MICROWAVE PROCESSING OF REMOTE-HANDLED TRANSURANIC WASTES AT OAK RIDGE NATIONAL LABORATORY*

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ABSTRACT

The Oak Ridge National Laboratory (ORNL) Waste Handling and Packaging Plant(1) (WHPP) is investigating the feasibility of applying microwave energy to melt Remote-Handled Transuranic (RH TRU) sludges. The initial bench-scale tests with surrogate sludges have shown that wet or dry surrogates can be processed into solid monoliths that meet the Waste Isolation Pilot Plant(2) (WIPP) waste acceptance criteria(3) (WAC). Sodium Nitrate ($NaNO_3$) binds the other solids when the wt% of $NaNO_3$ is greater than or equal to the wt% of the other solids. Microwave penetration depth experiments have shown that a wet slurrey absorbs microwave energy within a few cm of the slurry surface while dried surrogates below 100°C are heated throughout the depth (20 cm) of the surrogate volume. The latest bench scale processing of wet surrogates has demonstrated good process control, provided that certain diagnostics which monitor, temperature, boiling absorbed microwave power, and arcing are implemented.

INTRODUCTION

The ORNL WHPP is a facility that will process and repackage RH TRU liquid and solid wastes from ORNL and solids from other sites for shipment to the WIPP. The liquid RH TRU wastes, stored in stainless steel storage tanks, are thought to consist of a supernate/sludge mixture that contains by weight (neglecting water) approximately 75% $NaNO_3$ with the remaining 25% consisting of a complicated soup of chemicals containing the RH TRU wastes. This paper will focus on the WHPP liquids processing flowsheet which calls for evaporation of the free water followed by melting of the salt residues, which will then form, upon cooling, a solid monolith that meets the WIPP WAC. The $NaNO_3$ is used as the binding agent for the remaining chemicals so that free particulates are below the WIPP WAC. To avoid the requirement for extensive off gas processing (scrubbing) of the NOx gases in the WHPP, the temperature of the $NaNO_3$ melt needs to be limited to below 390°C. At present, the WIPP WAC allows soluble salts (such as $NaNO_3$) to be stored) as long as they are suitably packaged.

Currently, the WHPP process calls for three steps for evaporation and melting of the RH TRU wastes. They are a wiped film evaporator followed by an extruder, followed by microwave heating to maintain the temperature of a liner filled with molten salts. The WHPP project is investigating the feasibility of applying microwave energy to melt RH TRU sludges. Microwave heating of radioactive materials has the following important advantages over conventional heating.

1. Radiant heating and joule heating of radioactive dielectric materials require local heating elements near the highly radioactive, usually corrosive material, whereas microwave heating requires no local heating elements because the microwave heat is absorbed directly. With microwave heating, the radioactive material becomes its own heating element. No radiant heating elements are required, and this makes microwave heating much more reliable and easier to maintain in a radioactive material processing application where contamination of process equipment and maintenance exposures can be kept to a minimum.
2. Because microwave energy is absorbed directly by a large class of materials, microwave heating has the considerable advantage of much higher efficiency and faster process control, as compared with conventional radiant heating. For radiant heating, the entire oven must be brought to a working temperature, which requires more time and energy than the microwave method. This is because radiant energy heats all materials while microwaves do not effectively heat most metals or special low-loss ceramics, glasses, and plastics. Microwaves, however, can effectively heat other materials encountered in the nuclear industry such as clothing, gloves, shoe covers, concrete, metal powders, oxides, nitrates, sulfates, filtering media (nonmetallic), water, carbon, standard glasses, and many other dielectric materials.(4,5) This allows for

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considerable efficiency improvement over conventional radiant heating by careful selection of the materials in a microwave oven design. Because of this material selectivity, microwave ovens can heat materials to high temperatures while the microwave cavity remains relatively cool.

3. Microwave power can be transmitted through waveguides from generators that can be located safely outside a radioactive hot cell area where routine generator maintenance can be performed in a hands-on environment. Waveguide windows can effectively isolate the generator from the hot cell.
4. Microwave processes frequently generate the least amount of waste product, as compared with other chemical or mechanical processes, thus minimizing storage and transportation costs.
5. Microwave heating is effective for both wet and dry materials and has the potential to supplement or even replace conventional evaporation steps in slurry processing applications, thus greatly simplifying the overall process.

Several issues unique to microwave processing must be addressed before plant facilities can be designed.

1. The depth of penetration of the microwave power into the material must be measured to determine whether the microwaves penetrate into the interior of the material to produce bulk heating or they heat only the surface because of a small penetration depth. The microwave penetration depth is a function of material composition, temperature, and frequency of the microwave energy. The user can, therefore, exercise some control over the penetration depth by choosing the appropriate heating frequency (915 MHz or 2450 MHz) for the application. This information is crucial to understanding the effect of material geometry on the uniformity and controllability of microwave heating.
2. Container materials that are compatible with the radioactive material being processed must be investigated; in particular, ceramic and glass materials that are microwave transparent are highly desirable because they allow the microwave power to heat the radioactive material from all directions, thus improving efficiency and processing speed over the levels attained with metal containers. Metal containers, however, can be designed with rounded surfaces that minimize arcing; they would offer the advantages of low cost and resistance to thermal shock. Depending on the details of the process under consideration, corrosion resistance of the container material will also need to be addressed.
3. Because microwave heating is direct, fast, and very efficient, the possibility exists for thermal runaway if the local heating rate in the material exceeds the rate at which heat diffuses through the material.(6) This tends to produce hot zones in the material, which because of their higher temperatures, absorb more microwave power (microwave absorption usually increases with temperature in most materials). This leads to thermal runaway where hot zones become even hotter because of thermally enhanced microwave absorption and become thermally detached from the bulk of the material. This may lead to local boiling in liquids or slurries and cracking in solids. Thermal runaway can be prevented by (1) carefully controlling the microwave power while continuously monitoring the temperature of the material and (2) providing a uniform microwave illumination of the process material.
4. Finally, bench- and pilot-scale microwave processing experiments must be designed to be truly microwave compatible and produce good heating uniformity. Microwave arcing must be prevented when microwave equipment operates at the highest powers and smallest heating loads. This is achieved by eliminating sharp metallic edges and points in the microwave cavity which tend to draw microwave arcs. Smooth well-rounded edges and corners are preferred in a high-power microwave environment. Also, some means to decrease the inherent nonuniformity of microwave heating is essential for good process control. This can be accomplished by using one or more of the following: (a) a rotating metal fan (mode stirrer) to spatially move the complex microwave heating patterns in time, (b) a rotating turntable or conveyor belt to move the product at a set speed through the heating patterns, (c) multiple microwave feeds, and (d) microwave tubes that can be electronically frequency modulated.

ROCKY FLATS BENCH-SCALE TESTING

Work began early in CY 1989 at the Rocky Flats Plant (RFP) to demonstrate the feasibility of applying 2450 MHz microwave energy to heat surrogate sludges. The initial surrogate composition is shown in Table I. The bench-scale testing at the RFP was done using a 6-kW generator(7) connected by a waveguide transmission system to an aluminum batch oven (cavity) measuring 45.7-cm wide X 45.7-cm deep X 76.2-cm high. A 3-stub tuner was used to match the cavity impedance to reduce reflected microwave power propagating back to the generator. A turntable at the bottom of the cavity was used to rotate an insulated 8 l stainless steel beaker that contained the surrogate chemicals. Processing of the surrogate began by adding an initial charge of 1 Kg dry sludge to the beaker, with the beaker centered on the turntable. The input power was slowly increased to 3.5 kW. Initial melting occurred with 5-10 minutes. A screw feeder, enclosed in a 20-cm long by 3.2-cm ID tube to protect the interior of the screw from microwave arcing, was used to feed additional dry chemicals to the existing melt (microwave power was interrupted during feed operation). Subsequent 2 Kg additions of dried sludge were made to the beaker at 20 minute intervals. Sampling of the melt temperature was done at 5 minute intervals by interrupting the microwave power, opening the cavity door and inserting a type K thermocouple probe into the melt. The cavity was located under a hood and an NO_x meter was used to sample the NO_x gases evolved. The melt temperature was held to less than 400°C in order to prevent the evolution of excessive NO_x gases. Several scouting tests were run to determine the minimum nitrate concentration which could be processed without exceeding the temperature limit. A 54.8 wt% sodium nitrate mixture was determined to be the lowest nitrate concentration that would produce an acceptable waste form below 400°C. A total of nine immobilization test runs were conducted, three at 54.8 wt%, and six at 81 wt% sodium nitrate. Melt temperatures were maintained at approximately 305°C for both the 54.8 wt% and 81.0 wt% sodium nitrate sludge. Bulk powder densities averaged 1.40 g/cc before processing, final densities averaged 1.85 g/cc for both sodium nitrate concentrations. This increase in density translates into an average volume reduction of 24.3%. Generally, all of the sludge samples behaved similarly when placed in the microwave field. Processing times were controlled by visual inspection of the melt. Operating temperatures remained relatively constant for each trial. Finally, dry sludges with $NaNO_3$ concentrations above about 50% by weight can be solidified to an acceptable solid wasteform with few free particulates so that the wasteform meets the WIPP WAC.

TABLE I

INITIAL ORNL SURROGATE COMPOSITION

Component	wt%
$NaNO_3$	81.0
$CaCO_3$	8.30
Borax	4.45
Na_3PO_4	2.30
MgCl	1.97
Al_2O_3	0.69
Fe_2O_3	0.84
Ce_2O_3	0.45

A series of microwave penetration depth experiments were made with wet and dry sludges to understand where the microwave heat is deposited. The test apparatus consisted of a 8 l stainless steel beaker with four type K thermocouples penetrating the bottom approximately 2 cm from the side of the container. The stainless steel sheathed thermocouples were bent so that they remained parallel to the sides that were centered in the container. The thermocouple tips were 3 cm apart vertically; the top thermocouple was approximately 5 cm from the top of the container. Aluminum tape was used to wrap the thermocouples tightly together. A charge of dry sludge was placed in the container, and microwave power was applied for 30 minutes. The lowest thermocouple, placed 9.8 cm below the surface, heated first with a temperature drop of 10°C at each progressively higher thermocouple. A wet sludge with 10 wt% water was used next. The top thermocouple was 3.8 cm below the surface of the sludge. The microwave power was slowly increased from 2 to 5 kW over 10 minutes. The top thermocouple showed a steady increase in temperature to 110°C after 60 minutes. The next lowest thermocouple had a 60°C temperature, and the two bottom thermocouples had a 40°C temperature. From these two cases, we can conclude that dry sludges at temperatures of less than 75°C have penetration depths of about 10 cm while wet sludges at 110°C have penetration depths of 1-2 cm. Had the dried sludge been heated even higher in temperature to 200-300°C we feel that the microwave penetration depth would again decrease because the molten salt has a high electrical conductivity and would thus partially shield out the microwave energy.

ORNL BENCH-SCALE TESTING

Bench-scale work was initiated at ORNL to investigate the feasibility of microwaving wet sludges with sufficient water content to allow transport with simple pumping systems. This work was conducted at 2450 MHz in a modified 1 kw commercial microwave oven.(8) The cavity was chosen to be all stainless steel construction to avoid corrosion problems with the earlier aluminum cavity used at the RFP. Also, the oven power supply controls were replaced with an external silicon-controlled rectifier (SCR) controller to allow for fast, remote programming of the microwave power. This was in contrast to the RFP microwave generator which had a hand-operated 0% to 100% power control knob. Also, the RFP generator was a continuous wave (cw) source while the ORNL microwave oven power was duty cycle modulated to vary the power. A commercial temperature process controller and infrared sensor were used to continuously monitor sludge temperature during microwave processing. The measured temperature was compared to a pre-programmed heating profile stored in the temperature controller and the error signal was fed into the SCR controller. This was an improvement over the RFP work where temperatures were monitored only at 15 to 20 minute intervals between feed additions. The infrared sensor/programmable temperature controller/SCR controller combination proved to be very effective in preventing thermal runaway effects and allowed heating rates of about 0.5°C/min to be used without process upsets such as vigorous boiling, splattering, eruptions, or excessive NO_x generation due to thermal runaway.

The wet sludge was placed in a 400 ml Vycor(9) beaker. Vycor was chosen because it was an optically transparent and microwave transparent material that was compatible with the molten sludge. Earlier tests with Pyrex(9) glass showed that the molten sludge bonded very well to the Pyrex, then when the sludge solidified, it shrank in size and stressed the Pyrex beaker to the breaking point. Stainless steel beakers could have been used as in the RFP tests but they lowered the microwave coupling efficiency and they did not allow observation below the surface of the melt. The 1 kW microwave oven will ultimately be used in a hot cell to process samples from the actual waste storage tanks to study the off-gases generated. Therefore, for these studies, Vycor is an attractive material. For the larger 55 gallon drum liners required for the WHPP, a cheaper metal liner would be the most appropriate material, although other materials such as silica ceramic are not ruled out.

The most recent bench-scale tests at ORNL have used a modified surrogate shown in Table II. Sand, clay, and NaOH have been added to the surrogate to better reflect our perception of the actual waste storage tank contents, although at this writing, we have yet to take the first actual tank sample for analysis. As such information becomes available, the surrogate formulation will undoubtely change again. Nevertheless, much useful testing of processing technology can be accomplished even with best-guess surrogates. The amount of water added to the dry chemicals is done to produce a sludge that could be easily pumped into the microwave processing equipment. Also, the water aids in dissolving and mixing the dry chemicals which are usually pelletized in the dry form. Finally, the water content of the sludge allows the microwave energy to efficiently couple to the wet solids which in the dry state have much less microwave absorption at room temperature, but the solids absorb microwave energy better when their temperature exceeds 100°C.

TABLE II

REVISED ORNL SURROGATE COMPOSITION

Component	wt%
$NaNO_3$	41.4
H_2O	38.6
$Ca(NO_3)_2$	11.4
Bentonite Clay	2.61
Na_2Co_3	2.06
NaOH	1.67
Sea Sand	1.34
NaCl	0.83
$Al(NO_3)_2$	0.09

Initial experiments were done with an infrared sensor focused on the top surface of the sludge. Direct observation of the top surface worked well as long as the top surface did not boil vigorously. When vigorous boiling occurred, the effective emissivity of the surface decreased. This caused the apparent surface temperature to drop which caused the temperature controller to increase the microwave power output in an attempt to maintain the programmed temperature setting. This further increased boiling which lowered the surface emissivity still further. The solution to this instability was to relocate the sensor to the side of the microwave oven in order to view the outer surface of the side of the Vycor beaker, a stable surface that has a constant emissivity over a very wide temperature range. The slight penalty for this arrangement is a 5-10 s delay between the time the sludge sees an increase in temperature and the time the heat diffuses to the outer surface of the beaker. This delay can be easily compensated for by changing the time constants for the temperature controller and reprogramming to a more gradual heating rate.

Initial heating rates of 1.0°C/min were tried but this was still too fast a heating rate for the indirect temperature monitoring of the beaker. The rate was reduced to 0.5°C/min and this reduced the splattering of the boiling sludge. However, it became clear that a boiling indicator would be required to monitor boiling and produce a signal proportional to the degree of boiling that could be fed back negatively to the SCR controller so that the microwave power supplied to the sludge would be just balanced by the heat of vaporization of water vapor. Work on this detector is in progress.

At this point, a few words on the physical appearance of the sludge throughout the microwave heating process would be in order. After mixing the chemicals and water (300 ml total volume) in a 400 ml Vycor beaker, the mixture is light brown in color and has the texture of a runny milk shake. After the mixture stands over night, a clear 2 cm deep supernatant forms over a 6 cm deep sludge (approximately 225 ml). The mixture is heated and the top layer of supernatant begins to evaporate away. The supernatant is believed to be mostly a saturated solution of $NaNO_3$ and $Ca(NO_3)_2$. These salts produce a liquid which has a very good electrical conductivity which limits the microwave penetration depth to near the surface. As the supernatant is evaporated, the sludge begins to boil to a greater or lesser degree depending on the heating rate chosen. The sludge contains a large amount of bound water which is removed rather slowly as the sludge heats up. From about 120°C to 250°C, the sludge forms a liquid eutectic between $NaNO_3$, $Ca(NO_3)_2$ and the other salts with the clay and sand forming the undissolved solids phases. As the heating process progresses, the sludge bubbles pop and eject particles of sludge which stick to the walls of the beaker to form a thick ring of cooled sludge above the boiling pool in the center. This behavior persists until the temperature of the melt approaches 300°C where boiling becomes less pronounced and the dried ring of sludge on the side of the beaker begins to slump to the pool at the bottom. At the same time, the sludge becomes less absorbing of the microwave power because the microwave leakage power from the oven increases with temperature at a fixed input power. This effect is due to the molten salts high electrical conductivity which allows less and less microwave power to penetrate into the sludge to heat it. If sharp crystals are formed on the inside surface of the beaker walls, they may tend to draw small microwave arcs if the microwave input power is not limited.

Plans call for NO_x monitoring equipment to be installed to provide a direct indication of NO_x gases evolved during arcing along with an optical arc detector. In addition, an acoustic emission detector will be developed to prevent vigorous boiling. Development of these process controls will also be relevant for the pilot-scale equipment now under design.

CONCLUSIONS

Initial ORNL volume reductions for surrogates (dry components only) in 300 ml Vycor beakers are comparable with the RFP results in 8 l stainless steel beakers. Both processes result in ~25% volume reductions. The processing times for similar volumes are somewhat longer for the ORNL bench-scale tests than for the RFP tests, but the ORNL tests processed wet slurreys which required careful attention to limiting the heating rate to prevent vigorous boiling while the RFP tests only tried melting dry surrogates. In both the RFP and the ORNL tests, 2450 MHz microwave energy applied to the ORNL surrogate RH TRU wasteform has resulted in a solid monolith that meets the WIPP WAC. The ORNL WHPP project is proceeding with developing the microwave solidification/volume reduction process to the pilot-scale level so that fair comparisons between the microwave process and other processes such as the wiped-film evaporator and extruder can be made.

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