Microwave Calcination for Plutonium Immobilization and Residue Stabilization

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ABSTRACT
In the late 1980's development was begun on a process using microwave energy to vitrify low level mixed waste sludge and transuranic mixed waste sludge generated in Building 374 at Rocky Flats. This process was shown to produce a dense, highly durable waste form. With the cessation of weapons production at Rocky Flats, the emphasis has changed from treatment of low level and TRU wastes to stabilization of plutonium oxide and residues. This equipment is versatile and can be used as a heat source to calcine, react or vitrify many types of residues and oxides. It has natural economies in that it heats only the material to be treated, significantly reducing cycle times over conventional furnaces. It is inexpensive to operate in that most of the working components remain outside of any necessary contamination enclosure and therefore can easily be maintained. Limited testing has been successfully performed on cerium oxide (as a surrogate for plutonium oxide), surrogate electrorefining salts, surrogate residue sludge and residue ash. Future plans also include tests on ion exchange resins. In an attempt to further the usefullness of this technology, a mobile, self-contained microwave melting system is currently under development and expected to be operational at Rocky Flats Environmental Technology Site by the 4th quarter of FY96.

INTRODUCTION
Microwave vitrification was originally developed, at Rocky Flats in the late 1980's as a process to stabilize by-pass sludge generated in Building 374. By-pass sludge is generally a low level mixed waste (LLMW). Microwave was selected because it could economically reduce waste volume, treat to meet land disposal restrictions and immobilize the material for shipment. While the microwave's vitreous waste form was decidedly superior to the cemented grout process, with which it competed, life-cycle costs drove the selection of the process for treatment of this waste.

Initial work was performed on one and two liter containers of material that were heated by a variable, zero to six kilowatt (kW) power supply. These bench-scale experiments were very successful in treating a wide range of surrogate wastes as well as plutonium contaminated waste. The unit was also demonstrated on rasching rings, soils, ash, salts and other miscellaneous wastes. At this relatively small
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The microwave process uses a metal or ceramic container as part of the microwave chamber. After a heating/solidification cycle is completed, the inexpensive, single use containers are removed from the chamber to cool and become part of the waste form. Concurrent with cooling, the next run may proceed.

Subsequent work was performed with the aim of scaling the process up to thirty gallon drum size. This larger size in its current configuration uses a 60 kW generator for studies on surrogate by-pass sludge. Again this work was very successful. The system was designed to operate in a continuous or semi-batch mode filling the 30 gallon drum to 750 pounds. Figure 1 is a schematic of the microwave unit which includes the generator, wave guide, container as part of the cavity, and continuous feed. Figure 2 is a photograph of the large system. This large scale work is currently the subject of privatization negotiations.

RESIDUE AND OXIDE STABILIZATION
After the Rocky Flats weapons production mission was suspended in 1992, the site was confronted with the need to stabilize residues and plutonium oxide. Prior to that time, residues and plutonium oxide were accumulated for reprocessing. Conventional residue recovery technologies could conceivably have
been employed to stabilize all of the residues. However, many of the facilities at Rocky Flats have been shut down and are no longer available for residue and plutonium oxide processing. As a result new processes are necessary to treat residues and plutonium oxide.

Microwave heating is an attractive candidate for residue and plutonium oxide stabilization. It is a relatively mature technology with a 6 kW system currently operating in a plutonium contaminated glove box (see figure 3). It can be used as a generic heat source to vitrify, calcine, and react. It can produce waste forms that can readily be transported, stored, disposed of at the Waste Isolation Pilot Project (WIPP) or incorporated in the Defense Waste Pilot Facility (DWPF) via the can-in canister concept. Therefore, program emphasis has been shifted from LLMW and TRU sludges to residues and plutonium oxide. For these applications, criticality concerns make the smaller units (1 to 4 liters) more desirable than larger units (30 gallons). This fact is somewhat serendipitous, since the smaller units are much easier to control and will require very little additional development.

EXPERIMENTAL WORK

Sludges
Both surrogate and actual contaminated sludges have been processed in the bench-scale units.1,2,3,4,5 With the addition of a suitable source of silica, such as glass frit or crushed rasching rings, the resultant product is vitreous or crystalline with a specific gravity that can range above 3.0. Toxic Characteristic Leach Procedure, (TCLP) tests show that the resultant product is very resistant to leaching and would be a nearly ideal waste form. The plutonium also appears to remain bound up in the matrix material. TCLP studies were performed on surrogate sludges spiked with RCRA hazardous metals to levels representative of actual by-pass sludge at Rocky Flats. The metals of concern were chromium, nickel, lead, cadmium and silver. Several tests were performed with varying percentages of surrogate sludge to glass formers, simulating varying waste loadings. TCLP results demonstrated that for all spiked metals, the leachability could be reduced below the universal treatment standards for non-waste water as set forth in 40 CFR 268. In general leachability results were two to three orders of magnitude below the spiked sludge concentrations.3 Figure 4 is a photograph of the sludge waste form before and after vitrification.

Salts
Salts are not generally amenable to vitrification. However, the need for salt stabilization stems from reactivity concerns. Water that is tied up in the salts is available for hydrogen generation and the presence of reactive free metals such as calcium, sodium, and plutonium decrease the stability of the residue form. Heating in an oxidizing environment is an obvious method for stabilizing salts. Conventional stationary furnaces, without major modification, can perform this function in an eight hour shift. However, if a microwave ‘melter’ is employed, dramatically reduced cycle times can result. Because microwave energy directly heats the material and not the equipment or refractory, heating and cooling are rapid. Potentially, three or more batches per shift are possible. Microwave processing could be done in approximately one third the space for approximately one third the cost. Experimental work has been performed on electro-refining salt surrogates6 (Figure 5). Results of tests show that pure salt does not exhibit sufficient coupling with microwave energy to obtain temperatures necessary to oxidize the reactive metals. However, the addition of sodium carbonate, commonly used in salt
FIGURE 4
Surrogate Dried Sludge, Glass Frit and Vitrified Final Product
FIGURE 5
Microwaved Surrogate Electro-Refining Salt And Sodium Carbonate
stabilization as an oxidizing agent does result in sufficient coupling to oxidize the reactive metals and solidify the mixture.

**Oxides**
The Defense Nuclear Facility Safety Board (DNFSB) 94-3 requires stabilization of plutonium oxides at Rocky Flats. Microwave heating has been proposed to achieve this by calcining and/or vitrifying oxides for the same reasons that it was proposed for stabilization salts. The microwave process can heat the oxides faster and cheaper. Current microwave treatment systems were intentionally designed to be standard, uncomplicated equipment and therefore are unable to control temperature to the close tolerances that can readily be achieved in conventional furnaces. However, to achieve adequate stabilization, it has been determined that the oxide must be heated to a minimum of 1000°C. Since no upper temperature limit is necessary, the close temperature control available with standard furnaces is not required as long as the minimum temperature can be assured. Experimental results show that pure cerium oxide (surrogate for PuO₂) does not couple with the microwave field well enough to achieve this required temperature. Cerium oxide heated in non-glazed ceramic crucibles did not couple with the microwave energy, while samples heated in glazed crucibles produced a mixture of sintered oxide held together with remelted glaze. Impurities in the actual plutonium oxide may help to increase the coupling or crucibles made from silicon carbide or graphite (which do couple with the microwave field) could be used for this operation.

Additional tests were conducted in which borosilicate glass was added to the cerium oxide to improve the coupling with the microwave field. These mixtures produced a vitreous product upon heating (see Figure 6). The vitrified material completely eliminated all cerium oxide fines. Mixtures of up to 60 percent cerium oxide have been vitrified. These surrogate experiments demonstrate that microwave treatment has the potential for stabilizing plutonium oxide in crucibles which are compatible for storage in 3013 containers. Since the same piece of equipment is versatile and can be used for several other stabilization operations, microwave technology is an economical and practical method of processing oxides.

**Ash**
Both surrogate and contaminated ash have been vitrified. Ash makes an ideal feed for microwave vitrification. Its high silicon content allows it to be processed with little or no frit additive. Tests have demonstrated that up to 20% elemental carbon can be mechanically incorporated into the glass matrix. Microwave vitrification is a very attractive method for stabilizing ash.

**Ion Exchange Resins**
If a microwave 'melter' is available, it may be possible to use it to stabilize DNFSB 94-1 resins. Experiments in oxidation and pyrolysis are planned to determine the potential for this application. Some of the major technical questions that need to be resolved are:

1. What will happen when the resins are heated in air?
2. Will they spontaneously react due to their nitration?
3. Will the combustion products interfere with microwaving by causing arcing?
4. Are the pyrolyzed graphite resin beads a satisfactory storage/shipment form?

CONCLUSION
Microwave processing appears to be applicable to all of the residue forms studied and perhaps some others as well: (Sand, Slag and Crucibles, Raschig Rings, Graphite, Heels, Fire Brick etc.). The process was developed to treat LLMW and TRU sludges and consequently performs quite well on residue sludges. Initial results indicate that another good application is calcining and/or vitrifying oxides. Also salts could potentially be stabilized in the microwave melter. Testing with actual plutonium contaminated salts need to be performed to verify this. With little or no modification, a simple low-to-medium technology unit or duplicate units will be able to stabilize many different residue types.

However, there is one problem that has not been addressed. At Rocky Flats residues are stored in many locations and transporting them to one, or more, central microwave unit is an expensive process. One possible solution to this problem is to make a portable, modular unit(s).

A conceptual design for a prototype portable microwave system was prepared as part of the microwave technology transfer initiative. Additionally, a new small, portable microwave system has been designed for Safe Sites of Colorado (SSOC) (see Figure 7). The first physical unit should be available by the end of 3rd quarter FY96. This unit is being developed for processing residues in or near their storage location. This approach will save tremendous cost by eliminating or minimizing transfer operations.

![Figure 7. 6 kW Portable Microwave System](image)

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*Figure 7. 6 kW Portable Microwave System*
REFERENCES: ROCKY FLATS MICROWAVE VITRIFICATION


