

RF/MICROWAVE VOLUME-REDUCTION AND
STABILIZATION SYSTEM FOR RADWASTE RESINS

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ABSTRACT

Radio frequency (RF) heating of radioactive ion-exchange resins by means of microwave energy offers a simple and economic system for the volume reduction and chemical-physical stabilization of such radioactive waste materials. The electrical, physical, and chemical responses of four resins were developed for a drying temperature of 200°C or a pyrolysis temperature of 300°C. The volume reduction of resins produced by drying at 200°C or pyrolyzing at 300°C ranged from 52 to 80% depending on the solidification/packaging method for final disposal. Effluents from the process are small in volume, amount to less than 1 weight percent of the original resins, and can be easily treated. Pyrolyzed resins can be solidified in either cement or vinyl ester styrene (VES) to meet Nuclear Regulatory Commission (NRC) regulations, whereas dried resins are only compatible with VES.

INTRODUCTION

The costs of disposing of radioactive wastes from nuclear plants are increasing, and the more stringent requirements anticipated for future disposal of these wastes are expected to increase disposal costs still further. The development of advanced technologies capable of simultaneously reducing the volume and solidifying the radioactive waste into a stable mass will aid the nuclear power industry in meeting these requirements in an economic way.

Currently available technologies based on compaction, water removal, and incineration can reduce the cost of disposal by reducing the total waste volume. The amount of reduction depends on the type of radioactive waste and the treatment method. These have been discussed in previous EPRI reports.¹⁻⁷

Water removal is an important aspect of volume reduction for specific waste streams, such as the mildly radioactive ion-exchange resins. Conventional water removal systems, however, are complex, consume much space, and are often expensive. Typical problems associated with these systems include fouling of the heat transfer surfaces, the need to dispose of large quantities of hot gases, the introduction of particulates in the gaseous effluents, the need for scrubbers, and serious maintenance problems. Another concern is the stability of the dried waste in the final solidified/stabilized form. Some advanced radioactive waste treatment systems, such as radio frequency (RF) or microwave drying or pyrolysis,^{7,8} promise to eliminate or circumvent many of these problems.

Dielectric (RF or microwave) heating is a fundamentally different method of energy transfer to cause heating. Conventional heating methods, such as by hot gases, fluids, or heated particles, require physical contact with the surfaces of the material being heated and also require the establishment of a substantial temperature gradient if the material is to be heated within a short time. The heat diffuses into the interior of the material via thermal conduction from the heated surface. If a sizable volume of material is to be heated within a short time, the material must first be processed into small particles so that the diffusion time is acceptable. These circumstances generally require access to the entire volume of small

particles by the heat transfer agent (hot gases, liquids, or particles). If hot gases are used, the above combination of circumstances requires very large volumes of gases to cause a reasonable amount of heat transfer. If hot liquids or particles are used, a method must be devised to separate the heat transfer liquids or particles from the material being heated. At a final heating temperature in excess of 300°C, the thermal decomposition of the heat transfer liquids or particles must also be considered.

In addition, the radioactive resins will, if substantially heated, generate hazardous effluents that must be separated, or otherwise treated, from the heat transfer fluids. These concerns present serious design difficulties for conventional heating methods and can result either in complex effluent treatment designs, especially if large quantities of heat-transfer fluids are used, or in the emission of possibly hazardous materials.

Dielectric heating is a volumetric heating method. Access is required only at two generally opposing surfaces of the material being treated, and the volume of the material can be quite large. The heating can be done in a fully sealed container, which can capture all the effluents without their being diluted with other fluids or captured by other particles. Consequently, a much simpler design is possible.

The aforementioned properties become especially important if the resins are to be rendered physically inert to water or other destabilizing agents. We have found that by pyrolyzing resins around 300° to 350°C the sulfonate and amine groups are destroyed such that the volume-reduced resins will not rehydrate and swell. Others⁹ have found that if the final pyrolysis temperature exceeds 450°C, the final product again becomes unsuitable for solidification in cement. Thus, the temperature gradient or variation must be carefully controlled. This imposes design difficulties if conventional heat transfer processes are being considered.

The foregoing provides the rationale for the serious consideration of dielectric heating to reduce the volume of resin and to stabilize the final product. The process is illustrated in Fig. 1, which shows the flow patterns and functional blocks for the

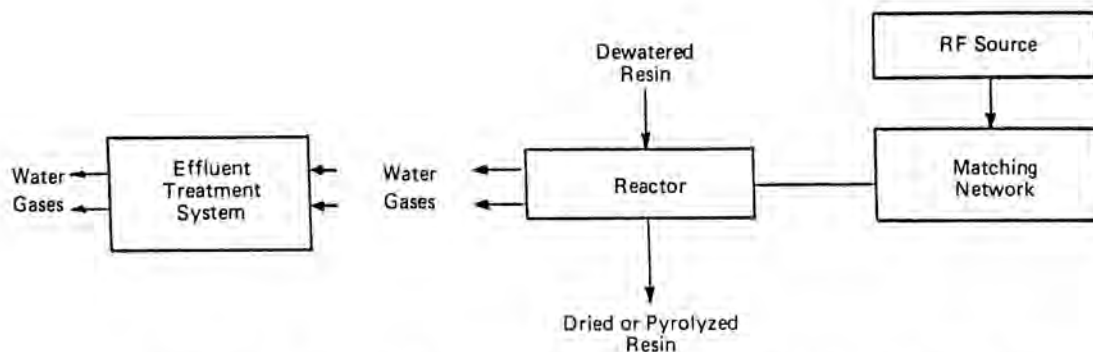


Fig. 1. Block Diagram of RF Drying and Pyrolysis Volume-Reduction System.

RF drying or pyrolysis volume-reduction method. The resins are pumped into the reactor and allowed to drain. RF power is supplied from a source remote from the reactor via a matching network and then by cables. Small quantities of gases and other effluents are generated along with water during the RF drying or pyrolysis heating step. These are treated by removing the toxic or hazardous components. The dried or pyrolyzed resins are then cooled and removed from the reactor via a resin removal duct. The volume-reduced resins are then placed in a high-integrity container (HIC) or mixed with an encapsulant.

This paper summarizes some of the results of an EPRI-sponsored research program⁸ conducted at IIT Research Institute (IITRI) to develop quantitative data on the volume reduction of ion-exchange resins using RF/microwave heating technologies. The results of volume-reduction experiments, characterization of the effluents and products obtained after volume reduction, and compatibility of the volume-reduced material with solidification agents are presented along with a brief description of RF system design and process economics. The program also considered other advanced techniques such as freeze drying, but the results of those experiments are not reported here. Details of the electrical property measurements, reactor design guidelines, and process economics are reported elsewhere.⁸

VOLUME-REDUCTION EXPERIMENTS

Volume-reduction experiments were conducted at IITRI using bench-scale equipment with 500 to 1,000 g of resin samples in both bead and powder form. The bead resins used in the experiments were spent resins from the condensate polishing operations at the Collins power plant of Commonwealth Edison Company. The powdered resins were obtained as fresh anionic and cationic resins (PCH and PAO) from Graver Chemical Company. The resin samples were heated to temperatures in the range of 100° to 300°C to determine the volume reduction possible with drying and pyrolysis techniques. The bulk of the heating experiments were conducted using external electrical heaters using heating protocols designed to simulate dielectric heating. Smaller samples of resins were also heated to temperatures over 300°C using dielectric heating in coaxial reactors, and these samples exhibited similar responses.

Figure 2 is a schematic diagram of the equipment used in the volume-reduction experiments. A preweighed quantity of the resin was poured into a graduated glass cylinder placed inside a furnace with split

heaters. The resin was heated to the required temperature using ohmic heaters and held there for a predetermined time. In some of the experiments the temperature was increased in stages, with intermediate soaking periods of constant temperature. Temperature was controlled by two thermocouples, one placed inside the resin and the other on the outside of the glass cylinder. Effluents from the glass cylinder were condensed using an air condenser, and the noncondensables were collected by displacing them over water. Samples of the noncondensable gases were obtained before and after water displacement for analysis by gas chromatography (GC) and mass spectroscopy (MS). The composition of condensate samples was also analyzed. The quantities of both condensable and noncondensable effluents generated during the treatment were measured along with the volume of the resin in the cylinder.

Figure 3 shows the results of one of the volume-reduction experiments using the spent resins. The reduction in the total volume of the resins as a percentage of the initial volume, and the volume of noncondensable gases generated during the heating, are

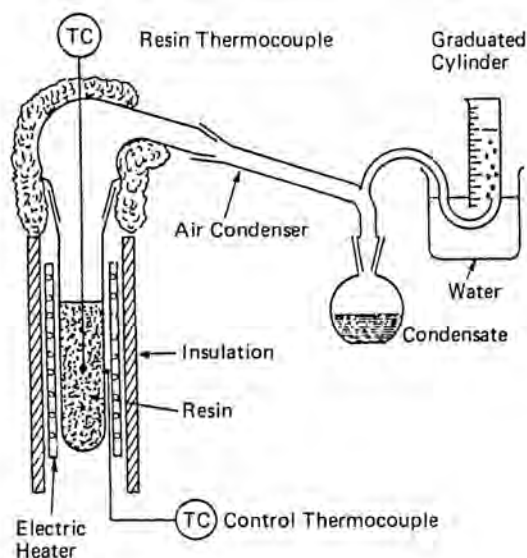


Fig. 2. Volume Reduction Apparatus.

TABLE I

Results of Volume-Reduction Experiments

Exp. No.	Sample	Temp., °C	Volume Reduction, %	Weight Reduction, %
B-1	Mixed Beads ^a	135	60.7	52.5
B-2	Mixed Beads ^a	225	60.7	57.8
B-3	Mixed Beads ^a	300	67.9	69.9
P-1	Mixed Powder ^b	140	35.7	58.0
P-2	Mixed Powder ^b	200	42.9	61.0
P-3	Mixed Powder ^b	300	57.1	73.7

^aSpent beads from Collins power plant

^bFresh powder from Graver Chemical Company

The effect of compaction pressure on the volume reduction of powdered resins is shown in Table II. By compacting the heated powder at a pressure of about 30 psi, the volume of the powdered resin was reduced by 54% after a treatment temperature of 135° to 140°C and by 70% after a treatment temperature of 300°C. Increasing the compaction pressure to 140 psi resulted in an additional 10% volume reduction. These results show that volume reductions of up to 80% are possible for powder resins at reasonable compaction pressures. In addition, the possibility of compacting the powders after heating permits a rather simple heating reactor design compared to the design in which simultaneous heating and compression are required. In fact, compression may not be necessary if the final solidification of the volume-reduced resin includes a mechanical mixing operation that homogenizes the resins with a solidification agent such as cement.

TABLE II

Summary of Volume Reduction of Resins by Thermal Treatment

Treatment Temp., °C	Volume Reduction, %			
	Beads	Powder		
		Without Compaction	With Compaction 30 psi	140 psi
135-140	60.7	35.7	54.1	64.8
200-225	60.7	42.9	55.0	63.1
300	67.9	57.1	69.6	79.8

The volume-reduction experiments conducted with both bead and powdered resins showed that volume reductions of 50 to 80% are possible depending on the heating temperature and the compression pressure used. The volume-reduced material in both cases was free flowing and did not show any tendency to stick to the walls of the reactors at temperatures up to 300°C. This will facilitate easy removal of the material from the RF heating reactor for final disposal. On the other hand, resins pyrolyzed substantially in excess of 300°C often stuck to the reactor walls or clumped together.

COMPOSITION AND QUANTITIES OF EFFLUENTS

To be acceptable, the volume-reduction process must not only reduce the volume of the resins; it must be environmentally safe as well. The gaseous and liquid effluents generated during heating and pyrolysis must be treated before being released into the atmosphere or reused inside the plant. The effluents produced by heating the bead and powdered resins were analyzed to determine treatment requirements.

Gas and liquid samples collected after heating the resin samples were analyzed by gas chromatography

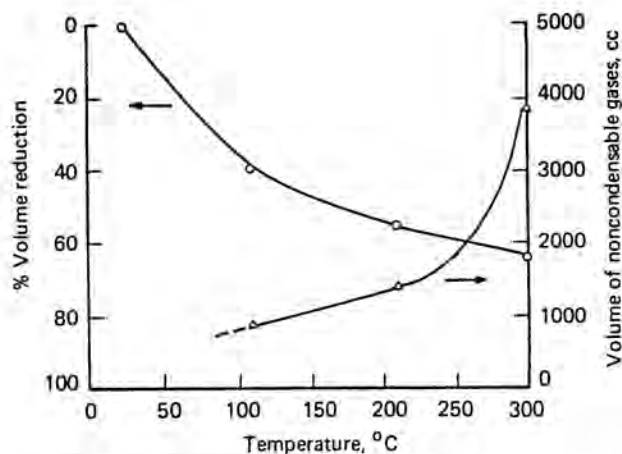


Fig. 3. Volume Reduction of Spent Resin.

shown as a function of temperature. Typically, the resins lost about 70 to 80% of their total water when held at about 110°C overnight. This was accompanied by a 50% reduction in the volume of the material. Continued heating of the resins to about 300°C resulted in further drying and subsequent pyrolysis of the resins. Final volume reduction was about 65 to 70%. Above 200°C, the generation of noncondensable gases increased, indicating rapid pyrolysis. The total volume of noncondensable gases was small (less than 1 scf per pound of resin), since no gases are artificially introduced into the system for heat transfer or other purposes.

The total weight of the resins also decreased with an increase in temperature. A major portion of the weight loss occurred at temperatures of 100° to 200°C due to evaporation of the water. Recovered water that condensed during the experiments accounted for most of the loss in weight of the original resin, with the noncondensable gases averaging about 1% by weight of the original resin.

Additional volume-reduction experiments were conducted to determine the effects of various parameters such as resin type, resin composition, heating temperature, and compressive load on the extent of volume reduction. The results of some of the experiments are presented in Table I. Through heating alone, the extent of volume reduction ranged from 60 to 68% for the beads, and from 35 to 57% for the powders. The beads retained their spherical shape even after they were pyrolyzed and packed into a compact form of individual spheres. The powder, on the other hand, formed small lumps, particularly at higher temperatures, and retained a large amount of air space. The high porosity of the powdered resins prevented good volume reduction through heating alone.

Experiments were conducted to determine if compaction can reduce the porosity and improve the volume reduction. An instrumented bench press was used for these experiments. Initial experiments with bead resin showed that compaction does not aid volume reduction. The beads behaved similarly to ball bearings, withstanding loads of up to a few hundred pounds without breakage, and the volume remained unchanged. The powders exhibited a completely different behavior. The loose agglomerates of dried or pyrolyzed powdered resin broke into fine powder and compacted into a solid mass at very low pressures.

(GC) to determine the quantities of major components and by mass spectroscopy (MS) to determine the concentrations of trace components. At low temperatures, the bulk of the noncondensable gases generated were carbon monoxide and carbon dioxide. At temperatures over 200°C, however, hydrocarbons such as methane and higher alkenes were generated. The generation of the fixed hydrocarbons indicates pyrolysis of the resins and destruction of the resin structure.

Anionic and cationic powdered resins were heated separately in stages to a temperature of 300°C to determine the effect of resin type on effluents. Both gaseous and liquid effluents were collected and analyzed using GC/MS techniques for their characterization. The results of the analysis are summarized below. The detailed composition of the effluents and their volumes are reported elsewhere.

1. The total volume of gaseous effluents ranged from 100 to 700 scf/ton of resin.
2. The bulk of the noncondensable gases are generated from cationic resins.
3. The gas obtained from heating cationic resin at 200°C overnight contained 96% SO₂, indicating decomposition of sulfonate groups at this temperature.
4. Noncondensable gases collected from heating anionic resins to 300°C contained 200 ppm of total mercaptans and had a strong odor.
5. Condensate samples collected from heating anionic resins at 200° and 300°C overnight contained 12% trimethylamine, indicating decomposition of amine groups in this temperature range.
6. Heating anionic resins to 300°C also produced small quantities of organic liquid, which was analyzed to be mostly aromatics (benzenes, styrenes, and xylenes were about 66% of the total).

The analysis of the effluents showed that contaminants in the effluents originate mostly from the anionic resin. The compositional data indicate that treatment of both the gaseous and liquid effluents will be necessary to prevent plant odors and to permit recycling of the water produced during drying. The relatively small quantities of these effluents, however, would permit small effluent treatment systems for their handling.

ANALYSIS OF VOLUME-REDUCED RESINS

We determined the elemental compositions of the resins, both as received and after volume reduction, in order to understand the relationship between volume reduction and composition, and to determine the fate of heavy metals during volume reduction. The samples used in this analysis were produced by heating spent bead resins from the Collins power plant. Figure 4 shows the weight ratios of carbon to hydrogen, carbon to sulfur, and carbon to nitrogen as a function of treatment temperature. Significant changes in the carbon-to-hydrogen ratio occur in the 200° to 300°C range. Similarly, the ratios of carbon to sulfur and carbon to nitrogen also decreased in the same temperature range. These results show that both pyrolysis and decomposition of functional groups in the resins commence at temperatures of over 200°C for the resin samples used in these experiments. For the resins pyrolyzed at 300°C the functional groups responsible

for the hydration properties of the resins as well as rehydration are largely destroyed. This is similar to the results noted by Matsuda;⁹ however, he also found that pyrolysis at temperatures above 500°C made the resins unsuitable for packaging in cement.

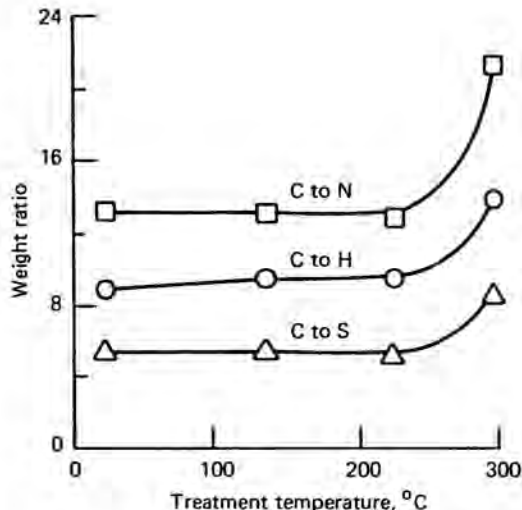


Fig. 4. Weight Ratios of Carbon to Nitrogen, Carbon to Hydrogen, and Carbon to Sulfur as a Function of Treatment Temperature.

SOLIDIFICATION AND ENCAPSULATION

The disposal of low-level radioactive wastes such as these resins by landfilling requires stabilization of the wastes to meet NRC regulations. The NRC requires that the resin mass be a free-standing monolith with less than 0.5% free-flowing water. In addition, the solidified mass must pass a 90-day immersion test followed by a compressive strength test in which the compressive strength of the solidified mass must exceed 50 psi. Some commonly used methods for solidification and disposal include solidification in binders such as cement, asphalt, and other proprietary materials, or packaging in high-integrity containers (HIC) without the use of any binders. Cement solidification is the least expensive method, but adding the cement and water required for its solidification may increase the total volume of the resin to be disposed of in the landfill.

Solidification and immersion tests were conducted using volume-reduced resins to determine their compatibility with common solidification agents. The two solidification agents used were cement and vinyl ester-styrene (VES, a proprietary Dow Chemical Company solidification medium). The compressive strength of the solidified resins using both of these binders was determined intermittently during their immersion in water and after a full 90-day immersion period. Results of the immersion and compression tests are shown in Table III. The tests showed that pyrolysis of the resins at 300°C is required to make them compatible with cement. VES was found to be compatible with resins produced by heating to all three temperatures considered.

The overall volume reduction of volume-reduced resins is shown in Table IV for both drying and pyrolysis using three methods of solidification/encapsulation. Volume reductions of 52 to 80% were noted, depending on heating temperature and the method

TABLE III

Results of Immersion and Compression Tests

Treatment Temp., °C	Resin/Solidification Agent	Resin as % of Total	Days of Immersion Prior to Failure	Compression Strength, psi
100	Beads/cement	33	18	--
100	Powder/cement	29	0	--
100	Beads/VES	60	--	7,750
100	Powder/VES	40	--	12,460
200	Beads/cement	34	33	--
200	Beads/VES	60	--	9,770
300	Beads/cement	46	00	295
300	Powder/cement	32	00	310
300	Powder/VES	40	--	14,940

of packaging. All of the samples showed compressive strengths in excess of 50 psi. It may be possible to improve the resin loading further, in particular with the cubes made using VES, in order to get an even greater overall volume reduction. The compatibility of the pyrolyzed resins with any of several disposal methods and the possibility of greater volume reduction make pyrolysis preferable to drying alone.

TABLE IV

Overall Volume Reduction of Resins After Solidification/Encapsulation

Solidification/Encapsulation Method	Volume Reduction, %	
	Drying at 200°C	Pyrolysis at 300°C
Cement	--	54 to 56
VES	52 to 59	73 to 75
HIC	43 to 63	57 to 80

SYSTEM DESIGN

Preliminary system design calculations were made using the electrical, chemical, and physical property data for heating resins for drying or pyrolysis in

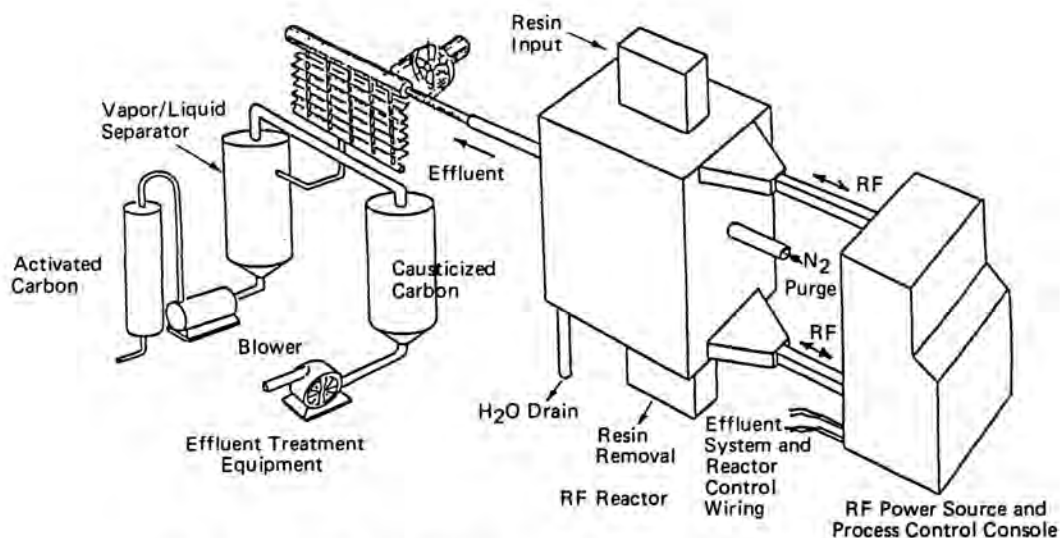


Fig. 5. Conceptual Design of RF Volume-Reduction System for Resins.

batch equipment. Figure 5 illustrates this conceptual design, which is capable of processing about 1000 to 3000 ft³/yr of resin at either 200° or 300°C. The elements consist of the RF power source, a control console, the RF reactor, and effluent treatment equipment.

The resins are sluiced into the reactor and allowed to drain. The reactor is first purged with nitrogen, then excited by electric fields developed from the RF source. When the temperature of the resins exceeds 100°C, water is driven off, and as the temperature approaches 300°C, the resins are substantially altered physically and chemically. During heating, the relatively small quantities of liquid and gaseous effluents are rendered innocuous by the effluent treatment equipment.

ECONOMIC ASSESSMENT

Based on a pre-solidified volume reduction of 55% for the 200°C treatment and 65% for the 300°C treatment, the maximum amount of capital that could be reasonably invested for the volume-reduction method was developed using the Equivalent Capital Investment (ECI) methodology. Solidification in cement, bitumen, and VES was compared with alternative methods. Depending on the evaluation period and cost escalation rates, the maximum capital that could be reasonably invested per 1000 ft³ of resin treatment per year ranged from \$752,000 to \$2,651,000. Volume reduction of the solidified resins produced by RF treatment is about 50% greater than that of the solidified resins produced by evaporator/extruder or thin-film evaporator. Hence, the maximum capital that can be invested is 40 to 50% higher. Preliminary cost studies suggest that the installed costs of the 300°C RF system can be comparable to or less than the ECI-allowed investment when only 1000 ft³ of resins are treated per year, and these installed costs should be substantially less than the ECI-allowed investment if greater yearly volumes are processed.

CONCLUSIONS

The technical and economic feasibility of RF drying and pyrolysis techniques for volume reduction

and physical-chemical stabilization of ion-exchange resins has been proven. The RF process offers advantages over alternative resin volume-reduction methods in five areas:

1. Simpler, less capital-intensive equipment.
2. Smaller effluent streams, which are more easily treated.
3. Lower power requirements and operating costs.
4. Dried product that is stable and compatible with a variety of solidification and packaging methods.
5. Greater volume reduction of solidified resin for a given quantity of effluent.

REFERENCES

1. "Advanced Radwaste Treatment Systems," NP-1600, Electric Power Research Institute, Palo Alto, California (October 1980).
2. "Non U.S. Advanced Radwaste Systems," NP-2055, Electric Power Research Institute, Palo Alto, California (September 1981).
3. "Assessment of Power Reactor Waste Immobilization by Vitrification," NP-3225, Electric Power Research Institute, Palo Alto, California (August 1983).
4. "Radwaste Incinerator Experience," NP-3250, Electric Power Research Institute, Palo Alto, California (October 1983).

5. "Identification of Radwaste Sources and Reduction Techniques," NP-3370, Electric Power Research Institute, Palo Alto, California (January 1977).

6. "Feasibility of Microwave Technology Drying for Radwaste," NP-2334, Electric Power Research Institute, Palo Alto, California (April 1982).

7. "Low Level Radwaste Solidification," NP-2900, Electric Power Research Institute, Palo Alto, California (March 1983).

8. "RF Volume-Reduction System for Radwaste Resins," In publication, Electric Power Research Institute, Palo Alto, California (June 1985).

9. "Volume-Reduction of Ion-Exchange Resins by Pyrolysis Technique." ANS Winter Meeting, San Francisco, California, November 1985. M. Matsuda, K. Funabashi, and S. Uchida.

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