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THE FEASIBILITY OF VITRIFYING EPICOR II ORGANIC RESINS

J. L. Buel
Pacific Northwest Laboratory
Richland, Washington 99352

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CONTENTS

ABSTRACT	iii
INTRODUCTION	1
PROCESS DEVELOPMENT	3
PROCESS TESTING	7
RESIN LOADING	7
PROCESS OPERATION	7
PARTICULATE ENTRAINMENT	8
RADIONUCLIDE BEHAVIOR	9
COMBUSTION EFFICIENCY	10
CONCLUSIONS AND FUTURE ACTIVITIES	13
REFERENCES	15

FIGURES

1	Feed Techniques Considered for Phase 1 Testing	4
2	Differential Scanning Calorimetry Analysis of EPICOR II Resins	5
3	Laboratory-Scale Process for Phase 1 Testing	6
4	Offgas Treatment and Sampling System	9
5	Offgas Analysis by Mass Spectrometry	11
6	Joule-Heated Ceramic Melter for Vitrifying EPICOR II Resins	14

TABLES

1	Composition of Glass Used in Process Operation	8
2	Retention of Simulated Radionuclides in the Glass Product	10

INTRODUCTION

Funded by the U. S. Department of Energy under the EG&G/TMI Waste Immobilization Program, Pacific Northwest Laboratory (PNL) has completed the first phase of a program in which a process designed to destroy EPICOR II® resins was tested for its feasibility. These resins were utilized to remove cesium and strontium from radioactively contaminated water in the Auxiliary Building at the Three Mile Island Unit 2 Reactor after the incident in March 1979. They are also being used as a polishing system for water processed through the submerged demineralized systems.

Two types of EPICOR II resins have been utilized at Three Mile Island:

- a mixture of anionic and cationic organic resins;
- a mixture of the organic resins and inorganic zeolite resins.

Only the organic resins were utilized for process testing in this study.

In a single step, the PNL process greatly reduces the volume of these resins by incinerating them and incorporating cesium, strontium and residual ash particles into glass. The objective of the first phase of the program was to develop and test the concept on a laboratory scale using resins loaded with simulated radionuclides. During the test, a stable glass product was produced in a canister 38 cm tall x 15 cm in dia. This report describes the process development and nonradioactive test results. The report concludes that EPICOR II resins can be destroyed in a single step with minimal waste byproducts.

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PROCESS DEVELOPMENT

Researchers at PNL have gained considerable expertise in vitrification from past experience in high-level waste programs (Bonner 1979). This experience, combined with that of other PNL researchers familiar with organic resins and incineration, helped develop a concept for the introduction of combustible EPICOR II resins into vitrification equipment. The selected technique was designed to expose the resins to combustion temperatures of over 600°C in contact with oxygen to allow complete combustion and with glass to absorb the radioactive elements of Cs and Sr. Residence time had to be adequate to allow combustion to be completed and to avoid entrainment of carbonaceous materials with the gaseous effluents.

Two different processes have been developed at PNL for waste vitrification. In the first, a joule-heated ceramic melter heats molten glass contained inside a refractory shell through dissipation of electric current in the melt. The resulting glass product continuously flows into a steel canister. In the second process, in-can melting, molten glass is heated directly in a stainless steel canister by external resistance heaters. Although the EPICOR II vitrification process is applicable to both the joule-heated ceramic and in-can melters, the first phase of this program concentrated only on the latter since the in-can melter test system is readily available for radioactive testing.

The four feed introduction techniques depicted in Figure 1 were evaluated during process development. Of these techniques, only below-surface entry (Number 4) assures contact of resins with glass to fix Cs and Sr in the glass product. The below-surface entry technique is similar to that employed in the molten-salt incinerator concepts (Rockwell 1980), except that molten glass is used instead of salt. The molten glass is also kept at higher temperatures (1050°C) to keep the glass fluid (less than 200 poise). These temperatures are well above the 600°C combustion temperature requirement for complete combustion. Figure 2 is a plot of the combustion behavior of EPICOR II resins in air obtained by differential scanning calorimetry analysis. The final portions of the exothermic curves, which are above the temperature limits of the

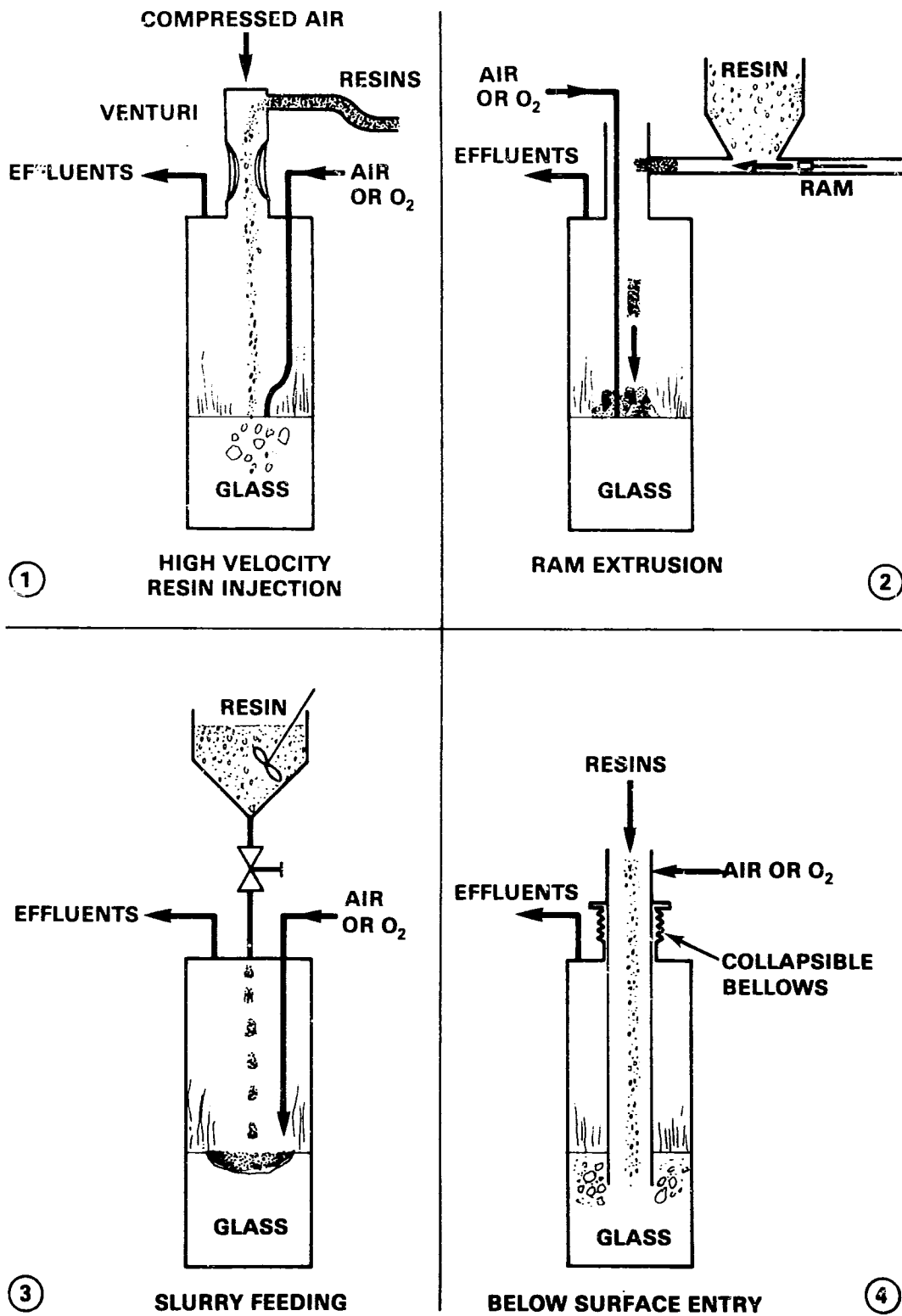


FIGURE 1. Feed Techniques Considered for Phase 1 Testing

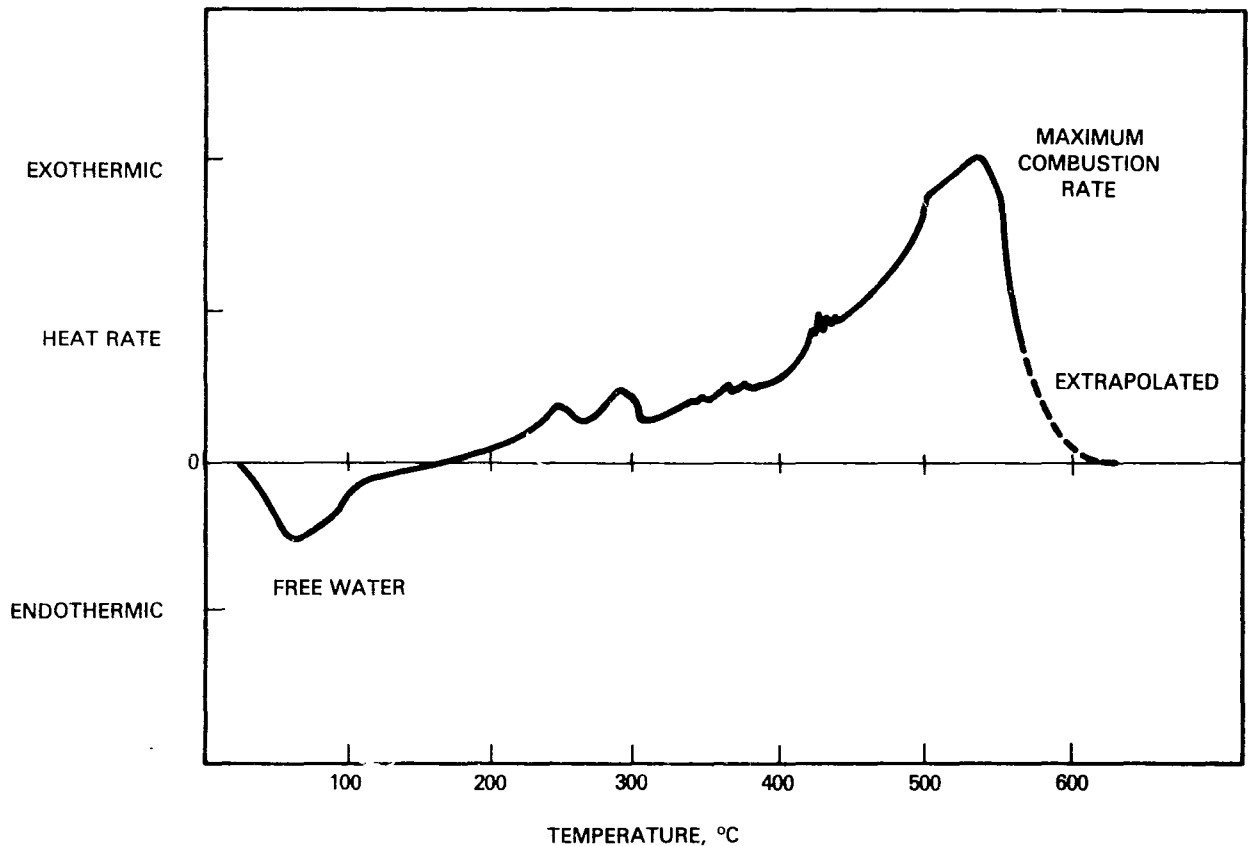


FIGURE 2. Differential Scanning Calorimetry Analysis of EPICOR II Resins

equipment used, are extrapolated, but other organic resins burn with similar exothermic behavior (Schultz 1972); therefore, we are confident that exothermic combustion reactions are complete at 600°C.

The process used for feasibility testing is depicted in Figure 3. Oxygen and resins loaded with nonradioactive Cs and Sr are fed through a sealed drop tube that penetrates the glass surface. The molten glass absorbs the Cs and Sr as the resins are destroyed. The drop tube is sized at 3.8-cm dia to keep vertical velocities between the drop tube and canister wall below 10 cm/s. This reduces the entrainment of particulates in the offgas and increases the residence time of combustibles at ignition temperatures. Most of the particulate carbonaceous material is fixed in glass until the oxygen completes combustion. Therefore, in the presence of O_2 the only materials retained in the glass product are Cs, Sr and noncombustible impurities or ash.

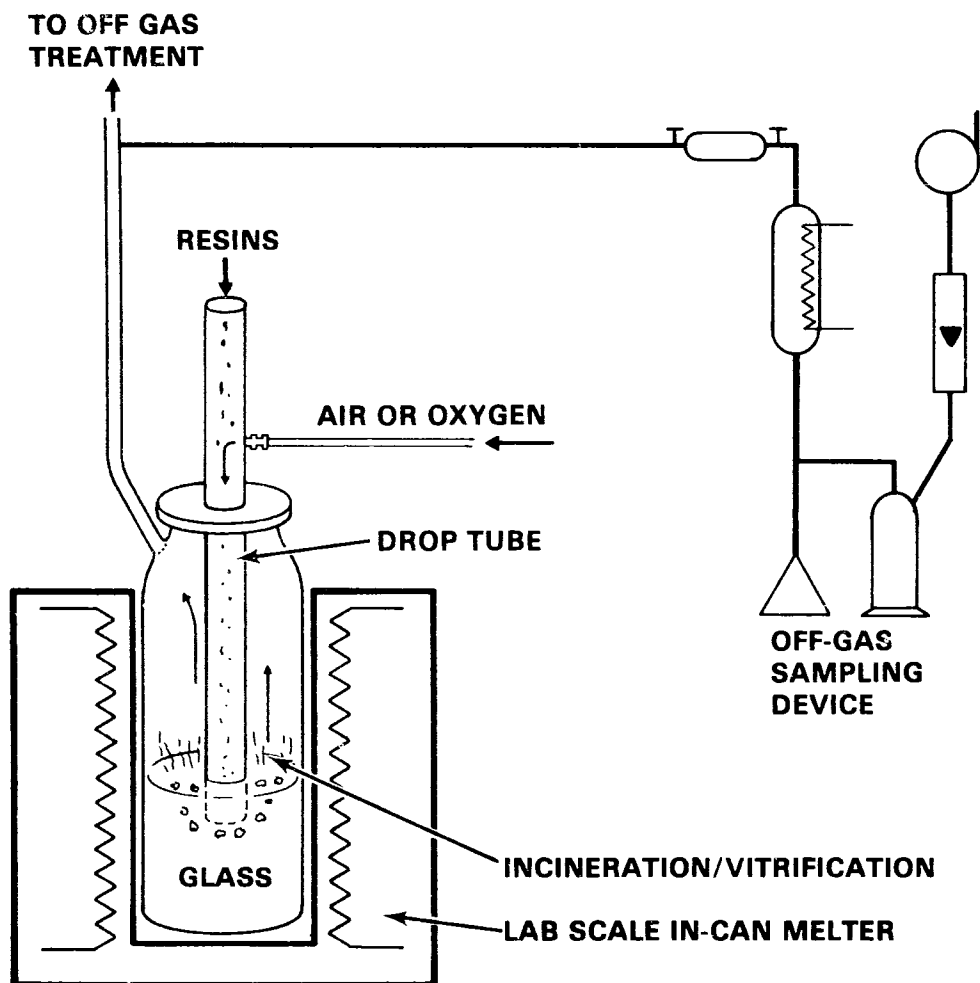


FIGURE 3. Laboratory-Scale Process for Phase 1 Testing

PROCESS TESTING

Two experimental runs were performed with EPICOR II resins loaded with nonradioactive Cs and Sr. The resins were fed through the drop tube into molten glass contained in a canister 38 cm tall x 15 cm dia. The canister was constructed of Inconel 690®, a nickel-chromium alloy. The gaseous effluents were continuously sampled, filtered, and sampled again before being scrubbed and exhausted to the stack. The sample streams were analyzed to identify the combustion products and Cs and Sr volatility behavior. The results were most encouraging and indicated that the carbonaceous material was completely converted to CO₂ with no detectable CO. Also, 99.3 to 99.8% of the Cs was retained in the glass along with 99.5 to 99.98% of the Sr.

RESIN LOADING

In order to determine the significance of the volatility data for Cs and Sr, understanding the basis for the degree of loading onto the EPICOR II resins is important. The loadings used in these tests were based on analytical detection limits of Cs and Sr in the glass. The loading of 0.012 g/g resin was chosen for both Cs and Sr because the final expected concentrations of these elements in the glass following the tests would be ten times the detection limit of 0.02 wt%. These loadings, which are many orders of magnitude higher than the expected loadings at Three Mile Island, will most probably give higher volatility numbers than would actually be expected for the EPICOR II resins at TMI.

PROCESS OPERATION

The loaded resins were metered through a clamped, vibrating polyethylene line. In both runs, 2400 g of resins were incinerated and vitrified in 9.8 kg of glass over a 4-hour period. Even though the feed-control method was crude, a steady vacuum of 25 cm H₂O was maintained in the canister throughout the

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operation. The glass was maintained between 950°C and 1050°C via automatic temperature control of the external heaters. The glass level was raised from 3.2 cm above the drop tube in Run I-A to 10 cm in the second run (Run I-B) to determine the effects of submergence on effluent behavior. No volume reduction data are reported because longer-term tests are needed to determine the maximum loading of the glass. The Cs and Sr concentrations in the glass at the completion of these runs were 0.24% and 0.35%, respectively. The glass used, whose composition is listed in Table 1, was a standard, off-the-shelf glass frit and was not designed to optimize product quality. However, the glass does fulfill the objective of determining process feasibility.

PARTICULATE ENTRAINMENT

The gaseous effluents passed through a HEPA filter, which was weighed to quantify the particulate entrainment. In the first run, 2.2% of the resins had collected on the filter in carbonaceous form. However, by raising the glass level, entrainment was reduced to <0.8%. The filter was also effective in removing all the detectable Cs and Sr in the off gas. Later phases of this program will demonstrate the concept of recycling the filter deposits back to the melter.

TABLE 1. Composition of Glass Used in Process Operation

<u>Component</u>	<u>Concentration by Specification, wt%</u>	<u>Concentration by Analysis, wt%</u>
SiO ₂	56.3	56.3
CaO	7.09	7.04
Na ₂ O	14.76	14.0
B ₂ O ₃	21.53	21.5
SrO	0	0.02
Cs ₂ O	0	<0.02
Impurities	0	1.24

RADIONUCLIDE BEHAVIOR

The most encouraging result has been the low concentration of Cs and Sr in the effluent stream. An offgas sampling system shown in Figure 4 condenses and scrubs the samples both before and after filtration. The second system is used to determine the efficiency of the filter in removing the radionuclides. After each run, the sample lines were flushed and all the solutions were analyzed. Although this is an accurate analytical procedure, the filter

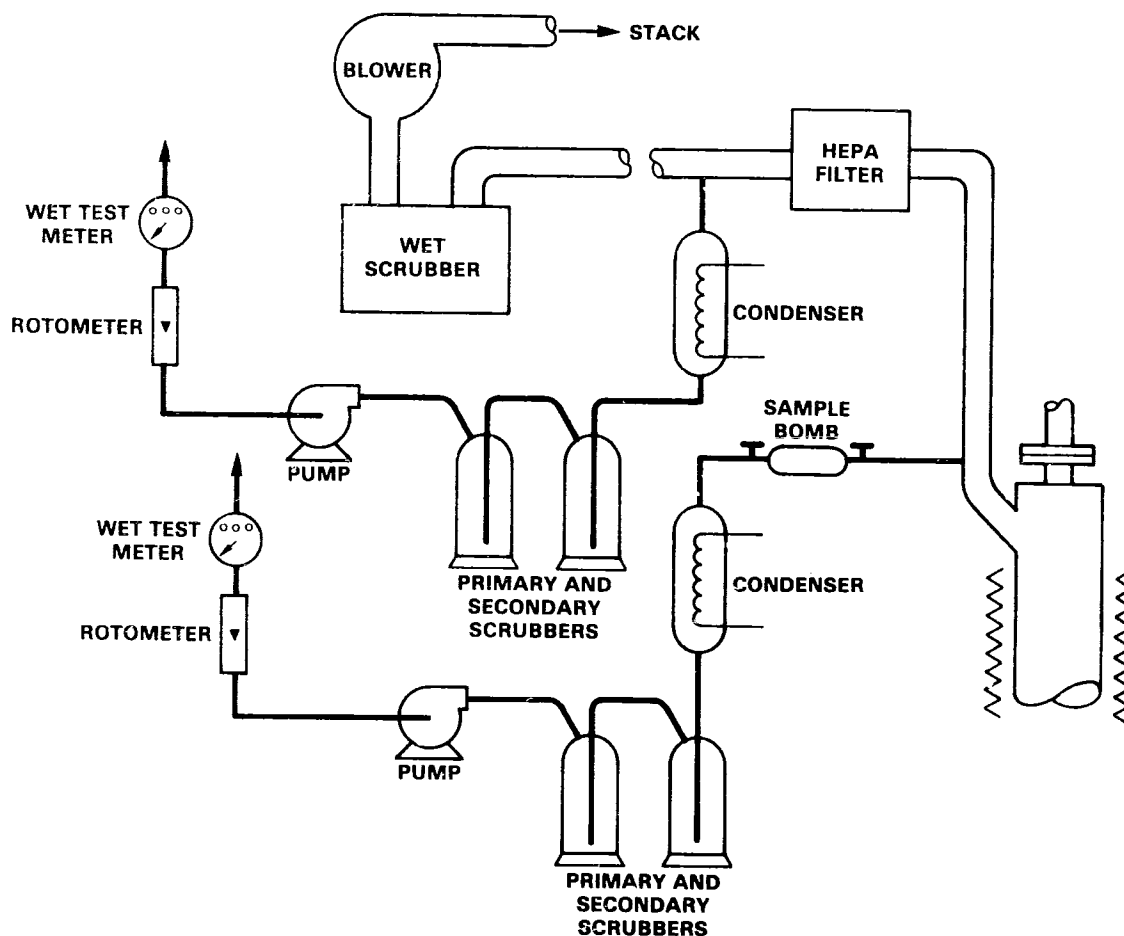


FIGURE 4. Offgas Treatment and Sampling System

particulates and glass product were also analyzed to serve as checks. Results are tabulated in Table 2.

The results in the first column indicate that radionuclide retention improved in the second run, which is attributable to the greater submergence of the drop tube. Interestingly, in Run I-A, where 2.2% of the resins were collected as carbonaceous particulates, only 0.24% of the Sr had been entrained into the offgas. Strontium is normally nonvolatile at the process temperature of 1050°C; thus, Sr effluent losses usually are proportional to particulate losses. However, the low entrainment of Sr in these tests indicates that Sr attains more affinity for the glass than partially combusted resins. Cesium, which is the more volatile component, also appears to behave independently of particulate losses.

COMBUSTION EFFICIENCY

The best indication of the degree of combustion is the CO/CO₂ ratio and amount of pyrolyzed resin. Mass spectrometric analysis of seven sample bombs collected from the offgas sampling system showed no detectable CO in any of the samples. This is attributable to the amount of excess oxygen, the high residence times of combustibles, and the high incineration temperatures. In only one instance (see Figure 5) did the pyrolysis product (hydrogen) concentration reach more than a negligible value. Apparently, a large quantity of resins was inadvertently introduced into the process at this time, as deduced from the high CO₂ and low oxygen concentrations. This indicates that feedrate control may be important. Pyrolysis products in the form of C_xH_y were always <0.5%.

TABLE 2. Retention of Simulated Radionuclides in the Glass Product

<u>Radionuclide</u>	<u>Run</u>	<u>Analytical Basis</u>		
		<u>Offgas Sample System</u>	<u>Filter Particulates</u>	<u>Glass Product</u>
Cesium	I-A	99.29%	99.5%	100%
	I-B	99.81%	>99.6%	94%
Strontium	I-A	99.76%	98.4%	100%
	I-B	99.98%	>99.6%	100%

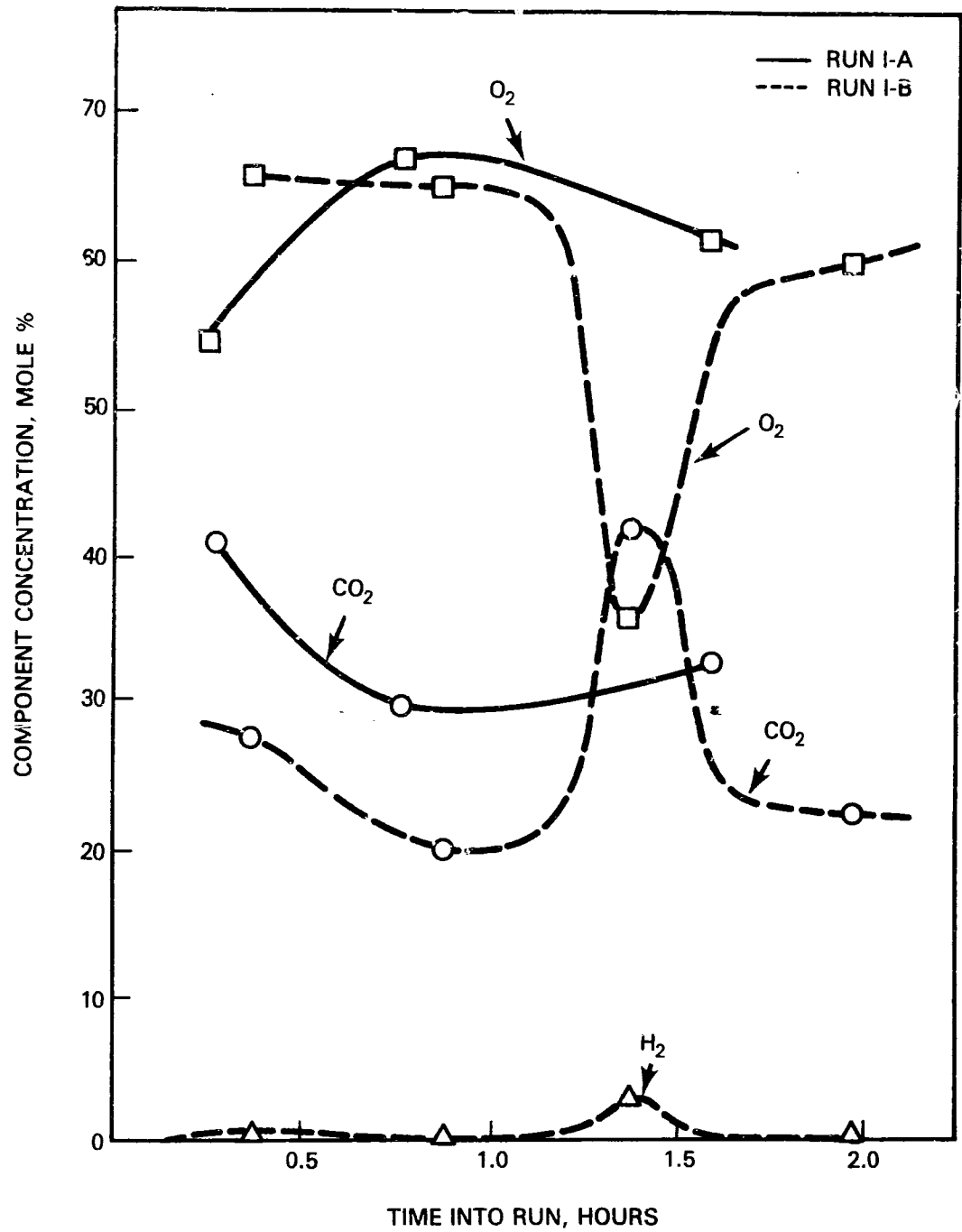


FIGURE 5. Offgas Analysis by Mass Spectrometry

CONCLUSIONS AND FUTURE ACTIVITIES

The feasibility tests with EPICOR II resin vitrification have developed some very encouraging data with respect to process operation. These include the following:

- Cs and Sr losses to the effluent stream are low. Cs volatility was controlled to 0.71 wt% and less; Sr losses were kept at 0.24 wt% and lower.
- Control of particulate and simulated radionuclide losses to the offgas is a function of the submergence depth of the drop tube.
- Sr and Cs appear to have greater affinity for molten glass than carbonaceous particulates, which tends to keep their losses very low.
- No CO was detected in any of the seven sample bombs collected throughout the tests. This means the process can operate safely without an afterburner and still keep emissions at a low level.

A number of additional developmental activities are being conducted with the resin vitrification process. These activities include longer-term testing with nonradioactive resins to determine volume reduction, processing rates, scale-up correlations, and material conformance to processing conditions. With this information, justification of the process can be determined.

The merits of the joule-heated ceramic melter (see Figure 6) for resin vitrification are being evaluated in the ongoing study. Since the ceramic melter operates with a constant glass level (as opposed to the rising-level in-can melter), an adjustable drop tube is not required. This difference may provide a distinct advantage for remote operation. The ceramic melter may also provide improvements in processing rates and product quality.

Another developmental activity being addressed is the formation of water-soluble sulfates on the surface of the glass product, which would create adverse effects on glass leachability. Sulfate groups exist in most cationic organic resins. Manring et al. (1967) postulate that sulfate

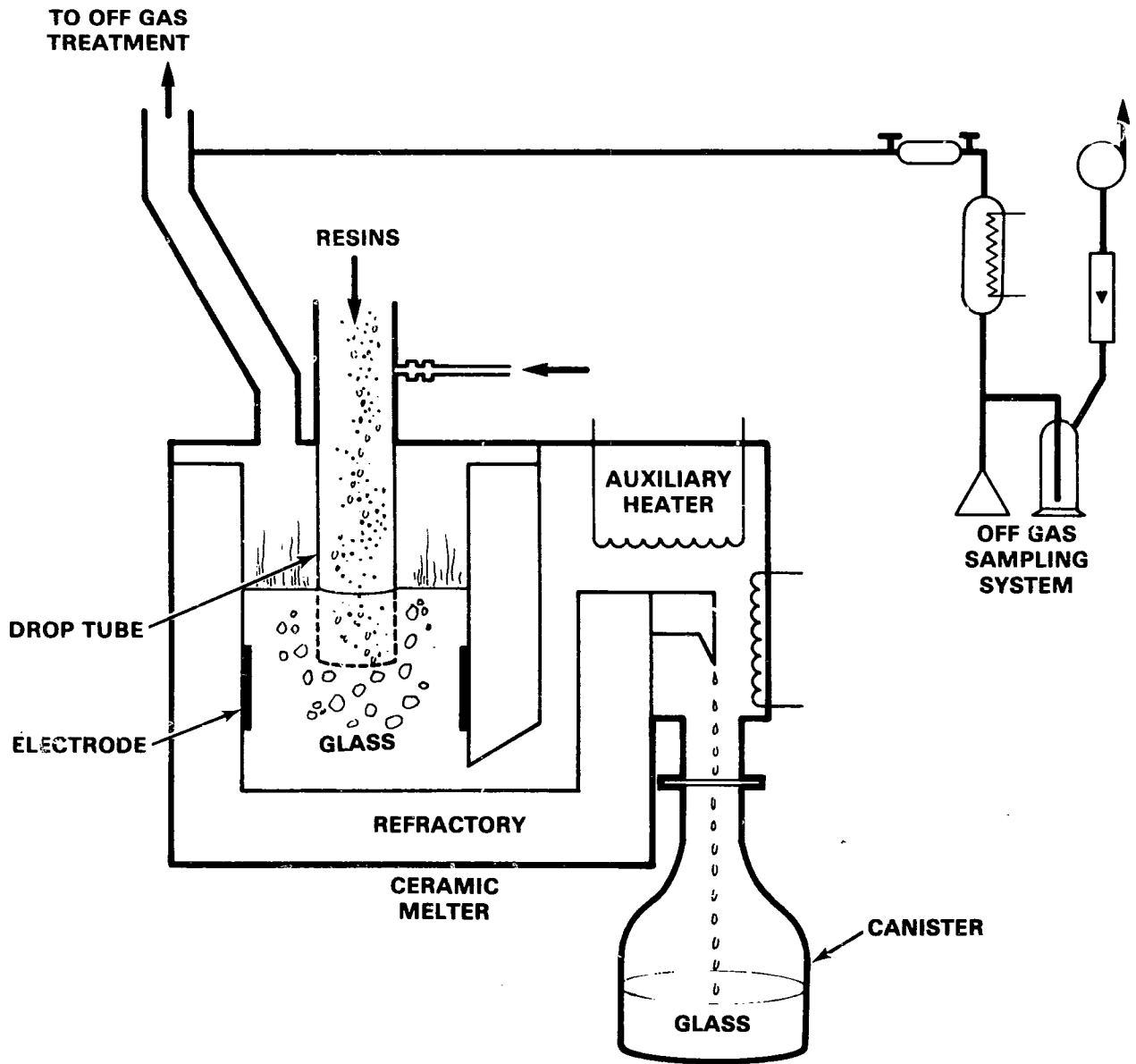


FIGURE 6. Joule-Heated Ceramic Melter for Vitrifying EPICOR II Resins

formation can be controlled in glass-forming processes by controlling the temperature and oxidizing conditions. Present activities address sulfate behavior when EPICOR II resins are vitrified.