a two-stage thermal treatment process. In the first stage, waste (either solid or liquid) is fed into a bed consisting of sodium carbonate for *in situ* neutralization of acidic off-gases and chromia-alumina oxidation catalyst. The bed is maintained at about 525-600 °C. The first stage is operated with less than the stoichiometric oxygen required for complete combustion so as to pyrolyze the feed. The combustible pyrolysis gases are carried into the second stage. Here the gases enter a bed of oxidation catalyst (chromia-alumina) fluidized with excess oxygen and maintained at the same temperatures as the first stage. The combustible gases are quickly converted to the inert products of complete combustion (*e.g.*, carbon dioxide and water vapor). The entire system is operated under negative pressure.

ADVANTAGES OF FLUIDIZED BED TECHNOLOGY

There are many advantages to using low temperature fluidized beds for the thermal treatment of mixed wastes. These are outlined below:

- Fluidized beds are unique in their ability to use *in situ* neutralization of acid gases. By incorporating sodium carbonate (Na_2CO_3) in the bed media, any acid gases produced (such as during the combustion of plastics) are quickly neutralized. Other thermal treatment processes do not have the turbulence necessary to exploit this capability and must rely on wet scrubbers. Scrubbers use large volumes of caustic water to neutralize the acid gases and are the source of a large volume secondary waste stream. Preliminary work at LLNL suggests that an indirect benefit of *in situ* neutralization is that it reduces the formation of toxic combustion by-products (including metals) and products of incomplete combustion (PIC's). This results from the immobilization or neutralization of some of the intermediates necessary to form PIC's.

- Because of its low operating temperature (~525-600 °C), RFP's fluidized bed requires no refractory lining. Refractories are fragile, absorb radionuclides, and increase the potential for radiation exposure to maintenance personnel. Further, the spent refractory becomes a secondary waste requiring treatment (containment and immobilization) when replaced.

- Because there is no refractory lining, the system can be of all-metal construction. Such construction facilitates quick start-ups and shut-downs. Refractories are fragile and have limitations on their heat-up and cool-down rates.

- Because of the all-metal construction, there is no concern of radionuclide migration into the refractory lining. This lack of migration improves criticality safety and facilitates accountability of radioactive species.

- Low operating temperatures, such as in RFP's fluidized bed process, are not conducive to NO_x formation. This is not true of most other thermal treatment processes.

- Elevated temperatures are known to volatilize radionuclides and other heavy metals.[1,2] RFP's fluidized bed system operates at a lower temperature than most other thermal treatment processes and hence is less prone to volatilization concerns. Quantifying plutonium, uranium, and americium volatilities is the topic of ongoing research being performed at Lawrence Livermore National Laboratory (LLNL). Preliminary studies show radionuclide volatile species nearly immeasurable over the operating temperature range of RFP's fluidized bed system (~525-600 °C).

- The turbulence of fluidized beds avoids the formation of "hot spots" (isolated regions of superheated material). This makes fluidized beds intrinsically explosion-proof.
- There are minimal secondary wastes associated with RFP's fluidized bed process. As explained above, *in situ*

neutralization is possible which obviates the requirement for a wet scrubber. The only secondary wastes come from catalyst and sodium carbonate attrition. These solids are easily collected with the ash and can be readily solidified by other methods (*e.g.*, polymer solidification, microwave solidification, or cementation). This solidified material would be the final waste form. Other thermal treatment processes require wet caustic scrubbers which produce a high volume aqueous secondary waste stream which would also require stabilization.

- Fluidized bed thermal treatment is compatible with a wide range of wastes including combustible solids, liquids, and sludges or non-combustibles with the addition of an auxiliary fuel. That portion of the waste feed which is not combustible is either removed by an extraction screw or eroded by the abrasive action of the bed. In either case, this material is collected and solidified as described above. While it is true that size reduction of the waste feed is necessary, this is easily performed by commercially available shredders. Past experience has shown size reduction to be quick and reliable.[3]

- RFP's fluidized bed is designed to operate at a negative pressure. This assures that any unexpected leakage would be from the outside into the FBU system. This fail-safe design assures containment of all wastes, secondary wastes, and exhaust gases. This is a major advantage when considering the radioactive and hazardous components of the waste.

PERFORMANCE DATA

The fluidized bed research program began at Rocky Flats in the 1970's with the purpose of developing a low temperature process for the combustion of typical plant waste.[4] Initial tests in the bench-scale system were successful, and a 9 kg/hr pilot unit was installed in 1973. Oxidation catalyst (chromia-alumina) was incorporated in the bed material to facilitate complete oxidation at temperatures of only 525-600 °C. Sodium carbonate (Na_2CO_3) was added to the bed to quickly neutralize any acidic off-gases before they left the vessel (*in situ* neutralization). Such gases are produced in the combustion of many plastics. Tests in this unit were successful, and data from its operation were used to design a full-scale, 82 kg/hr, demonstration unit. This unit was called the Fluidized Bed Incinerator, or FBI.

The FBI was fabricated in 1977 and went through start-up testing in 1978. In tests performed through the early 1980's, the demonstration unit successfully destroyed approximately 21,500 kg of low-level solid plant wastes and over 5600 liters of liquid plant waste.[3] One of the highlights of the program was a test burn of polychlorinated biphenyls (PCB's) in the pilot unit. This test was performed in 1981 and was monitored by the EPA. Results showed the system achieved a destruction efficiency in excess of 99.9999% ("six-nines").[5]

PROPOSED MODIFICATIONS TO THE FBI

The FBI operated quite satisfactorily; however, much has changed in fluidized bed design, off-gas treatment, and regulatory requirements since the FBI's construction in 1977. For these reasons, several modifications are being considered for the design of the new system. The new fluidized bed incineration program is known as the Fluidized Bed Unit, or FBU. The most notable modifications being considered are to the fluidized bed design and off-gas treatment.

One desirable modification would be to eliminate the cyclone between the first and second stages of the process. Combustible gases from the first stage pyrolysis could then go directly to the second stage to complete combustion. The cyclone between the stages of the old FBI design removed a considerable amount of solids (*e.g.*, charred material and carbon) that could have been treated further in the second stage to get greater destruction and volume reduction. Instead, these solids were removed with the ash.

Two alternatives recommended by West Virginia University (WVU) are being considered. The first is a "hybrid" fluidization system. The bottom of the unit has a relatively slow superficial gas velocity (on the order of 0.5 m/sec) and operates as a "bubbling" bed. This section is similar to the design of the primary stage in the FBI (*i.e.*, oxygen deficient operation, pyrolysis of the waste). The upper section of the hybrid bed is a "fast" fluidized bed. Here the gas flow is much greater, on the order of several meters per second. Additional gas is injected at the intersection of the "bubbling" and "fast" sections, and there is a reduction in the cross-section of the system to create these higher velocities. Jets along the length of the fast section add additional air and nitrogen. The fast section operates oxygen rich to complete the combustion of the waste. The higher gas velocities carry much of the waste catalyst and sorbent out of the bed. The disengagement section at the top of the bed slows the gas, allows final reactions to occur, and maintains an inventory of fluidized catalyst and sorbent. Solids carried out of the bed are separated from the gas by a cyclone, and are returned to the bed. This fast, recirculating design assures that the wastes are completely destroyed.

The second option suggested by WVU is a totally "fast" fluidization system. The lower portion of the bed is operated in an oxygen deficient mode. Above this section, jets introduce additional gas and oxygen to create an oxygen excess in the upper part of the column to complete the combustion. Again, uncombusted solids are separated and returned to the bed to complete destruction.

Other modifications have been considered for the off-gas treatment system. One was the "hold-test-release" (HTR) concept. The off-gas would be captured, liquefied, stored, and tested to ensure there was no contamination present before releasing it to the atmosphere.[6] A Peer Review Panel consisting of representatives from DOE, EPA, DOE site contractors, and experts in the fields of air pollution control and waste incineration reviewed the proposal. The group ultimately recommended there is no need for the addition of the HTR process versus conventional continuous pollution control measures. They felt the technology would add unnecessary complexity to the process without reducing the risk of escape of contaminants.

One modification to the off-gas system that will be adopted is the use of one or more stainless steel HEPA filters. One concern about mixed waste incineration is that there is "only a piece of paper between the process and the public." There was concern that in the event of a high temperature excursion or fire, the HEPA filters would be consumed, and radioactive species could pass unimpeded into the environment. The new stainless steel HEPA filters are able to withstand such temperatures. Conventional HEPA filters will also remain in the off-gas chain.

CURRENT FBU DEVELOPMENT PROGRAM

The FBU's development is a nationwide program incorporating input from national laboratories, universities, regulatory agencies, and private companies to assure the most current technology is utilized.

A plexiglas Flow Visualization Unit (FVU) has been constructed at the Colorado School of Mines (CSM) in Golden, CO. This system has a computer-interfaced data acquisition and control system. The FVU is used by both EG&G employees and CSM faculty for ambient temperature fluidization studies in support of the FBU Project. Its location at CSM has facilitated public access for demonstrations of the technology that would not be easily accommodated if the unit was located at Rocky Flats.

Los Alamos National Laboratory (LANL) is performing research on techniques to monitor for radionuclides in the off-gas. Dr. Oscar Krikorian at Lawrence Livermore National Laboratory (LLNL) is studying the volatility of radionuclides and heavy metals over the temperature range of 500-1200 °C. Calculations indicate that aerosol formation, particularly of plutonium oxyhydroxide, is minimal at the proposed operating temperature of the FBU, but increases exponentially with temperature.

The Department of Energy's (DOE) Morgantown Energy Technology Center (METC) is expert in the area of fluidization. Along with West Virginia University (WVU), they are providing information on state-of-the-art fluidized bed systems and monitoring techniques.

EPA's Risk Reduction Engineering Laboratory (RREL) is the interface to the regulatory requirements for licensing the FBU. Realizing that licensing a thermal treatment process for mixed waste would be difficult, Dr. C. C. Lee of RREL established the National Technical Workgroup on Mixed Waste Incineration (NTW). NTW has selected the FBU to serve as a case study to determine what is necessary to license thermal treatment processes for mixed waste. The NTW membership includes a representative from the primary contractor at each of the DOE sites, a representative from DOE headquarters, the EPA Offices of Solid Waste, Radiation, and Air Quality and Planning Standards, the EPA Regional Offices, the EPA Risk Reduction Engineering Laboratory, industrial representatives for mixed waste incineration, the Nuclear Regulatory Commission, and representatives from State Environmental Departments in states where mixed waste incineration is under active consideration.

EPA-RREL has sub-contracted with Energy and Environmental Research Corporation (EER) to perform a study of continuous off-gas pollution control techniques and monitoring technology. The S-Cubed Division of Maxwell Laboratories was sub-contracted by EER to look at state-of-the-art technologies for the monitoring of radionuclides in the off-gas.

The National Institute of Standards and Technology (NIST) in Boulder, CO is working with FBU team members on developing gas separation membranes that may be useful in separating nitrogen and hydrocarbons from carbon dioxide in the off-gas. The NIST facility in Gaithersburg, MD is assisting in accelerated life testing of metals proposed for FBU construction.

Finally, the EG&G Rocky Flats Waste Systems Development Group has been involved in designing prototypes of the waste feed system, selecting materials of construction, and providing technical and administrative support for the project.

In FY '93, thermally hot tests of the FBU concept will be performed using an existing fluidized bed incinerator away from the Rocky Flats site. These tests are being coordinated by the EPA-RREL. Initial studies will focus on verifying the effectiveness of the sodium carbonate *in situ* neutralization of acidic off-gases. Later studies will verify the FBU's ability to meet the emissions requirements set forth by the EPA and the State of Colorado.

SUMMARY

The FBU project at Rocky Flats has an aggressive national program to develop this thermal treatment technology. By operating at low temperatures and incorporating *in situ* neutralization in its design, the FBU has numerous technical advantages over other thermal treatment processes. In an independent study performed by Science Applications International Corporation (SAIC) and funded by Martin Marietta Energy Systems, fluidized beds were rated as the top overall conventional thermal treatment technology for the destruction of mixed waste.[7] FBU technology has been successfully demonstrated at Rocky Flats in bench-scale, pilot-scale, and full-scale tests. This paper has provided a cursory view of the technical activities in the FBU development program. More detailed information on FBU technology and on community relations activities in preparation for licensing may be found in the literature.[8,9]

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