125
1-16-95 JS (2)
RFP-4966

May 17, 1995

RFP-4966

May 17, 1995

**Two Stage, Low Temperature, Catalyzed Fluidized Bed Incineration
with *In Situ* Neutralization for Radioactive Mixed Wastes**

Technology Review and Status Report

Jonathan F. Wade and Paul M. Williams

Rocky Flats Environmental Technology Site
PO Box 464
Golden, Colorado 80402-0464

U.S. Department of Energy
Contract DE-AC04-90DE62349

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

May 17, 1995

UC-706
DOE/OSTI-TID-4500
RFP-4966

Two Stage, Low Temperature, Catalyzed Fluidized Bed Incineration with *In Situ* Neutralization for Radioactive Mixed Wastes

Technology Review and Status Report

Jonathan F. Wade and Paul M. Williams

Subject Descriptors

Air Emissions
Air-Pollution Control
Ash Stabilization
Hazardous and Radioactive Mixed Waste Treatment
Incineration
Off-Gas Treatment
Organic Destruction
Polychlorinated Biphenyl (PCB) Treatment

Rocky Flats Environmental Technology Site
PO Box 464
Golden, Colorado 80402-0464

U.S. Department of Energy
Contract DE-AC04-90DE62349

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RFP-4966

Table of Contents

Table of Figures and Tables.....	iv
----------------------------------	----

Introduction

Abstract.....	1
Executive Summary	1

Off-Gas Treatment and Air Emissions

Summary Description of the Fluidized Bed Unit Process.....	3
<i>In Situ</i> Neutralization Effectively Captures Greater than 99% of the HCl.....	5
<i>In Situ</i> Neutralization Will Minimize HCl and Cl ₂ Emissions.....	7
Minimizing Chlorine Effectively Suppresses Dioxin and Furan Production	9
Low Temperatures Significantly Reduce Radionuclide Volatility	10
Radionuclide Stack Emissions During Demonstration-Scale Testing Met or Exceeded Air Quality Requirements	13
Rocky Flats Established Conservative, Upper Bounds for Air Emission Estimates .	15
Proposed Air Pollution Control Measures Capture Nearly All Metal Particulates	16

Ash Treatment

Cementation or Polymer Encapsulation Can Successfully Immobilize FBU Ash.....	17
---	----

Equipment and Process Design Considerations

Molybdenum, Manganese, Vanadium, and Other Metal Oxides May Meet or Exceed Chromium Oxide Performance as a FBU Catalyst Material.....	21
Recirculating Beds May Increase Combustion Efficiency but Decrease Cost Effectiveness.....	22
Off-Gas Recycle or Capture Technologies May Not Improve Efficiency or Safety .	23
Semi-Permeable Membranes May Help Meet Future, More Stringent Emission Requirements	25

Process Selection Considerations

Fluidized Bed Units Have Stable Process Control Capabilities	25
Fluidized Bed Technology is Preferable for Mixed Waste Treatment.....	26
Public Acceptance and Licensing Remains Difficult but Is Improving.....	28
FBU Capital Cost Estimates	29

Status

Recommendation.....	29
---------------------	----

RFP-4966

Table of Figures and Tables

Figure 1. Block Diagram for the Fluidized Bed Unit Process.....	4
Figure 2. "Burping" Shown on a Fluidized Bed Model.	7
Table I. Experimentally Derived Estimates for the Mass of Americium, Plutonium, and Uranium Volatilized Yearly from an Incinerator as a Function of Temperature.	11
Table II. Experimentally Derived Estimates for the Mass of Americium, Plutonium, and Uranium Entering an APC System Assuming Different Operating Scenarios.	12
Table III. Demonstration-Scale FBU Testing, November 1978 through January 1988.....	14
Table IV. Building 776 Stack 202 Annual Actinide Air Emission Data, January 1979 through January 1988.....	15
Table V. Preliminary Emission Spectroscopy Data for Pilot- and Demonstration- Scale FBU Ash, Analysis of Fraction Less than 100 μm Particle Size.	18
Table VI. Fluidized Bed Ash Particle Sizes.....	19
Table VII. Best and Worst Ash Surrogate Compositions for Cementation Study.	20
Table VIII. TCLP Data from Cemented "Best Case" Surrogate Ash, 30% Ash Content.....	21
Table IX. TCLP Data from Cemented "Worst Case" Surrogate Ash, 30% Ash Content.....	22
Table X. TCLP Data from Cemented "Worst Case" Surrogate Ash at 20 and 30% Ash Content.	23
Table XI. Effect of Encapsulating Surrogate Ash with Low Density Polyethylene at 50% Waste Loading.	24
Table XII. TCLP Extract Data for Polymer Encapsulation of FBU Chromia- Alumina Catalyst.....	25
Figure 3. Configuration of a Hybrid Fluidized Bed Reactor.....	26

Two Stage, Low Temperature, Catalyzed Fluidized Bed Incineration with *In Situ* Neutralization for Radioactive Mixed Wastes

Technology Review and Status Report

Jonathan F. Wade and Paul M. Williams

Abstract

A two stage, low temperature, catalyzed fluidized bed incineration process is proving successful at incinerating hazardous wastes containing nuclear material. The process operates at 550°C and 650°C in its two stages. Acid gas neutralization takes place *in situ* using sodium carbonate as a sorbent in the first stage bed. The feed material to the incinerator is hazardous waste—as defined by the Resource Conservation and Recovery Act—mixed with radioactive materials. The radioactive materials are plutonium, uranium, and americium that are byproducts of nuclear weapons production. Despite its low temperature operation, this system successfully destroyed poly-chlorinated biphenyls at a 99.99992% destruction and removal efficiency. Radionuclides and volatile heavy metals leave the fluidized beds and enter the air pollution control system in minimal amounts. Recently collected modeling and experimental data show the process minimizes dioxin and furan production. The report also discusses air pollution, ash solidification, and other data collected from pilot- and demonstration-scale testing. The testing took place at Rocky Flats Environmental Technology Site, a US Department of Energy facility, in the 1970s, 1980s, and 1990s.

Executive Summary

In 1994 the Rocky Flats Fluidized Bed Unit (FBU) successfully demonstrated that its *in situ* neutralization feature captures 99 to 99.9% of all hydrogen chloride (HCl) gas generated by low temperature incineration.

This compares favorably to the 95% HCl capture efficiency typical for conventional incineration with wet off-gas¹ scrubbing. Despite its low temperature operation, the FBU successfully destroys hazardous waste as shown by destroying poly-chlorinated biphenyl (PCB) at a 99.99992% destruction and removal efficiency (DRE).

The successful HCl capture efficiency data validates the FBU's waste minimization strategy to meet or exceed all applicable air emission requirements. The FBU only relies on its air-pollution control (APC) system to remove particulates; APC systems are highly effective and reasonably efficient at removing particulates from incineration off-gas. The FBU system relies on its two stage, low temperature, catalyzed oxidation process with *in situ* neutralization to meet or exceed all other air emission requirements.

Low temperature combustion with *in situ* neutralization produces minimal amounts of acidic gases, dioxin and furan, volatile radionuclides, and volatile hazardous and toxic metals. Minimizing these hazards is beneficial because APC systems are generally ineffective or inefficient at removing these pollutants. *In situ* neutralization and low temperature operation combine to make the FBU the safest, most effective, demonstrated incineration technology for hazardous, radioactive mixed waste treatment.

The ability of the FBU's *in situ* neutralization to capture acidic gases is a significant engineering advance in waste minimization technology. The technol-

¹ "Off-gas" denotes the mixture of gases and vapors generated by combustion.

ogy minimizes the HCl, chlorine gas (Cl_2), and chlorinated organic products of incomplete combustion (PICs) produced by incineration. For example, incinerating surrogate waste containing 60% polyvinyl chloride (PVC) in the FBU would produce off-gas containing only 10 to 20 parts per million (ppm) HCl. This low HCl concentration is upstream of the APC system. This results in only 0.004 kilograms per hour (kg/hr) HCl gas entering the APC system, well below the 1.8 kg/hr regulatory limit allowed to leave the APC system through stack emissions. In addition, *in situ* neutralization also precludes production of other acidic gases such as sulfur oxides (SO_x).

Several independent experimental studies verified the low acidic content of FBU off-gas and support the chlorine capture findings are real and repeatable. Furthermore, new 1994 data corroborate pilot- and demonstration-scale data collected at the Rocky Flats Environmental Technology Site in the 1980s.

In situ neutralization also minimizes dioxin and furan production. This is because commingling chlorine with hydrocarbons at 200 to 500°C creates dioxins and furans. Consequently, eliminating chlorine prevents dioxin and furan production in both stages of the FBU process.

The FBU's relatively low operating temperatures volatilize fewer radioactive species than is possible with higher temperature treatment technologies. For example, experiments with FBU technology conducted at Lawrence Livermore National Laboratory show the 550°C first stage bed converts only about 5×10^{-13} grams per year (g/yr) plutonium to volatile forms. If all this plutonium passes through the second stage bed (as it does), then this plutonium enters the APC system. This compares to about 2×10^{-1} g/yr plutonium that would enter an APC system while incinerating at 1200°C using similar waste feed and gas flow conditions. Consequently, low temperature operation results in a 12 order-of-magnitude reduction for plutonium entering the APC system.

Low temperature combustion also minimizes the volatilization of other radionuclides and all hazardous metals except mercury. Therefore, the FBU relies less

on APC measures to remediate combustion off-gas than other thermal treatment technologies. Fewer radionuclides and metals entering the APC system improves system safety. This is a significant reason why Rocky Flats favors the FBU over other incineration technologies.

The FBU relies on a state-of-the-art APC system to remove about 99.999999% of all particulates from the FBU off-gas stream. This APC system is safer and more effective than other off-gas treatment options. The APC system also includes design features to prevent dioxin and furan formation, thereby providing an integrated redundant safety feature. Since the APC system will not remove mercury, mercury removal will take place on the few applicable waste forms before FBU treatment.

Several immobilization methods can prepare the FBU ash from the APC system for safe, long term disposal. Initial polymer encapsulation tests show that low density polyethylene containing 40 to 50% ash surrogate can successfully pass the Toxicity Characteristic Leaching Procedure (TCLP) test. Immobilizing with Portland cement at a 20 to 30% ash content also appears feasible. Improving the ash-to-matrix ratio appears possible with both technologies. Since FBU ash is about 11 to 25 times smaller in volume than waste entering the FBU, the overall chain of treatment steps significantly reduces waste volume. Furthermore, since FBU treatment does not require off-gas scrubbing, there is no secondary waste liquid to treat and dispose.

This paper identifies these advances and discusses why Rocky Flats chose to pursue developing the FBU system. Implicit in this discussion is information describing how the Rocky Flats FBU design improves upon other fluidized bed technologies. The provided data supports assertions that FBU technology is the most mature thermal treatment system for hazardous radioactive mixed waste. This report finishes by discussing the cost estimates associated with building a low level radioactive mixed waste FBU treatment facility. References to source documents are throughout this report to assist interested readers locate additional information.

Summary Description of the Fluidized Bed Unit Process

This section describes the FBU process in its simplest form. The intent of this section is to identify the major process concepts only. This discussion omits equipment design, process control, associated support systems, and radioactive containment features of the FBU. Omitting description of these systems simplifies this discussion.

The FBU system is a two stage, flameless combustion process for converting solid or liquid combustibles to a chemically stable, dry ash. A block process schematic (see Figure 1, page 4) shows that two reactor vessels compose the heart of the system. The two vessels are the primary fluidized bed, called the *primary bed*, and the secondary fluidized bed, or *afterburner*. These vessels contain beds of fluidized solids in which wastes decompose and oxidize.

Fluidization is the operation by which solid particles transform into a fluid-like state through suspension in a gas or liquid. This gas or liquid is the "fluid." In the FBU the fluid is a combination of heated air and nitrogen gas. Passing the fluid upward through a bed of fine particles at a low flow rate merely causes the fluid to percolate through the void spaces between the stationary particles. This is a *fixed bed*.

With an increase in flow rate, particles move apart and a few vibrate and move in restricted regions. This is an *expanded bed*. At a higher velocity, the upward flowing fluid reaches a point where it can just barely suspend all the particles in its stream. At this point the frictional force between the particles and the fluid just balance the weight of the particles; the vertical component of the compressive force between adjacent particles disappears; and the pressure drop through any section of the bed about equals the weight of fluid and particles in that section. The bed is just fluidized and is an *incipiently fluidized bed*.

Increasing the fluid flow rate beyond the incipient fluidization point causes large instabilities with bubbling and channeling in the bed. At higher flow

rates, agitation becomes more violent and the movement of solids becomes more vigorous. In addition, the volume of the bed does not expand much beyond its volume at incipient fluidization. Such a bed is a *bubbling fluidized bed*.² Further increasing the fluid flow rate, so that average particles entrain in the gas stream and flow out of the reactor vessel, results in a *fast fluidized bed*.

Both the FBU's primary bed and afterburner reactor vessels contain bubbling fluidized beds. Bubbling fluidized beds have excellent heat transfer properties, so uniform temperatures exist throughout each bed. A fluidized bed is the recommended technology whenever there is ample exothermic heat, possibility of a temperature runaway or explosion, and when strict and reliable temperature control is of paramount importance.³

Waste enters the primary bed as either a solid or liquid. Solid wastes must enter the reactor as small pieces. Consequently, bulk solids often require size reduction followed by sorting to remove undesirable materials. Size reduction and sorting take place by shredding and classifying. Coarse shredding breaks the waste down to about 1 inch diameter particles. Air classifying and metal removal steps remove smaller, undesirable dense and metal objects. Fine shredding breaks the waste down to about 0.25 inch diameter pieces for feeding into the FBU.

A screw continuously feeds the particulate solid waste into the primary bed. Fine solids, resins, and liquids can feed directly into the bed without the pretreatment steps. A valve associated with the feed screw helps quickly isolate the solid feed from the bed, if required.

In the primary bed, the waste gasifies and pyrolyzes at about $550 \pm 50^\circ\text{C}$ in the presence of heated air, nitrogen, catalyst, and sorbent. Methanol is the fuel for heating the bed while starting up the system. No auxiliary bed heating takes place after start-up, rather the

² Daizo Kunii and Octave Levenspiel. *Fluidization Engineering*. Boston: Butterworth-Heinemann, 1991, p. 1-2.

³ *Ibid.*, p. 34.

heat of the oxidizing waste maintains the bed temperature. The ratio of air-to-nitrogen fed into the bed controls the rate of waste pyrolysis and heat generation. The catalyst allows pyrolysis to occur at the low temperature and provides a "thermal inertia" effect that helps stabilize the operating temperature. The sorbent provides an effective neutralizing media for acidic off-gas. Small particles of combustion byproducts from the pyrolysis reaction continuously elutriate out of the bed with the gas flow and the screw feeder continuously adds new waste to the bed.

A cyclone separator removes the fly ash and salt generated from the sorbent/chlorine reaction from the process off-gas before it enters the afterburner. The afterburner contains catalyst and operates at $650 \pm 50^\circ\text{C}$ and oxidizes the off-gas in the presence of air and catalyst to form carbon dioxide and water vapor.

Particulates and gases departing the afterburner enter the APC system. In the APC system, a cyclone separator removes the coarsest particles. Sintered

metal filters remove particulates larger than a 5 micron (5×10^{-6} meter) diameter. A catalytic converter polishes⁵ any small amount of hydrocarbons in the off-gas stream. Glass high efficiency particulate air (HEPA) filters remove the smaller particles, and metal HEPA filters provide a backup to the glass HEPA filters. Heating the cyclone, lines, sintered metal filters, and catalytic converter to above 500°C prevents dioxin and furan production in the APC system. Ash from the cyclones and filters are the only solid byproduct and collect for storage or additional treatment. Cementation or polymer encapsulation treatment immobilize any heavy metals present in the ash.

The motive force for transferring gas and particles from the bed through the APC system is the air ejector. The air ejector keeps the entire system below atmospheric pressure so that any leaks result in gas flow into the system. HEPA filters after the ejector provide additional particulate removal before the gases pass to

⁴ Jonathan Wade illustration.

⁵ "Polish" in this context signifies converting to carbon dioxide and water vapor.

the building plenum and an additional four stage HEPA filtration system. Since the sorbent captures virtually all acidic gases in the primary bed, the APC system does not require wet off-gas scrubbing. In this way the FBU is different than other thermal treatment technologies that need to treat large volumes of contaminated water from the scrubber. This is a major advantage of the FBU system when compared to other thermal treatment systems.

Another advantage of the FBU system is its all metal materials of construction. Neither the primary nor the afterburner reactor vessels require a refractory ceramic lining. The system does not require a lining because the system operates at temperatures low enough to allow use of nickel, chromium, or cobalt based superalloy metals as the materials of construction for reactor vessels and process piping.

Since refractory ceramics are sensitive to thermal shock, eliminating the lining enables faster start-up and shut-down of the FBU system than is possible with other incineration processes. Fast response capability contributes to FBU system safety.

Ceramic refractory linings also assimilate heavy metals and radionuclides. Therefore, eliminating the refractory lining also eliminates a radioactive secondary waste form from the process that would require RCRA treatment upon its removal. Eliminating the refractory lining also simplifies accounting for radioactive material inventory during ongoing system operation. Finally, eliminating the refractory lining obviates repairing and replacing the refractory as it wears, thereby reducing radiation exposure to workers.

***In Situ* Neutralization Effectively Captures Greater than 99% of the HCl**

Initial experiments show that soda ash, sodium carbonate (Na_2CO_3), is performing at a level that constitutes a significant scientific advance in waste treatment technology. Tests conducted at Energy & Environmental Research Corporation (EER) in Irvine, California, using their fluidized bed test facility demonstrated:

An *in situ* bed of sodium carbonate can efficiently capture (absorb) greater than 99.9% of the chlorine which passes into it. This was achieved during tests in which pure HCl was mixed with the hot fluidization gas upstream of the bed. The HCl concentration of the fluidization gas before the bed during these tests was approximately 3% (30,000 ppm). The measured HCl concentration after the bed was 10 to 20 ppm. This rate of HCl addition to the bed corresponds to incinerating a Rocky Flats waste containing 60% PVC [polyvinyl chloride], which is a high value based on the Rocky Flats waste.

Greater than 99.5% of the chlorine added to the fluidized bed during gasification of PVC was captured (absorbed) by the *in situ* sodium carbonate sorbent. The rate of PVC addition to the fluidized bed during these gasification tests corresponds to the rate expected from a Rocky Flats waste containing 50% PVC, which is a high value based on the Rocky Flats waste.⁶

Therefore, both experiments with HCl and PVC showed chlorine capture efficiency better than 99.5%. Because the bed configuration for these tests was not optimal, additional improvements in HCl capture efficiency are possible.

Substantial verification of the EER tests took place at the Colorado School of Mines (CSM) in Golden, Colorado. As part of their scope of work, CSM studied the evolution rate of HCl vapors from the degradation of PVC, and the effect of HCl evolution rate on *in situ* neutralization. The results showed HCl evolution from PVC spans the temperature range from 250 to 350°C and does not take place at one unique temperature. This study shows *in situ* neutralization effectiveness is independent of HCl generation rate. Excel-

⁶ G. D. Kryder, W. Clark, and W. R. Seeker, Energy and Environmental Research Corporation, Irvine, California. *Criteria Development and Performance Testing of Mixed Waste Incineration: In situ Chlorine Capture in a Fluidized Bed Unit*, EPA Contract 68-CO-0094, Work Assignment 3-6, conducted for Risk Reduction Engineering Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, September 30, 1994, p. 3-4.

lent neutralization occurs whenever the bed has the proper weight ratio between sodium carbonate-to-PVC (greater than 9-to-1) and these materials have good physical contact with each other. The sodium carbonate sorbent reduced the peak generation rate of HCl vapors by 99.75% while increasing the PVC temperature at 10°C per minute (°C/min), and by 99.9% while increasing at a 100°C/min rate.⁷

Another small-scale project between CSM and Ecova Corporation in Golden, Colorado, replicated the high HCl capture efficiency.⁸ The observed HCl capture was about 99% over the entire test while adding HCl gas to the sodium carbonate bed. Furthermore, in tests with PVC in the bed, the sodium carbonate neutralized the HCl generated, and chemical analysis of the combustion gas samples for PICs did not find any chlorinated organic compounds. This last result is very promising and deserves additional validation and investigation.

The recent sorbent efficiency data correlates successfully with data collected during the 9 kg/hr pilot-scale testing at Rocky Flats in the late 1970's and early 1980's. Pilot-scale experiments burned waste containing known amounts of PVC to test the efficiency of *in situ* acid neutralization. Since no accurate, continuous HCl gas analyzers were available, the analyses scrubbed a small bleed stream from the incinerator off-gas and analyzed the scrub solution for dissolved HCl. A comparison took place between the chlorine in the off-gas and in the waste. Chlorine capture efficiency of greater than 99 percent was typical during these tests.⁹

⁷ Robert M. Baldwin, *Progress Report Fluidized Bed Reactor Model Project, Accomplishments for Period of September 1, 1993, to September 30, 1993*, Chemical Engineering and Petroleum Refining Department, Colorado School of Mines, Golden, Colorado, October 19, 1993, p. 3.

⁸ Craig M. Young, Ecova Corporation, *Combustion Testing Report; Prepared for: Colorado School of Mines*, Golden, Colorado, May 11, 1994, p. 1.

⁹ L. J. Meile, F. G. Meyer, A. J. Johnson, and D. L. Ziegler. *Rocky Flats Plant Fluidized Bed Incinerator, RFP-3249*. Golden, Colorado: Rockwell International for US Department of Energy, Rocky Flats Plant, March 8, 1982, p. 56.

The 81 kg/hr demonstration-scale FBU also efficiently neutralized acidic gases other than HCl. During treatability testing on ion exchange resins [tributyl phosphate, (C₄H₉O)₃PO] and solvents in the 1980s, virtually all of the phosphorus pentoxide (P₂O₅) generated by incineration converted to sodium phosphate (Na₃PO₄). Furthermore, the Na₃PO₄ partitioned to the residue as a dry, stable solid. The P₂O₅, if not treated, readily absorbs moisture forming phosphoric acid (H₃PO₄) that is very corrosive to ferrous metals and alloys. Data indicates that sulfur dioxide (SO₂) and trioxide (SO₃) also neutralize at the point of generation in the presence of sodium carbonate sorbent.¹⁰ Without treatment these compounds could form corrosive sulfuric and sulfurous acids.

In all the years of testing, only one experiment showed HCl capture efficiency at less than 99%. This took place May 19, 1981, during the successful incineration of a PCB-solvent mixture with 12% chloride content in the pilot-scale system. In this test the HCl capture efficiency was only 98%.¹¹ This low efficiency probably resulted from a less-than-optimal conical vessel geometry. Testing partially confirmed this hypothesis in 1994 when CSM tested a double-truncated, cylindrical geometry like the demonstration-scale unit that caused "burping" in the fluidized bed. Figure 2 (page 7) shows this phenomena. A similar effect may account for the lower HCl capture recorded during the pilot-scale PCB testing. A new, flat bottom, cylindrical primary reactor vessel geometry developed in 1994 eliminated the burping problem. The flat bottom vessel geometry consistently yielded 99 to greater than 99.9% HCl capture efficiency.

Several experiments also investigated chlorine gas generation. Recent work shows Cl₂ barely forms over the FBU operating temperature range. The vapor pressure of Cl₂ is approximately six orders-of-magnitude

¹⁰ *Ibid.*, p. 56-57.

¹¹ A. J. Johnson, F. G. Meyer, D. I. Hunter and E. F. Lombardi. *Incineration of Polychlorinated Biphenyl Using A Fluidized Bed Incinerator, RFP-3271*. Golden, Colorado: Rockwell International for US Department of Energy, Rocky Flats Plant, September 18, 1981, p. 8.

lower than HCl, or typically less than 1 part per trillion (ppt).¹²

***In Situ* Neutralization Will Minimize HCl and Cl₂ Emissions**

In order to satisfy the emission standards of the Boiler and Industrial Furnace (BIF) rule, HCl and Cl₂ emissions from a future Rocky Flats incinerator must not exceed risk based ground level ambient air concentrations at the location of the maximum exposed individual. These reference air concentrations (RACs) are 7×10^{-6} grams per cubic meter (g/m³) and 0.4×10^{-6} g/m³ for HCl and Cl₂ respectively. To meet the RACs, the HCl and Cl₂ concentration at the stack exit must not exceed 920 ppm and 53 ppm.¹³ These calculations assume a facility specific atmospheric dilution factor of 200,000. FBU technology can exceed these requirements without the use of off-gas scrubbing. Eliminating scrubbing obviates its high capital and operating costs.

Assuming only a 98% HCl capture efficiency in the new FBU, the resulting stack HCl concentration is 65 ppm, or 0.02 kg/hr. This level is considerably lower than the 920 ppm HCl stack concentration required to meet the RAC and the 1.8 kg/hr emission rate necessary to meet RCRA incinerator emission limits.¹⁴ If the FBU captures 99.9% of all HCl as current testing indicates is possible, the HCl emissions are ~15 ppm, or 0.004 kg/hr. Because the neutralization takes place *in situ*, the 0.004 kg/hr is the HCl concentration entering the APC system. Consequently, the FBU does not require off-gas scrubbing because the off-gas met or exceeds HCl quality requirements before the APC sys-

tem. Similar, favorable results also apply to Cl₂ emission estimates.

A recent report commenting on the FBU system mistakenly indicated a "wet/dry" system would lead to better removal of "the high chloride content" in FBU off gases. Implicit in the report is the assertion that wet/dry scrubbing would lead to better metal removal

Figure 2. "Burping" Shown on a Fluidized Bed Model. The model is Plexiglas™, about 0.9 m wide, 3.5 m tall, and 0.2 m deep. Air is being blown upward through the particle bed, thereby "fluidizing" the bed. This model simulates a slice of the demonstration-scale FBU used at Rocky Flats in the 1980s. The dark area in the center is a region of poor gas/particle mixing, called "burping." The cause of the burping is the double-truncated cylindrical bottom design. The gas flow rate is higher than usual to exaggerate the effect for the photo. Rocky Flats corrected this problem by building a flat bottom bed that improved gas/particle mixing. The model is at the Colorado School of Mines in Golden, Colorado.

¹² *State-of-the-Art Assessment of APC Systems and Monitoring Technology for the Rocky Flats Fluidized Bed Unit, Final Report.* Irvine, California: Energy and Environmental Research Corporation, EPA Contract 68-CO-0094, for US Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, and US Department of Energy, Rocky Flats Office, Rocky Flats Plant, November 30, 1992, p. 7-14.

¹³ *Ibid.*, p. 7-14.

¹⁴ *Ibid.*, p. 7-18.

and better prevention of dioxin formation than possible with the FBU's *in situ* neutralization. However, some facts quoted in the report did not support this assertion. For example, the report cited that Joy Energy Systems of Charlotte, North Carolina, believed they could achieve 95% HCl removal by spraying the off-gas with a wet lime slurry before the bag house.¹⁵ AIRPOL, Inc., of Teterboro, New Jersey, recommended a dry scrubber to remove 90 to 99% of HCl.¹⁶ Neither of these numbers meets the 99 to 99.9% HCl removal efficiency of the FBU. The FBU is superior to these industry standard performance estimates. Furthermore, the report did not convey the authors understood that *in situ* neutralization led to a low chlorine content in FBU off-gas.

It would be possible (though undesirable) for Rocky Flats to add liquid off-gas scrubbing to the FBU APC system. The HCl stack emissions from the FBU with off-gas scrubbing technology would range from 0.0002 to 0.0011 kg/hr. This calculation assumes the 95% efficiency for the industry standard systems can apply to the low HCl concentration in the FBU off-gas. The 95% estimate comes from the previous industry examples and illustrate what is typical for off-gas scrubbing technologies. However, the trade-off is higher capital and operating costs for the APC system, and higher treatment and disposal costs for the evaporated salt from the off-gas scrubbing technology.

While liquid off-gas scrubbing could help meet future, more stringent emission regulations, other, more beneficial alternatives exist to improve APC performance, if required. The best option is to perfect the *in situ* neutralization process. Optimizing *in situ* neutralization is preferable to off-gas scrubbing and its undesirable aqueous waste byproducts. Another option is to use a carbon filter back-up to the *in situ* neutralization. The carbon filter, if required, could provide a

more economically prudent approach to meeting future air emission requirements than adding liquid off-gas scrubbing technology. Using semi-permeable membranes to partition unwanted hydrocarbons from the off-gas is another innovative, though less proven possibility for meeting emission requirements.

This analysis brings up an important difference between the FBU and most incineration technologies. The common industry approach assumes the APC system performs independently of the incineration technology. This type of thinking results in systems consisting of the best incinerator coupled to the best APC system. The Rocky Flats approach differs by integrating APC into the incineration technology itself, and results from looking for the best overall solution to the Rocky Flats waste problem in the context of the operating environment.

In the FBU, minimizing air pollution starts by minimizing hazardous off-gas, radionuclides, and heavy metals created while incinerating. At the same time, the FBU minimizes solid waste production. Minimizing waste production is an urgent requirement while working with radioactive materials and merely beneficial in most industrial hazardous waste treatment applications. Minimizing waste is an urgent requirement because of the cost of secondary waste treatment and the shortage and expense of disposal sites for radioactive wastes. The FBU minimizes primary waste by making ash, which is smaller in size than the original waste. The FBU minimizes secondary wastes by eliminating evaporator salts resulting from treating off-gas scrubbing solutions and by eliminating immobilized refractory vessel linings. Therefore, low temperature operation with *in situ* neutralization contributes to meeting or exceeding air pollution requirements while helping to minimize secondary waste production. This waste minimization or pollution prevention strategy can avoid capital costs, lower operating costs, and the EPA strongly supports this philosophy.¹⁷

¹⁵ [Carl Cooley]. *Industrial Response to Requirements For The Air Pollution Control System For A Referenced Fluidized Bed Incinerator*. Washington, D.C.: US Department of Energy, Office of Environmental Restoration and Waste Management, Office of Technology Development, March 1993 [Revised July 1993], p. B-11.

¹⁶ *Ibid.*, p. B-15.

¹⁷ *Strategy for Hazardous Waste Minimization and Combustion*, EPA530-R94-044. Washington, D. C.: US Environmental Protection Agency, Solid Waste and Emergency Response, November 1994.

Minimizing Chlorine Effectively Suppresses Dioxin and Furan Production

Fly ash in contact with chlorine containing off-gas in the 200 to 400°C range creates dioxins, and in the 200 to 500°C range creates furans.¹⁸ Rocky Flats' combustion strategy precludes this problem by incorporating multiple, independent features in the incineration and APC systems to prevent formation of these toxic, gaseous species. This strategy takes advantage of safety features integral to the FBU design.

Eliminating chlorine production during incineration is a preferred waste minimization or pollution prevention strategy; removing dioxins and furans using only off-gas scrubbing is merely a waste remediation strategy. As the data from the sorbent experiments show, Rocky Flats is having success eliminating HCl from off-gas through use of sodium carbonate sorbent. This data is both credible and independently verified.

The rest of this report uses the simple term "dioxin" to refer to both dioxins and furans. While this is not strictly correct, this convention significantly streamlines sentence structures and improves clarity. The gaseous species referred to are polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

There are two zones where dioxin formation occurs in typical waste combustion systems. The first is inside the combustion zone where poor mixing and very low temperature pathways of less than 400°C can let dioxin escape oxidation. There are several alternative theories regarding how dioxin formation occurs in the combustion zone. All of these theories agree that if dioxin experiences high temperatures with sufficient oxygen then destruction will occur with extremely high efficiency. Modern waste combustion furnaces now incorporate "good combustion practices" as part of their design. These practices are a set of design and operation parameters specifically focused on minimizing organic emissions. The practices include uniform,

high temperatures within the furnace; enhanced fuel/air mixing; and minimization of the carryover of unburned carbonaceous particulate matter.¹⁹

The FBU avoids the dioxin problems inherent to other incinerator designs. A main advantage of fluidized bed technology is its destruction and removal efficiency (DRE). With sufficient oxygen the DRE changes as time, temperature, and turbulence vary. If any one factor increases, the other factors can decrease and maintain the same DRE. The fluidized bed technology exploits this relationship by increasing the residence time and turbulence to allow high DRE at lower temperatures. The increased turbulence results from fluidized bed technology's inherent design and the increased residence time results from the FBU's two stage process. The advantages of low temperature operation include lower radionuclide, metal, NO_x emissions, and safer operation. The higher turbulence eliminates very low temperature pathways and leads to dioxin destruction.

Dioxin formation is often a problem in the destruction of poly-chlorinated biphenyls (PCB's). Tests conducted on the pilot-scale incinerator on May 19, 1981, showed:

A trial burn of polychlorinated biphenyl (PCB) transformer fluid in a fluidized bed incinerator has been completed at Rocky Flats Plant (RFP). Extensive sampling procedures were used to assess the efficiency of the burn; analysis by Rocky Flats Plant laboratories of the samples collected gave a 99.99992 percent PCB destruction efficiency. This compares well with the independent EPA analysis indicating that 99.9999 percent of the PCB was destroyed.²⁰

The report includes complete analysis data and a discussion of all analytical techniques; the analysis did not detect dioxins in the off-gas stream. This destruction

¹⁸ *State-of-the-Art...*, *op. cit.*, Figure 7-15, p. 7-35.

¹⁹ W. R. Seeker, W. Clark, W. S. Lanier, and G. Rizeq, EER Corporation, "Combustion Byproducts From Mixed Waste Thermal Treatment Processes: Formation and Control," *Proceedings of the Mixed Waste Thermal Treatment Symposium*, Denver, Colorado, April 12-14, 1994, p. 159-160.

²⁰ A. J. Johnson, *et. al.*, *op. cit.*, p. 1.

efficiency occurred using the pilot-scale FBU operating at an average of 595°C in the primary bed, and 695°C in the afterburner.

The second zone of dioxin formation is downstream of the combustion process. The zone results from a catalytic mechanism in which dioxin precursors react with metals in the fly ash to form dioxin. This zone is usually the dominant source of dioxin formation in many waste combustion devices. The temperature of the off-gas particles and the off-gas quench rate significantly influence this process.²¹

The FBU has three independent mechanisms to prevent dioxin formation while cooling of the off-gas. They are:

1. Eliminating the chlorine from the waste stream by *in situ* neutralization;
2. Using heaters to keep the off-gas warmer than 500°C until it passes through the sintered metal filters to eliminate commingling between ash and off-gas within the temperature range of concern; and,
3. Quickly cooling the off-gas only after removing the fly ash.

Low Temperatures Significantly Reduce Radionuclide Volatility

Minimizing radionuclide emissions is a crucial safety concern at Rocky Flats. A recent assessment of the FBU did not adequately address radioactive emission requirements because the industrial representatives contacted for the report lack understanding of radionuclides. By the report's own admission, "the [incineration] industry has almost no experience with radionuclides in mixed waste."²² Fortunately, Rocky Flats personnel are better versed in radionuclide volatility and emissions than the industrial representatives.

Combustion does not destroy radionuclides. Radionuclides must either exit the combustion chamber in the ash as a solid or in the off-gas as a vapor or par-

ticle. Rocky Flats has a twofold strategy to minimize radionuclide emissions: minimize their production and remove them in the APC system.

Since minimizing the plutonium and other radionuclides in the off-gas emissions is a high priority safety concern, Rocky Flats initiated a significant experimental effort at Lawrence Livermore National Laboratory (LLNL) to provide real data to understand and engineer a successful overall system. The LLNL data shows that actinide emission suppression in the FBU takes place by three separate but related effects: low temperature operation, the presence of sodium carbonate, and low chlorine concentration in the off-gas. The FBU system minimizes radionuclide emissions to a greater extent than is possible by remediation with APC technology alone.

The LLNL data in Table I (page 11) shows how increasing only the operating temperature of a typical incinerator from 550 to 1200°C increases the radionuclide emissions. Elevating the temperature increases the plutonium volatilized by the reactor from 5×10^{-13} grams per year (g/yr) to 2×10^{-1} g/yr, a twelve order-of-magnitude increase. The americium increases from 3×10^{-16} g/yr to 2×10^{-4} g/yr, another twelve order-of-magnitude increase. The uranium volatilization increases from 8×10^{-5} g/yr to 9×10^4 g/yr, a nine order-of-magnitude increase. The additional radionuclides dramatically increase the burden on an APC system. These lower temperatures are relevant because the primary stage of the proposed FBU system at Rocky Flats would operate at 550 to 600°C, while rotary kilns and other incinerators typically operate at 1200°C and above. Because the FBU operates at a lower temperature than other thermal treatment systems it produces less radioactive metals for the APC system to remediate.

The data is significant because most plutonium, uranium, and americium releases to the environment would happen via vapor transport. A typical APC system in the DOE complex can remove about 99.9999% of the particulates in off-gas using three or four stage HEPA filtration, with each HEPA filter operating at a 99.97% efficiency. This constitutes a six order-of-

²¹ W. R. Seeker, *et. al.*, *op. cit.*, p. 160.

²² [Carl Cooley], *op. cit.*, p. B-2.

magnitude particulate reduction. However, HEPA filters and many other APC devices only remove metal particulates and cannot remove metal vapors. So the tiny portion of metal vapors that do not condense into particulates in the APC system pass through to the environment. From just the lower temperature effect, the FBU has a nine to twelve order-of-magnitude reduction in volatilized radioactive emissions passed to the APC system compared to other types of thermal treatment. This decrease is far greater than the entire effect of typical HEPA filtration in most APC systems.

To acquire the data for Table I, LLNL used the transpiration method²⁴ to experimentally determine the volatility of plutonium, americium, and uranium. The measured quantities are the volatile species emanating from solid plutonium oxide (PuO_2) and from a solid solution of 1,000 ppm americium oxide in plutonium oxide ($\text{PuO}_2/(1,000 \text{ ppm})\text{AmO}_2$). The environment for these tests included steam and oxygen, both at 0.1 atm, at temperatures of 957 to 1,057°C. The volatile species are $\text{PuO}_2(\text{OH})_2$ and $\text{AmO}_2(\text{OH})_2$ gases, respectively; these gaseous species are plutonium- and americium-oxyhydroxides. Other experiments also found the amount of uranium volatilizing from solid uranium

Table I. Experimentally Derived Estimates for the Mass of Americium, Plutonium, and Uranium Volatilized Yearly from an Incinerator as a Function of Temperature.²³

Temperature °C	Mass Americium grams/year*	Mass Plutonium grams/year*	Mass Uranium grams/year*
550	3×10^{-16}	5×10^{-13}	8×10^{-5}
600	9×10^{-15}	1×10^{-11}	1×10^{-3}
700	2×10^{-12}	2×10^{-9}	8×10^{-2}
800	6×10^{-10}	2×10^{-7}	1×10^{-1}
900	2×10^{-8}	1×10^{-5}	2×10^1
1,000	8×10^{-7}	6×10^{-3}	8×10^2
1,100	1×10^{-5}	2×10^{-2}	9×10^3
1,200	2×10^{-4}	2×10^{-1}	9×10^4

*Error approximately $\pm$ one-half order-of-magnitude

oxide (U_3O_8) in the presence of steam and oxygen. The volatile species are uranium trioxide (UO_3) and oxyhydroxide [$\text{UO}_2(\text{OH})_2$] gases.²⁵

LLNL also had to assume the operating characteristics for a typical incinerator to compile Table I. The waste feed included sufficient plutonium, uranium, and americium to saturate the off-gas in the system. The plutonium and americium are present as solid PuO_2 with 1,000 ppm AmO_2 in solid solution. Uranium is present as solid U_3O_8 . Incinerator operating conditions are 1 atm total pressure with 0.1 atm O_2 gas and 0.1 atm H_2O gas at a gas flow rate of 40 kilomoles per hour (kmols/h). Operational time is 6,000 hours per year.²⁶ Table I values do not consider actinide volatilization from the formation of oxychlorides and oxyfluorides.

In addition to lower temperatures, the FBU also has a sodium carbonate bed that further suppresses the volatility of actinides. The presence of sodium carbonate in the FBU reduces the volatility of uranium by about a factor of ten, and mildly suppresses the formation of volatile americium- and plutonium-oxyhydroxides.²⁷ The formation of disodium uranate (Na_2UO_4) causes the large reduction in uranium volatilization. The Na_2UO_4 forms in the presence of so-

²³ Oscar H. Krikorian; Bartley B. Ebbinghaus; Martyn G. Adamson; Alfred S. Fontes, Jr.; and Dennis L. Fleming. *Experimental Studies and Thermodynamic Modeling of Volatilities of Uranium, Plutonium, and Americium from Their Oxides and From Their Oxides Interacted with Ash*, UCRL-ID-114774. Livermore, California: University of California for US Department of Energy, Lawrence Livermore National Laboratory, September 15, 1993, p. 75, Figure 12 [Data shown in Table I manually interpolated from the figure].

²⁴ In the transpiration method, a known amount of carrier gas is slowly passed over a solid or liquid in a furnace chamber, such that any volatile gases produced become entrained in the carrier gas and are swept out of the chamber where the volatilized gas is then condensed and analyzed. The carrier gas may also contain reactive gases that contribute to forming the volatilizing species. *Ibid.*, p. 5.

²⁵ *Ibid.*, p. 73-76.

²⁶ *Ibid.*, p. 74-75.

²⁷ *Ibid.*, p. 1, 73.

Table II. Experimentally Derived Estimates for the Mass of Americium, Plutonium, and Uranium Entering an APC System Assuming Different Operating Scenarios.

Scenario	Experimental Conditions	Mass Americium grams/year	Mass Plutonium grams/year	Mass Uranium grams/year
1. Typical incinerator at correct temperature but with artificially low chlorine gas concentration (from Table I)	1,200°C 1 atm total pressure 0.1 atm O ₂ 0.1 atm H ₂ O 40 kmols/hr gas flow 6,000 hr/yr operation	2×10^{-4}	2×10^{-1}	9×10^4
2. Typical incinerator at artificially low temperature with typical chlorine concentration	550°C 1 atm total pressure 0.1 atm O ₂ 0.05 atm H ₂ O 10,000 ppm Cl ₂ 40 kmols/hr gas flow 6,000 hr/yr operation	4.4×10^{-9}	2.2×10^{-5}	1.5×10^0
3. FBU without sorbent or chlorine gas (from Table I)	550°C 1 atm total pressure 0.1 atm O ₂ 0.1 atm H ₂ O 40 kmols/hr gas flow 6,000 hr/yr operation	3×10^{-16}	5×10^{-13}	8×10^{-5}
4. FBU without sorbent but with chlorine gas	550°C 1 atm total pressure 0.1 atm O ₂ 0.05 atm H ₂ O 10 ppm Cl ₂ 40 kmols/hr gas flow 6,000 hr/yr operation	6.8×10^{-14}	3.3×10^{-10}	3.5×10^{-5}
5. FBU with sorbent but without chlorine gas	550°C 1 atm total pressure 0.1 atm O ₂ 0.1 atm H ₂ O Na ₂ CO ₃ bed 40 kmols/hr gas flow 6,000 hr/yr operation	$<2 \times 10^{-17}$	2×10^{-13}	1.7×10^{-9}

dium oxide (Na₂O). The Na₂O forms because of the sodium carbonate. This emission suppression is on top of the effect caused by the lower temperatures in the FBU. For example, results from these studies allow an assessment of the FBU's afterburner emissions. This analysis gives volatilization rates of 2×10^{-13} g/yr Pu,

1.7×10^{-9} g/yr U, and less than 2×10^{-17} g/yr Am.²⁸ Table II, Scenario 5 shows these values for comparison with other estimates. These are the estimated rates for these metals entering the FBU's APC system.

In another separate study LLNL estimated variations in actinide volatilization during combustion caused by varying only the chlorine concentration in the off-gas. The concern was that HCl could significantly increase the volatilities of all actinide species. Chlorinated oxide gases of UO₂Cl₂, PuO₂Cl₂, and AmO₂Cl₂ are the volatile species in the presence of HCl. The vapor pressure of UO₂Cl₂ is available from thermodynamic data. Recent thermodynamic data on PuO₂(OH)₂ volatility can provide predictive estimated thermodynamic data for PuO₂Cl₂. The assumption is that AmO₂Cl₂ and PuO₂Cl₂ have the same vapor pressure, but for AmO₂Cl₂ the pressure relates directly to the AmO₂ mole fraction in the PuO₂ solid solution. For this study the partial pressures of oxygen and water gas were 0.10 and 0.05 atm, respectively.

In a typical incinerator technology such as a rotary kiln, the chlorine in the waste produces a $\sim 10^{-2}$ atm ($\sim 10,000$ ppm or $\sim 1\%$) HCl gas pressure in the combustion chamber. For this type of system, the calculated actinide volatilization rates in the off-gas are 1.5 g/yr U, 2.2×10^{-5} g/yr Pu, and 4.4×10^{-9} g/yr Am.

²⁸ *Ibid.*

However, these calculations assume the technology could operate at 550°C.²⁹ Once again, typical incinerators operate at greater than 1200°C, so these values are unrealistically low. Assuming the FBU operates with 99.9% HCl capture efficiency, the HCl concentration is 10 ppm. At 10 ppm HCl the calculated actinide volatilization rates in the FBU off-gas are 3.5×10^{-5} g/yr U, 3.3×10^{-10} g/yr Pu, and 6.8×10^{-14} g/yr Am. Once again, these calculations are for 550°C, which is a realistic operating temperature for the FBU.³⁰ Table II, Scenarios 2 and 4 show these values for comparison with other estimates. These are concentrations of actinide metals entering the FBU APC system. These data show the chlorine concentration in most thermal treatment processes significantly increases the volatility of actinides. However, the low HCl presence in the FBU only causes a minor addition to radionuclide volatilization. The FBU produces significantly fewer radionuclides that enter the APC system than other thermal treatment technologies.

Radionuclide Stack Emissions During Demonstration-Scale Testing Met or Exceeded Air Quality Requirements

Rocky Flats has stack emissions data associated with the operation of the pilot- and demonstration-scale FBUs for combustion of radioactive and mixed waste. Both units are in Building 776. The off-gas and ventilation air from the incinerator area exhaust through HEPA Filter Plenum 202 and a stack designated as the Building 776 Plenum 202 Stack. This plenum receives room ventilation air along with off-gas from the pilot- and demonstration-scale FBU.

Pilot-scale testing on a 35.5 cm diameter, 9 kg/hr unit took place from February 13, 1975, to July 13, 1980, and consisted of 47 runs over 3,275 operating

hours. The operating time does not include the 304 hours of start-up, shut-down, or idle periods. The fast start-up and shut-down are possible because the FBU's low operating temperatures eliminate the need for a ceramic refractory lining that can easily crack during thermal cycling. The pilot-scale unit treated about 17,667 kg of liquid and solid wastes in this period. Waste burned in these tests include what is now known as low level mixed waste.³¹ One run on May 19, 1981, treated 12.74 kg of Pyronol™ transformer fluid and kerosene. The chemical analysis of the Pyronol shows the 4 hour test burned 2.1 kg of Aroclor-1254™, a type of PCB.³²

Demonstration-scale FBU testing on a 91 cm diameter, 81 kg/hr unit took place over several periods from 1978 to 1988. The 1979 to 1981 tests incinerated some waste materials from radioactive process areas. Table III (page 14) lists these waste materials as "suspect solid waste" and "suspect compressor oil." These wastes had a very low level of radionuclide contamination, well below 10 nanocuries per gram (nCi/g) of alpha radionuclides. Used engine oils from the Rocky Flats fleet garage, new diesel oil, and a minor amount of solid PVC and plastics were the primary wastes burned during equipment testing between 1985 and 1987.

Table IV (page 15) shows Building 776 Stack 202 exhaust system annual radioactive air emission data from January, 1979, through January, 1987, the time of the demonstration-scale testing. Comparing Table III to Table IV shows no discernible correlation between FBU operation and radionuclide emissions. Even under upset conditions for the FBU, the off-gas would proceed through the multi-stage HEPA filtration system before release.

Table IV shows levels of radioactive emissions many orders-of-magnitude higher than predicted by LLNL research shown in Table I (page 11). Comparing the data suggest the level of radioactive emissions from the FBU is imperceptible when measured against

²⁹ Oscar H. Krikorian, Bartley B. Ebbinghaus, and Martyn G. Adamson. *An Estimate of Chlorine-Induced Volatilities of Actinides in the Rocky Flats Plant Fluidized Bed Incinerator*, UCRL-ID-115788. Livermore, California: University of California for US Department of Energy, Lawrence Livermore National Laboratory, December 1993, p. 1.

³⁰ *Ibid.*, p. 9-12 [Values calculated from information provided].

³¹ Rocky Flats Databooks 1583, 1663, 1664, 1766, 1832, and 1908.

³² A. J. Johnson, *et. al.*, *op. cit.*, p. 6-7.

Table III. Demonstration-Scale FBU Testing, November 1978 through January 1988.³⁴

<i>Run date (week)</i>	<i>Operating hours</i>	<i>Waste quantity (kg)</i>	<i>Waste type</i>
November 6, 1978	48	1,217	Office trash
April 22, 1978	53	2,139	Office trash
June 10, 1979	114	641	Suspect solid waste
		5,976	Office trash
August 12, 1979	62	3,187	Suspect solid waste
August 24, 1980	111	5,874 ³⁵	Suspect solid waste
October 2, 1980	27	318	Suspect compressor oil
March 2, 1981	102	2,526	Suspect compressor oil
October 6 and 7, 1985	51	307	Waste oil (nonhazardous, nonradioactive)
October 27, 1985	103	2,318	Waste oil and diesel oil (nonhazardous, nonradioactive)
March 9, 1986	less than 3	Not recorded	New diesel oil
April 11, 1986	less than 3	Not recorded	New diesel oil
May 1 to 5, 1987	~5	Not recorded	New diesel oil
May 26 to 29, 1987	~11	Not recorded	New diesel oil
June 1 to 5, 1987	~12	Not recorded	New diesel oil
June 8 to 9, 1987	~5	Not recorded	New diesel oil
June 15, 1987	less than 3	Not recorded	New diesel oil
June 22 to 23, 1987	~10	48	New diesel oil, new PVC and plastic
June 29 to July 1, 1987	~50	Not recorded	New diesel oil
July 13 to 17, 1987	~30	Not recorded	New diesel oil, new PVC and plastic
July 23 to 24, 1987	~60	Not recorded	New diesel oil, new PVC and plastic
September 29, 1987	~2	Not recorded	New diesel oil
October 6, 1987	~4	Not recorded	New diesel oil
October 29, 1987	~4	Not recorded	New diesel oil
December 1, 1987	~4	84	New diesel oil
January 14, 1988	~4	73	New diesel oil

the emissions resulting from ongoing Rocky Flats operations. The data suggests that dilution air from the Building 776 was a greater source of radionuclide releases than was the FBU system. Furthermore, all releases were below the allowable air pollution permit levels which ranged between 0.10 and 0.18 μCi .³³ The variation in permitted release levels is consistent with allowable release being related to the activity concentration.

³³ Gary L. Potter, Director, Waste Programs, EG&G Rocky Flats, Inc., Rocky Flats Plant, Golden, Colorado, to Madeline Newar, Environmental Studies and Statistics Branch, Office of Radiation Programs, Washington, D. C. *Waste Incineration Off-Gas System*. Letter Reference 91-RF-1254, March 12, 1991, Appendix, Figure 1.

Since nearly all radionuclides leave the FBU as particulates, filtration provides a successful means of control. As Table IV shows, Rocky Flats has significant, credible data to support permit applications and public discussions regarding FBU technology.

The 3,275 hours of pilot-scale testing and 881 hours of demonstration-scale testing validated more than just the air emission system, it also verified many other features of the FBU system. An example of this successful verification is the cyclone separators. The primary cyclone downstream from the primary reactor and the cyclone downstream from the afterburner

³⁴ *Ibid.*, Appendix, Tables I and II. Correction as noted.

³⁵ Corrected. New value from Rocky Flats Databook 1908, p 20.

Table IV. Building 776 Stack 202 Annual Actinide Air Emission Data, January 1979 through January 1988.³⁷

Year	Months	Effluent Volume m ³	Release ²³⁹ Pu, ²⁴⁰ Pu grams/period	Release ²³³ U, ²³⁴ U grams/period	Release ²³⁸ U grams/period	Release ²⁴¹ Am grams/period
1979	12	1.092 x 10 ⁸	4.8 x 10 ⁻⁷	2.1 x 10 ⁻⁶	1.4 x 10 ⁻¹⁴	—
1980	12	6.6 x 10 ⁷	1.7 x 10 ⁻⁷	1.3 x 10 ⁻⁶	4.0 x 10 ⁻¹⁵	—
1981	12	8.184 x 10 ⁷	6.3 x 10 ⁻⁷	*	9.7 x 10 ⁻¹⁵	—
1982	12	1.003 x 10 ⁸	1.1 x 10 ⁻⁶	*	2.1 x 10 ⁻¹⁴	—
1983	12	8.917 x 10 ⁷	3.7 x 10 ⁻⁷	*	6.2 x 10 ⁻¹⁴	—
1984	12	8.327 x 10 ⁷	8.7 x 10 ⁻⁷	*	3.8 x 10 ⁻¹⁴	—
1985	12	9.713 x 10 ⁷	1.6 x 10 ⁻⁶	2.4 x 10 ⁻⁷	2.4 x 10 ⁻¹⁴	1.8 x 10 ⁻⁷
1986	12	7.565 x 10 ⁷	3.0 x 10 ⁻⁷	3.6 x 10 ⁻⁷	4.9 x 10 ⁻¹⁵	1.7 x 10 ⁻⁸
1987	13	8.961 x 10 ⁷	3.3 x 10 ⁻⁷	1.9 x 10 ⁻⁶	4.3 x 10 ⁻¹⁵	1.8 x 10 ⁻⁸

*²³³U and ²³⁴U values reported with ²³⁸U values in 1981 through 1984.

"performed efficiently without operational problems or modifications."³⁶

Rocky Flats Established Conservative, Upper Bounds for Air Emission Estimates

Air pollution control system performance is a crucial safety concern for the FBU system. Evaluating these systems is complex, time consuming, and expensive. To enable modeling of the preliminary designs for the FBU APC system, Rocky Flats made a conservative assumption about APC technology performance, which is:

Filtration penetrations (at a single particle size) were assumed to be multiplicative. This would be a poor assumption for a polydisperse particle-size distribution since the finer particles which tend to

escape the first filter would also be most likely to escape the second filter. However, this assumption is justified in this case because the particle size distribution has been assumed to be mono-disperse at the size most likely to escape the filter. The particles entering the second filter are no different from the particles entering the first filter, and thus the particle capture efficiency should not be affected by the order of the filter in the [air-pollution control] chain.³⁸

This assumption is credible, easy to use, and leads to estimating conservative, upper limits for particulate emissions. Even using this assumption, the appropriate calculations estimate the Rocky Flats APC system far exceeds performance requirements established by applicable state and federal regulations.

Industrial practice is to achieve low emissions without the dependence on expensive HEPA filters, unless specified by the customer. The FBU requires HEPA filters because they are a fundamental part of the DOE's radiation control strategy and specified in various DOE orders. While this differs from industrial practice, the use of HEPA filters at DOE facilities builds upon a mostly successful tradition of engineering safe facilities for containment of radionuclide bearing materials. However, because of the FBU sys-

³⁶ L. J. Miele, *et. al.*, *op. cit.*, p. 48.

³⁷ Gary L. Potter, *op. cit.*, Appendix, Table III. Data for this table calculated from the source document. For this estimation, the proportion of each isotope are approximated as the isotopic mix found in FBU ash. (EG&G Rocky Flats Analytical Requisition 460164, From 776 FBI Ash. October 3, 1994.) The proportions of ²³⁹Pu to ²⁴⁰Pu are estimated at 94:6 respectively. The ²³³U to ²³⁴U uranium isotopes were estimated at 50:50 because isotopic data was unavailable. Since each of these uranium isotopes has similar activity, the error caused by this approximation is very small. Specific activity data came from an accepted handbook. (Bernard Shleien, editor. *Health Physics and Radiological Health Handbook*. Silver Springs, Maryland: Scinta, Inc., 1992.)

³⁸ *State-of-the-Art...*, *op. cit.*, p. 7-21.

tem's low emissions, the system relies less on off-gas remediation and final HEPA filtration than many other incineration systems.

Proposed Air Pollution Control Measures Capture Nearly All Metal Particulates

Like radionuclides, metals are not destroyed during combustion; therefore, they must exit the combustion chamber either as solid in the bottom ash, or as vapor and particulate in the off-gas. Estimating the metals vaporized during mixed wastes combustion in the FBU took place using the thermodynamics equilibria model CET85 developed by the National Aeronautics and Space Administration's (NASA's) Lewis Research Center. The model estimates radionuclide and heavy metal behavior once they enter the APC system. The estimated stack emissions of particulate matter after the APC system is 1×10^{-5} grains per dry standard cubic foot (gr/dscf). This value is well below the 0.08 gr/dscf BIF Tier III standard or the 0.015 gr/dscf municipal waste standard that Rocky Flats personnel anticipate Colorado authorities will impose.³⁹

The NASA model assumes all reactions achieve chemical equilibrium in the combustion chamber and all elements mix intimately. This equilibrium approach is conservative, meaning it gives an upper limit for metal vaporization. The estimates err toward the conservative side because most combustors do not always maintain equilibrium and perfect, thorough mixing. Kinetics and mass transfer tend to inhibit the vaporization of metals, so actual vaporization is lower than predicted by the model. Currently there is not sufficient kinetic data for all possible compounds that may form during combustion to formulate a comprehensive kinetic model. However, the thermodynamic data available for this model is very good, so the analysis is state-of-the-art.

Calculations on 14 metal and three radioactive constituents assessed the APC system's ability to capture metals emitted from the FBU system. The metals

are antimony, arsenic, barium, beryllium, cadmium, cesium, chromium, lead, mercury, nickel, selenium, silver, strontium, and thallium. The radioactive constituents are americium, plutonium, and uranium. All calculations assumed HCl concentrations at both 0 and 1,000 ppm which represent values lower and higher than expected in the FBU. These calculations conservatively estimate volatilization because some solid trapping and matrix effects are not part of the estimation. The presupposed metal content in every different type of Rocky Flats combustible, low level mixed waste matrix is 1 ppm for each metal and radionuclide. This is likely higher than the metal and radioactive content most applicable Rocky Flats wastes.

The model's calculations indicate americium and plutonium isotopes are relatively refractory but significant vaporization occurs at 1,300°C when moderate levels of chlorine are present at fuel lean conditions. These estimates concur with the LLNL experimental calculations (see Table I, page 11). Cesium exemplifies the behavior of a volatile metal because calculations estimate the 1 ppm is fully in the vapor phase at temperatures higher than 600°C. Strontium and uranium are of intermediate volatility and exemplify the greatest dependence on chlorine and stoichiometry. For example, uranium is fully volatile at temperatures of 1,000°C under fuel rich conditions. However, uranium is fully volatile at temperatures as low as 700°C under fuel lean conditions due to the formation of oxyhydroxides and chlorinated oxyhydroxides. Strontium on the other hand becomes less volatile under fuel lean conditions. Thus thermal treatment devices operating at high temperatures are more likely to drive these metals to the vapor phase. These metals later condense into a fine fume that oblige the overuse of particulate control devices.

The investigation included several combinations of different particulate control devices including cyclones, sintered metal filters, and HEPA filters with off-gas cooling to 80°C. Condensation and aerosol dynamics determine the size of the metallic particles. The calculations considered how removal efficiency of each device varied as a function of particle size.

³⁹ *Ibid.*, p. 7-22.

The estimation is the FBU APC system will remove all metals (except mercury) and radionuclides with a 99.999999% efficiency. This system is three orders-of-magnitude more efficient at removing particulates than most DOE APC systems. The two key design components of particulate control devices are the efficient gas cooling to allow volatile metal condensation followed by capture of submicron size particles with metal and glass HEPA filters.⁴⁰ Rocky Flats would like to conduct a mock trial burn using surrogate wastes at a licensed facility in California to demonstrate this system's efficiency.

Mercury is a highly volatile metal and in most cases remains in the vapor phase even at low APC device temperatures. Particulate APC devices will not capture mercury from the vapor phase. The inability of particulate control devices to capture mercury is as true for the FBU as for any other incineration technology. Mercury requires special management to prevent its presence in the waste or special technology to remove it from off-gas. Mercury off-gas scrubbing technology is expensive and creates waste byproducts. Therefore, the prudent strategy at Rocky Flats is to prevent the presence of bulk mercury in the waste by characterizing and segregating mercury bearing wastes from combustible wastes to prevent their entry into the FBU. In addition, Rocky Flats would pursue a permit that would allow treatment of wastes containing only suspect mercury levels or levels below detectable analytical limits.

The strategy to remove all mercury from the waste before FBU treatment appears feasible. Process knowledge characterization data show that only two of the 17 waste forms considered for FBU processing may contain mercury.⁴¹ These are the "FBI oils" and "excess chemicals" waste types. Chemical analysis of the 90.31 cubic meter (m^3) of FBI oils shows the mer-

cury content is less than 0.94 ppm.⁴² Additional data suggest that 0.94 ppm mercury concentration in the FBI oils waste form would not cause the FBU to exceed the BIF RAC emission limits for mercury.⁴³ The 23.91 m^3 of excess chemicals consist of out-of-date chemicals packaged for disposal from throughout the plant site, acid waste, and solid, expired chemicals. Segregation and analysis of this waste before initiating FBU treatment should provide a simple option for controlling mercury releases. Treatment methods other than incineration for the very small portions waste containing mercury may prove more economically prudent than incorporating mercury scrubbing technology into the APC system for the FBU.

Cementation or Polymer Encapsulation Can Successfully Immobilize FBU Ash

The Technology Development organization at Rocky Flats is pursuing several strategies for managing radioactive ash generated by FBU treatment. Efforts underway include characterizing ash generated by the pilot- and demonstration-scale FBU systems and feasibility testing several immobilization technologies using surrogate ash. Data collected using surrogate ash shows that at this time immobilizing with Portland cement at a 20 to 30% waste loading or polymer encapsulation at a 40 to 50% loading appears feasible. Immobilizing with microwave melting technology also remains possible. Immobilization using radioactive ash from the pilot- and demonstration-scale FBU process will occur with all three immobilization technologies in fiscal year 1995.

Characterization

Rocky Flats manages ash from the pilot- and demonstration-scale systems in several different programs. Rocky Flats manages 0.84 m^3 incinerator ash as transuranic (TRU) mixed wastes, and 8.3 m^3 as low

⁴⁰ W. R. Seeker, *et. al.*, *op. cit.*, p. 159.

⁴¹ *Annual Land Disposal Restriction Progress Report, Revision 0*. Golden, Colorado: US Department of Energy, Rocky Flats Office, March 31, 1994, Tables 2-1, 4-9, and B-1.

⁴² *Diversified Scientific Services Inc.; Waste Analysis Report; Data Log 6996*, September 27, 1994.

⁴³ *State-of-the-Art...*, *op. cit.*, pp. 7-19 to 7-23 and Table 7-6.

level mixed wastes.⁴⁴

TRU mixed wastes have radionuclide concentrations greater than or equal to 100 nCi/g, and low level mixed wastes contain less than 100 nCi/g. The low level- and TRU-mixed wastes have EPA codes based on

process knowledge and

limited analytical characterization. These codes are for arsenic (D004), barium (D005), cadmium (D006), chromium (D007), lead (D008), mercury (D009), selenium (D010), silver (D011), and spent solvents (F001, F002, and F005). These EPA code assignments result from the EPA's derived-from rule: the ash is hazardous for these constituents because it derives from combustible wastes originally containing these constituents.

Rocky Flats is in the process of characterizing ash from the pilot- and demonstration-scale FBU. Waste drum sampling took place in September and December 1994 for one subpopulation of the radioactive ash. Data validation for these samples is not yet complete, so data reported here is preliminary. Samples drawn from low level mixed waste drums 04932 and 04898 show that alpha radiation levels in the drums are 25.5 and 29.2 picocuries per gram (pCi/g) and beta radiation levels are less than 122 pCi/g.⁴⁵ Table V shows the relative concentrations of other anions and metals. Although the emissions spectrography data are not defensible for RCRA use, it provides an expeditious assessment of the ash composition while awaiting certified data. Table VI (page 19) shows particle analysis data. Organic analysis, TCLP, and other RCRA-required determinations are not yet complete. Rocky Flats personnel anticipate compilation, certification, and release of additional data in 1995.

Table V. Preliminary Emission Spectroscopy Data for Pilot- and Demonstration-Scale FBU Ash, Analysis of Fraction Less than 100 μ m Particle Size.⁴⁶

<i>Less than 100 ppm</i>	<i>100 to 1,000 ppm</i>	<i>1,000 to 10,000 ppm⁴⁷</i>	<i>Greater than 10,000 ppm</i>
Ag, As, B, Ba, Be, Bi, Ca, Cd, Co, Ga, Ge, Hg, In, Ir, Mg, Mn, Mo, Nb, Ni, Sb, Sr, Te, Tl, V, and Zr	Al, Fe, and Zn	Cr, Cu, K, P, Pb, Si, and Sn	Na

Rocky Flats personnel also gathered ash for immobilization development while collecting samples for the analytical characterization. Treatability studies took place using this radioactive ash and a pilot-scale, twin screw polymer extrusion unit in Building 779, Room 270 during the second week of February 1995. A similar treatability study used Portland cement with the ash in a laboratory-scale cementation facility in Building 779, Room 218, during the third week in February 1995. Immobilization treatability studies with this radioactive ash will take place before the end of fiscal year 1995 using the bench-scale microwave solidification unit in Building 774, Room 210.

Cementation

Several studies evaluated immobilization technologies using nonradioactive ash surrogates. Cementing uses Portland cement and polymer encapsulating uses low density polyethylene to immobilize the ash. The cementation study took place using a "best case" and a "worst case" surrogate matrix. Table VII (page 20) shows these formulations. Preparing the surrogate waste required spiking each matrix with 1,000 ppm silver, barium, cadmium, lead, and nickel; chromium spiking took place by adding chromia-alumina catalyst from the demonstration-scale FBU. Testing included

⁴⁴ *Comprehensive Treatment and Management Plan, Version 1.3*. Golden, Colorado: US Department of Energy, Rocky Flats Office, June 9, 1992. Tables 3.1 and 3.2, pp. 3-2 to 3-6.

⁴⁵ *371 PARC Analytical Report Rad Screens, FBI Ash*, EG&G Rocky Flats Analytical Laboratories, September 23, 1994.

⁴⁶ *EG&G Rocky Flats Emission [sic.] Spectroscopy Analysis (SQ) Analytical Report, Drum 04898*, October 18, 1994.

⁴⁷ The low chromium levels shown in this table are thought to occur because only the fraction smaller than 100 μ m was examined in this analysis. The chromia-alumina catalyst is quite hard and higher levels of chromium are likely in the ash fraction larger than 100 μ m.

mixing the cement to form samples containing 30% surrogate waste, curing the samples, and submitted the samples for TCLP analysis. Table VIII (page 21) and Table IX (page 22) show how cementing immobilized all heavy metals but chromium to within applicable treatment standards for the TCLP extract.

Because cementing with a 30% ash content did not adequately immobilize all chromium, preparation took place of additional samples containing 20% and 30% surrogate ash. These cemented samples contained the chromium but not the other RCRA-listed heavy metals. Table X (page 23) shows the samples with 20% ash content met the EPA treatment standard of 5 ppm for chromium. However, the samples containing 30% surrogate waste once again failed the TCLP.⁴⁹ The treatment standards shown in these tables are current treatment standard values from the EPA's new *Universal Treatment Standard* regulation. This regulation provides some temporary regulatory relief for some characteristic waste forms.⁵⁰ Within the next few years these treatment standard values will decrease. Rocky Flats will evaluate treating these wastes to the new, lower treatment standards in fiscal year 1995.

Table VI. Fluidized Bed Ash Particle Sizes.⁴⁸

Size Micrometers (μm)	Weight Percentage
Greater than 1,000	13.3
500 to 1,000	52.6
212 to 500	24.2
147 to 212	4.2
43 to 147	3.9
30 to 43	0.8
20 to 30	0.4
10 to 20	0.4
5 to 10	0.1
Less than 5	Less than 0.1

Polymer Encapsulation

A polymer encapsulation scoping study immobilized surrogate FBU ash. The study's samples included six metals (barium, cadmium, chromium, lead, selenium, and silver) spiked into surrogate ash at concentrations of 50, 500 and 5,000 ppm. The surrogate ash was different from cementation study surrogate. Two types of fly ash (types C and F) were the surrogates, and fly ash spiking took place using an incipient wetness technique.⁵¹ Both untreated and polymer encapsulated ashes were subject to TCLP analysis. The polymer encapsulated waste content was 50% spiked ash, 50% low density polyethylene (LDPE). Both sample types omitted the sodium carbonate found in the actual ash to simulate a "worst case" demonstration.⁵² The situation was worst case because the sodium carbonate in the FBU ash can act to neutralize the acidity in the TCLP analysis, thereby lowering the amount of heavy metal in the final TCLP leachate. Consequently, all analysis using real ash, containing 5 to 25% sodium carbonate, should yield better TCLP analysis than are shown in this test.

Table XI (page 24) shows the results of TCLP analysis for the polymer encapsulation study. In both

⁴⁸ EG&G Rocky Flats, Inc., *Analytical Report, Lab 794-60*, November 29, 1994.

⁴⁹ Gary B. Semones, and Jeffrey A. Phillips. *Cementation Development Year End Project Summary, FY 94, TD-94-022*. Golden, Colorado: EG&G Rocky Flats Inc., Technology Development, for US Department of Energy, Rocky Flats Environmental Technology Site, September 15, 1994, p. 19-20.

⁵⁰ "Land Disposal Restrictions, Phase II—Universal Treatment Standards for Organic Toxicity Characteristic Wastes and Newly Listed Wastes; Final Rule." Washington D. C.: *Federal Register*, Vol. 59, p. 47982-48110, September 19, 1994, pp. 48275-48277, 48281-48282.

⁵¹ The incipient wetness impregnation technique first requires determination of the point of incipient wetness. Incipient wetness is defined as the volume of water required to completely wet the solid without any standing water being left on the solid. Unfortunately, fly ash behaves like a clay, slowly absorbing water and creating a thick sludge. This obscures the point of incipient wetness and makes mixing difficult. To ensure the exposure of all the fly ash to the spiking solution, a small excess of water was used. This produced a slurry that could be easily mixed and still absorb all of the water within a few minutes. The volume of solution required was estimated to be approximately 0.45 milliliter per gram of ash.

⁵² Boyce W. Logsdon, Andrea M. Faucette, James H. Oldham, and Robert J. Yudnich. *Heavy Metal Leachability From Polyethylene Encapsulated Nitrate Salt Waste At Rocky Flats*. Golden, Colorado: EG&G Rocky Flats, Inc., for US Department of Energy, Rocky Flats Environmental Technology Site, March 30, 1993, p. 16-17.

untreated and treated wastes, the TCLP values were significantly lower than the levels of metal spiked into the fly ash matrix. Two factors contributed to the low concentration of metals in the leachate. First, the fly ash neutralized some of the acidity of the TCLP leaching solution and precipitated the metals as hydroxides. Second, some metal ions adsorbed onto the surface of the ash. The first of these two contributors probably had the greatest effect, resulting in a final pH of the extract of 11 for fly ash type C, and 10 for type F. Large increases in the metal spiking values generally led to only small increases in metal leaching.⁵³

Overall, the encapsulation

process resulted in improved stabilization of the fly ash.⁵⁵ All of the treated samples met the newest applicable RCRA

treatment stan-

dards, except cadmium spiked at 5,000 ppm. However, as Table V (page 18) shows, the smallest size fraction of FBU ash contains less than 10 ppm cadmium, so problems encapsulating at higher cadmium levels are

not relevant. Selenium does not appear in Table V, as the selenium levels are likely very low. Consequently, immobilizing selenium is not likely to cause a problem. However, knowing the actual levels of selenium in the FBU ash will require complete laboratory certified heavy metal analysis that is not yet available. Surprises are possible.

Polymer encapsulation tests also occurred using only the chromia-alumina catalyst material. Testing took place on three samples using the TCLP procedure on the following: unencapsulated catalyst, 50% catalyst in LDPE, and 40% catalyst in LDPE. Chro-

Table VII. Best and Worst Ash Surrogate Compositions for Cementation Study.⁵⁴

<i>Material</i>	<i>"Best Case" Weight Percent</i>	<i>"Worst Case" Weight Percent</i>
Chromia/alumina catalyst	20.70	32.00
Sodium carbonate	24.10	5.70
Sodium chloride	14.80	19.90
Sodium sulfate	4.6	4.0
Coconut charcoal - ground carbon	6.9	5.0
Class F fly ash	28.90	33.40
TOTAL	100	100

mium was the only hazardous constituent present, but was present at a loading of 18% chromium by weight.

Table XII (page 25) shows the results of the TCLP analysis. The unencapsulated catalyst failed the TCLP with a concentration of over 221 ppm in the extract. Encapsulation in LDPE at the 50% level reduced the chromium concentration in the extract to 5.4 ppm, which barely fails the 5.0 ppm treatment standard. Reduction of the catalyst loading to 40% in LDPE resulted in a TCLP extract concentration of 3.2 ppm, which easily passes. Therefore, LDPE encapsulation effectively stabilizes FBU ash. These surrogate test results will guide the experimental studies with the radioactive ash.

An advantage of the FBU is the ash is the only waste from the FBU. Since there is no aqueous off-gas scrubbing, there is no need to develop an immobilization technology for evaporator salts. Also, since the FBU is an all metal system, there is no need to develop an immobilization technology to bind up heavy metals

⁵³ This is consistent with the major stabilization mechanisms being neutralization of the solution rather than strong adsorption onto the ash surface. At the same time, the increase in metal spiking interfered with the ability of the ash to neutralize the leachate, resulting in a lower final solution pH. This, in turn, resulted in higher metal concentration in the leachate solution. Encapsulating the spiked fly ash in LDPE reduced the exposure of fly ash to the leachate solution. This was demonstrated by the reduced ability of the fly ash to neutralize the leachate solution and resulted in a final pH of about 5.2. Even though the LDPE also reduced exposure to the metals, the lower pH solution more effectively leached the metals. These two competing effects tended to slightly increase the leach rates at lower spike levels and greatly decrease leach rates at higher spike levels. This is a favorable situation for most metals. However, cadmium failed the TCLP in the encapsulated ash, where it has passed in the unencapsulated fly ash.

⁵⁴ Gary B. Semones, and Jeffrey A. Phillips, *op. cit.*, p. 22.

⁵⁵ Boyce W. Logsdon, *et. al.*, *op. cit.*, p. 25, 28.

and radionuclides that migrate into a refractory lining during operation. In addition, there are reductions in radiation exposures to maintenance personnel because there is no need to change a refractory lining on a regular basis.

Molybdenum, Manganese, Vanadium, and Other Metal Oxides May Meet or Exceed Chromium Oxide Performance as a FBU Catalyst Material

Rocky Flats is pursuing the selection of an improved catalyst material for the FBU. Several good reasons exist to eliminate the chromia-alumina catalyst and substitute a more environmentally benign catalyst. At this time, using molybdenum-, manganese-, or vanadium-oxides, or other metal oxides as a combustion catalyst appears feasible.

The baseline catalyst intended for use in the FBU contains chromium. Recent data show the hexavalent chromium (Cr^{+6}) in untreated incinerator ash ranges from 3.9 to 120 ppm.⁵⁶ As the immobilization discussion (above) shows, cementation and polymer encapsulation technologies can safely bind the chromium in the ash to safe levels established under RCRA regulations. However, it seems ethically undesirable to treat organic waste via the FBU, and, at the same time, add a hazardous constituent, chromium.

Also, chromium is 1,000 times more volatile than uranium, plutonium, or americium. Minimizing the incineration temperature and off-gas chlorine concentration minimizes metal volatility. Nevertheless, a chromium based catalyst almost guarantees some amount of chromium emission from the APC system,

even if the amount of chromium emissions remains within BIF RAC values. Consequently, the search for a new catalyst is part of the overall waste minimization or pollution prevention strategy for the FBU.

Chromia-alumina catalyst is under consideration for the FBU by default: the catalyst performed successfully during the pilot- and demonstration-scale tests. However, a better understanding of the catalytic mechanisms may lead to the selection of a better cata-

Table VIII. TCLP Data from Cemented "Best Case" Surrogate Ash, 30% Ash Content.⁵⁶

Sample	Cadmium ppm	Chromium ppm	Barium ppm	Lead ppm	Silver ppm	Nickel ppm
1	< 0.025	14.60	0.317	< 0.025	< 0.050	< 0.025
2	< 0.025	16.70	0.283	< 0.025	< 0.050	< 0.025
3	< 0.025	14.60	0.329	< 0.025	< 0.050	< 0.025
4	0.034	13.20	0.342	< 0.025	< 0.050	< 0.025
5	< 0.025	11.40	0.283	< 0.025	< 0.050	< 0.025
$\bar{x}_{\text{AVG}}$	0.027	14.10	0.311	< 0.025	< 0.050	< 0.025
σ	0.004	1.96	0.027	—	—	—
90% UCL*	0.032	16.61	0.345	0.250	0.050	0.025
Treatment Standard	1.0	5.0	100	5.0	5.0	5.0
Status	Pass	Fail	Pass	Pass	Pass	Pass

*Upper control limit

lyst. Since the chosen catalyst can alter the products of the combustion process, finding a catalyst that produces more HCl, less Cl_2 , and less chlorinated hydrocarbons—like vinyl chloride—would minimize off-gas emissions from the FBU. A catalyst that favors HCl production is desirable because the chlorine in HCl readily absorbs in the sodium carbonate sorbent.

Work selecting a new catalyst material is taking place at CSM. The research used thermogravimetric analysis and other techniques to evaluate the catalyst materials, and the evaluation is usually focusing on the break-down of PVC. The catalysts evaluated include supported oxides (like chromia-on-alumina) and unsupported bulk metal oxides. At this time the selection process has narrowed the evaluation to a proprietary AmocoTM catalyst, chromia-alumina (the existing Rocky Flats baseline), vanadium oxide (V_2O_5), manga-

⁵⁶ Gary B. Semones, and Jeffrey A. Phillips, *op. cit.*, p. 22.

⁵⁷ Lockheed Analytical Services, *Common Ions and Additional Analytes, TCLP Extract, Method 7196*, October 7, 1994.

nese oxide (MnO_2), molybdenum oxide (MoO_3), and cobalt oxide (Co_3O_4).⁵⁸ The selection process will conclude during fiscal year 1995.

Recirculating Beds May Increase Combustion Efficiency but Decrease Cost Effectiveness

Rocky Flats began investigating recirculating bed technology in 1992. A technology review by DOE's Morgantown Energy Technology Center (METC) and West Virginia University prompted the investigation. The METC work recommended recirculating fluidization processes prevalent in industry and often found in the oil and gas industry.⁶⁰ In 1994 Rocky Flats built a "hybrid" flow visualization model at the Colorado School of Mines (CSM) in Golden, Colorado, to evaluate recirculating bed technology.

The CSM hybrid system incorporates relatively minor geometry changes to the FBU to significantly improve combustion performance. The hybrid system incorporates a bubbling bed bottom section with a fast fluid bed on top. Figure 3 (page 26) shows the configuration of the hybrid model. The motivation to pursue this design is to facilitate better burning. Unburned hydrocarbons in the ash could contain hazardous or-

ganic constituents; hydrocarbon data from the pilot- and demonstration-scale FBU configuration are inconclusive regarding FBU combustion efficiency. The hybrid system would provide greater residence time and two stages of solid combustion to favor more complete combustion.

The hybrid system may also minimize ash production and improve life cycle costs. Solids previously considered part of the final waste will circulate back to

Table IX. TCLP Data from Cemented "Worst Case" Surrogate Ash, 30% Ash Content.⁵⁹

Sample	Cadmium ppm	Chromium ppm	Barium ppm	Lead ppm	Silver ppm	Nickel ppm
1	0.044	11.10	0.775	< 0.025	< 0.050	< 0.025
1-Dupl.	< 0.025	14.20	0.899	< 0.025	< 0.050	< 0.025
2	0.028	13.20	0.828	< 0.025	< 0.050	< 0.025
3	0.026	15.70	0.694	< 0.025	< 0.050	< 0.025
4	0.041	14.30	0.876	< 0.025	< 0.050	< 0.025
5	0.026	14.30	0.761	< 0.025	< 0.050	< 0.025
$\bar{x}_{\text{AVG}}$	0.032	13.60	0.806	< 0.025	< 0.050	< 0.025
σ	0.009	1.54	0.077	—	—	—
90% UCL	0.043	15.58	0.904	0.250	0.050	0.025
Treatment Standard	1.0	5.0	100	5.0	5.0	5.0
Status	Pass	Fail	Pass	Pass	Pass	Pass

the primary bed for reuse in the hybrid system. The recirculated solids are waste, catalyst, and sorbent particles greater than about 40 μm diameter. Table VI (page 19) shows that 98.2% of the ash in the current FBU configuration is greater than 43 μm . Recirculating this material could improve the waste-to-ash ratio. However, the current FBU system waste-to-ash ratio varies from about 11:1 to 25:1, depending on the type of waste. This ratio is very good, so improvement does not appear absolutely necessary.

Although volume reduction appear less than those reported for other incinerators, the ash from the FBU constitutes the sole waste from the process, already converted to a dry, pulverized form for immobilization and disposal. The waste produced by aqueous off-gas scrubbing in most thermal treatment processes are usually disregarded in weight and volume reduction figures and, indeed, completely ignored as being a sec-

⁵⁸ Michael J. Gordon, Robert M. Baldwin, Sidhartha Gaur, and John O. Golden, Colorado School of Mines. "Bulk Metal Oxides as Low Temperature Catalysts for Combustion of Mixed Wastes." Presented at *Rocky Mountain AIChE National Conference*, San Francisco, California, November 14-18, 1994.

⁵⁹ Gary B. Semones, and Jeffrey A. Phillips, *op. cit.*, p. 23.

⁶⁰ E. K. Johnson, and G. J. Morris, Editors. *Conceptual Design of a Fluidized Bed Combustor For Volume Reduction of Waste*. Morgantown, West Virginia: West Virginia University for Morgantown Energy Technology Center, US Department of Energy, June 1992.

ondary waste that requires additional treatment for conversion to a disposable waste.⁶¹

The trade off with the hybrid design is that the overall system throughput may decrease and operating costs may increase. However, a recent report cited a Government Accounting Office estimate that radioac-

Off-gas capture involves capture and storage of all combustion gases produced by the FBU. The purpose is to test all off-gas for hazardous and radioactive contamination before release to the environment and to guarantee 100% compliance with all applicable emission standards. Rocky Flats explored several off-gas

Table X. TCLP Data from Cemented "Worst Case" Surrogate Ash at 20 and 30% Ash Content.⁶²

Sample, 20% Waste Content	Chromium ppm	Sample, 30% Waste Content	Chromium ppm
1	1.280	1	11.50
2	2.430	2	12.90
3	1.360	3	N/A
4	1.940	4	10.60
5	2.500	5	8.71
$\bar{x}_{AVG}$	1.902	$\bar{x}_{AVG}$	10.93
σ	0.574	σ	1.755
90 % UCL	2.637	90% UCL	13.18
Treatment Standard	5.0	Treatment Standard	5.0
Status	Pass	Status	Fail

tive waste disposal costs are \$7,000 to \$14,000 per drum.⁶³ Therefore, even small improvements in system efficiency may lead to significant programmatic cost reductions. Rocky Flats built the hybrid model at CSM, in part, to evaluate these life cycle cost factors and determine the system configuration that leads to the greatest system wide efficiencies. Current testing with the completed hybrid model is on hold because of DOE budget reductions.

Off-Gas Recycle or Capture Technologies May Not Improve Efficiency or Safety

Rocky Flats considered recycling off-gas from the APC back into the FBU. Evaluating off-gas recycle technologies took place while evaluating off-gas capture options. The idea for off-gas capture originated at LLNL during the early development of their combustion treatment facility. Rocky Flats considered this idea for the FBU.

capture concepts during this evaluation. Rocky Flats investigated off-gas liquefaction and contracted Los Alamos National Laboratory (LANL) to study absorption processes, chemical conversion processes, and adsorption processes.

Off-gas liquefaction involves the capture of carbon dioxide (CO₂) and water vapor generated by

the combustion process. Rocky Flats investigated high and low pressure liquefaction systems. Either system would convert the FBU to a closed loop design, lead to some advantages in smaller emission volumes, and improve combustion efficiency. Of the two options, the low pressure system seemed preferable because of its lower costs and substantial industrial experience.⁶⁴

LANL investigated off-gas absorption and chemical conversion processes. The two off-gas absorption processes explored were base- and alkanol-amine-absorption. Base-absorption would only collect CO₂ gas; the investigators did not understand what influence, if any, N₂, H₂O, and other trace gases would have. What is known is these trace gases would only complicate the process. Alkanol-amine processes are simple and commercially available; however, they are highly corrosive. The two chemical conversion processes LANL investigated were the production of urea,

⁶¹ L. J. Miele, *et. al.*, p. 57-58.

⁶² Gary B. Semones, and Jeffrey A. Phillips, *op. cit.*, p. 23.

⁶³ [Carl Cooley], *op. cit.*, p. D-1.

⁶⁴ Dennis M. Stull, and John O. Golden. *Liquefaction and Storage of Thermal Treatment Off-Gases*, RFP-4485. Golden, Colorado: EG&G Rocky Flats for US Department of Energy, Rocky Flats Environmental Technology Site, September 1993.

Table XI. Effect of Encapsulating Surrogate Ash with Low Density Polyethylene at 50% Waste Loading.⁶⁷

		<i>Metal Concentrations In TCLP Extracts</i>					
		<i>Silver</i> ppm	<i>Barium</i> ppm	<i>Chromium</i> ppm	<i>Lead</i> ppm	<i>Selenium</i> ppm	<i>Cadmium</i> ppm
Treatment Standard→		5.0	100	5.0	5.0	5.7	1.0
Fly ash C, 50 ppm spike	Before	0.05	10.10	0.04	0.36	0.54	0.62
	After	0.01	1.08	0.04	0.03	0.11	0.06
	Status	Improved	Improved	Not Improved	Improved	Improved	Improved
Fly ash F, 50 ppm spike	Before	0.03	0.84	0.02	0.40	0.17	1.00
	After	0.01	0.85	0.09	0.04	0.09	0.06
	Status	Improved	Not Improved	Not Improved	Improved	Improved	Improved
Fly ash C, 500 ppm spike	Before	0.05	10.60	0.04	0.04	0.54	0.62
	After	0.12	1.03	0.43	0.11	0.19	0.12
	Status	Not Improved	Improved	Not Improved	Not Improved	Improved	Improved
Fly ash F, 500 ppm spike	Before	0.05	0.54	0.04	7.38	0.54	7.43
	After	0.14	0.98	0.83	0.16	0.34	0.49
	Status	Not Improved	Not Improved	Not Improved	Improved	Improved	Improved
Fly ash C, 5,000 ppm spike	Before	0.05	7.43	0.04	0.98	0.54	10.60
	After	1.72	1.02	4.58	0.73	1.65	0.90
	Status	Not Improved	Improved	Not Improved	Improved	Not Improved	Improved
Fly ash F, 5,000 ppm spike	Before	0.01	1.43	1.01	9.41	0.54	170.00
	After	0.77	0.28	0.80	1.93	2.75	3.0
	Status	Not Improved	Improved	Improved	Improved	Not Improved	Improved

and the production of methane and/or alcohol.^{65,66} Both processes generated a product that could not receive commercial application because there is no *de minimis* limits for their radioactive contaminated products. Consequently, none of the processes appeared desirable to attach to an FBU treating radioactive mixed wastes.

⁶⁵ Nancy N. Saurer. *Analysis of Chemical Technologies for CO₂ Off-gas Containment*, LA-UR-91-3326. Los Alamos, New Mexico: University of California, Los Alamos National Laboratory, for US Department of Energy, September 30, 1991.

⁶⁶ M. W. Burkett, W. J. Parkinson, D. C. Nelson, and A. L. Bowman. *Rocky Flats Plant Incinerator Off-Gas Handling & Storage Concept Evaluation*, LA-UR-91-3142. Los Alamos, New Mexico: University of California, Los Alamos National Laboratory, for US Department of Energy, September 1991.

LANL also investigated activated carbon adsorption to store the CO₂ gases. The advantage of gas adsorption storage over compressed gas storage is that some fraction of the gas in storage is in a liquid-like phase that is much more dense than compressed gas. While this system is simple and easy to operate, it is costly. A preliminary cost analysis indicates the capital and operating costs are about \$6,000,000 and \$2,000,000 per year, respectively.⁶⁸ The cost-to-benefit ratio of this technology did not appear attractive.

⁶⁷ Boyce W. Logsdon, *et al.*, *op. cit.*, p. 26-27.

⁶⁸ Charles O. Grigsby. *Activated Carbon Adsorption Storage of Incinerator Off-Gases At Rocky Flats: Preliminary Design*, LA-UR91-3206. Los Alamos, New Mexico: University of California, Los Alamos National Laboratory/Los Alamos Technology Office/Rocky Flats Plant, for US Department of Energy, October 3, 1991.

After evaluating all of the off-gas storage techniques, a peer review panel recommended suspending further effort on the off-gas capture concept for three reasons. They were:

1. Even the simpler off-gas capture systems are unnecessarily complex;
2. Representative samples of the captured CO₂ may be difficult to obtain, and regulator experience with these systems would hinder start-up; and,
3. The additional complexity of these systems (including off-gas recirculation systems) makes the perception of additional safety or efficiency from these systems unfounded.⁷⁰

Instead, Rocky Flats is pursuing a state-of-the-art air pollution monitoring and control system as the safest, most cost effective APC option.

Semi-Permeable Membranes May Help Meet Future, More Stringent Emission Requirements

In the process of investigating off-gas capture and storage, Rocky Flats investigated membrane technology. The intent was to use membrane technology to assist with the capture and storage technology. This work to considering membranes for partitioning unwanted hydrocarbons from the off-gas. While tests at the National Institute of Standards and Technology (NIST) in Boulder, Colorado, showed the success of this innovative membrane application,⁷¹ Rocky Flats is finding that membrane technology is not necessary to meet

⁶⁹ Boyce W. Logsdon, *et. al.*, *op. cit.*, p. 28.

⁷⁰ [Karen Rhine Itomura, Activate, Inc., Benton, Illinois, Facilitator.] *Peer Review Panel Summary Report for Technical Determination of Mixed Waste Incineration Off-Gas Systems for Rocky Flats*. Golden, Colorado: EG&G Rocky Flats, Inc., for US Department of Energy, September 15-17, 1992. As found in Dennis M. Stull, and John O. Golden, *Liquefaction and Storage of Thermal Treatment Off-Gases*, RFP-4485, EG&G Rocky Flats, Inc., for US Department of Energy, Rocky Flats Plant, Golden, Colorado, September 8, 1992, Appendix A, p. 25-30.

⁷¹ Dennis M. Stull, Boyce W. Logsdan, and John J. Pellegrino. *An Investigation Of Gas Separation Membranes For Reduction Of Thermal Treatment Emissions*, RFP-4641. Golden, Colorado: EG&G Rocky Flats, Inc., for US Department of Energy, May 16, 1994.

Table XII. TCLP Extract Data for Polymer Encapsulation of FBU Chromia-Alumina Catalyst⁶⁹

	Chromium content in TCLP extract
	ppm
Unencapsulated	221
50% waste loading	5.4
40% waste loading	3.2

and far exceed current APC standards. This membrane technology may prove valuable as emission regulations become more stringent.

Fluidized Bed Units Have Stable Process Control Capabilities

Beyond the need to meet all regulatory concerns, mixed waste treatment will require the strictest process control capabilities to reap public acceptance. Fluidized bed technology is the most accepted technology by engineers for tight process control, and has a long history of success in applications requiring a tight safety envelope.

Fluidized beds are commonly used in industry because of their safe operating characteristics. A chemical engineering textbook describes the commonly understood assumptions about fluidized bed technology this way:

In most cases, the fluidized bed is the reactor of choice whenever the exothermic heat is great, when there is a danger of a temperature runaway or explosion, and thus when strict and reliable temperature control is of paramount importance. Also, because of its large temperature flywheel effect, one can use much higher concentrations of feed in fluidized bed, well within the flammability region, resulting in significant cost savings.⁷²

A large number of fluidized bed uses are for synthesis reactions, but hydrocarbon cracking, carbonizing, gasifying, calcining, roasting, halogenating, reducing, biofluidizing, power generating and waste incinerating processes all have fluidized bed applications. These

⁷² Daizo Kunii and Octave Levenspiel, *op. cit.*, p. 34.

Figure 3. Configuration of a Hybrid Fluidized Bed Reactor. The design incorporates a bubbling bed reactor (FBU Reactor #1) on the bottom and a fast fluid bed (FBU Reactor #2) on top. In 1994, Rocky Flats personnel built this full-scale, ~10 m tall, Plexiglas™ model at the Colorado School of Mines in Golden, Colorado.⁷⁴

applications include the production of phthalic-anhydride through the catalytic partial oxidation of naphthalene, Fisher-Tropsch synthesis using carbon monoxide and hydrogen to produce an aliphatic gasoline substitute, and acrylonitrile production by the oxidation of propylene and ammonia. These processes are all extremely exothermic and use fluidized bed technology to prevent hot spots or a runaway reaction.⁷³ In addition, these processes have operated safely in industries since the mid-1940s.

Rocky Flats is working toward a state-of-the-art instrumentation, monitoring, process control, and materials of construction for the new FBU. Evaluation of engineering and reference manuals,⁷⁵ and description

⁷³ *Ibid.*, p. 27-34.

⁷⁴ Chad Talley illustration.

⁷⁵ L. J. Meile. *Rocky Flats Plant Fluidized Bed Incinerator, Engineering Design and Reference Manual*, RFP-3372. Golden, Colorado: Rockwell

of the 1980s demonstration-scale unit's instrumentation system⁷⁶ shows the instrumentation level for that system is not consistent with today's currently accepted requirements. Rocky Flats has developed an improved instrumentation and control concept for a new FBU system.⁷⁷ In addition, Rocky Flats personnel carefully reviewed materials of construction for reactor vessels and all other system components. This review recommended materials to guarantee they are resistant to corrosion from ongoing operations, and can successfully contain the radioactive materials, even in upset conditions.⁷⁸

Fluidized Bed Technology is Preferable for Mixed Waste Treatment

The commercial incineration industry primarily uses rotary kilns, controlled air or high temperature, single stage fluidized bed incinerators. However, industry does not treat mixed wastes, and the

radioactive component in the mixed waste substantially alters treatment technology selection criteria.

Many independent technical evaluations rank fluidized bed technology as the safest and most effective for mixed waste treatment. A 1989 study ranked

International for US Department of Energy, Rocky Flats Plant, December 23, 1982.

⁷⁶ William F. Tosney and Andrew J. Johnson. *Data Acquisition and Control Instrumentation for Fluidized Bed Incineration System*, RFP-3013. Golden, Colorado: Rockwell International for US Department of Energy, Rocky Flats Plant, June 20, 1980.

⁷⁷ Gary B. Semones. *Conceptual Control Room Design for the Fluidized Bed Unit Reactor*, Internal Report WC-91-001, EG&G Rocky Flats, Inc., for US Department of Energy, Golden, Colorado, February 7, 1991.

⁷⁸ Nathaniel R. Quick, "Accelerated-Life Testing in Hostile Environments," *ASM Advanced Materials and Processes*, Vol. 144, No. 4, October 1993.

fluidized bed technology first among all technologies evaluated, including controlled air and rotary kiln incineration, for recovering plutonium residues.⁷⁹ A 1990 report ranked fluidized bed technology first for treating combustible, low level mixed wastes. The review considered twelve alternative technologies, including both rotary kiln and controlled air incinerator technologies.⁸⁰ An Oak Ridge study ranked fluidized bed technology as the first choice for treating mixed wastes among twenty-four technologies, including controlled air and rotary kiln technologies.⁸¹ An SAIC study resulted in similar results.⁸² A joint DOE/EPA initiative in 1994 ranked fluidized bed technology first among nine technologies evaluated, including rotary kiln and controlled air technologies.⁸³ Rocky Flats has also evaluated nonincinerative alternatives to FBU treatment.⁸⁴ None of the alternatives appear feasible for all applicable waste forms at this time. Another influence is a 1995 independent technical review of the LANL controlled air incinerator recommending deactivation

of that facility in favor of a "new, certifiable, continuous throughput incinerator."⁸⁵

Furthermore, a two-stage system with sodium carbonate sorbent is a Rocky Flats innovation and provides superior performance to other fluidized bed technologies. The higher temperature, single stage, calcium carbonate bed recommended by some industrial contacts is 1 to 2 orders-of-magnitude less effective than the Rocky Flats FBU at chlorine removal. This is interesting in light recent criticism that fluidized beds (probably calcium based) have historically not been totally effective at acid gas control.⁸⁶

The principal reasons cited for ranking fluidized bed technology highly for mixed waste treatment are effectiveness, a high degree of process control, and successful radioactive containment because of the few moving parts required. An industry source cites another good reason:

For waste feeds suitable for incineration using both fluidized beds and rotary kilns, the capital cost for [fluidized beds] is 15 to 40% less than [rotary kiln units] having the same feed rates. Operating cost for fluidized beds is also likely to be lower. Pressure drops through the beds are higher than through rotary kilns, but the power consumption is compensated by the lower excess air. The operating labor is also usually less for fluidized beds. Absence of moving parts and less thermal shock due to presence of bed solids (with their large total heat capacity) lead to less maintenance cost.⁸⁷

⁷⁹ T. K. Thompson, et. al., *Plutonium Recovery Modification Project Volume Reduction System, Final Report*. Golden, Colorado: Rockwell International for US Department of Energy, November 2, 1989.

⁸⁰ A. F. Sferrazza, *Federal Facilities Compliance Agreement/Compliance Order Treatment Plan Number 1*. Golden, Colorado: EG&G Rocky Flats, Inc., for US Department of Energy, March 1990, p. 5-13.

⁸¹ *An Assessment of Thermal Destruction Technologies for Application to Department of Energy Mixed Wastes, Volume 1, Technology Assessment*. Prepared under contract DE-AC05-84-OR21400 for US Department of Energy by Hazardous Waste Remedial Actions Program, Martin Marietta Energy Systems, Inc., Oak Ridge, Tennessee, n. d.

⁸² Robert L. Gillins and E. Malone Steverson, "A Compilation and Assessment of Thermal Treatment Technologies for Application to Department of Energy Wastes," *Proceedings of the 1991 Incineration Conference*, Knoxville, Tennessee, May 13-17, 1991, p. 273-278.

⁸³ *Development and Application of Thermal Treatment Technology Selection Criteria for DOE/Rocky Flats Mixed Wastes*. Irvine, California: Energy and Environmental Research Corporation under EPA Contract 68-CO-0094 for US Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, June 30, 1994.

⁸⁴ David L. Shuck, and Michael C. Skriba, Fluor Daniel Environmental Services, and Jonathan Wade, EG&G Rocky Flats, Inc. "Evaluating Non-Incinerative Treatment Of Organically Contaminated Low Level Mixed Waste." *Proceedings of Waste Management '93, Vol. 1*, Tucson, Arizona, February 28-March 4, 1993, p. 683-690.

⁸⁵ *Independent Technical Review of The Controlled Air Incinerator and the Proposed Expansion of Material Disposal Area G at Los Alamos National Laboratory*, LA-UR-95-275. Los Alamos, New Mexico: University of California, Los Alamos National Laboratory for US Department of Energy, January 1995, p. iii-2.

⁸⁶ [Carl Cooley], *Industry Response to Requirements for The Air Pollution Control System For A Referenced Fluidized Bed Incinerator*, as cited in *State-of-the-Art...*, pp. 7-14 to 7-18.

⁸⁷ Pasupati Sadhukhan, and Mike Bradford. "Fluidized Bed Incineration of Hazardous Chemicals and Waste Solids With Simultaneous Control of Air Pollutants," *Proceedings of the 1992 Incineration Conference*, Albuquerque, New Mexico, May 11-15, 1992, p. 121-128.

Public Acceptance and Licensing Remains Difficult but Is Improving

Rocky Flats is seeking meaningful public involvement for its waste management and environmental remediation efforts. If the public feels that decisions are made without their involvement, even the best treatment projects run the risk of being shelved. Therefore, a key element in project success is early, meaningful public involvement. This includes not only providing accurate, up-to-date information, but going a step further to provide mechanisms to address community concerns and opportunities for meaningful feedback to the decision making process.

Public involvement began early in the process of considering a new FBU for Rocky Flats. The first step was the initiation of a public involvement plan and the formation of a Citizens Review Group (CRG) in 1992. Composed of 20 representatives from local business, environmental groups, state and local governments, academia and special interest groups, the CRG participated in weekly half-day briefings, panel discussions, and facility tours to gain a better overall perspective on hazardous waste and proposed treatment technologies. The CRG presented the EPA with a 20 page document of suggested changes and comments to the plant's planning efforts. Although the CRG acknowledged public concerns about incineration, it did not rule out the possibility of incineration as a waste treatment process, provided public participation was part of the decision making process. Public involvement and communication efforts also include tours of the Fluidized Bed Flow Visualization Model at CSM, promoting awareness through the Rocky Flats Speakers Bureau, and publishing the *Environmental Restoration Update* newsletter.⁸⁸ Public participation work is continuing with a Citizens Advisory Board as part of the Rocky

⁸⁸ Gary B. Semones, Paul M. Williams, Steven P. Stiefvater, Doyle L. Mitchell, and Bryan D. Roecker. "Technical Progress and Community Relations Activities For The Fluidized Bed Thermal Treatment Process At The Rocky Flats Plant." *Proceedings of Waste Management '93, Vol. 1*, Tucson, Arizona, February 28-March 4, 1993, p. 633-637.

Flats *Site Treatment Plan* required under the Federal Facility Compliance Act.

Rocky Flats also founded a National Technical Workgroup (NTW) on Mixed Waste Incineration. The first meeting was November 6, 1991. Nineteen participants from EPA, DOE, Nuclear Regulatory Commission (NRC), and private industry attended. The initial goal NTW was to review the DOE's mixed waste incineration strategy. The group now includes state regulators and other DOE stakeholders. NTW sponsored a workshop for regulators in 1993,⁸⁹ and in April 1994, sponsored a public workshop about mixed waste incineration.⁹⁰

The NTW surveyed existing mixed waste and hazardous waste incinerators to compile lessons learned and to put together a regulatory roadmap. The roadmap shows the steps required to receive a license to operate a mixed waste treatment facility. The survey identified facilities licensed by the NRC. These incinerators include low level radioactive incinerators at 17 domestic utility facilities, 42 medical and institutional facilities, 18 industrial facilities, and 4 governmental facilities.⁹¹ However, the survey identified only three commercial facilities that may burn mixed waste.

Review of the literature on these permitted commercial mixed waste incinerators illustrated the various areas of conflict between the philosophy and the requirements imposed by hazardous waste regulations as opposed to nuclear management guidelines. These conflicts include:

- The NRC's and DOE's nuclear as low as reasonably achievable (ALARA) approach with the EPA's hazardous "analyze and treat it" approach;

⁸⁹ *Proceedings of the April, 1993, National Technical Workgroup (NTW) Workshop on Mixed Waste Incineration*. Irvine, California: Energy & Environmental Research Corporation, July 22, 1993.

⁹⁰ *Proceedings of the Mixed Waste Thermal Treatment Symposium*. Denver, Colorado: EG&G Rocky Flats for US Department of Energy, April 12-14, 1994.

⁹¹ *Development of a Regulatory Compliance Roadmap*. Irvine, California: EER Corporation, for EG&G Rocky Flats, Inc., Golden, Colorado, April 1, 1994, p. 73-75.

- Specific regulatory requirements including waste sampling and analysis, facility inspection, and enforcement;
- Duplication of regulatory specific requirements which could be more economically combined including waste packaging manifests, record keeping, financial assurance requirements, facility monitoring requirements, emergency preparedness and prevention requirements, and post closure failure scenarios; and
- Duplication of effort because of similar licensing and permitting procedures.⁹²

The successfully permitting and operation of a controversial hazardous incineration facility near Denver may help Rocky Flats. The facility is a submerged quench incinerator to treat 11 million gallons of liquid waste removed from the former Basin F surface impoundment at the Rocky Mountain Arsenal. The wastes are residuals from nerve gas production at the facility. This incinerator is now operating. A computer modem connects the effluent monitoring system of their incinerator to the regional offices of the EPA and the Colorado Department of Public Health and the Environment. The permit effort also included substantial public involvement in the selection process for the incineration technology. Facility costs for the Arsenal incinerator are about \$80,000,000. All waste destruction at the Arsenal will take place within a two year period. The Army has no future plans for using this facility after treating the Basin F waste.

FBU Capital Cost Estimates

Rocky Flats is in the process of evaluating the cost of an FBU system. Initial capital cost estimates for this project are \$38,000,000. This estimate includes decontamination, decommissioning, and renovating 15,000 square feet (ft²) on the first floor of Building 707 within Modules E, F, and G. In addition 3,000 ft² will require renovation on the second floor for required

ventilation modifications. The estimate includes a 1,500 ft² loading dock with drive lanes added to the west face of Building 707 to facilitate liquid storage and treated waste shipment.⁹³

The basis for the cost estimates come from Department of Energy lessons learned documentation and on lessons learned at the Department of the Army, Rocky Mountain Arsenal. The cost estimate does not include ash immobilization facilities because these facilities are being built as part of other capital projects. The estimate includes a real time monitoring similar to the Arsenal system to facilitate permitting. Building selection took place in 1994. Capital design work by an architectural engineering firm would begin in the second quarter of fiscal year 1997 in order to keep pace with current compliance agreements.⁹⁴

Recommendation

EG&G Rocky Flats, Inc., recently recommended that DOE Rocky Flats Field Office (RFFO) place development of the FBU on hold pending a decision to take place in late 1996. At that time, RFFO and their contractors will decide whether to pursue thermal treatment of its combustible low-level mixed waste streams, or to pursue a suite of non-thermal technologies. This decision is taking place under the aegis of a compliance agreement with the Colorado Department of Public Health and the Environment and EPA Region VIII.

⁹³ *Conceptual Study for CTMP Solvent Contaminated Wastes Treatment System—Thermal (Treatment System 1A), Authorization 446308.*

Golden, Colorado: EG&G Engineering & Technology Department, EG&G Rocky Flats, Inc., for US Department of Energy, Rocky Flat Plant, October 1994, p. Part 0—Summary. May contain Unclassified Controlled Nuclear Information, Department of Energy approval before release required.

⁹⁴ *Site Selection Alternatives for CTMP Solvent Contaminated Wastes Treatment System—Thermal, Engineering Study, Job Number 986442-50.* EG&G Rocky Flats, Inc., for US Department of Energy, Golden, Colorado, April 15, 1994. May contain Unclassified Controlled Nuclear Information, Department of Energy approval before release required.

⁹² *Ibid.*, p. 80-81.

At this time, EG&G management is sufficiently confident that if combustion is the selected option in 1996, sufficient technical and cost information is available for a fair appraisal of fluidized bed technology when compared to other thermal treatment technologies, and that remaining development work required for implementing this technology can take place concurrently with the capital installation project. Discontinuing development at this time seems a prudent risk that does not compromise the ability to implement this process, if selected, and allows EG&G to concentrate current development efforts on non-thermal technologies in order to more fairly evaluate them.

EG&G's FBU Team took an innovative, cost-saving approach to develop this technology using a variety of industry, academic, and governmental experts and resources. Resuming work on the FBU project is possible and may prove beneficial to other incinerator projects within the DOE as a way to quickly and inexpensively test air-pollution control and monitoring strategies and equipment.⁹⁵

⁹⁵ Thomas L. Rising, Director, Technology Development, EG&G Rocky Flats, Inc., Rocky Flats Environmental Technology Site, Golden, Colorado, to William J. Primack, US Department of Energy, Rocky Flats Field Office, Golden, Colorado. *Fluidized Bed Unit*. Letter Reference 95-RF-01774, February 15, 1995, p. 1.