

FINAL REPORT

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**Chemical Characterization of  
Organic Ion-Exchange Resins  
Supplied by Arkansas Power  
and Light Company**

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May 1985

Prepared for the  
Arkansas Power and Light Company  
under Contract 2311205862



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Little Rock, Arkansas 72203  
under Contract 2311205862

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## SUMMARY

Evidence for an exothermic reaction in a bed of dewatered ion exchange resin was observed at Arkansas Power and Light Company (AP&L), Arkansas Nuclear No. One (ANO) on January 15, 1983. Battelle, Pacific Northwest Laboratories (Battelle-Northwest) has conducted extensive studies in support of Arkansas Power and Light Company in an effort to determine the cause of this exothermic event.

No unequivocal cause of the exothermic event detected in a bed of dewatered ion exchange resin on January 15, 1983, at Arkansas Power and Light Company, Arkansas Nuclear No. One was determined. Studies conducted by Battelle, Pacific Northwest Laboratories included: 1) extensive analytical analyses to determine the cations and anions present in resin samples submitted by AP&L; 2) a determination of whether oxidants, reductants, acids, or bases were present in the resin samples submitted by AP&L; 3) determination of "free" organics; 4) thermal stability of the resins used by AP&L; 5) solidification of resins in cement; 6) an evaluation of microorganism growth in resins; 7) simulated dewatering tests; and 8) a thermodynamic evaluation of resin stability. None of the studies conducted indicated a definitive cause for the exothermic event.

However, the studies conducted by Battelle-Northwest do eliminate several potential causes of the exothermic event. The studies also indicate the potential significance of extensive microorganism growth in the resins being a contributing factor to the exothermic event.

The results obtained by Battelle-Northwest's studies conducted in support of Arkansas Power and Light Company are summarized as follows:

- Phase I studies gave no evidence of the presence of oxidants (i.e., nitrates, chlorine, chlorates, etc.) in resin samples from Cask A and Cask B in sufficient quantity to cause the resin destruction observed in Cask A after the exothermic event.

- Phase I studies found no alcohols, citric acid, hydrazine, or aromatic compounds on resins from Cask A or in solutions obtained from Cask A after the exothermic event.
- Additional studies identified the organics found in small quantities in Cask A and Cask E as very stable aliphatic compounds; their stability is also indicated by the fact they were still present in Cask A after the exothermic event.
- Phase I studies did find significantly greater quantities of Iron, Copper,  $\text{Cl}^-$ , and other ions present in Cask A resins in comparison to resins obtained from Cask B. Cation and anion analyses were not conducted on other cask samples.
- Solidification in cement of both cask and new resin samples supplied by AP&L resulted in no significant or unexpected temperature increase. Heats of solidification obtained from the laboratory studies were less than reported values of the heat of hydration for "normal" Portland cement. These findings allowed AP&L to successfully solidify the resins contained in Casks A, B, C, D, and E in cement for disposal.
- Verbal information was conveyed to Battelle-Northwest by AP&L personnel that some previous resin solidifications resulted in significant heat generation. This heat generation is attributable to the heat of neutralization (acid-base reaction) released by the addition of  $\text{Ca}(\text{OH})_2$  during the solidification procedure if the resins are in the  $\text{H}^+$  form.
- All new resins supplied by AP&L were stable in air to temperatures greatly exceeding the boiling point of water. DSC studies indicated the least thermally stable resin was ARA-9371. All resins will air-oxidize if the temperature is sufficiently great.
- Thermodynamic calculations assuming a representative resin composition, removal of all water at  $100^\circ\text{C}$ , water and carbon as end products of oxidation and utilization of all available oxygen for combustion showed that the reaction rate would be slow. Although oxidation of Cask A resin by either oxygen (air) or by chemical oxidant (such as  $\text{NO}_2^-$  or  $\text{NO}_3^-$ ) would have released sufficient energy to cause the observed exotherm in Cask A,

the initiation of air oxidation of the resins is expected to be kinetically unfavorable under normal conditions of cask dewatering.

- Laboratory-scale dewatering tests gave no evidence of temperature increase. However, Battelle-Northwest believes better results would be obtained using fully-instrumented dewatering tests on actual resin disposal casks.
- The presence of a variety of microorganisms in all cask samples was definitively shown. Furthermore, these microorganisms, or tester organisms believed to have similar characteristics, were shown to be capable of growth under anaerobic conditions, apparently using only residual organics and the sulfonate groups of the resin to support growth. The presence of significant quantities of these microorganisms in Cask A could have been a contributing factor to the exothermic event that occurred either through direct oxidation of the microorganism or its metabolic products. If this oxidation of the microorganism occurred, it may have provided sufficient heat to raise the resin bed to a temperature at which air oxidation of the resin began and continued until the event was detected.

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## INTRODUCTION

Evidence for an exothermic reaction in a bed of dewatered ion exchange resin was observed at Arkansas Nuclear No. One (ANO) on January 15, 1983. A contract was established between Arkansas Power and Light Company (AP&L) and Battelle-Pacific Northwest Laboratories (Battelle-Northwest) to chemically characterize resin samples from this cask and other related sources. This is regarded as Phase I of the study. The final report of Phase I, dated April 22, 1983, did not reveal any unequivocal cause for the exothermic reaction. The report did identify oxygen in air as the most likely oxidant, and stated that additional characterization of the exothermic reaction possibility would require a detailed examination of mechanisms of air oxidation of the resins.

Subsequent to the work described above, additional studies by Battelle-Northwest were authorized by Arkansas Power and Light Company. These additional studies are described in Amendment 1 to BNW Contract No. 2311205862, and are divided into Phase II and Phase III categories.

Phase I studies were conducted on resin samples supplied by Arkansas Power and Light Company, and represented resins from Cask A, Cask B, and Unit 1, T13. Phase II and Phase III studies were conducted on resins obtained in a joint Battelle-Northwest/Arkansas Power and Light Company cask sampling effort; samples of new resins were supplied by Arkansas Power and Light Company.

Studies conducted under the Phase II and Phase III categories have largely been reported in Summary Progress Reports dated October 6, 1983; January 12, 1984; and June 25, 1984. The present final report incorporates the information previously submitted in the Phase I final report, the Summary Progress Reports and also the information obtained in other studies conducted but whose results have not previously been submitted in report form to Arkansas Power and Light Company.

The total studies conducted by Battelle-Northwest included: 1) extensive analytical analyses to determine the cations and anions present in the resin samples submitted by Arkansas Power and Light Company; 2) a determination of whether oxidants, reductants, acids or bases were present in the resin samples; 3) determination of "free" organics; 4) thermal stability of the

resins used by Arkansas Power and Light Company; 5) solidification of resins in cement; 6) an evaluation of microorganism growth in resins; 7) simulated dewatering tests; and 8) a thermodynamic evaluation of resin stability.

The results of the studies indicated above are reported in the following text. The studies did not result in a definitive answer as to the cause of the exothermic event that occurred during resin dewatering. However, the studies have shown that the exothermic event was not caused by "normal" chemical reaction of the resin.

### CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the studies conducted in support of Arkansas Power and Light Company, Battelle-Northwest has concluded the following:

- The exothermic event detected in Cask A was not the result of a "normal" chemical reaction, i.e., reaction caused by strong oxidants such as nitric acid, permanganate, etc.
- Air oxidation is believed to have been the cause of the exothermic event noted in Cask A.
- The presence of significant quantities of microorganisms in Cask A may have provided the source of easily oxidized material that initiated the exothermic event.

Some comments on air oxidation of resins may also be made.

- Air oxidation of the resins themselves is not expected to occur during cask dewatering except in very unusual circumstances. The presence of significant quantities of microorganisms may have provided the conditions necessary to initiate the exothermic event detected in Cask A. The presence of certain metal ions, particularly Cu and Fe, are also known to promote the ease of oxidation and the presence of significant quantities of these ions loaded on the resin sites may also have contributed to the initiation of resin oxidation.
- Air oxidation of the resins is not expected to result in a "runaway" reaction under normal cask dewatering conditions. This is supported by the thermodynamic calculations used to predict the length of time required to reach the temperatures believed necessary to cause the degree of resin degradation found in Cask A after the exothermic event. Thus, temperature monitoring of the resin bed during cask dewatering should give adequate information to determine if heat generation is occurring and the reaction could then be terminated by refilling the resin bed with water.

The studies conducted by Battelle-Northwest and the information supplied by AP&L indicate several "unusual" aspects related to the resin contained in Cask A. First, the resin in Cask A had been in a resin holding tank for several years and was not easily removed from the holding tank. Second, a strong odor, similar to that normally associated with anaerobic microbial growth (e.g., septic tank) was present during the load-out of the resin into Cask A and during the dewatering of Cask A. Third, unequivocal evidence of the presence of several types of microbial organisms capable of sustained growth on the resin in Cask A under anaerobic conditions was obtained. Both the greater than normal time for dewatering and the difficulty in removing the resin from the holding tank may have resulted from microbial growth in the resin. Thus, it is our conclusion that these "unusual" aspects may be "indicators" of extensive microbial growth in the resin contained in Cask A and that the presence of these microorganisms resulted in conditions favorable to air oxidation, thereby resulting in the exothermic event detected in Cask A on January 15, 1983.

It is Battelle-Northwest's recommendation that fully instrumented temperature monitoring of cask dewatering be conducted as a means of assuring early detection of excessive heat generation in the resin bed as a result of resin oxidation during dewatering. As previously mentioned, normal cask dewatering conditions are not expected to result in "runaway" air oxidation of the resins; any excessive heat generation in the resin bed as a result of air oxidation should be easily terminated by discontinuing air flow and refilling the cask with water.

## REVIEW OF PHASE I RESULTS

A mixed-bed organic ion exchange disposal liner designated Cask A, was dewatered for the 6th cycle on January 15, 1983, at Arkansas Power and Light Company, Arkansas Nuclear No. One, Russellville, Arkansas. Eight hours after the 6th cycle dewatering, steam was observed coming from the cask and liner. The resin in the cask had been collecting on the bottom of a spent resin holding tank for approximately 4 years prior to its removal and loading of the cask. AP&L assumed the resin was ARA-9371 (anion) and ARC-9358 (cation). A second resin disposal cask, designated Cask B, also contained resin from the same spent resin holding tank, but had only been partially dewatered and had not exhibited an exotherm.

To determine the probable cause of the exothermic reaction in Cask A, AP&L requested that Battelle-Northwest analyze the resins in Casks A and B to determine the oxidizing agents present (i.e., nitrates, chlorine, chlorates), test samples of Cask A resin taken before and after steam release, and determine if the samples of resin submitted would exhibit similar reactions and heat release.

Battelle-Northwest suggested a variety of analytical approaches to identify the cause of the exothermic reaction, including titration of resin samples with reducing-oxidizing agents to observe mV changes, analyzing for "free" organics, conducting acid-base titrations of the resins, determining enthalpy differences, and complete cation and anion analyses. Specific methods proposed for characterization were to be selected after receipt of the samples and modified if the above methods were not beneficial.

## SUMMARY OF PHASE I RESULTS

Laboratory experiments and analyses were conducted to determine the probable cause of the exothermic reaction in an Arkansas Power and Light Company dewatered resin cask and liner. No unequivocal cause for the exothermic reaction was determined after exhaustive chemical analyses of the Cask A resins and associated water. Resin from Cask A taken before the exotherm, resin from Cask B which was only partially dewatered at the time of the incident, and resin from Unit I, T13, were also tested.

Battelle-Northwest's investigation included a thorough physical review of each sample upon receipt; photographs of each sample; chemical analyses of the resins and water samples to determine the cation and anion content; a systematic search for organics, hydrazine, and citric acid contamination of the resins and water; a study to determine the thermal stability of the resins as received and of new resin loaded with suspected chemical initiators; a review of chemical oxidants and their possible impact on initiating an exothermic reaction; and an investigation to determine if oxidants were associated with the resins at the time of the exothermic reaction.

The information obtained can be summarized as follows:

- Cask A samples taken during and after the exothermic reaction contained mixtures of macroporous and gel-type resins. Cask A samples taken prior to the exotherm and samples from Unit I, T13 contained only gel-type resin.
- Samples from Cask A taken during the exotherm contained  $\text{Fe}_2\text{O}_3$  solids, some of which had such a small particle size that the sample looked like a red solution. No red solids were found in Cask A samples taken after the exotherm. The solids, if present prior to dewatering, may have contributed to the unusually large number of dewatering cycles required (6 vs. 3) to complete the dewatering cycle.
- Cask A resin was badly damaged and had released large amounts of sulfate and ammonium ion into the aqueous solution. Unusually large amounts of Fe, Cu, and  $\text{Cl}^-$  and other ions were found in the Cask A resin as compared to resins from Cask B and Unit I, T13.
- No alcohols, citric acid, hydrazine or aromatic compounds were found on the Cask A resin or in solution.
- Differential scanning calorimetric analyses of the AP&L resins in air showed no exothermic reaction which alone could have caused the incident.

New gel-type resins loaded with suspected initiators ( $\text{NO}_2^-$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ) failed to cause an exotherm of unusual nature.  $\text{Cu}^{2+}$  is a well-known catalyst for redox reactions particularly where  $\text{O}_2$  is an oxidant.<sup>(a)</sup> Anion resin (ARA-9371) was found to be stable to about 200°C, at which temperature an exothermic reaction occurred. The cation resin (ARC-9358) was stable to 310°C.

- No oxidants were detected in sufficient quantity in the resins to cause the resin destruction observed in Cask A or even cause a temperature rise of greater than about 10°C, if they had reacted completely with the resin.

#### PHASE I CONCLUSIONS

No unequivocal cause for the exothermic reaction was determined. No components were found, other than the resin itself (in combination with oxygen from the air), which would provide enough energy to cause the observed exothermic reaction, and the resin did not react exothermically under the conditions examined in this study. Until the mechanism is determined, it is not possible to specify which component or components need to be characterized to assure safety.

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(a) Basolo, F. and R. G. Pearson. 1967. Mechanisms of Inorganic Reactions 2nd ed. p. 500. Wiley. New York.

## PHASE II STUDIES

Five ion exchange resin disposal casks designated Casks A, B, C, D, and E located at Arkansas Power and Light Company, Arkansas Nuclear No. One, contained resin removed during cleanout of the resin storage tank. The objective of the Phase II studies was to provide data to support AP&L decisions regarding offsite shipment and disposal of the resin contained in the five casks located at ANO. The specific work conducted under Phase II included: 1) sampling of resin casks and discussions at ANO; 2) laboratory solidification of cask resins in cement; 3) investigation of the role of supplied air; 4) studies of the reactions at elevated temperatures (thermal analysis studies); 5) identification of organics present and, 6) simulated dewatering tests.

### SAMPLING AND DISCUSSIONS AT AP&L

Battelle-Northwest personnel, L. G. Morgan and J. L. Ryan, traveled to Arkansas Nuclear No. One on July 31, 1983, and remained at the site through August 4, 1983.

The primary purpose of the visit was to observe/participate in obtaining core samples of each of five ion exchange resin disposal casks present at ANO. These five disposal casks contained resin removed from the plant's radwaste spent resin storage tank during cleanout operations. Removal of some of the resin required the use of very high pressure water streams. Cask A, the cask that experienced the exothermic event detected on January 15, 1983, was the first of the five casks to be loaded with spent resin during the cleanout of the resin storage tank, and was the only cask to have completed dewatering.

In addition, during the visit Battelle-Northwest personnel discussed the exothermic event with all personnel involved in the event and ANO's subsequent operations. They also became much more familiar with ANO's plant operations related to all ion exchange resin systems, with particular emphasis given the radwaste system.

Prior to the trip to the ANO site, Battelle-Northwest personnel designed and constructed a core sampling device for use in obtaining resin samples from each of the five casks described above. The core sampler was brought to ANO by Morgan and Ryan and was used to obtain the desired resin samples. The core sampler was left at the ANO site after its use.

Resin samples obtained from Casks A, B, C, D, and E contain resins whose identity is unknown; i.e., the manufacturer and resin-type (anion or cation) is not known. It was possible to determine approximate volume ratios of gel and macroreticular resins in the casks. Descriptions of the cask resins and of their visual microscopic examination are given as Appendix A of this report.

The acquisition of the samples and the information obtained during the site visit concluded this aspect of the Phase II studies. The significant results of this portion of the Phase II studies are given below.

- Battelle-Northwest is satisfied the resin samples obtained from each cask are representative samples and adequately describe the contents of each cask. Thus, prediction of cask behavior made as a result of studies on the resin samples obtained should be valid. No one should be able to question any prediction on the basis of inadequate sampling of the casks.
- Discussions at ANO resulted in Battelle-Northwest being fairly confident that the exothermic event was not the result of what will be designated "operator error." Items of concern prior to the visit included the possibility of inadvertent dumping of strong oxidants such as nitric acid into the resin storage tank or the cask, the use of very hot air (such as might be obtained from portable space heaters) during dewatering of Cask A, and severe resin degradation because of high radiation levels. Battelle-Northwest found no indication of "operator error." In fact, plant operations essentially preclude most of the concerns regarding "operator error" that Battelle-Northwest personnel had prior to the visit.
- Discussions at ANO resulted in Battelle-Northwest being able to define the known history of the resins contained in each cask. Detailed information concerning the dewatering and solidification processes used

for resins at ANO was also obtained. These aspects become more important when combined with results obtained under other categories, such as "Role of Supplied Air."

#### SOLIDIFICATION OF ION EXCHANGE RESINS

Five ion exchange resin disposal casks, designated Casks A, B, C, D, and E, located at Arkansas Power and Light, Arkansas Nuclear No. One, contained resin removed during cleanout of the resin storage tank. Cask A, the cask that experienced the exothermic event detected on January 15, 1983, was the first of the five casks to be loaded with spent resin and was the only cask to have completed dewatering. Solidification and subsequent disposal of the ion exchange resins contained in the five casks was an option available to ANO if laboratory studies of the solidification process indicated no unusual or unexpected temperature behavior. Battelle-Northwest conducted instrumented solidification tests on a laboratory scale and concluded that no excessive temperature increases would be experienced in solidification of the resins contained in Casks A, B, C, D, and E using the CHEM-NUCLEAR SYSTEMS INC. (CNSI) solidification procedure. The laboratory-scale resin solidification studies conducted by Battelle-Northwest are described in the following text.

ANO requested that Battelle-Northwest conduct the laboratory solidification tests in accordance with the procedures used by CNSI. The CNSI solidification procedure is proprietary to CNSI and was provided to Battelle-Northwest by ANO. Written permission to provide Battelle-Northwest with the CNSI procedure was given by CNSI to ANO for the purpose of conducting the laboratory solidification tests. A copy of the CNSI solidification test procedure is provided as Appendix B of this report. No further dissemination of the CNSI procedure should be made without written permission of CNSI.

Battelle-Northwest modified and expanded the CNSI procedure for the purposes of the instrumented laboratory studies. Modification consisted primarily of not placing the cement-resin mixture in an oven but rather in an instrumented dewar for temperature monitoring. A complete description of the laboratory resin solidification procedures used by Battelle-Northwest is given in this report as Appendix C.

Laboratory-scale solidification tests were completed for the following ion exchange resins obtained from AP&L, ANO site: A101D, C20-H, RWA-78, Rohm and Haas 200C, ARA-9371, Mixed 150 L/C, Rohm and Haas 900C, ARC-9358, and samples representing the contents of Casks A, B, C, D, and E.

The numerically designated resins were resins supplied to Battelle-Northwest by AP&L and whose designations correspond to those on the sample containers as received by Battelle-Northwest. It is Battelle-Northwest's understanding that these resins are "as supplied" to AP&L by the various manufacturers. No treatment of the resins other than that described in the laboratory solidification procedures was done by Battelle-Northwest. Brief descriptions of these resins are given in this report as Appendix D.

Solidification of both new and cask resins was conducted in accordance with the procedures given in Appendix C. Additions of  $\text{Ca(OH)}_2$  to some of the new resin slurries generated heat. The increase in temperature indicated that the new resin was in the hydrogen-form and a simple acid-base neutralization reaction occurred, releasing the heat of neutralization. No increase in temperature was found when  $\text{Ca(OH)}_2$  was added to the actual cask resins, thereby indicating that no significant amount of hydrogen-form resin remained. Any resin in the casks that was originally in the hydrogen-form had already been converted to some other cation form before being loaded into the cask. Consequently, new resin samples that showed an increase in temperature when  $\text{Ca(OH)}_2$  was added were allowed to return to ambient temperature before addition of cement and temperature monitoring of the solidification process.

#### Solidification Test Results

Summary data of the solidification tests are given in Table 1. Temperature vs. time plots are also given for each test in Figures 1-14.

#### Heats of Solidification and Heat Capacities of Solidified Resin Samples

The experimental heats of solidification for the resins were determined, as were the experimental heat capacities of the solidified resin samples. The results of these studies indicated that the heats of solidification were less than values reported for "normal" cement solidification. Experimental details are given in Appendix E.

TABLE 1. Resin Solidification Test Results

<u>Type of Resin</u>	<u>Test No. 1</u> Diamond Shamrock A101D as recvd	<u>Test No. 2</u> Diamond Shamrock C20-H as recvd	<u>Test No. 3</u> RWA-78 as recvd	<u>Test No. 4</u> Rohm & Haas 200C as recvd	<u>Test No. 5</u> ARA-9371 as recvd	<u>Test No. 6</u> Mixed 150L/C as recvd	<u>Test No. 7</u> Rohm & Haas 900C as recvd
Weight of 100 ml of settled and then "dewatered" resin	72.9 g	79.7 g	72.7 g	90.0 g	73.8 g	77.0 g	69.7 g
Weight of water in solidification beaker	35.9 g	33.3 g	33.9 g	34.0 g	34.7 g	32.4 g	39.5 g
Initial pH of resin slurry	5.5	5.0	5.5	5.5	6.0	5.5	5.5
Final pH of resin slurry	13.0	12.5	13.0	13.0	12.5	12.5	12.5
Weight of Ca(OH) <sub>2</sub> added	5.0	9.0	5.0	5.0	5.0	5.0	5.0
Temperature after Ca(OH) <sub>2</sub> addition	*	*	*	*	*	*	*
Weight of cement added	107.7	119.7	87.3	87.1	115.9	112.7	87.4
Temperature after cement addition	23.2°C	22.8°C**	22.6°C	22.8°C	24.2°C	23.4°C	*
Maximum temperature observed	29.0 °C	27.0°C	23.5°C	25.8°C	26.6°C	29.6°C	25.5°C

\* Not Observed

\*\*After return to ambient temperature prior to cement addition

TABLE 1. Resin Solidification Test Results - Con't

Type of Resin	Test No. 8	Test No. 9	Test No.10	Test No.11	Test No.12	Test No.13	Test No.14
	ARC-9358 as recvd	Cask A/Core1 Smple 1,1/3 Smple 2,1/3 Smple 3,1/3	Cask A/Core2 Smple 1, 1/8 Smple 2, 7/8	Cask B Represent. Sample	Cask C Represent. Sample	Cask D Btm 6" 1/8; Represent. Smple, 7/8	Cask E/Core1 Smple 1, 1/4 Smple 2, 3/4
Weight of 100 ml of settled and then "dewatered" resin	82.4 g	78.0 g	79.4 g	79.2 g	80.9 g	79.9 g	85.8 g
Weight of water in solidification beaker	31.6 g	40.4 g	31.4 g	32.7 g	32.9 g	34.2 g	30.0 g
Initial pH of resin slurry	5.5	5.5	5.5	5.5	5.5	5.5	5.5
Final pH of resin slurry	12.5	12.5	12.5	12.5	13.0	13.0	12.5
Weight of Ca(OH) <sub>2</sub> added	11.0	5.0	5.0	5.0	5.0	5.0	5.0
Temperature after Ca(OH) <sub>2</sub> addition	*	21.0°C	21.0°C	21.0°C	21.0°C	21.0°C	21.0°C
Weight of cement added	115.6	88.5	95.9	97.6	100.5	95.6	84.9
Temperature after cement addition	23.6°C	21.8°C	21.6°C	21.0°C	21.6°C	21.8°C	23.2°C
Maximum temperature observed	24.9°C	24.0°C	23.8°C	22.4°C	22.4°C	22.4°C	23.8°C

\* Not Observed

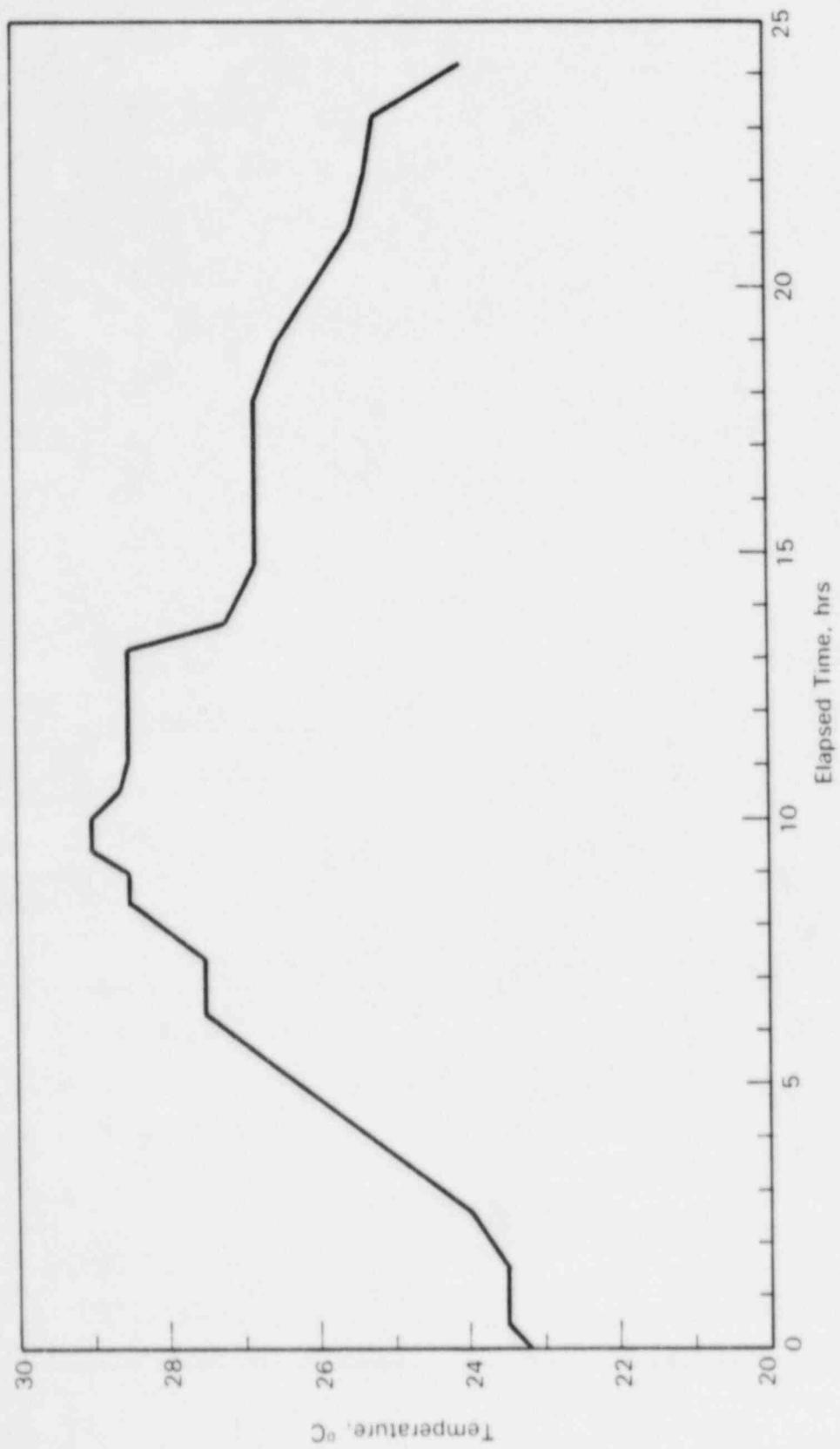


FIGURE 1. Temperature Profile for Cement Solidification of Diamond Shamrock A101D

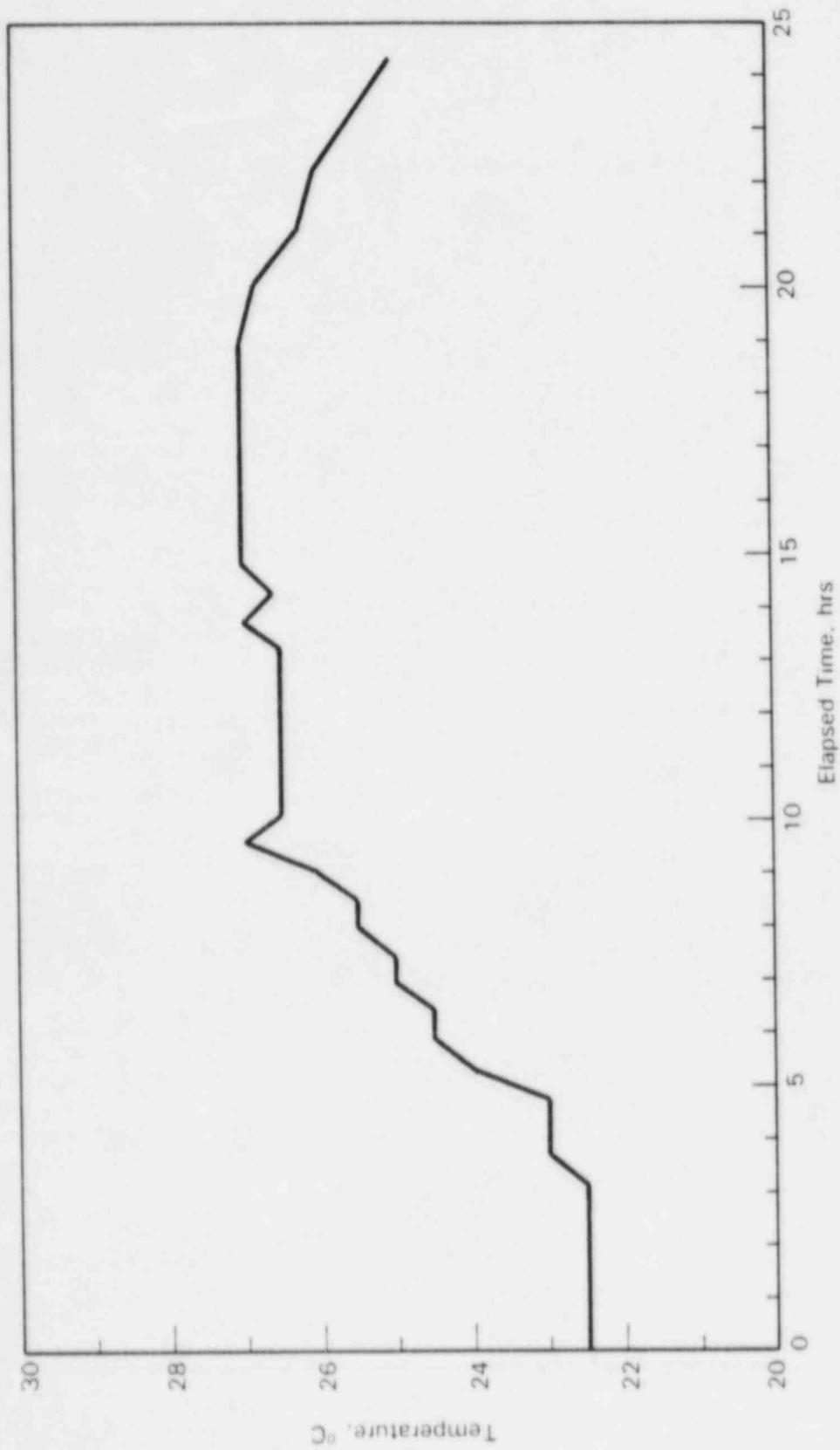


FIGURE 2. Temperature Profile for Cement Solidification of Diamond Shamrock C20-H

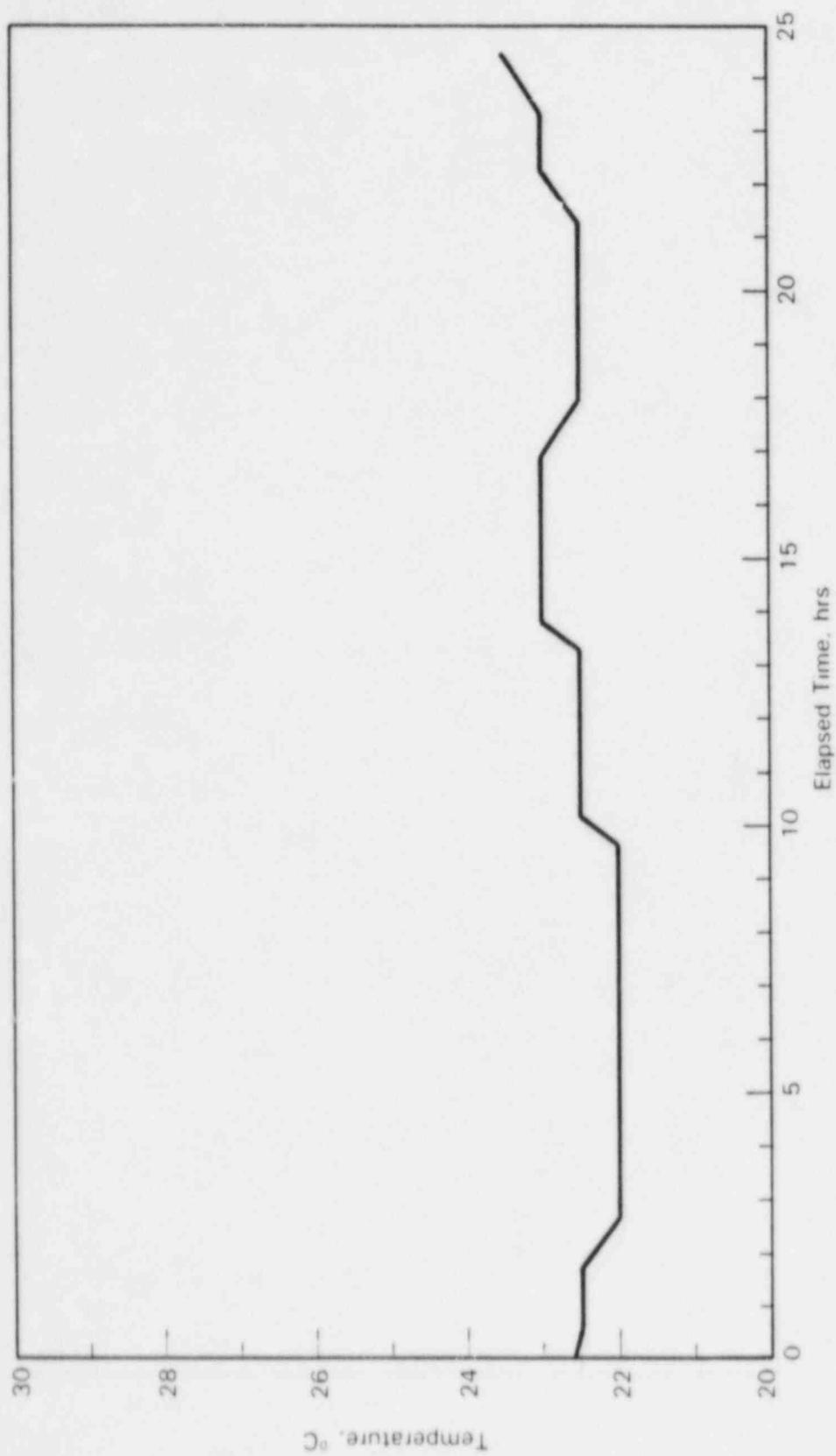


FIGURE 3. Temperature Profile for Cement Solidification of RWA-78

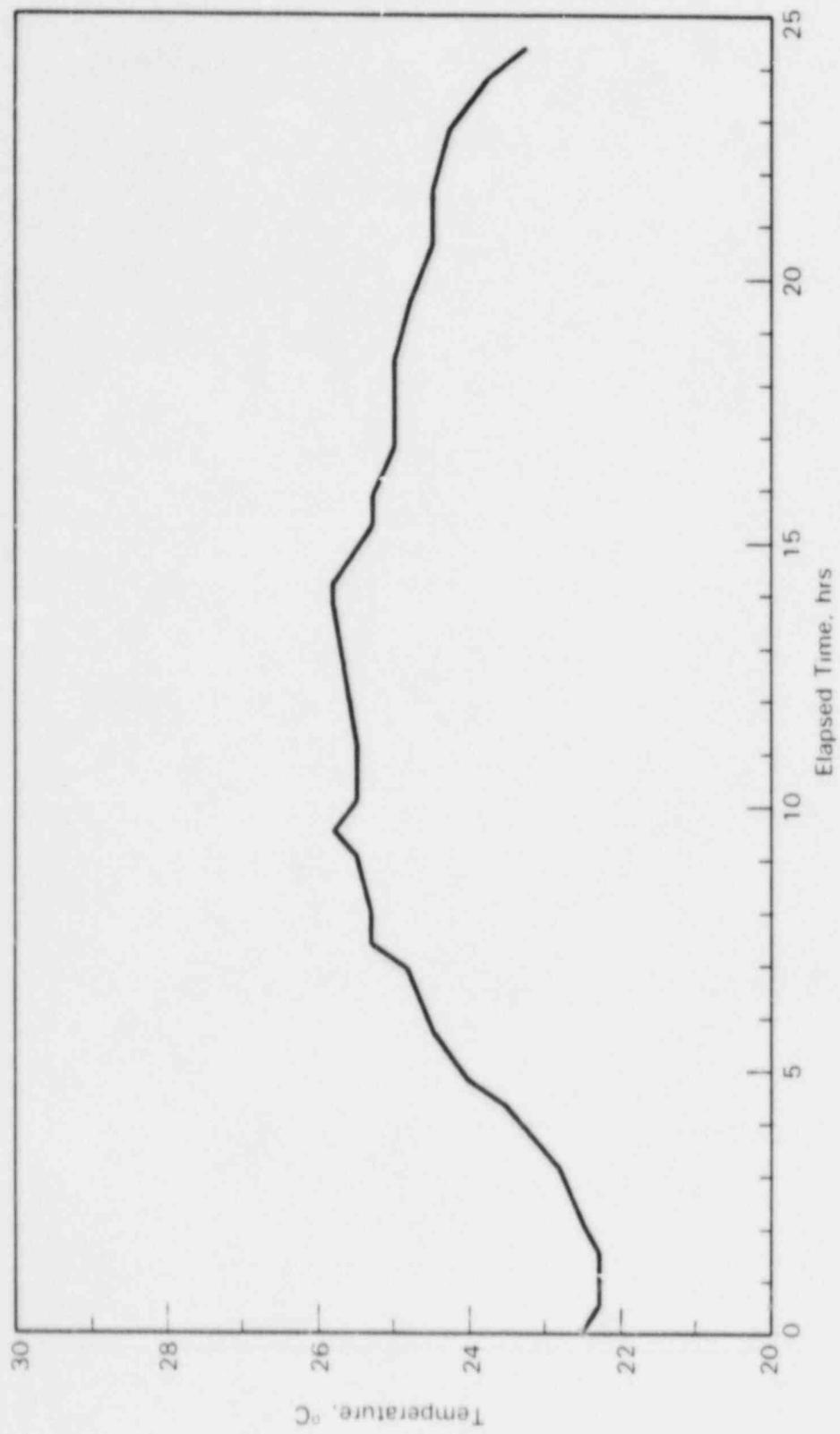


FIGURE 4. Temperature Profile for Cement Solidification of Rohm & Haas 200C

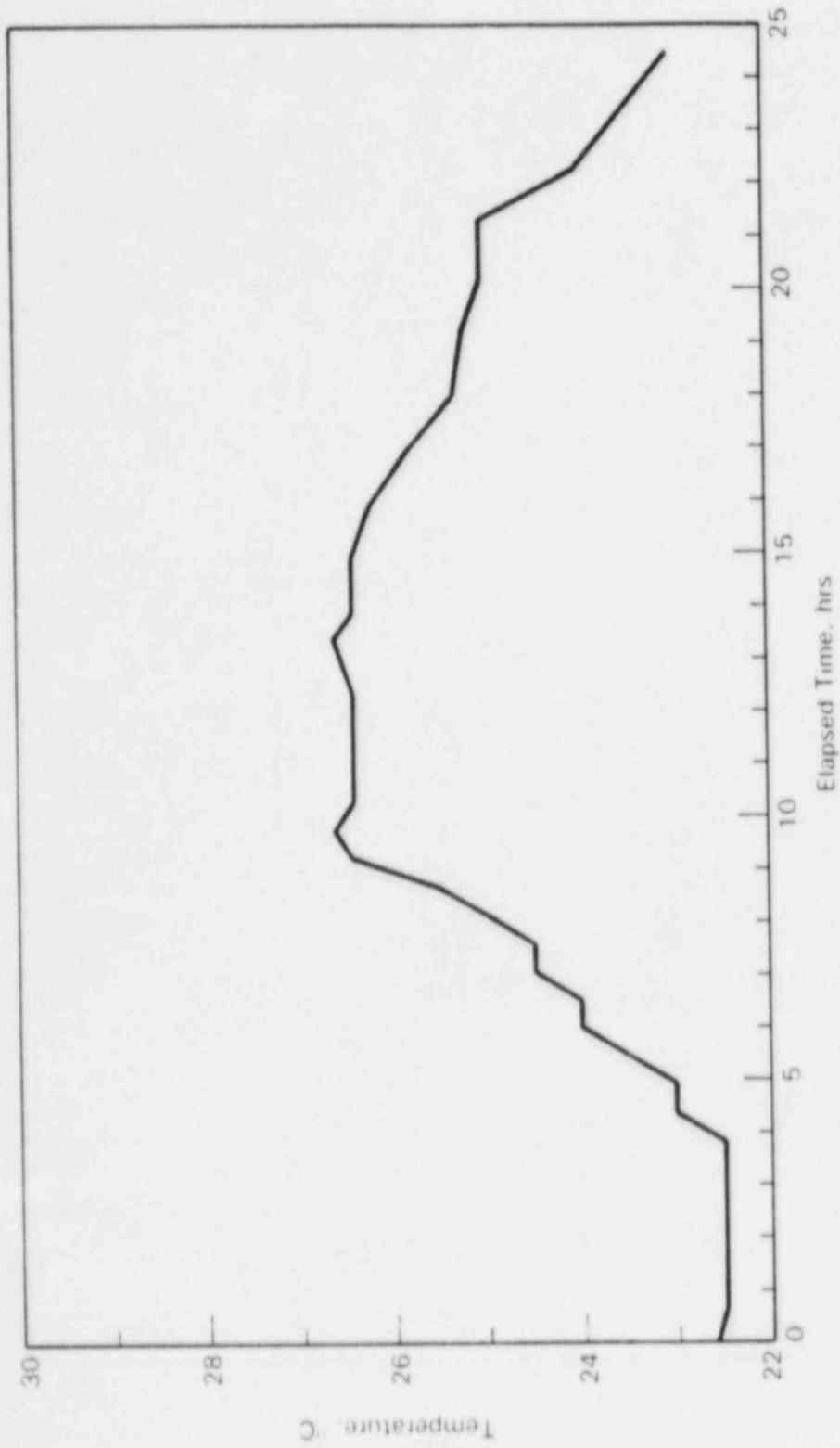


FIGURE 5. Temperature Profile for Cement Solidification of ARA-9371

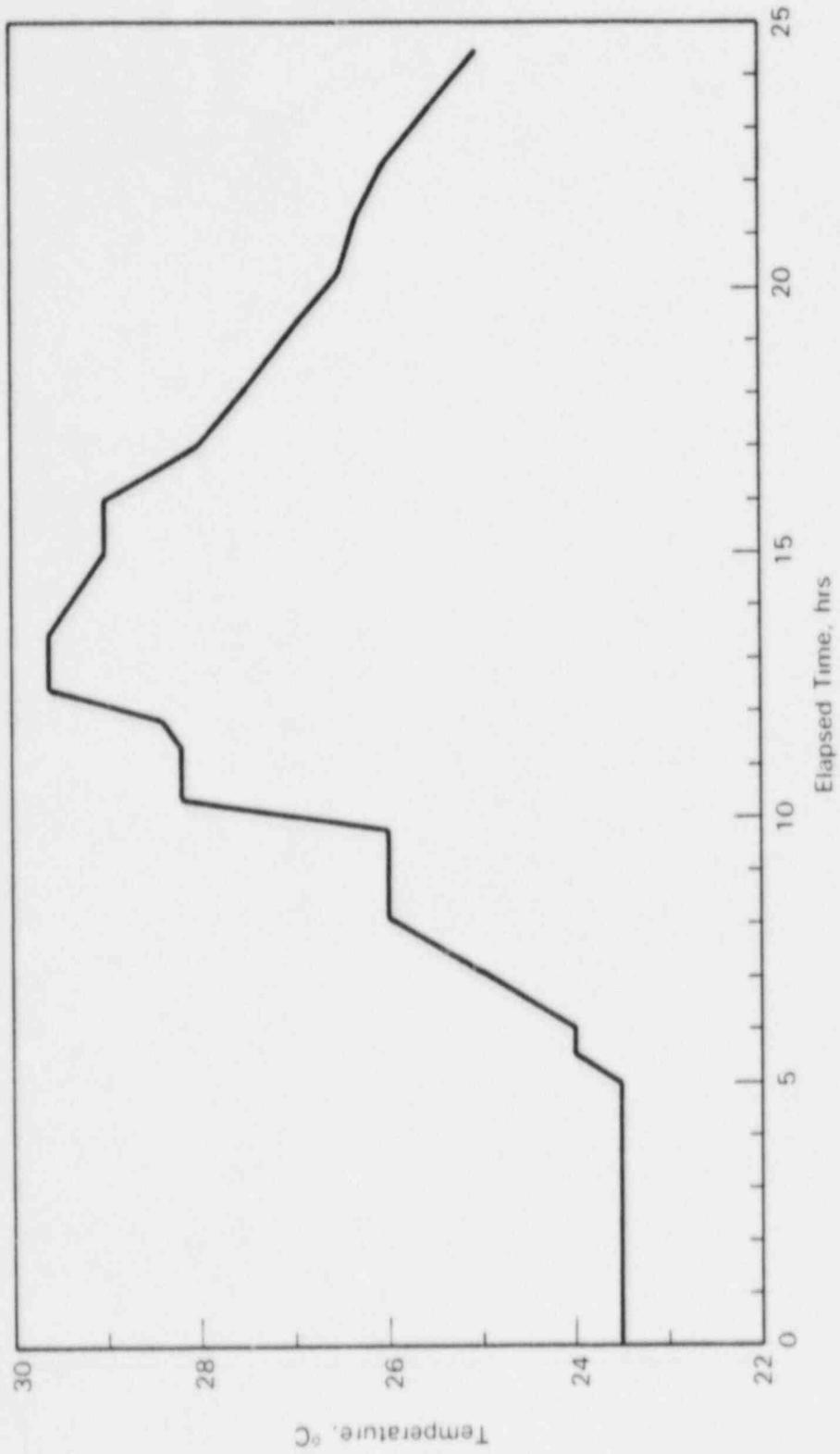


FIGURE 6. Temperature Profile for Cement Solidification of Mixed 150 L/C

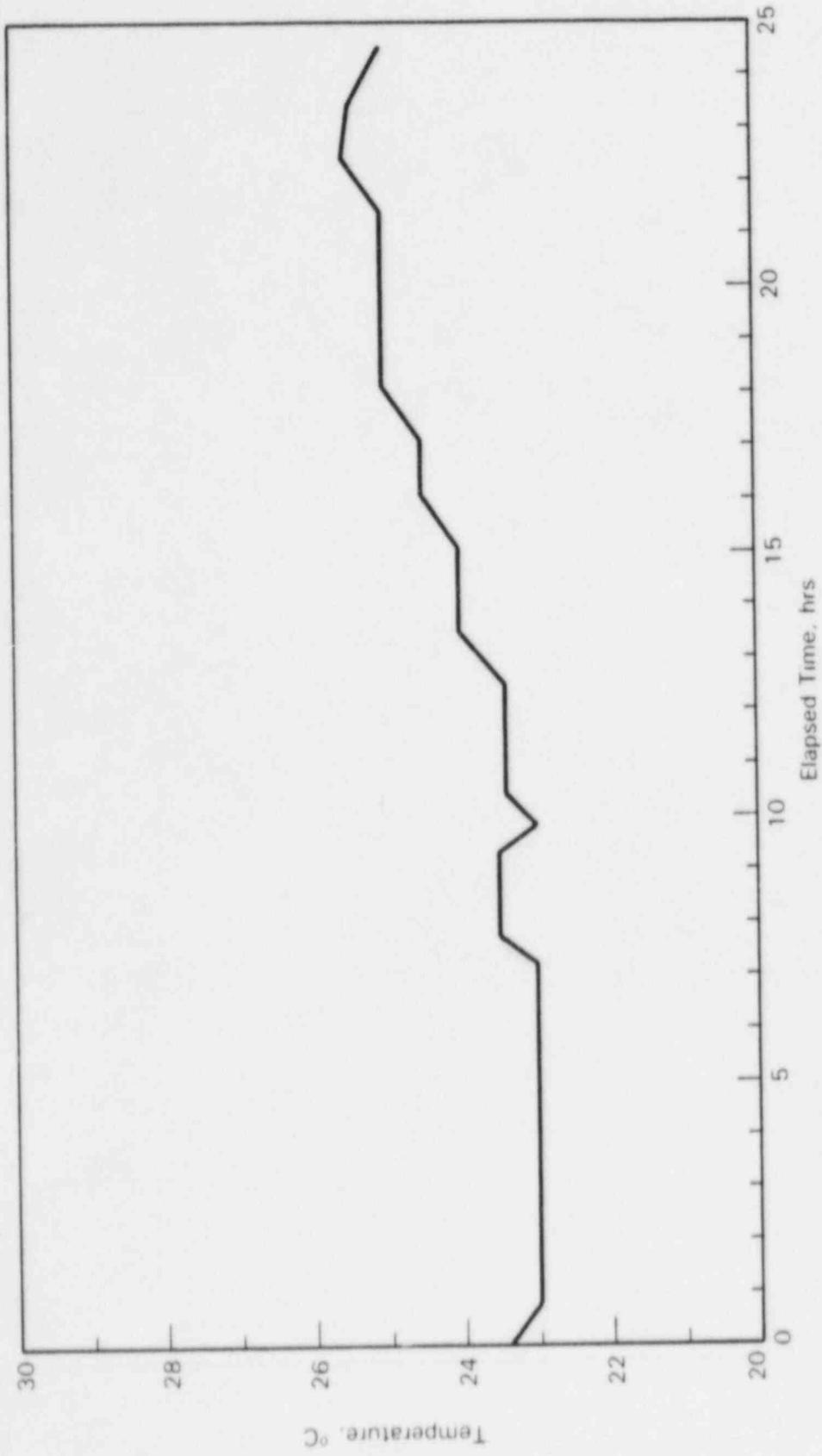


FIGURE 7. Temperature Profile for Cement Solidification of Rohm & Haas 900C

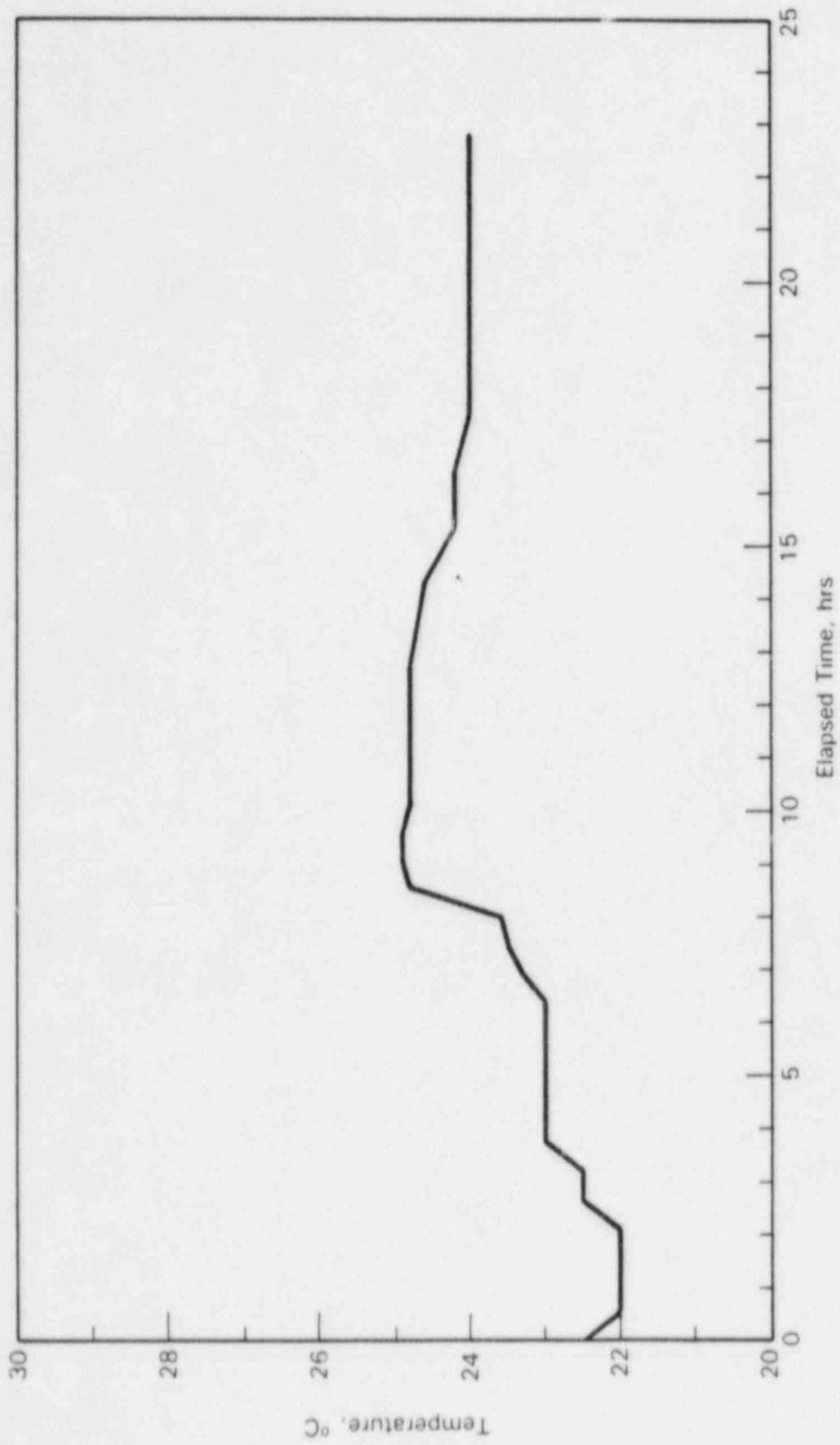


FIGURE 8. Temperature Profile for Cement Solidification of ARC-9358

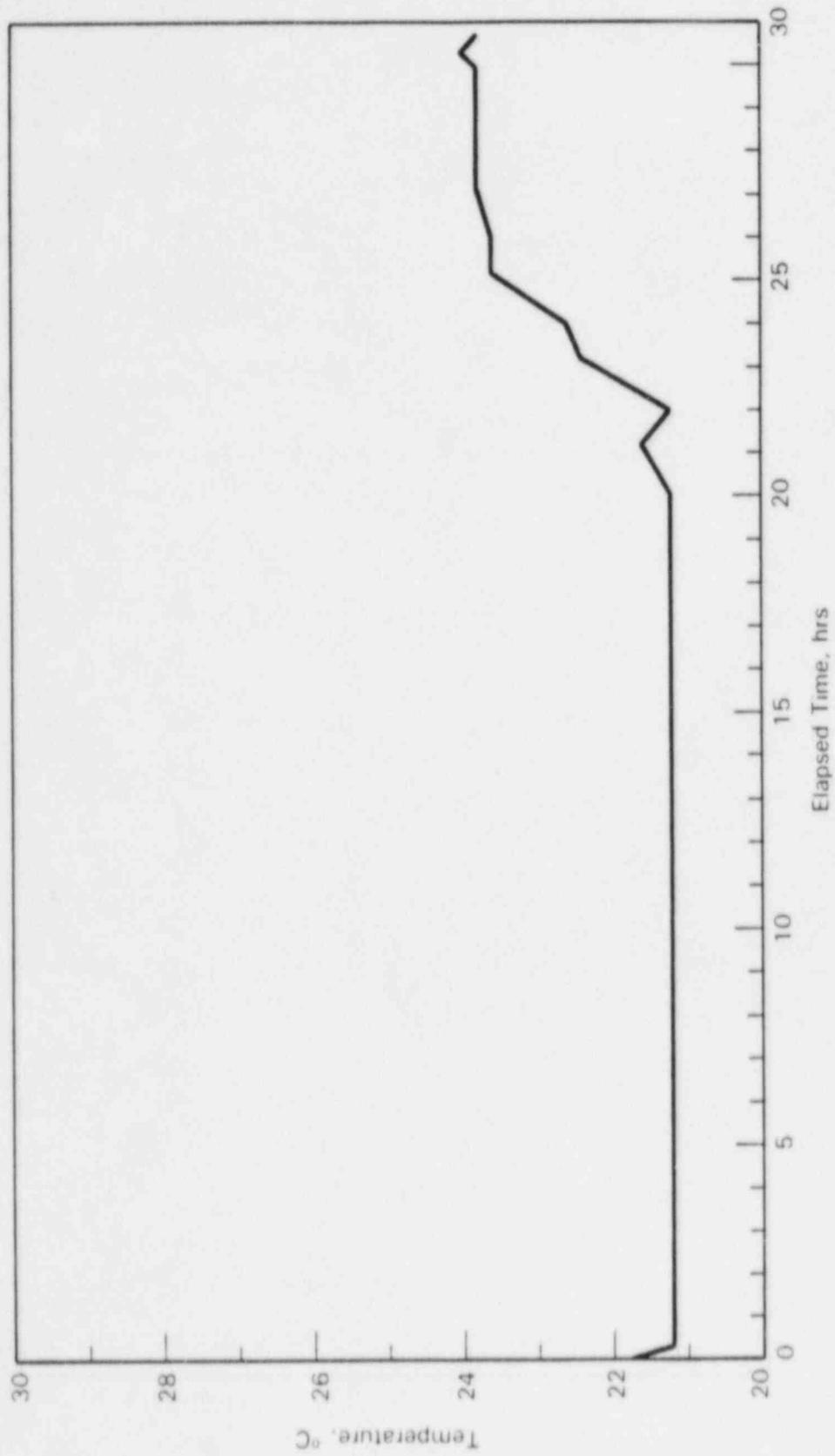


FIGURE 9. Temperature Profile for Cement Solidification of Cask A, Core #1

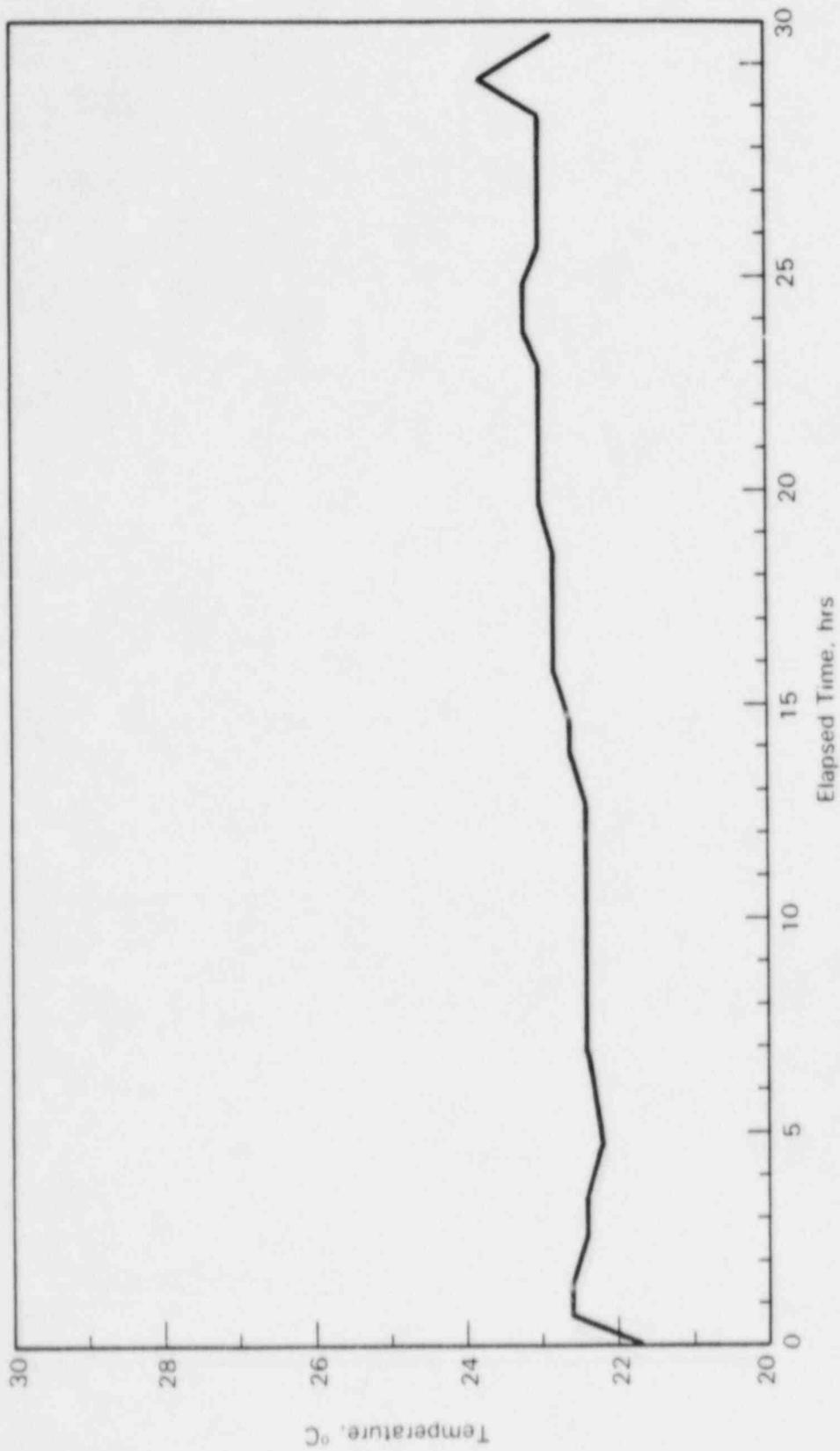


FIGURE 10. Temperature Profile for Cement Solidification of Cask A, Core #2

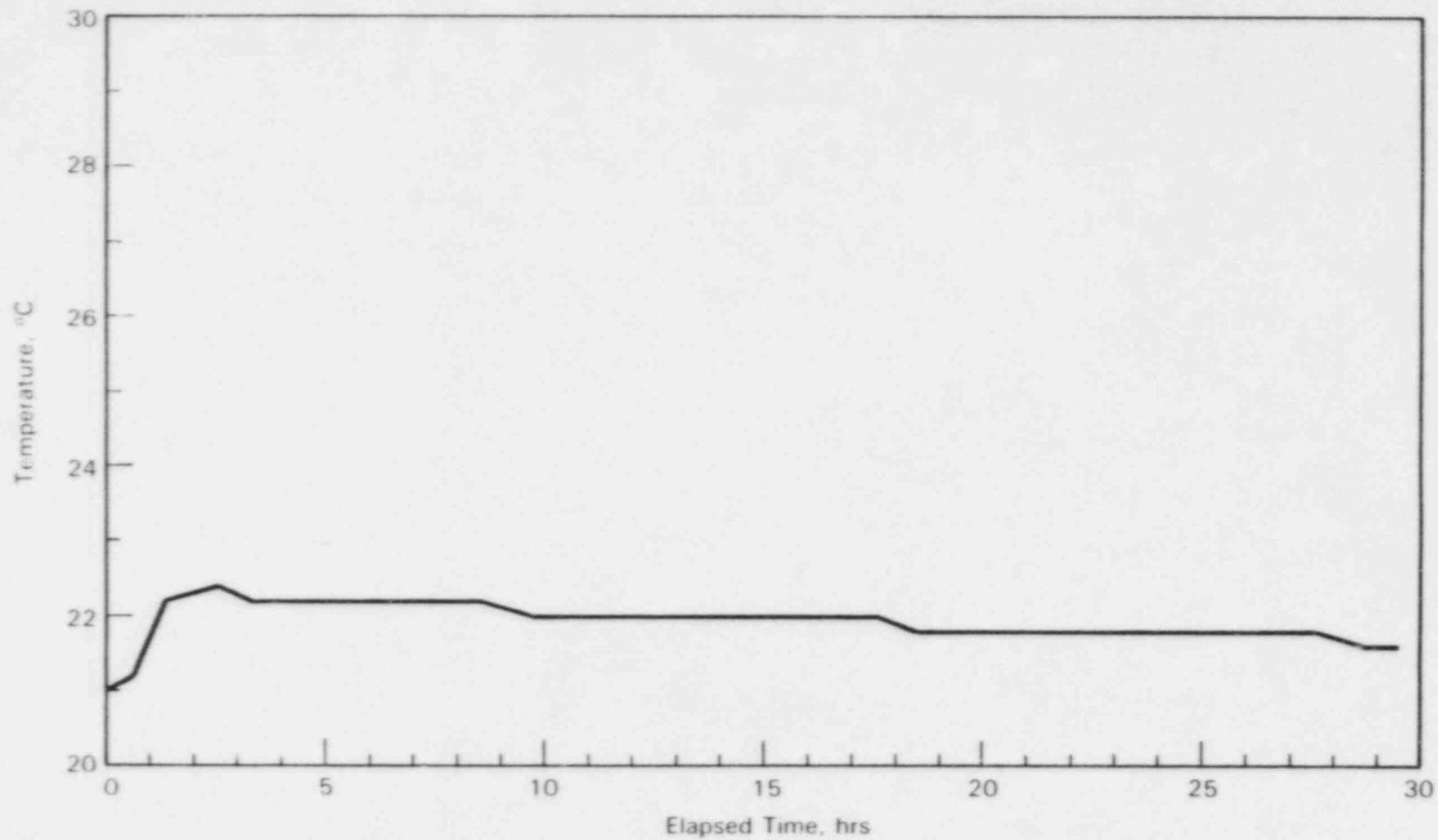


FIGURE 11. Temperature Profile for Cement Solidification of Cask B Representative Sample

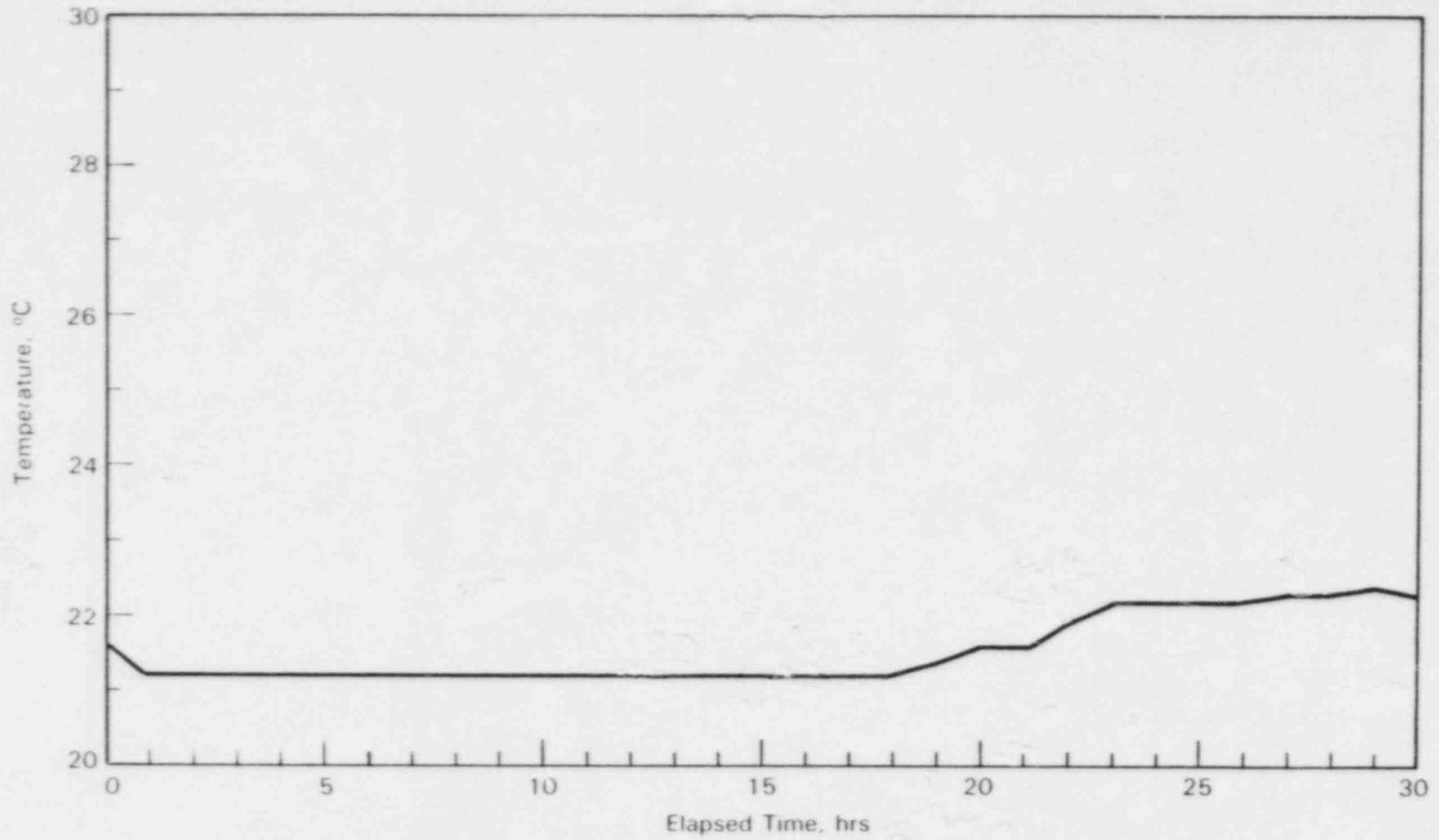


FIGURE 12. Temperature Profile for Cement Solidification of Cask C Representative Sample

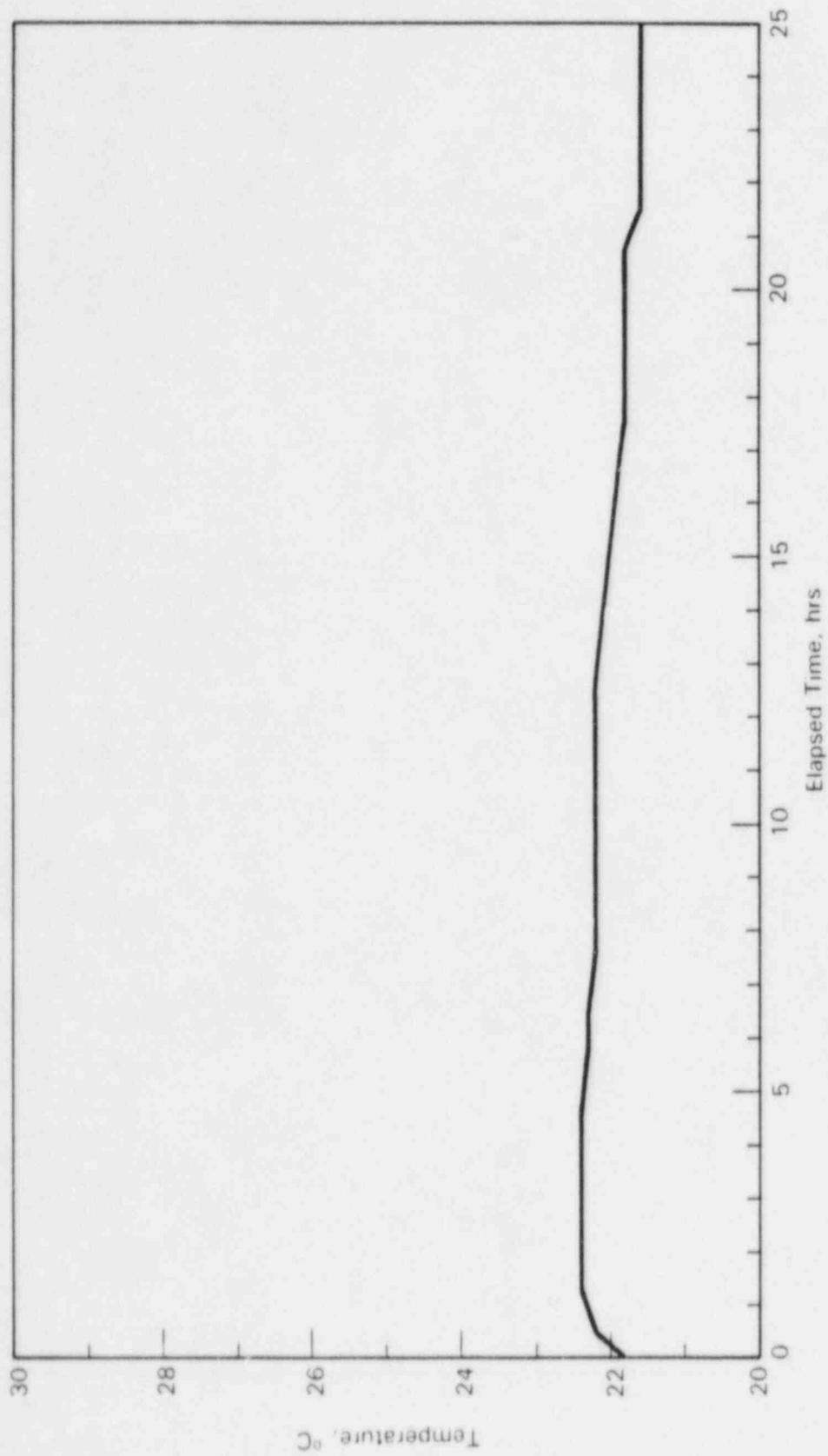


FIGURE 13. Temperature Profile for Cement Solidification of Cask D1 (1/8) and D2 (7/8)

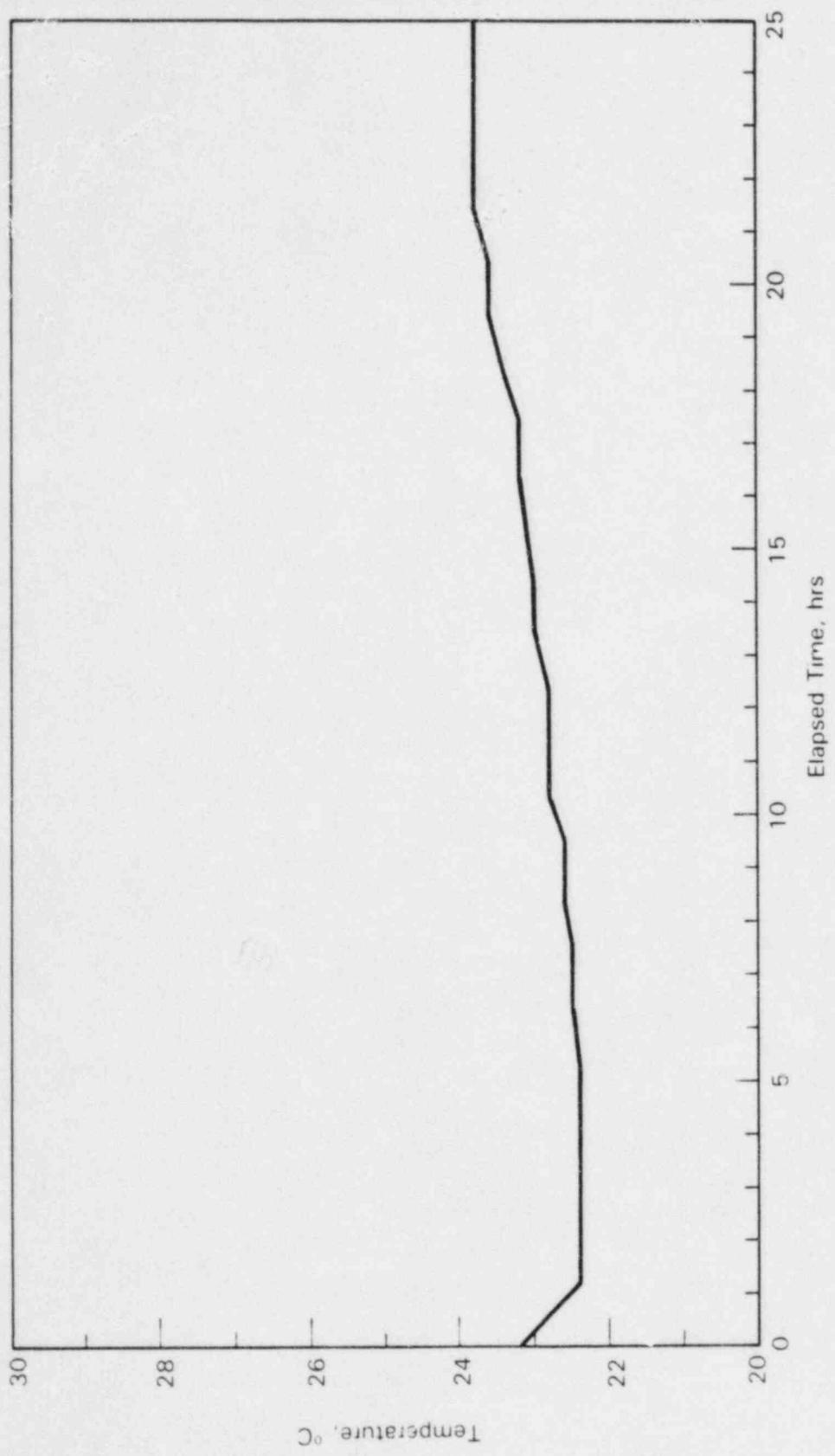


FIGURE 14. Temperature Profile for Cement Solidification of Cask E, Core #1

The heat capacity of cement solidified resin samples was measured using Differential Scanning Calorimetry (DSC) and found to be within the range reported for normal cement samples<sup>(a)</sup>. Samples from the solidification study using Diamond Shamrock C20-H and Rohm & Haas 200C resins had heat capacities of 0.222 cal/g/deg and 0.312 cal/g/deg, respectively.

The heats of solidification were calculated using

$$\Delta H (\text{solidification}) = \Delta H (\text{system}) + C_p \Delta T$$

where

$\Delta H (\text{system})$  = amount of heat lost to the system

and

$C_p \Delta T$  is the enthalpy change of the cement-solidified resin

The experimentally determined heat capacity values reported above (from DSC studies) and the heat loss to the system used for solidification of the cask resins result in a  $\Delta H (\text{solidification})$  range of 21.8 cal/g to 22.0 cal/g, for solidification Test No. 9 (Cask A, Core 1). Similar values are obtained for all the other tests. Lea<sup>(a)</sup> reports heats of hydration for "normal" cement of 61 cal/g at 3 days of curing, 79 cal/g at 7 days of curing, and 96 cal/g at 28 days curing. "Normal" cement was not defined by Lea<sup>(a)</sup>. Variations of water/cement ratios (0.4 to 0.6) can change the heat values by 10-15%, and the type of cement can change the heat values by 15-30%. The experimental values are 21-57% lower than reported values<sup>(a)</sup> based on the heat of hydration for 3 days of curing and therefore indicate no reason for concern regarding the heat of solidification of both new resin- and cask-cement

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(a) Lea, F.M. 1971. The Chemistry of Cement and Concrete, 3rd ed. Chem. Pub. Co., Inc., New York.

compositions. Any major exothermic enthalpy change other than the heat of hydration would have been detected.

#### Discussion of Resin Solidification Studies

The instrumented solidification studies indicated no significant differences in behavior between new and cask resins supplied by AP&L. Slight variations in the maximum temperatures obtained are within the deviations expected for this type of study.

No hazardous or unexpected exothermic reactions were noted in any of the solidification tests. The maximum temperatures obtained for the cask samples were: Cask A, Test #9, 24.0°C after 30 hours; Cask A, Test #10, 23.8°C after 30 hours; Cask B, Test #11, 22.4°C after 2.5 hours; Cask C, Test #12, 22.4°C after 29 hours; Cask D, Test #13, 22.4°C after 1 hour; and Cask E, Test #14, 23.8°C after 21 hours. Ambient air temperature was approximately 21°C. These temperatures are more than 100°C less than those noted to cause visual changes in appearance of the new resins supplied by AP&L and more than 200°C less than the temperature required to cause visible resin degradation.

The data reported above for the actual cask resins resulted in an experimental heat of solidification for Cask A, Test #9, of ~22 cal/g. This value is less than that found in the literature for the heat of hydration of "normal" cement. The calorimetric cells have a fairly high rate of heat loss and this contributes to the error of long-term experiments. However, the significant fact to note is that there was essentially no difference in the solidification behavior of new and cask resins.

Based on the laboratory resin solidification tests, Battelle-Northwest predicted no excessive temperature increases would be experienced in solidification of the resins contained in Casks A, B, C, D, and E using the CNSI procedure. No significant temperature differences between lab-scale and full-scale tests are expected.

In addition, solidification excludes oxygen from the resin. As stated in the Phase I report, we believe oxygen was the oxidant necessary for the exotherm noted in Cask A in January 1983.

## ROLE OF SUPPLIED AIR

Battelle-Northwest postulated at the conclusion of Phase I that oxygen (in the air) was the oxidant necessary for the exothermic event in Cask A. Phase II studies in this category further addressed this question using both thermodynamic calculations based on assumed reactions and correlation of resin degradation with temperature. The significant results obtained are:

- Phase I studies gave no evidence of strong oxidants being present in either Cask A or Cask B in sufficient quantity to be a concern; i.e., no significant quantity of nitrate, nitrite, chromate, permanganate, etc., was found. This finding strongly indicated that the oxidant was not present as an ion loaded on the ion exchange resin. Furthermore, if nitric acid, nitrate, or nitrite had been the oxidant we would expect oxides of nitrogen to have been present in the gases evolving from Cask A during the exotherm. No oxides of nitrogen were noted by ANO personnel at the time the exotherm was detected.
- Resin oxidation with air can occur. Theoretically a large enough mass of resin with air pulled through at the proper rate will oxidize, retain the heat of combustion, and the temperature of the resin will increase. However, pulling air at the operating rate and at ambient temperature through the resin in the cask is not expected to result in any significant oxidation of the resin and therefore no temperature increase would be expected. This is supported by general knowledge of ion-exchange resin properties and by the successful use of the dewatering procedure by many different utilities, including ANO operations prior to the exothermic event.

Additional information regarding the role of supplied air, i.e., thermodynamic calculations and correlation of resin degradation with temperature, are reported in the Phase III portion of the present report.

## REACTIONS AT ELEVATED TEMPERATURE

Thermal analysis studies of resin behavior were conducted. These studies and their results are reported in the Phase III portion of the present report.

## IDENTIFICATION OF ORGANICS

Organic material was found as a coating on resin beads in samples from Cask A. Samples of Cask A resin were washed with xylene, carbon tetrachloride, and ethanol. Each solvent removed some of the organic material, but xylene removed the greatest amount and carbon tetrachloride the least.

Oily material was also found on top of the aqueous phase in Cask E and samples of this material were also examined. The material was an emulsion of organic and aqueous phases and was quite resistant to phase separation. The phases were separated by prolonged centrifugation.

The organic material from Cask A and Cask E was examined using infrared spectroscopy and gas chromatography. The organic material found in these casks is very similar. The material has a high boiling point and consists mainly of aliphatic hydrocarbons. Small amounts of organic acids and esters are probably present, and there is evidence of traces of aromatic materials.

Battelle-Northwest concluded that there were no significant differences in the organic material found in Cask A and Cask E. Furthermore, this material is not expected to be easily oxidized because of its high molecular weight and aliphatic nature. Support for stability of this organic material is given by the fact it is still present in Cask A after the exothermic event. Our most likely guess is the material is a lubricating oil that entered the radwaste system by some means.

The presence of this organic material may also have contributed to the difficulty experienced in emptying the resin holding tank. The organic material could act as a binder to form an aggregated resin mass that would not be easily removed using the standard technique to transfer resin from the holding tank to a disposal cask.

If this resin mass existed long enough in the holding tank, then microorganism growth that fed on the foreign organic material in essentially anaerobic conditions is a possibility. The microorganisms themselves, or their metabolic products, may have provided the easily oxidized material that initiated the exothermic event in Cask A during dewatering (the dewatering

procedure providing oxygen from the air as the necessary oxidant). The possibility of extensive microorganism growth was examined; the results of these studies are reported in Phase III of the present report.

#### LABORATORY-SCALE DEWATERING TESTS

Laboratory-scale dewatering tests were conducted on new resins, actual cask resins, and resins containing significant microorganism growth. No exothermic reactions were detected. Because these dewatering tests were conducted after the completion of the microorganism studies, the complete details and results of these tests are reported in Phase III of the present report.

### PHASE III STUDIES

Phase III studies were directed toward understanding the mechanism or mechanisms whereby the exotherm observed in Cask A became possible. Several studies originally proposed under Phase II were conducted under Phase III because they aided in determining what conditions do or do not produce an exotherm. The specific work conducted under Phase III included: 1) a thermodynamic evaluation of resin stability, 2) elevated temperature studies, 3) microorganism growth in resins, and 4) simulated dewatering tests.

#### THERMODYNAMIC EVALUATION OF RESIN

The following is a theoretical study concerning the energies involved in obtaining resin bed temperatures high enough to cause exothermic reactions with only the resin itself and oxygen as reacting components. The calculations are in three parts: 1) heat required to pyrolyze the resin, 2) heat released by resin oxidation, and 3) time for resin bed to reach pyrolyzing temperature.

The four resins considered are ARC-9358, ARA-9371, IRA-200C, and IRA-900C. As shown in Table 2, these represent two sulfonic acid exchangers, a quarternary ammonium exchanger, and a polyamine exchanger. Two are gel-type, and two are macroreticular. Three are based on polystyrene, and one on an epoxy-polyamine. These are representative of most resin types. Resin ARA-9371 pyrolyzes at the lowest temperature, ~200°C. ARC-9358 was found to pyrolyze at 335°C-350°C. However, as shown below, calculation of the total heat evolved is not very sensitive to the final temperature reached within this range.

Table 2 lists properties of the resins used for calculations. To calculate the heat required for pyrolyzation, the following assumptions were made:

- 1) Resin bed consists of 1/4 by volume of each resin listed above:  
388 g H<sub>2</sub>O/L + 366 g exchanger/L.
- 2) Ambient temperature, 20°C.

- 3) Heat capacity of the resin is within acceptable limits of polyethylene, 0.3 cal/deg/g.
- 4) All water evaporates at 100°C with no binding energy to the resin.
- 5) No heat loss occurs to the air being pulled through the bed.
- 6) The final resin bed temperature was 300°C uniformly throughout the bed.

TABLE 2. Resin Properties<sup>(a)</sup>

Description	Resin	Percent H <sub>2</sub> O <sup>(b)</sup>	Bulk Density, kg/L
Epoxy-polyamine gel	ARA-9371 (Used data for A-30)	53-57	0.730
Styrene sulfonate gel	ARC-9358 (Used data for C-20)	43-46	0.817
Styrene sulfonate macroreticular	IRA-200C	48	0.80
Styrene ammonium macroreticular	IRA-900C	60	0.67

- (a) Values reported by manufacturers for resins in Na<sup>+</sup> and Cl<sup>-</sup> forms.  
 (b) Experimental determination of water content on an equivolume mixture of the four resins listed after conversion to H<sup>+</sup> and OH<sup>-</sup> form gave a water content of 50% H<sub>2</sub>O vs the 51.5% H<sub>2</sub>O predicted using the table values. This difference in water content is about what is expected because of the different form and does not greatly affect the thermodynamic calculations.

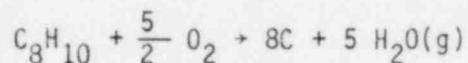
The heat required to raise the resin bed to 300°C is:

$$\begin{aligned}
 & (100^0 - 20^0) [C_{H_2O} (\text{wt. } H_2O/L) + C_{\text{resin}} (\text{wt. resin/L})] \\
 & + \Delta H_{\text{vap}}^{H_2O} (\text{wt. } H_2O/L) + (300^0 - 100^0) C_{\text{resin}} (\text{wt. resin/L}) \\
 & = 80^0 [(1 \text{ cal/g/deg}) (388 \text{ g/L}) + (0.3 \text{ cal/g/deg}) \\
 & (366 \text{ g/L})] + (540 \text{ cal/g/deg}) (388 \text{ g/L}) + (200^0) \\
 & (0.3 \text{ cal/g/deg}) (366 \text{ g/L}) = 271 \text{ kcal/L.}
 \end{aligned}$$

It should be noted that water evaporating below 100°C, or a lower final temperature, would lower the heat requirement. However, the largest term is the  $\Delta H_{\text{vap}}^{\text{H}_2\text{O}}$ . If not all the water evaporates from the total resin bed, or if the water content is lower than estimated, or if only the lower part of the resin bed lost all of its water and reached 300°C, a much greater difference in the heat requirement would be observed. Comparison of manufacture's values with experimental determinations gives confidence to the water content values used. However, a real possibility exists that not all the water was vaporized.

To calculate the heat released during oxidation of the resins, the following assumptions were made:

- 1) Combustion goes to completion
- 2) Since the heat of combustion will vary between resin types and the exact composition of the resin in Cask A was unknown, a representative value was selected. Water and carbon would be the products under a oxygen-deficient, low-temperature combustion. The representative compound chosen for these calculations was ethylbenzene:



$$\Delta H = -114.4 \frac{\text{kcal}}{\text{mole O}_2}$$

- 3) Cask A was full of resin,  $103 \text{ ft}^3 = 2916 \text{ L}$
- 4) Sandpiper pump pumped air at  $1.5 \text{ gal/sec} = 2.04 \times 10^4 \text{ L/h}$

At 20°C, 114.7 L of air contains one mole  $\text{O}_2$ . The oxygen flow rate in Cask A would be:

$$(2.04 \times 10^4 \text{ L/h}) (114.7 \text{ L/mole O}_2)^{-1} = 178 \text{ moles O}_2/\text{h}.$$

This is equivalent to  $0.0612 \text{ moles O}_2/\text{L/h}$  or  $(0.0612 \text{ mole O}_2/\text{L/h}) (114.4 \text{ kcal/mole O}_2) = 7.00 \text{ kcal/L/h}$ .

To release 271 kcal/L would require  $(271 \text{ kcal/L}) (7.00 \text{ kcal/L/h})^{-1} = 38.8$  hours.

#### Discussion of Thermodynamic Evaluation of Resin Results

The thermodynamic evaluation of resin oxidation given above is believed to be a reasonable approximation of the results expected from air oxidation of the resin. Uncertainties exist in this evaluation, and these have been stated in the discussion. Specifically, the resin composition is not known, and we assumed all water was removed at 100°C, that water and carbon were the products of the oxidation, and that all available oxygen was utilized in combustion.

Similar calculations were performed using benzene ( $C_6H_6$ ), ethane ( $C_2H_6$ ), and trimethylamine hydrochloride ( $(CH_3)_3NHCl$ ) as representative compounds of combustion. Little difference in the results exists when comparison of the heats of combustion are made on a per mole of  $O_2$  basis. Oxidation of  $C_2H_6$  with nitrite or nitrate ion also yields similar thermodynamic results.

Oxidation of the Cask A resin by either oxygen (air) or by chemical oxidant (such as  $NO_2^-$  or  $NO_3^-$ ) would have released sufficient energy to cause the observed exotherm in Cask A. However, the process must be initiated and the initiation of air oxidation of the resins is expected to be kinetically unfavorable under the normal conditions of cask dewatering.

The time required to raise the resin bed temperature from ambient to 300°C by oxidation of the resin with air pumped through under the operating conditions was calculated to be ~39 hours. While this time length is not unlikely for the dewatering process, it does indicate a slow reaction rate.

#### THERMAL STABILITY OF RESINS

The objective of these studies was to observe the temperatures necessary to obtain resin characteristics similar to those observed in the cask resin samples (Appendix A). Two tests were run on new ion exchange resins supplied by AP&L: 1) a qualitative description of resin materials after heating the resins in air for prolonged time periods (16-20 h), and 2) determination of resin decomposition temperature by differential scanning calorimetry (DSC).

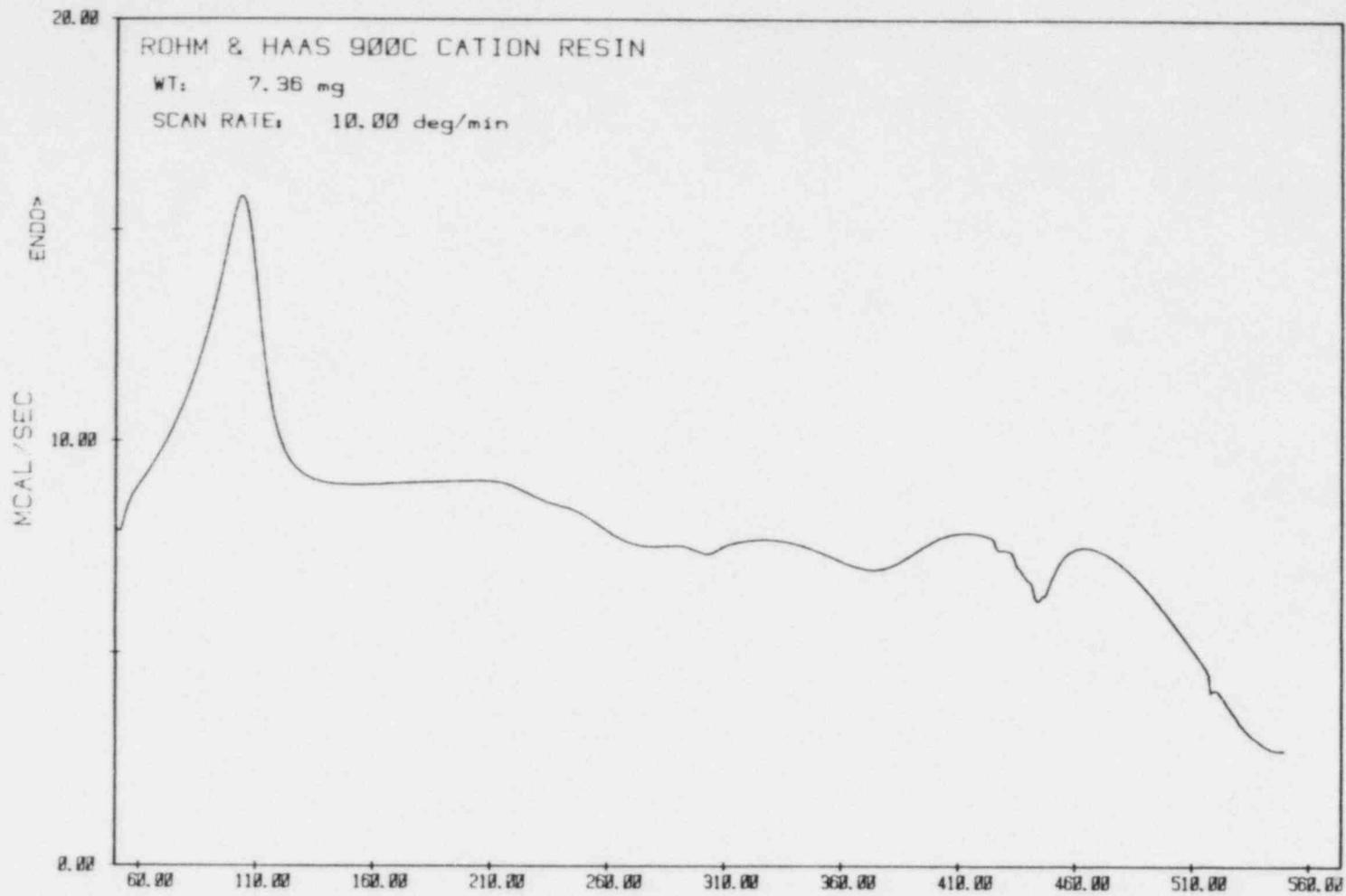
In the former test, resin samples were placed in open glass vials inside an oven. All resins began to show visible changes in appearance (darkening) by at least 150°C. However, a minimum temperature of ~250°C was necessary to produce obvious resin degradation (loss of bead structures, pyrolysis, etc) in any of the samples. The ARA-9371 resin was the least stable and at 350°C, was a bubbling, pyrolyzing mass that finally produced a solid char. Some bead structure was still apparent, however, in the product of ARA-9371 degradation. Table 3 presents observations noted during these studies. The DSC studies indicated that all the resins were stable to 200°C in air with the possible exception of ARA-9371. After its initial water loss, this resin (ARA-9371) has a slow constant exothermic drift which may or may not be a return to baseline by additional water loss. Figures 15-22 present the actual DSC decomposition curves for the resins. Decomposition temperatures for the new resins, as determined by the DSC studies, are summarized in Table 4.

Based on the appearance of new resin as a function of heating temperature and an examination of the variety of resin samples obtained from Cask A, it was concluded that essentially all the resin present in Cask A probably reached a minimum temperature of 300°C during the exothermic event; zones within the cask may have approached a temperature of 400°C.

TABLE 3. Observations of Resin Thermal Stability<sup>(a)</sup>

Temperature Exposure Time	Diamond Shamrock A101D	Diamond Shamrock C20-H		Rohm & Haas 200C	ARA-9371	Mixed 150 L/C	Rohm & Haas 900C	ARC-9358
			RWA-78					
As received	Light tan	Dark brown	Medium brown	Dark beige	Medium tan	Medium brown	Medium beige	Dark tan
149°C 16 hr.	Very sl. darker	Black. Grey film on glass	No change	Very sl. lighter	Dark tan	Mixed, medium tan & dark	Dark beige	Black, hard lumps that were not easily broken. Slight grey film on glass.
197°C 16 hr.	Darkened to med. brown	Same as 149°C	Dark tan	Same as 149°C	Very dark brown, almost black	Same as 149°C-beads darker	Darker beige	Same as 149°C Lumps seem harder.
254°C 20 hr.	Black beads in small clumps.	Black-loose beads.	Black-loose beads.	Black-loose beads. Sl. grey film on glass.	Black-heavy clump. Brown film on glass.	Black-loose beads. Sl. grey film on glass.	Black-loose beads.	Large black clumps. Slight grey film on glass.
306°C 20 hr.	Black beads. Slight grey film on glass.	Black beads. Small clumps. Slight grey film on glass.	Black beads. Slight grey film on glass.	Black beads. Slight grey film on glass.	Black heavy clump. Massive degradation. Heavy brown film on glass.	Black beads. Slight grey film on glass.	Black beads. Slight grey film on glass.	Large black clump- some loose beads. Slight grey film on glass.

(a) In the sample descriptions, black color was observed with the naked eye with the sample exposed to air. It does not necessarily imply that the samples were carbonized.



RD SCHEELE FILE: RH900.DA  
 DATE: 84/01/09 TIME: 13:59

TEMPERATURE (C)

DSC

PERKIN ELMER Thermal Analysis

FIGURE 15. DSC of Rohm & Haas 900C with Air Purge

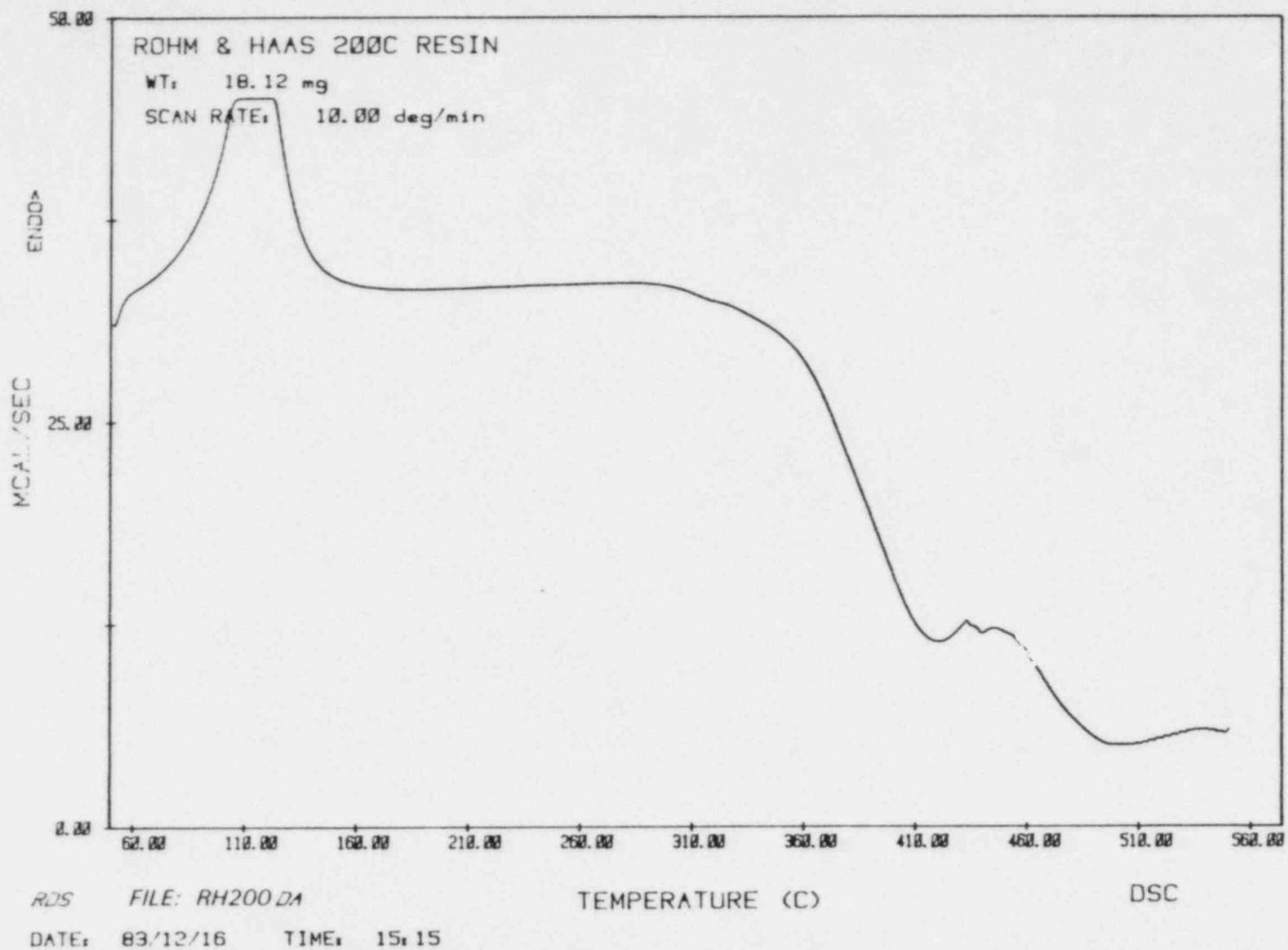


FIGURE 16. DSC of Rohm & Haas 200C with Air Purge

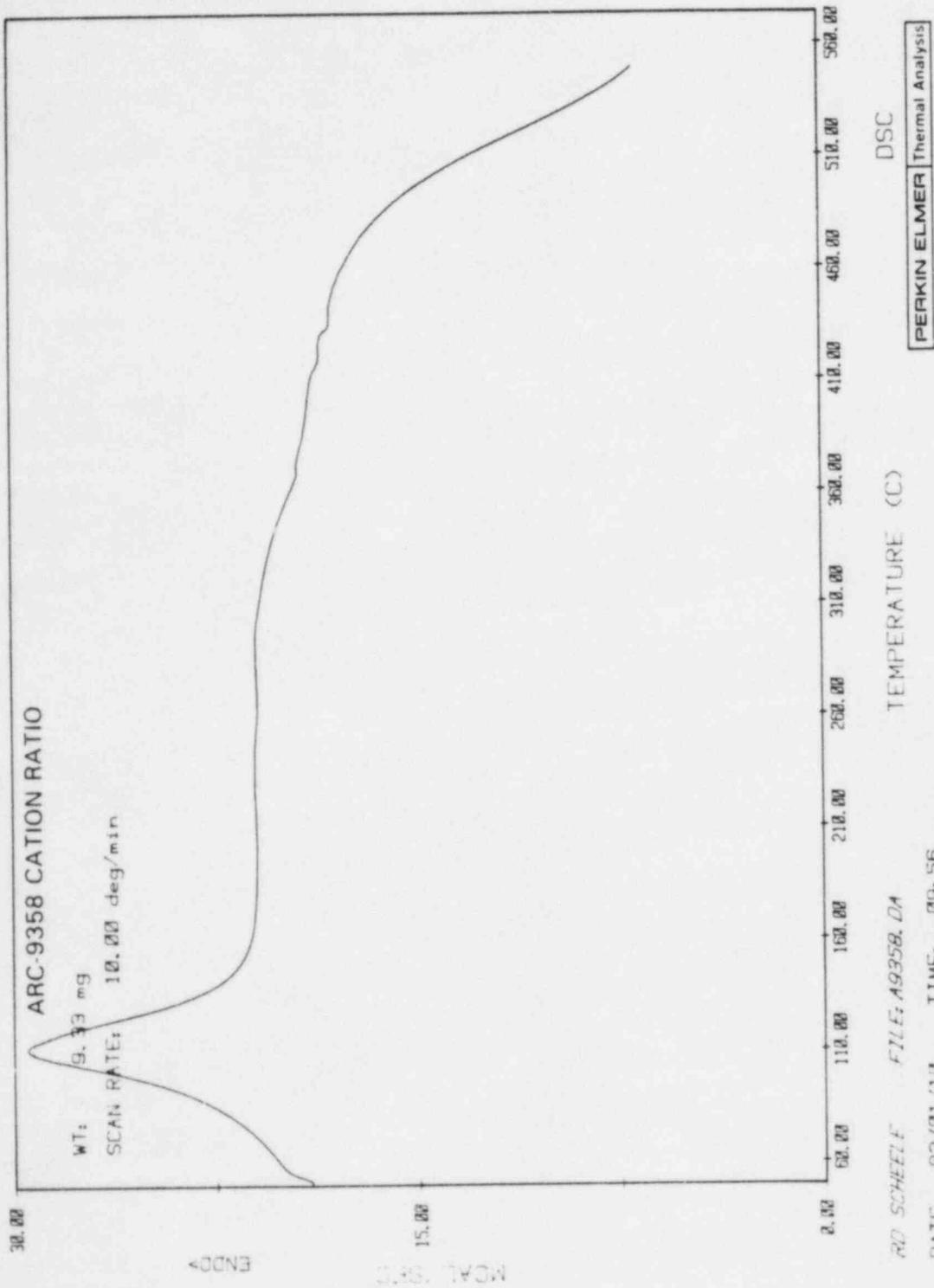


FIGURE 17. DSC of ARC-9358 with Air Purge

44

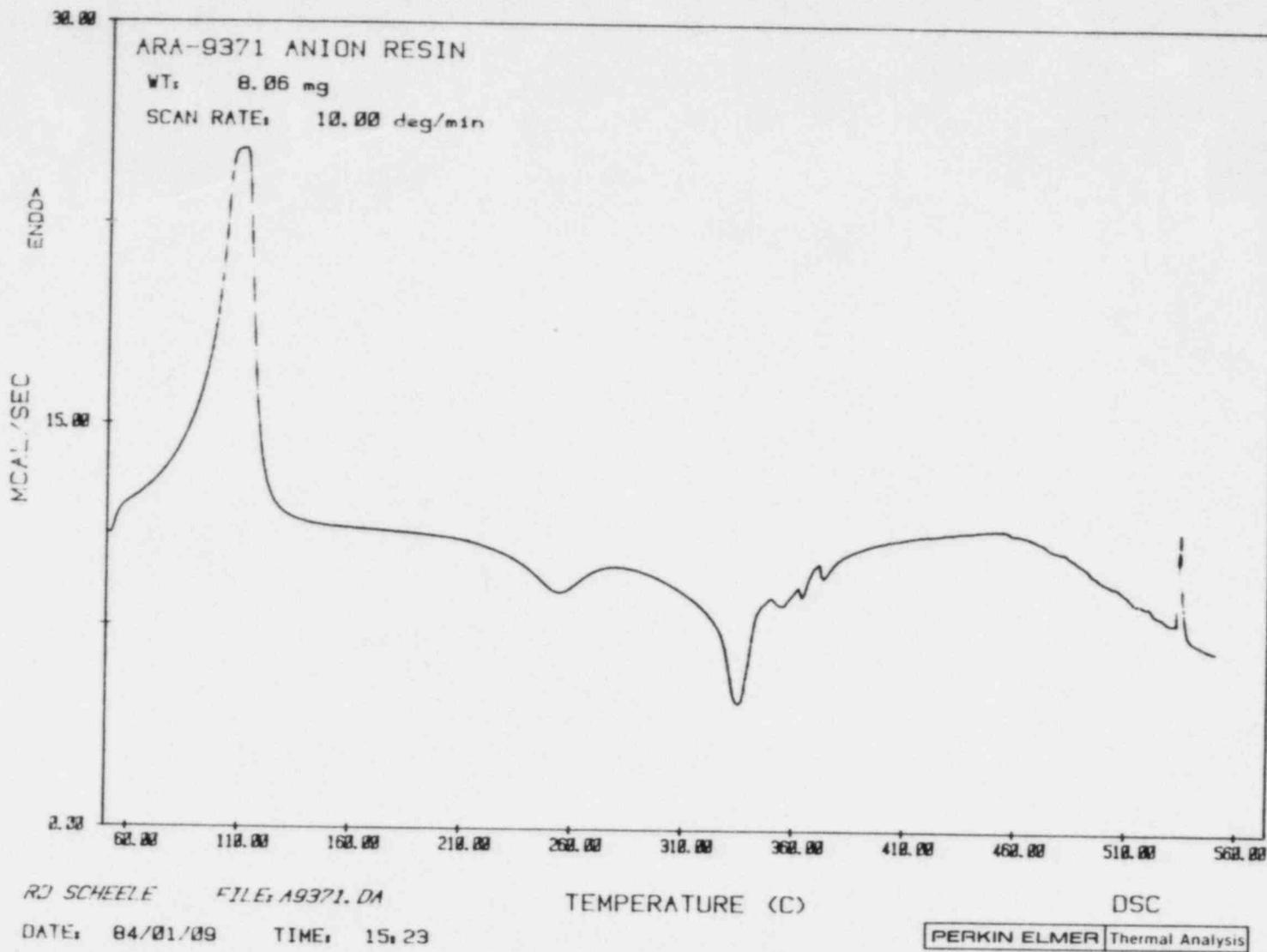


FIGURE 18. DSC of ARA-9371 with Air Purge

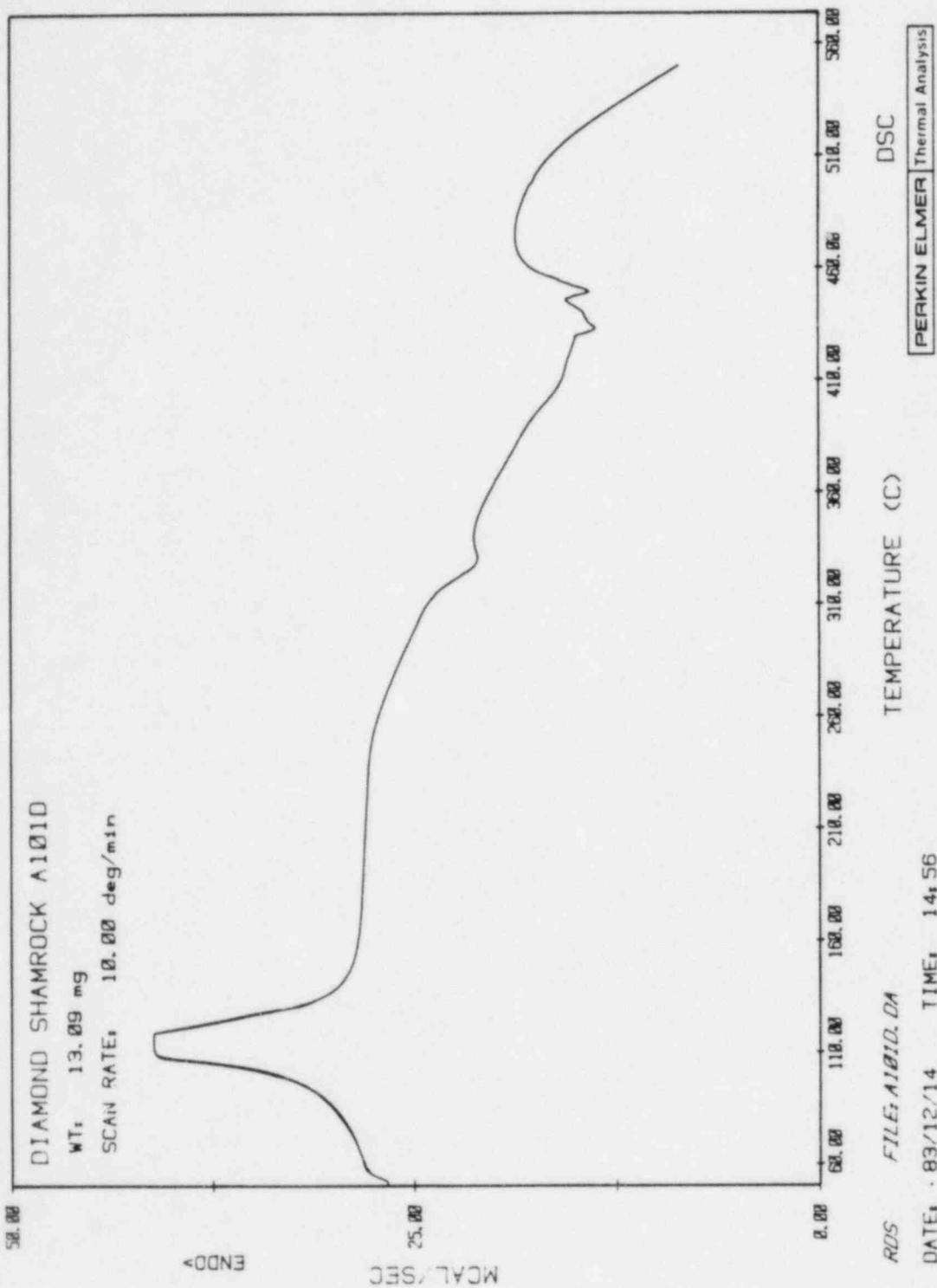


FIGURE 19. DSC of Diamond Shamrock A101D with Air Purge

46

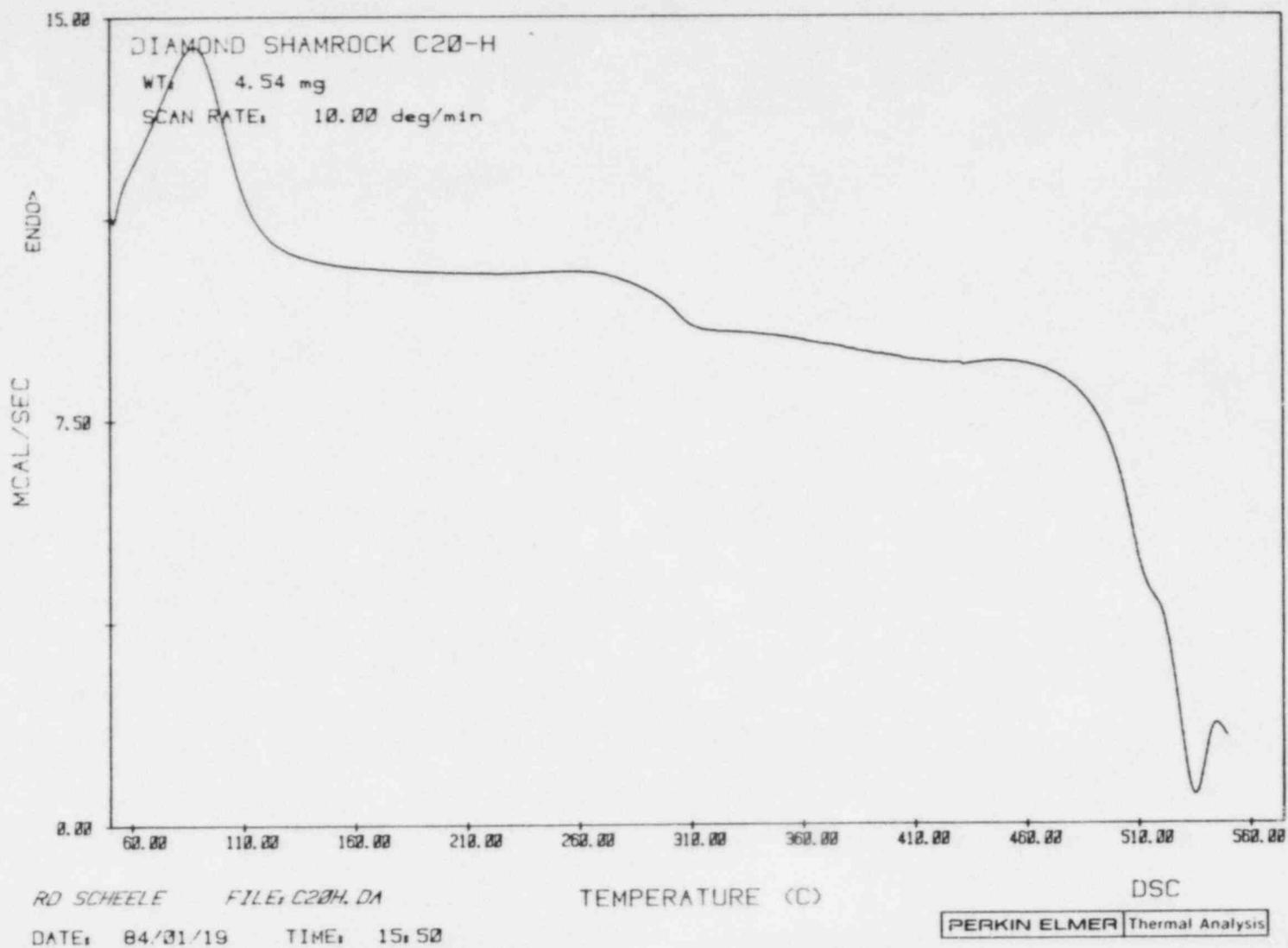


FIGURE 20. DSC of Diamond Shamrock C20-H with Air Purge

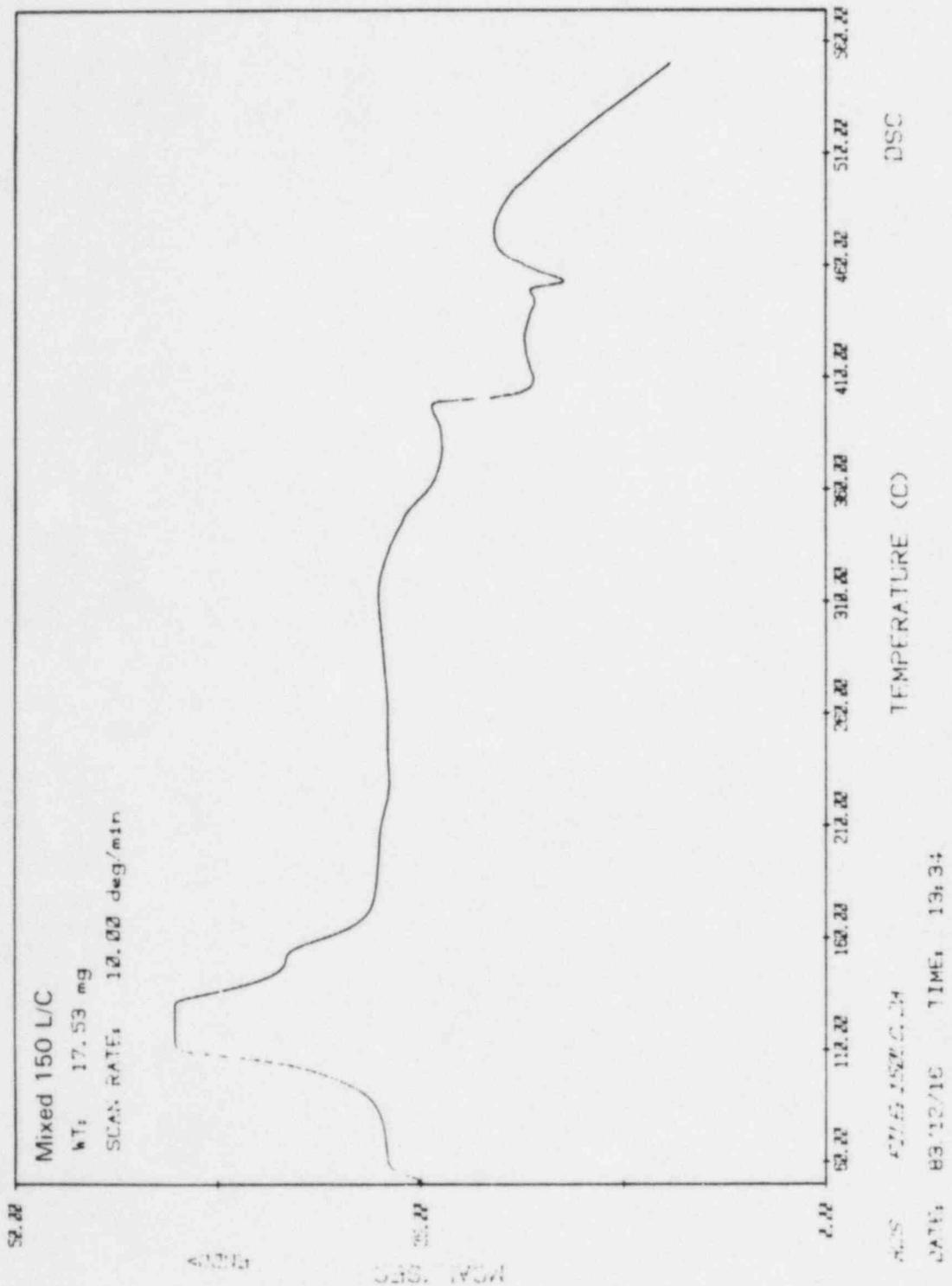


FIGURE 21. DSC of Mixed 150 L/C with Air Purge

48

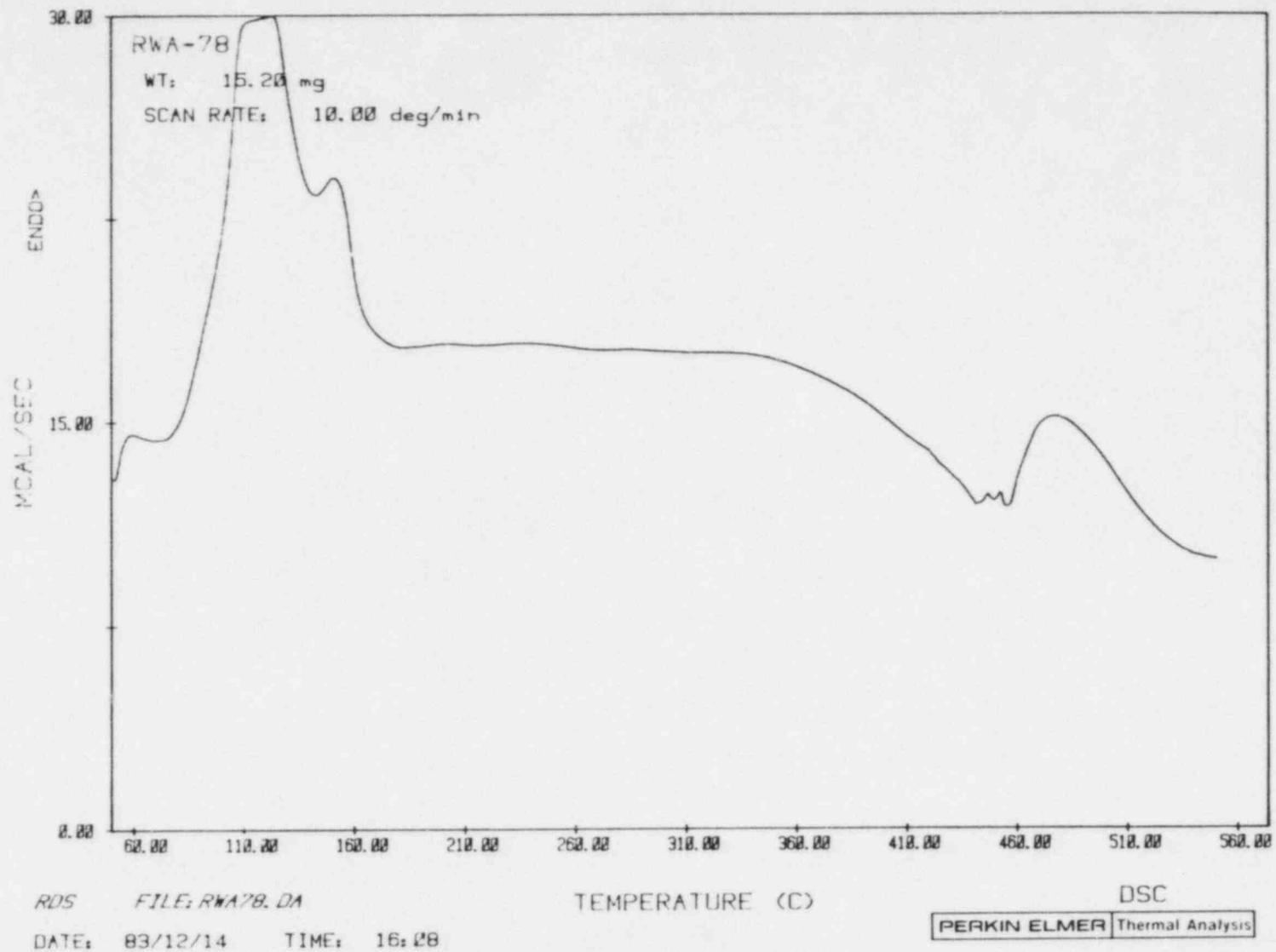


FIGURE 22. DSC of RWA-78 with Air Purge

TABLE 4. Resin Decomposition Temperature

<u>Resin</u>	<u>Decomposition Temperature, °C (DSC Results)</u>
Rohm & Haas 900C	210
Rohm & Haas 200C	290
ARC-9358	300
ARA-9371	140-200
Diamond Shamrock A101D	240
Diamond Shamrock C20-H	250
Mixed 150 L/C	>200
RWA-78	340

#### MICROORGANISM GROWTH IN RESINS

Five ion exchange resin disposal casks, designated Casks A, B, C, D, and E, located at Arkansas Power and Light, Arkansas Nuclear No. One, contained resin removed during cleanout of the resin storage tank. Cask A, the cask that experienced the exothermic event detected on January 15, 1983, was the first of the five casks to be loaded with spent resin and was the only cask to have completed dewatering.

The results of Phase I indicated the absence of any significant quantity of strong oxidants in either Cask A or Cask B. Thus, Battelle-Northwest concluded that oxygen in air was the likely oxidant. The question then was: How did the resin degradation (oxidation) initiate?

Battelle-Northwest proposes that the presence of significant quantities of microorganisms could have provided the ingredients necessary to initiate the exothermic event detected in Cask A. The presence of significant quantities of microorganisms could have contributed to the initiation of the exothermic event by the following mechanisms.

First, microorganisms generate heat as a byproduct of their metabolism. Population growth of microorganisms can also be extremely rapid if favorable

growth conditions exist. If enough heat is generated and is retained by the bulk material in which the microorganism is found, the temperature of the bulk material will increase. These effects are commonly observed in compost piles. If the temperature increase is sufficient, auto-oxidation of materials can occur, finally resulting in combustion (rapid oxidation) of the bulk material - this is the cause of the so-called "green-hay" fires.

Second, both aerobic (oxygen using) and anaerobic (non-oxygen using) microorganisms exist. Most anaerobic microorganisms can utilize sulfur in their metabolism; sulfur is present in the structure of most of the resins used at ANO. The presence of either live or killed microorganisms is a source of finely divided organic material. The high surface area to mass ratio of the microorganisms favors their oxidation at a lower temperature than either direct resin oxidation, or oxidation of stable organics. As oxidation occurs, heat is generated and can be retained by the bulk material until the temperature of the bulk material increases to the value required for its combustion (rapid oxidation).

Third, the metabolic products of the microorganisms may be more easily oxidized than either the organic resins or other organics originally present.

Thus, the presence of significant quantities of microorganisms in the casks could possibly result in an exothermic event being initiated by one or more of the mechanisms described above.

The purpose of the microorganism studies described in this report was to determine if the mechanisms described above could have existed in Casks A, B, C, D, and E.

#### Experimental Plan

Battelle-Northwest states at the outset that it is not a straightforward microbiological problem to determine the possibility that bacterial metabolism initiated the exothermic reaction that occurred during dewatering of Cask A.

The studies are a basic research problem, not an engineering problem. Therefore, a predetermined set of procedures do not exist that can be applied to answer the question: Did the exothermic event in Cask A have a biological origin? Moreover, unless the conditions in the cask just preceding the

exothermic event can be reconstructed, it cannot be concluded that negative results imply lack of a biological component in the exothermic reaction.

Reconstruction of conditions existing in Cask A prior to dewatering is very difficult. The environment in the cask prior to the exothermic event is unknown. In addition, the high temperatures attained during the exothermic reaction probably destroyed biological evidence that would have been of assistance in determining if there was a biological origin to the exothermic event.

Finally, funding resources and time constraints limited what could be achieved.

These reservations are stated so that it is clearly understood that Battelle-Northwest is not claiming that its studies completely addressed the potential importance of microbial metabolism on the stability of organic ion exchange resins containing low level nuclear waste materials.

Battelle-Northwest does believe that its studies indicate the potential importance of microbial action in spent resins. Furthermore, Battelle-Northwest believes these studies have shown that the exothermic event that occurred in Cask A could have had a biological origin.

#### Experimental Rationale and Design

If microbial metabolism was important in preparing the system for the exothermic event detected in Cask A, several conditions should have been met:

- 1) The total metabolism and growth of microbes preceding the exothermic event should have been extensive. Therefore, the resins in the cask, plus the material bound or coated on the resins, must be able to support microbial growth. As a consequence, biological polymers (i.e., DNA), metabolic byproducts, and cell and/or microcolonies should have existed in the casks and may be detectable.
- 2) The casks (and the resin storage tank) were probably anaerobic (without oxygen) prior to dewatering. Therefore, bacterial metabolism was probably fermentative or linked to anaerobic respiration. Fermentative metabolism requires fermentable substrates (sugars, some organic acids,

etc.). Cask A did not contain more than trace levels of fermentable substrates, hence these studies concentrated on anaerobic respiration as the main probable cause of microbial activity.

Battelle-Northwest's studies attempted to demonstrate that indicators of microbial growth were present in the resins from the casks that were not dewatered (Casks C, D, and E), partially dewatered (Cask B), and in the cask that underwent the exothermic event (Cask A). These studies also attempted to show that both resins from the casks and new "as-received" resins are capable of supporting microbial growth and metabolism.

Anaerobic respiration has three common origins. Both bacterial nitrate reduction and bacterial sulfate reduction are probable. Methanogenesis (production of methane) by carbon dioxide reducing bacteria cannot, a priori, be excluded. However, these studies concentrated on some form of sulfate reduction as the most likely form of metabolism in the casks for the following two reasons:

- 1) Several of the ion exchange resins used at ANO contain sulfonate groups as part of the basic repeating polymeric unit of the resin. The sulfonate ( $-SO_3-H^+$ ) group is a potential electron acceptor for sulfate reducing bacteria.
- 2) The resin in Cask A had a strong odor during dewatering (and is still present in Cask A resin samples) that was possibly caused by reduced sulfur compounds.

Thus, the microorganism studies attempted to enrich sulfate reducing bacteria present in cask resins, and to demonstrate the growth of sulfate reducing bacteria in inoculated resins. Battelle-Northwest's studies were limited to one type of sulfate reducing bacteria for the inoculated resin tests.

#### Materials and Methods

Five representative cask samples (radioactive) and eight representative resins (nonradioactive) were studied. The representative cask samples were obtained as follows:

- Cask A - approximately equal quantities of resin from
  - Core Sample No. 1, Sample No. 1
  - Core Sample No. 1, Sample No. 4
  - Core Sample No. 1, Sample No. 5
  - Core Sample No. 2, Sample No. 2
- Cask B - Representative sample
- Cask C - Representative sample
- Cask D - approximately equal quantities of resin from
  - Sample from bottom 6 in. of core.
  - Representative sample from 8 in. above the bottom of the core to the top.
- Cask E - approximately equal quantities of resin from
  - Core Sample No. 1, Sample No. 1
  - Core Sample No. 1, Sample No. 2
  - Core Sample No. 2, Sample No. 1
  - Core Sample No. 2, Sample No. 2
  - Core Sample No. 2, Sample No. 3

The eight representative resin samples were obtained from AP&L, ANO site and are designated: A101D, C20-H, RWA-78, Rohm & Haas 200C, ARA-9371, Mixed 150 L/C, Rohm & Haas 900C, and ARC-9358.

The numerically designated resins were resins supplied to Battelle-Northwest by AP&L and those designations correspond to those on the sample containers as received by Battelle-Northwest. It is Battelle-Northwest's understanding that these resins are "as supplied" to AP&L by the various manufacturers. No treatment of the resins was done by Battelle-Northwest. Brief descriptions of these resins are given in Appendix D.

Resin samples obtained from Casks A, B, C, D, and E contain resins whose identity is unknown; i.e., the manufacturer and resin-type (anion or cation) is not known. It was possible to determine approximate volume ratios of gel and macroreticular resins in the cask. Descriptions of the cask resins are given in Appendix A.

A 4-gram slurry of each sample or resin was prepared and divided equally into four sterile test tubes. Reduced Postgate medium either with or without lactate was added to the appropriate tube. Two tubes, one with lactate and one without lactate, were inoculated with a 0.1 mL aliquot of a 48 hour culture of *Desulfovibrio desulfuricans*. The other two tubes received no organism. Appropriate organism controls, media controls, and H<sub>2</sub>O controls were also prepared. All tubes were incubated in an anaerobic jar at 30°C for seven days. At the end of the initial incubation period, all tubes were observed for growth and gram stains of each broth culture were prepared. The gram stain provided a method of distinguishing two major subgroups of the bacteria *Proccayotes*. Incubation was allowed to continue after the initial seven days; additional observations for growth were noted and additional gram stains were prepared.

#### Initial Results

The following describe the results of the initial studies described above.

Cask A. Evidence of sulfate reducing bacteria in the uninoculated samples with or without lactate was observed based on the production of H<sub>2</sub>S (see Table 5 for the results obtained for all cask samples). There was no apparent difference in growth or H<sub>2</sub>S production between the samples either in the presence or absence of lactate. This observation indicates that sulfate reducing bacteria were probably present in this cask.

Cask B. The results were similar to those observed for Cask A with the exception that less growth and H<sub>2</sub>S production were exhibited in the samples without lactate.

Cask C. There was evidence that other bacteria were present in this cask because of excessive gas production and lack of H<sub>2</sub>S production in the uninoculated samples. Resin particles were pushed to the top of the culture tubes by the excessive gas production in both inoculated and uninoculated resin samples. H<sub>2</sub>S production was present only in the inoculated samples. Microscopic examination of the inoculated samples indicated a mixture of bacteria were present. Gram negative short curved rods and long rods, gram positive rods with spores, and gram positive cocci were observed. These short rods were extremely mobile when observed under wet mount preparation.

TABLE 5. Growth Characteristics of Radioactive Cask Resins

	Cask A <sup>(a)</sup>			Cask B			Cask C			Cask D <sup>(a)</sup>			Cask E <sup>(a)</sup>		
	Density	H <sub>2</sub> S	Gas	Density	H <sub>2</sub> S	Gas	Density	H <sub>2</sub> S	Gas	Density	H <sub>2</sub> S	Gas	Density	H <sub>2</sub> S	Gas
<u>Lactate Present</u>															
Inoculated	4+	+	-	4+	+	-	4+	+	+	4+	+	-	4+	+	-
Uninoculated	4+	+	-	3+	+	-	4+	-	+(c)	4+	-	+(c)	4+	tr	+
<u>Lactate Absent</u>															
Inoculated	4+	+	-	4+	+	-	4+	tr	+(c)	2+	+	-	2+	+	-
Uninoculated	4+	+	-	2+	+	-	4+	-	+(c)	4+	-	+(c)	2+	tr	+

(a) Pooled samples (See Materials and Methods Section)

(b) Growth density is a visual measurement of the amount of turbidity and H<sub>2</sub>S production on top and throughout the sample (i.e., 4+, 3+, 2+, 1+, tr).

(c) Excessive gas production (resin particles pushed to the top of the tubes).

Cask D The results for Cask D were similar to those obtained for Cask C.

Cask E. The results for Cask E were similar to those obtained for casks C and D. However, a trace of H<sub>2</sub>S was also present in the uninoculated samples. Microscopic examination also indicated a variety of morphologically different bacteria. Both sulfate reducing bacteria and other anaerobic bacteria appeared to be present in Cask E.

Nonradioactive Resins. All inoculated samples of the nonradioactive resins had evidence of H<sub>2</sub>S production and bacterial growth with the exception of C20-H and ARC-9358. The inoculated samples without lactate showed less growth than those samples with lactate.

All uninoculated samples had no evidence of bacterial growth or H<sub>2</sub>S production with the exception of the RWA-78 resin. In RWA-78 samples, a mold-like growth occurred on the surface of the resin in both the inoculated and uninoculated samples containing lactate. In addition, the uninoculated sample of RWA-78 showed a trace of H<sub>2</sub>S production indicating some sulfate reduction occurred.

#### Discussion of Initial Results

The initial results reported above established the following:

- 1) The sulfate reducing bacteria *Desulfovibrio desulfuricans* used to inoculate the various resin samples was shown to grow in reduced Postgate medium containing resins from each of the casks (Casks A, B, C, D, and E). This organism produced H<sub>2</sub>S in these experiments, both in the presence and absence of lactate in the medium. Lactate is a suitable carbon source for this organism, and was added for enrichment of the sulfate reducing bacteria in certain samples of the total experimental matrix. However, growth in the samples without lactate indicates a suitable substrate or energy source existed in the cask resins.
- 2) *Desulfovibrio desulfuricans* was shown to grow in reduced Postgate medium containing each of the nonradioactive resins with the exception of C20-H and ARC-9358. However, samples without lactate seemed to show less bacterial growth than those samples containing lactate. In addition,

the uninoculated sample of RWA-78 showed a trace of H<sub>2</sub>S production indicating some sulfate reduction occurred.

- 3) Resins from Casks A, B, and E when inoculated alone into reduced Postgate medium showed bacterial growth and H<sub>2</sub>S production, possibly indicating the presence of *Desulfovibrio desulfuricans* or other anaerobic sulfate reducers in the resins. Bacterial growth and H<sub>2</sub>S production occurred with these resins whether lactate was present or absent from the medium, indicating a sufficient energy source for anaerobic bacterial growth was present in these resins without the addition of lactate. A small gram negative curved rod was found to be the predominant organism in gram stains of cultures from resins obtained from Casks A and B.
- 4) Resins from Casks C, D, and E indicated a variety of morphologic bacterial types on microscopic examination. These included gram-negative rods, gram-positive rods with or without spores, and gram-positive cocci.

#### Additional Results

Following the initial studies, additional experiments were conducted to more fully define the potential for bacterial growth in resins obtained from Casks A, B, C, D, and E. Preliminary efforts to isolate and identify specific microorganisms from these casks were also conducted.

The results of these additional studies are described below:

- 1) Resins from Casks A, B, C, D, and E gave no evidence of bacterial growth when incubated in sterile distilled water.
- 2) Resins from Casks A through E in reduced Postgate medium containing no sulfate in the medium supported bacterial growth and H<sub>2</sub>S production when inoculated with *Desulfovibrio desulfuricans* and incubated anaerobically. The Postgate medium used in all of the initial tests contained sulfate in the medium. The presence of bacterial growth and H<sub>2</sub>S production in the present tests indicates the added organism can grow in the presence of the resins alone, apparently using the organic

residuals and sulfonated groups present in the resins to establish growth.

- 3) Samples from Casks A, B, and E incubated anaerobically in Postgate medium without sulfate showed H<sub>2</sub>S production (indicating sulfate reduction) after 7 days; samples from Casks C and D did not show H<sub>2</sub>S production under identical conditions.
- 4) A number of organisms isolated from the various resins in Postgate medium without sulfate were partially identified. 0.1 mL aliquots from each of the resin-medium tubes showing bacterial growth were plated onto Postgate-sulfate agar and nutrient agar. These plates were then incubated both aerobically and anaerobically at room temperature.

All resins were found to contain a gram-negative rod which was oxidase positive and is a *Pseudomonas* species. Although usually found as an aerobe, these organisms can respire anaerobically using nitrate as a final electron acceptor.

A gram-positive spore-forming anaerobe, a *Clostridium* species, was isolated from resins obtained from Casks A, C, D, and E. This organism is capable of producing copious amounts of gas (not H<sub>2</sub>S).

A medium sized gram-positive rod which did not produce spores and grew both aerobically and anaerobically was isolated from resins obtained from Casks C, D, and E. Based on microscopic and colonial morphology, this organism appears to be a *Corynebacterium* species.

Finally, a small vibrioid gram-negative rod was isolated from resin obtained from Cask B. This organism is a strict anaerobe (i.e., *Desulfovibrio* species) which is fairly fastidious and seemed to be lost easily on transfer.

#### Discussion of Additional Results

A variety of morphological bacterial types were shown to exist in resin samples obtained from Casks A, B, C, D, and E. Further, both added known sulfate reducing bacteria and the bacterial types existing in the cask resins were shown to be capable of bacterial growth in the absence of both added sulfate and lactate. Certain bacterial types that produced copious amounts of

gas (not H<sub>2</sub>S) under anaerobic conditions were shown to be present in all casks except Cask B.

### Conclusions

The purpose of the microorganism studies was to determine if the presence of microorganisms in organic ion exchange resins contained in Casks A, B, C, D, and E could be shown. Further, if these microorganisms existed, would they show growth under conditions approximating those expected for the casks and the resin holding tank from which the casks were loaded?

It has been shown unequivocally that a variety of morphological bacterial types existed in the resin samples obtained from Casks A through E.

Bacteria contained in Casks A, B, and E were shown to be capable of growth under anaerobic conditions, apparently utilizing only residual organics and the sulfonate groups of the resin to support growth. It is significant to note that Casks A, B, and E contained resins which had been in the resin holding tank for the greatest period of time. However, all cask resins were capable of supporting sulfate-reducing bacterial growth as was shown in those samples inoculated with *Desulfovibrio desulfuricans*. Thus, time is expected to be a significant factor in determining the level of bacterial growth present in any given cask, and may also determine the predominant bacterial species.

It has also been shown unequivocally that most of the new resins supplied to Battelle-Northwest by AP&L are capable of supporting bacterial growth. The nonradioactive resins (C20-H and ARC-9358) which inhibited growth of the tester organism are similar in their polystyrene matrix and are known for their chemical resistance. This chemical resistance may not allow the organism to attack the resin and therefore inhibits or prevents the reduction of the sulfonate groups. The H<sup>+</sup> form of both C20-H and ARC-9358 resins may also contribute to their resistance to microorganism growth.

To our knowledge, the area of microbial growth in organic ion exchange resins has received little previous study. Organic fouling of resins is a well-recognized phenomena that is somewhat related, but the main concern has been the resultant loss in exchange capacity, not the potential for microbial

growth. Our studies have indicated that microbial growth in ion exchange resins may be an area requiring additional studies, particularly if our hypothesis that the presence of a significant microbial population contributed to the initiation of the exothermic event detected in Cask A is shown to be a plausible hypothesis.

#### SIMULATED DEWATERING TEST

The objective of the simulated dewatering test was to monitor events potentially leading to the exotherm observed in Cask A. Samples from: Casks A, B, C, D, and E; Cask E spiked with the microorganism *Desulfovibrio desulfuricans*; and new ion exchange resins obtained from AP&L (Rohm & Haas 200C, Diamond Shamrock A101D, Mixed 150 L/C, RWA-78, ARC-9358, Diamond Shamrock C20-H, ARA-9371, and Rohm & Haas 900C) were temperature monitored under various air flow rates. In no case was a significant temperature rise observed.

Experimental parameters for the simulated dewatering tests were selected based on calculations with known AP&L operating conditions and laboratory limitations. AP&L parameters for the resin bed included: 2900 L volume; 17,037 cm<sup>2</sup> cross-sectional area, 2.6-6.5 L/sec air flow rate; and 30-40% void volume. Scaling the airflow rate on a face velocity basis for the laboratory resin bed volume of 300 mL resulted in a value of 650-1625 mL/min; a value not practical for laboratory operation. Therefore, the airflow rate was ratioed by resin bed volume resulting in a recommended laboratory airflow of 26-65 mL/min.

Calculations based on assumptions made in the thermodynamic studies predict a temperature rise of 7-23 °C/h, if 100% of the oxygen is used for resin combustion in the 300 mL laboratory resin bed. Details of these and previously mentioned experimental parameter calculations pertaining to the simulated dewatering test are given in Appendix F.

#### Simulated Dewatering Test Results

A summary of the simulated dewatering test results is provided in Table 6. Two air flow rates were used in Tests No. 1, 2, and 4. Samples in Test No. 4 were preheated before temperature monitoring began.

TABLE 6. Summary of Simulated Dewatering Tests

Test No. Sample(s)	1		2		3	4	
	Cask A, Cask B, Cask C, Cask D		Cask E, Cask E with Microorganism Spike		New Ion Exchange <sup>(a)</sup> Resins	A101D, Mixed 150 L/C, ARC-9358, ARC-9371	
Air flow rate mL/min	40	80	40	80	35-45	0	40
Initial Temp., °C	20	21	22-23	20.5	22-24	58-69	54-62
Temp. range, °C, over total run period	20-24	20.5-21.8	20.5-23	20-22.5	20-24	dropping to 22	dropping to 28-32
Maximum time of run, hours	109	95	122	165	115	79	6

(a) New resins are Rohm and Haas 200C, Diamond Shamrock A101D, Mixed 150 L/C, RWA-78, ARC-9358, Diamond Shamrock C-20H, ARA-9371, and Rohm and Haas 900C.

### Discussion of Simulated Dewatering Test Results

The instrumented simulated dewatering tests indicated no significant increase in temperature during the process for either the new or cask resins supplied by AP&L. Minor fluctuations in temperature obtained are within the expected deviations for this type of study.

Because we believe oxygen (in air) was the required oxidant for the exothermic event noted in Cask A on January 15, 1983, a continuous airflow was maintained during the dewatering tests to maximize the availability of oxygen. The air flow rates were also increased on most tests after several days at the calculated cask-equivalent airflow rates. No temperature changes were noted at any of the flow rates used. In addition, other tests used the actual dewatering cycle of 8 hours of airflow (pumping) and 16 hours of static conditions (dewatering cycle times should be considered proprietary information); no temperature changes were noted for these tests. Thus, no significant changes in the temperature of the resin were found using the laboratory conditions specified.

Laboratory-scale dewatering tests suffer from the inevitable scaling factor required to conduct the work. The laboratory-scale tests utilize a resin volume  $\sim 10^4$  less than the volume of the actual cask. Although the laboratory tests were conducted in insulated vessels to try and maintain adiabatic conditions, the actual cask and resin has a much greater potential for retaining any heat generated during dewatering. The fact that no significant temperature changes were noted during the laboratory-scale tests does not preclude temperature changes occurring in the actual cask under otherwise identical conditions.

The uncertainties associated with any laboratory-scale dewatering tests are largely those of scale, but the effects of the scaling cannot be accurately predicted for these studies. Battelle-Northwest recommends that fully instrumented dewatering tests be conducted on actual resin disposal casks in accordance with accepted dewatering practices. The instrumented full-scale dewatering would give an experience base useful in detecting any abnormal behavior such as a significant increase in temperature. Furthermore, any abnormal behavior is expected to be easily detected without fear of an

extremely rapid or "run-away" reaction if air-oxidation was the cause of the exotherm in Cask A.

## APPENDIX A

### DESCRIPTION OF CASK RESINS

Resin samples from Casks A, B, C, D, and E, located at ANO, were obtained by using a core sampler designed, constructed, and furnished by Battelle-Northwest. Each core sample was divided into the various samples described in the following text. Sample descriptions include those recorded during the actual cask sampling. Additional descriptive information was obtained later at Battelle-Northwest. Visual examination of various cask resin samples were also conducted using optical microscopy.

### DESCRIPTION OF CASK CORE SAMPLES

Core samples of the resins contained in Casks A, B, C, D, and E, located at ANO, were obtained. The following text describes these core samples.

#### Cask A, Core Sample No. 1

Cask A was a 103 cubic foot resin disposal liner. The cask had been refilled with water on January 15, 1983, after the exothermic event had been detected. The cask was not sealed but was inside a plastic "greenhouse." Core Sample No. 1 was obtained on August 2, 1983, at about 1030 hours.

Core Sample No. 1 was obtained by inserting the sampler vertically into the resin bed about ten inches from the exact center of the cask. Some resistance was experienced in inserting the sampler into the resin bed; this was apparently caused by a crust on the resin bed.

Some resin was lost from the sampler during its withdrawal from the resin bed because the shutter on the sampler was not completely closed. Later inspection of the resin core and sampler showed that about four inches of resin from the core were lost.

The liquid that initially drained from the sampler upon its withdrawal was black and then turned clear. We believe the initial black appearance was caused by resin escaping from the incompletely closed shutter.

A faint odor was present when the sampler was withdrawn from Cask A. The odor could best be described as "sewer-like," "sewer-gas," or similar to that of a just-opened septic tank. It did not have any characteristic amine odor.

The resin in the bottom of the sampler appeared black for about the lower ten inches of the core. There was a gradation in appearance for about another ten inches, and the remainder appeared to be a brown/black mixture. The resin core had about a one-eighth inch thick crust at the top of the core.

The following samples were obtained from Cask A, Core Sample No. 1.

- Sample No. 1. The bottom six inches of the core. All of the resin had a black appearance.
- Sample No. 2. Representative material from 6 in. above the bottom to 18 in. above the bottom of the core.
- Sample No. 3. A solid "chunk" of resin located seven inches from the bottom of the core.
- Sample No. 4. Representative material from 1 ft. 6 in. above the bottom of the core to the top of the core, 3 ft. 2 in.

Resin "chunks" were found randomly throughout the entire core sample; each of the above samples contained at least one. The resin "chunks" are all very dark. The resin beads in the "chunks" appeared to be somewhat smaller and had a glassy-look with a red/black color.

The resin core was 3 ft. 2 in. in depth; the original depth of resin (before some loss occurred during withdrawal of the sampler from the cask) appeared to have been about 3 ft. 6 in.

#### Cask A, Core Sample No. 2

Cask A, Core Sample No. 2, was obtained on August 2, 1983, at about 1300 hours. Core Sample No. 2 was an attempt to obtain resin from near the liner wall at the bottom of the cask. The sampler was inserted at an angle with the sampler entering near the center of the cask opening, and the bottom of the sampler ending at the liner wall on the cask bottom.

Several gas bubbles were observed when the sampler was inserted into the resin. Gas bubbles had also been noted when the sampler was inserted to obtain Core Sample No. 1.

The personnel inserting the sampler indicated it took "an effort" to push the sampler through the surface crust at the top of the resin bed.

There was no apparent resin loss from the sampler when it was withdrawn from the cask.

The resin at the bottom of the core was black in appearance but did not appear to be as dark as that found at the bottom of Core Sample No. 1. The remainder of the resin core appeared to be a brown/black mixture as observed in Core Sample No. 1.

The following samples were obtained from Cask A, Core Sample No. 2.

- Sample No. 1. Material from the lower six inches of the core. One large chunk of resin was included in this sample.
- Sample No. 2. Representative material from 6 in. above the bottom of the core to the top of the core.
- Sample No. 3. The crust from the top of the core and a chunk of material obtained about 8 in. from the top.
- Sample No. 4. A thin 3/4 in. thick layer about 8 in. above the bottom of the core. This material was not stuck together but had a different visual appearance. All lighter color resins in this sample were from the inability to prevent some mixing when taking the sample.

#### Cask B, Representative Sample

Cask B contained resin that had been removed from the resin holding tank immediately after Cask A was filled. Cask B had undergone two cycles of dewatering but was backfilled with water after the exothermic event in Cask A was detected. Cask B was not sealed and was inside the "greenhouse" with Cask A. Algae or similar growth was very apparent in the liquid on the top of the material in Cask B; this is not unusual because of the long time period the cask had been open to the atmosphere.

A single core sample was obtained from Cask B on August 2, 1983, at about 1430 hours. The core was obtained by inserting the sampler vertically into the resin bed near the center of the cask opening.

Some gas bubbles were observed during the sampling, but there was no apparent odor at Cask B.

The very bottom 1 in. of the core contained mostly whitish resin beads which were later identified as a macroreticular resin. The total depth of the resin core sample was 3 ft. 6 in.

A single sample, representative of the total core was taken. This sample excluded the whitish resin at the very bottom and the very top which obviously contained "pond muck" as a result of the water draining through the core. The resin in the core was "brown;" i.e., it didn't look like new resin, but it did not have the mixed brown/black appearance of the core samples from Cask A. However, there are dark resin beads present in the core from Cask B - this may indicate that the dark resin is not necessarily associated with the conditions of the exothermic event that occurred in Cask A.

#### Cask C, Representative Sample

Casks C, D, and E had approximate internal volumes of 164 cubic feet whereas Casks A and B were smaller, having volumes of approximately 103 cubic feet. Casks C, D, and E also were filled after additional spent resin had been added to the resin storage tank. The approximate total mixture of "old" and "newer" resins in the resin storage tank at the time of loading Casks C, D, and E was ~130 cubic feet of "old" resin and ~270 cubic feet of "newer" resin.

Casks C, D, and E had been sealed since their filling and were opened just prior to obtaining the core samples. The distinctive odor associated with Cask A was not apparent in any of these casks.

A single core sample was obtained from Cask C on August 3, 1983, at about 0930 hours. The core was obtained by inserting the sampler vertically into the resin bed near the center of the cask opening. No difficulties were observed in inserting the sampler.

Resin was lost from the sampler during the withdrawal because the shutter did not completely close. Later examination indicated that as much as 12 in. of resin may have been lost. The length of the core was 3 ft. 6 in., but indications are that the resin bed in the cask was 4 ft. 6 in. deep.

The bottom few inches of the core were somewhat darker in color to the eye, but the core generally contained resin that was "new" in appearance, i.e., yellowish in color, not brown or black. A single sample was obtained by sampling the entire core to obtain a representative sample. Material at the very top of the core was excluded from the representative sample. Microscopic observation of a sample obtained from the darker region of the core showed the presence of a very few dark resin beads.

#### Cask D, Representative Sample

A single core sample was obtained from Cask D on August 3, 1983, at about 1100 hours. The core was obtained by inserting the sampler vertically into the resin bed near the center of the cask opening. No difficulties were observed in inserting the sampler.

The resin core separated in two places during transport, but no resin was lost nor should the profile have been changed. The length of the resin core was 4 ft. 4 in.

The resin located in the lower six inches of the core was darker than the remainder of the core. The personnel doing the sample transfers from the core to the sample bottles stated there were very dark or black resin beads throughout the core.

Microscope samples taken at 2 in. from the bottom of the core indicated the presence of grayish macroreticular resin, brown macroreticular resin, and several black beads. A microscope sample taken at 2 ft. 6 in. above the bottom of the core had clear gel resins, amber gel resins, and black and/or very reddish beads.

The following samples were obtained from Cask D.

- Sample Cask D1. Bottom 6 in. of core.
- Sample Cask D2. Representative sample from 8 in. above the bottom of the core to its top.

#### Cask E, Core Sample No. 1

Cask E was the last cask loaded during the cleanout of the resin storage tank. The final cleanout of the resin storage tank required the use of high pressure water streams to remove "caked" resin from the walls, and this material was loaded into Cask E.

Cask E was opened and sampled on August 3, 1983, during the afternoon. The individual who opened the cask stated there was a "rotten" smell present when the cask lid was first removed. However, within fifteen minutes no odor was apparent to several people who approached the cask opening. It was also stated by the individual who opened Casks C, D, and E, that Casks C and D also had the same "rotten" smell when their lids were first removed.

The surface of the liquid in Cask E was completely covered (visual observation through the cask opening) with a layer of oily scum, with some clear oil floating in globules. A sample of the oily material was taken. The thickness of the scum layer in the cask was measured to be about 3/8 in. - 1/2 in.

Core Sample No. 1 was obtained by inserting the sampler vertically into the cask near the center of the cask opening. Bubbles were released during the time period of obtaining the core sample. The personnel conducting the core sampling stated the rotten smell was present when the sampler was inserted and withdrawn. However, all personnel stated the "rotten" odor detected in Casks C, D, and E was not that associated with Cask A.

The depth of the resin bed in Cask E was only one foot; the remainder of Cask E contained only water with the oily material at the liquid surface.

The following samples were obtained from Cask E, Core Sample No. 1.

- Sample No. 1, Resin from the lower 3 in. of the core.
- Sample No. 2. Resin from the upper 6 in. of the core.

Microscopic evaluation of samples taken from the core indicated the lowest 3 in. of the core contained essentially all gel-type resins while the upper portion of the core contained mostly macroreticular resin.

A sample of water was also taken from Cask E.

#### Cask E, Core Sample No. 2

Core Sample No. 2 was taken to obtain resin from near the liner walls. The core was obtained by inserting the sampler at an angle from near the center of the cask opening and having the bottom of the sampler at the liner wall on the bottom of the cask.

The core sample was ten inches deep. The lower three inches of the core contained darker resins. Grayish macroreticular resins predominated in the remainder of the core. The following samples were obtained from Cask E, Core Sample No. 2:

- Sample No. 1. Some sludge and resins taken at the very bottom of the core.
- Sample No. 2. Red-looking resin beads located at the bottom of the core.
- Sample No. 3. Sampled core from ~3 in. above bottom to top. Mostly macroreticular resins. Sludge from the very top of the resin core was excluded.

#### MICROSCOPIC EXAMINATION OF AP&L CASK RESINS

Visual examinations of various core samples obtained from Casks A, B, C, D, and E were obtained using optical microscopy. The purpose of these studies was to determine the type of resin present (gel or macroreticular) and the resin appearance. The following text identifies the samples examined by optical microscopy and describes these observations.

Cask A, Core No. 1, Sample No. 1

Examination of this sample in the sample bottle with a bright light indicated that all beads were a bright (glistening) shiny black except for a very small portion (~2%) of macroreticular beads.

Examination of this sample under a microscope indicated that not all the beads were black charred beads. It appeared that many gel-type beads were present with an oily film on their surface, and that this film contained fine black material (probably char). It was very difficult to determine how many beads were truly black and how many were only coated. Many (most) of these beads floated on water and appeared hydrophobic.

Three samples of this resin were washed with 3 solvents;  $\text{CCl}_4$ , ethanol, and xylene. All of these removed appreciable brown color, xylene the most, and  $\text{CCl}_4$  the least, and after such treatment, the beads no longer appeared coated.

Examination After Xylene Wash. No  $\text{H}_2\text{O}$  was added. After some evaporation of xylene, the beads, although not appearing coated as before, still appeared hydrophobic with most floating and appearing to stick together somewhat. The sample was then washed twice with acetone and again placed in  $\text{H}_2\text{O}$ . At this point very few beads floated, and the resin was not surface coated.

Less than 10% of the beads were macroreticular. Various stages of pyrolysis appeared to be present in both the gel-type and macroreticular resin. These ranged in appearance from what appeared to be carbon beads through strongly colored but clear to only yellow beads. Many fragments were present, including both resin fragments and carbon particles. Probably much less than 10% of resin was totally carbonized, but many beads were very dark and appeared to have some spots of carbonization on them.

One brown macroreticular bead was present with sufficient breakage to see that its interior was white. Other brown to tan macroreticular beads were often cracked, but the cracks were not sufficiently open to see the interior of the bead.

Cask A, Core No. 1, Sample No. 2

This resin appeared to have an oily film and to be somewhat hydrophobic but did not have the mass of fine black material on the bead surfaces. After two acetone washes this oily film appeared to have been removed. The resin (except for totally blackened beads) appeared to be about 80% macroreticular. Some of the gel-type resin, and a very few macroreticular beads, appeared to have the grey surface coating described above, but this appeared to be less extensive and not as great on each bead as in the sample immediately below. There did appear to be a slightly higher proportion of totally opaque (charred) black beads but fewer black fragments. Most of the black beads appeared quite solid although several showed extensive surface cracking in a network very similar to the surface-cracked brown macroreticular beads observed before, and of which there are a few in this sample. These black beads definitely looked different and were certainly much less cracked, broken, and distorted than the black beads in the lower portion of the core. A few very grey opaque beads were seen. One grey bead had at least four round spots where it appeared to have touched other beads. The round spots were white macroreticular resin showing through. Except for this area, one can see only a slight amount of light resin showing through. Another macroreticular bead had many grey spots that appeared almost as if they were nucleation sites for crystallization of porous metal.

It appeared that a major portion of the truly opaque carbonized beads were produced from macroreticular beads. One large grey macroreticular bead was broken and was largely off-white inside but with two or three discrete grey spots inside the bead. It appeared that this may have been due to the beginning of carbonization.

During solvent cleaning this material did not have any appreciable fine black solids suspended in the organic, unlike the samples in the lower portion of the core. This, again, points to the greater physical stability of the charred beads in this region.

A very small amount of brick-red, porous looking particles were found which were not shaped like resin beads at all. The sample also contained some broken chips (fines) of both gel-type and macroreticular resin.

Cask A, Core No. 1, Sample No. 3

This sample consisted of a resin lump which was sufficiently hard that it made a crunching sound when a 1/2 in. piece was cut off with a scoopula. The lump (1/2 in. piece) was washed with acetone (removing very little color) to rinse "tramp" beads off the lump. The small lump was examined and found to be completely pyrolyzed with sintering. No unpyrolyzed beads were observed.

Cask A, Core No. 1, Sample No. 4

Although this sample appeared to have a slight hydrophobic film, it did not appear to have any black particulates on the beads. H<sub>2</sub>O was added, and the resin was easily examined without solvent washing. The resin suspension was clean with fines being almost entirely broken, uncharred bead fragments.

This resin was also mostly (~75-80%) macroreticular. It contained somewhat fewer carbonized beads than the zone just below. Otherwise, the sample was similar in that the charred beads appeared to be intact, often with "alligator hide" surface cracking but also often with a shiny surface. There were some dark brown macroreticular beads, including ones showing lighter spots where they had contacted other beads. The gel-type beads were not coated with grey material, although there appeared to be some (but less than samples obtained lower in the core) on the carbonized beads.

One macroreticular bead was observed with several (~100) very discrete dark grey spots with sharp boundaries. The grey was an opaque metallic grey, as also noted in a few beads in Core No. 1, Sample No. 2. Reflection (these may be incipient localized nucleated charring) faces occurred in these dark grey spots but were too small to determine with certainty if they were crystal faces. The charred beads were 10 to 15% of the total.

Cask A, Core No. 1, Resin Above 30 in. Level (only a microscope sample was taken)

This sample was in H<sub>2</sub>O and not solvent washed. It had a lot of fine cream-colored particles much smaller than the resin beads floating in the water. It had some resin in clumps with the void spaces completely filled with what appeared to be this same material. It looked very much like it might be biofouling. This sample looked much like the one just below in quantity and nature of carbonized beads. The gel-type and charred beads had a large amount of greyish surface "crud" on them unlike the sample below.

Cask A, Core No. 2, Sample No. 1

The resin in this sample had an oily film similar to the same region in Core 1. Acetone was added to the sample but the sample was not washed; the oil film came off. The sample had many carbon particles and broken carbonized beads. The resin was mostly gel-type. Many, but not all of the carbonized beads were coated with tan to brown crud as were many of the noncharred gel-beads. Many carbon shells of beads exist. The resin in this sample is probably 30+% carbonized.

Cask A, Core No. 2, Sample No. 2

This sample, as obtained in H<sub>2</sub>O, showed all of the features seen in a composite of all samples of Core 1 above the 8 in. level. This included about the same percentage of carbonized beads, macroreticular resin, surface crud, possible biofouling, brown macroreticular beads, grey macroreticular beads, etc.

Cask A, Core No. 2, Sample No. 4

This resin was probably about 20% macroreticular. The resin (gel) varied from black to clear beads with relatively few (10-20%) actual charred beads. Most of the near black or deep red beads had blobs and patches of porous grey to grey-brown material on the surface. Not all beads had this (only one or two macroporous beads were found with it). The material appeared somewhat similar to grey metallic sponge and showed up on some (most), but by no means

all, of the light colored gel beads. It was definitely not present to as great an extent in the sample of the bottom six inches of resin, despite beads of varying colors from pale yellow to jet black being present in that solvent washed sample.

Cask E, Core No. 2, Sample No. 3

This sample had some resin clumps with beads or bead fragments cemented together with light crusty material. Some other beads had some surface crusting of light to greyish material. Among the gel-type beads, there were some very deep red beads. All beads, but in particular the macroreticular ones, showed some surface crazing that appeared to be impact related. This may be related to the high pressure water stream used to remove this resin from the resin storage tank. Some of the brown surfaced macroreticular beads had been chipped, and these appeared to be whiter inside than on the surface.

In contrast to this sample, the Cask B macroreticular resin (bottom of core) was much shinier on the surface (less surface chipping, etc.) and also appeared to be whiter (less brown beads). Also, in this sample, there did not appear to be any surface deposits or cementing.

In Core 1 of Cask E, the macroreticular resin appeared similar to that in Core 2 of Cask E, but no crusty deposits were observed in the microscope sample.

APPENDIX B

CNSI SOLIDIFICATION WORKSHEET 1  
(PCP SOLIDIFICATION OF PARTICULATE WASTES)

Appendix B contains proprietary information and has been withheld from public disclosure per the provisions of 10 CFR 2.790.

APPENDIX C

BATTELLE - NORTHWEST  
LABORATORY PROCEDURES

FOR

SOLIDIFICATION OF ION EXCHANGE RESINS

Appendix C contains proprietary information  
and has been withheld from public disclosure  
per the provisions of 10 CFR 2.790.

## APPENDIX D

### DESCRIPTION OF NEW ION EXCHANGE RESINS FURNISHED BY ARKANSAS POWER AND LIGHT COMPANY, ARKANSAS NUCLEAR No. ONE

Ion exchange resins are used for various purposes by Arkansas Power and Light Company at Arkansas Nuclear No. One. Specific resins are selected by AP&L in accordance with their desired use and the normal purchasing practices of AP&L. Samples of new resins were furnished to Battelle-Northwest by AP&L for the purpose of conducting resin solidification tests. The manufacturers and identification codes are given.

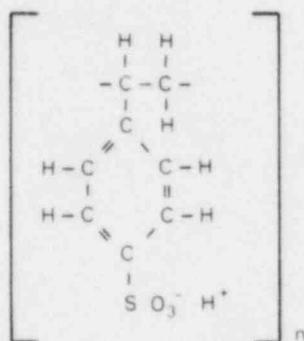
Visual examination of the various core samples obtained from the casks indicated varying amounts of gel and macroreticular resins present in each cask. The functional group, or polymeric unit, of the resins in the casks was not determined. Thus, the casks contain resins known to have been used at ANO, but the manufacturer, identification code, and functional group of the resins in the casks is not known.

Battelle-Northwest's resin solidification studies were conducted, using the Chem-Nuclear Systems, Inc. solidification procedure, to determine if potentially hazardous or unanticipated reactions would occur as a result of solidification of the spent resins contained in Casks A, B, C, D, and E. Solidification tests of the new resins furnished by AP&L were conducted as a reference to those conducted with cask resins. Therefore, solidification of cask resins should give results within the range of results obtained for the new resins if no unusual or unexpected reactions occur as a result of solidifying the cask resins.

Brief descriptions of the new resins furnished by AP&L are given in the following text. More detailed information should be obtained from the manufacturers.

### IRA-200C

IRA-200C is the trade name of a strongly acidic cation exchange resin manufactured by Rohm and Haas Company. The polymeric unit is shown below with brief comments also given.

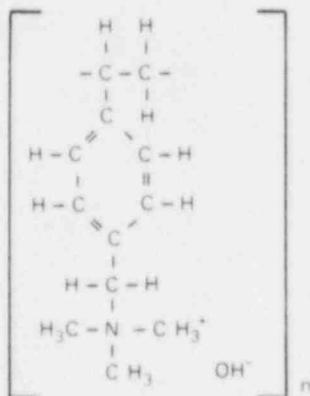


The resin is crosslinked with about 20% divinylbenzene, meaning that about every fifth benzene ring is attached to two aliphatic chains. Because divinylbenzene normally contains up to 50% ethylstyrene, there will also be ethyl groups, not part of the polymer chain, attached to some benzene rings.

This is a macroreticular resin.

### IRA-900C

IRA-900C is the trade name of a strongly basic anion exchange resin manufactured by Rohm and Haas Company which derives its exchange activity from quaternary ammonium groups. The polymeric unit is shown below.



This resin is also crosslinked with divinylbenzene - see comments given for IRA-200C.

This is a macroreticular resin.

#### A-101 D

Duolite A-101 D is the identification number of a strong-base anion exchanger manufactured by Diamond Shamrock Chemical Company. The basic repeating unit is the same as for IRA-900C. The crosslinking is done after the polymerization is complete (unlike most other polystyrene resins). We do not know the crosslinking agent, but there are reasons to believe it is not divinylbenzene.

The sample we received from AP&L is a gel-type resin.

#### ARC-9358

ARC-9358 is believed to be Duolite ARC-358, the identification number of a strongly acidic cation exchange resin manufactured by Diamond Shamrock Chemical Company. The basic repeating unit is the same as that for IRA-200C, but with only 8% divinylbenzene crosslinking.

This is a gel-type resin.

#### C20-H

Duolite C20-H is the identification number of a resin manufactured by Diamond Shamrock Company. It is the same resin as ARC-358 but is a standard grade whereas ARC-358 is a high purity grade.

This is a gel-type resin.

#### ARA-9371

ARA-9371 is believed to be ARA-371, the identification number of an intermediate strength basic anion exchange resin manufactured by Diamond Shamrock Company. ARA-371 is an epoxy-polyamine resin, but we do not know its exact structure. A possible structure based on the condensation of polyethyleneamine and epichlorohydrin is given below.

This is a gel-type resin.



## APPENDIX E

### HEAT CAPACITY AND HEATS OF SOLIDIFICATION STUDIES

Thermal analysis techniques were utilized to determine the heat capacity of cement-solidified resin samples. In addition, laboratory-scale solidification tests were conducted in calorimetry cells on both cask and new resin samples. The heat capacity and rate of heat loss from the calorimetry system were also determined. These results were combined, as shown below, to determine the heats of solidification for the cement-solidified resins.

#### Heat Capacities of Cement-Solidified Resins

The heat capacity,  $C_p$ , of cement-solidified resin samples was determined using a Perkin-Elmer DSC-2 differential scanning calorimeter (DSC). A DSC measures heat changes in a material or chemical system as a function of temperature; the measurements may be obtained either isothermally or at a constant temperature increase.

The heat capacity,  $C_p$ , is the change in heat content,  $\Delta H$ , as a function of a change in temperature,  $\Delta T$ .

$$C_p = \Delta H / \Delta T$$

A DSC measures  $\Delta H / \Delta t$ , where  $\Delta t$  is the change in time at a constant  $\Delta T / \Delta t$ . Therefore,  $C_p$  can be determined using the relationship

$$C_p = \frac{\Delta H / \Delta t}{\Delta T / \Delta t}$$

The experimentally determined heat capacities for the cement-solidified resin samples and for a sapphire standard are given in Table E-1.

TABLE E-1. Heat Capacities of Selected Cement-Solidified Resin

Temp., K; (°C)	$C_p$ , cal/g/deg			
	Sapphire, Actual	Sapphire, Experimental	Diamond Shamrock <sup>(a)</sup> C20-H, Solidified	Rohm & Haas, <sup>(a)</sup> 200C, Solidified
298; (25)	0.185	0.185	0.222	0.312
303; (30)	0.188	0.183	0.244	0.350
313; (40)	0.192	0.191	0.310	0.439
323; (50)	0.197	0.199	0.407	0.567
333; (60)	0.201	0.204	0.544	0.737

(a) Linear regression,  $C_p = a + bT$  where the temperature,  $T$ , ranged from 298-333°K for Diamond Shamrock C20-H and Rohm & Haas 200C gave the following respective results:  $r^2$ , correlation coefficient = 0.967, 0.98;  $a = -2.487, -3.28$ ; and  $b = 0.009, 0.012$ .

The cement-solidified Diamond Shamrock C20-H sample contained a large relative amount of resin, while the cement-solidified Rohm and Haas 200C sample contained a low relative amount of resin. These two samples were chosen as "representative" samples of the resin solidification tests. Agreement between actual and experimental values of the heat capacity of sapphire are quite good. The variation in heat capacity between the two actual cement-solidified resins chosen for analysis was probably caused by differences in water content. A rerun of the cement-solidified Rohm and Haas 200C sample showed a large decrease in heat capacity, especially at 60°C; this decrease is attributable to loss of water during the first DSC test. The heat capacity values for cement solidified resins were used to determine the heats of solidification as described in the report.

Measurement of the Heat Capacities and Rate of Heat Loss of the Calorimetric Cells Used for Temperature Monitoring of Resin Solidification in Cement

The objective of this work was to measure the heat capacity of the large and small dewar calorimetric systems used to measure the temperature rise for the cement solidification of Arkansas Power and Light ion exchange resins. This was accomplished by introducing a measured amount of energy to the system and determining the heat loss. The experimental apparatus, the method used, and the results of these experiments are described.

To determine the energy lost from the calorimeter, a known amount of electrical energy was converted to heat energy and used to heat up a known quantity of deionized (DI) water. The amount of energy absorbed by the water was calculated using its heat capacity and the temperature increase. The amount of heat absorbed by the calorimeter was the difference between the heat input and that absorbed by the water. After the temperature of the water was raised 10°C, corresponding to the rise seen in the cement solidification tests, power was shut off and the water temperature allowed to return to ambient. This allowed calculation of the rate of heat loss. The equations used were:

$$1) \Delta H_{\text{input}} = I^2 R t$$

where  $I$  is the current in amperes,  $R$  is the resistance in ohms, and  $t$  is the time in seconds. The units of this calculation are joules. The units may be converted to calories by dividing by 4.184.

$$2) \Delta H_{\text{H}_2\text{O}} = C_p \Delta T m$$

Where  $C_p$  is the heat capacity of water (4.2 J/g/K),  $\Delta T$  is the change in temperature, and  $m$  is the mass of the water.

$$3) C_{p_{\text{cell}}} = (\Delta H_{\text{input}} - \Delta H_{\text{H}_2\text{O}}) (\Delta T)^{-1}$$

$$4) \text{Rate of Heat Loss} = (-\Delta H_{\text{H}_2\text{O}}) t^{-1}$$

Figure E-1 is an electrical schematic of the experimental system, and Figure E-2 is a schematic of the calorimetric cell. The heater was made from nichrome wire and had a resistance (R) of  $2.55 \mu$  with current flowing. The voltage drop across the heater was measured using a digital multimeter every 120 sec and monitored by a small laboratory computer. The temperature of the water and of room air was monitored using the lab computer. The current used in the  $\Delta H$  input calculation was calculated based on the measured voltage drop and electrical resistance, i.e. ( $I = \frac{V}{R}$ ).

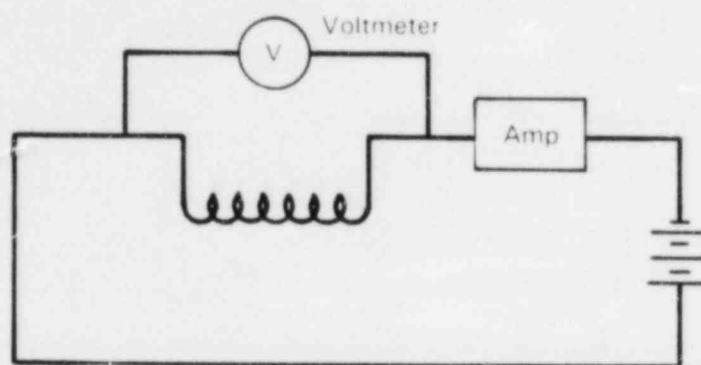


FIGURE E-1. Electrical Schematic of Technique Used to Determine Heat Capacities of Calorimetric Cells

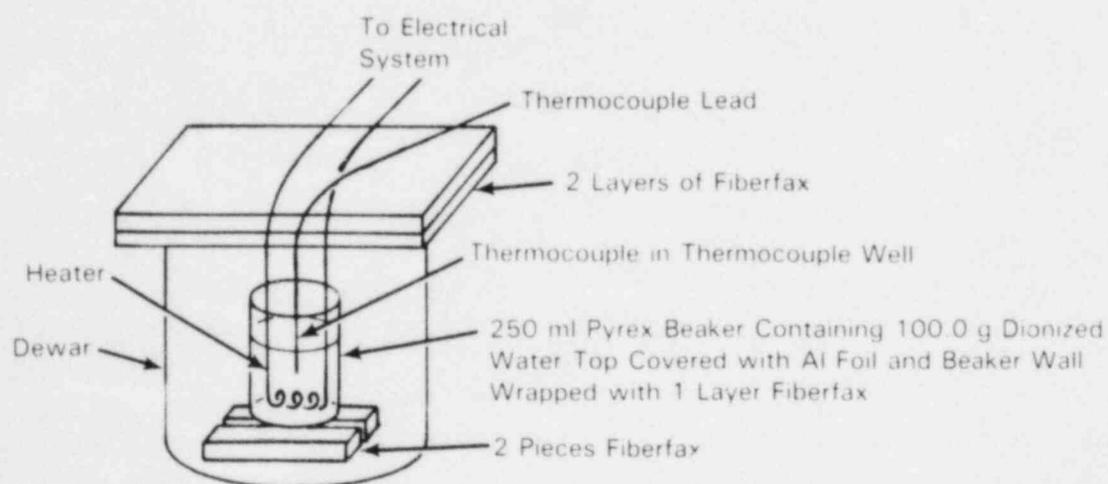


FIGURE E-2. Schematic of Calorimetric Cell

The results of these experiments are presented in Table E-2. In both cases, 40% of the input energy was lost to the calorimetric cell. The heat loss and the heat loss rate were both greater for the large dewar, probably because of the increased mass of the system.

TABLE E-2. Heat Capacities and Heat Loss Rate for Calorimetric Cells Used in Resin Solidification Tests<sup>(a)</sup>

System	$\Delta H_{\text{input}}, \text{ J}$	$\Delta H_{\text{H}_2\text{O}}, \text{ J}$	$\Delta H_{\text{loss}}, \text{ J}$	$C_p(\text{cell}), \text{ J/K}$	Heat loss, J/sec
Small Dewar <sup>(b)</sup>	7660	4770	2880	253	0.17
Big Dewar <sup>(c)</sup>	8820	5310	3510	278	0.25

(a) Results reported in joules; units may be converted to calories by dividing by 4.184.

(b) Dewar used for solidification tests with cask resins.

(c) Dewar used for solidification tests with new resins.

#### Heats of Solidification

The heats of solidification for the laboratory-scale resin solidification tests were determined as shown below:

$$\Delta H (\text{solidification}) = \Delta H (\text{system}) + C_p \Delta T$$

where  $\Delta H (\text{system}) = C_p (\text{calorimeter cell}) \Delta T + \Delta H (\text{lost from system})$

$C_p \Delta T$  = enthalpy change noted from the cement-solidified resin sample.

$\Delta T$  = maximum temperature attained minus initial temperature.

Using Solidification Test #9 (Cask A, Core 1) as an example we have

$$\Delta T = (24.0^\circ\text{C} - 21.8^\circ\text{C}) = 2.2 \text{ deg.}$$

$C_p$  (calorimeter cell) = 253 J/K = 60.47 cal/K  
 $C_p$  (cement sample) range = 0.222 to 0.312 cal/g/deg  
Rate of Heat Loss from System = 0.17 J/sec = 146.27 cal/h  
Time to Reach Maximum Temperature = 30 h  
Mass of Cement/Resin Sample = 211.9 g

This gives a heat of solidification of

$$\begin{aligned}\Delta H (\text{solidification}) &= \Delta H (\text{system}) + C_p \Delta T \\ &= C_p (\text{calorimeter}) \Delta T + \Delta H (\text{lost from system}) \\ &\quad + C_p (\text{cement}) \Delta T\end{aligned}$$

$$\begin{aligned}\Delta H (\text{solidification}) &= (60.47 \text{ cal/K})(2.2 \text{ K}) \\ &\quad + (146.27 \text{ cal/h})(30 \text{ h}) \\ &\quad + (0.222 \text{ cal/g/K})(2.2 \text{ K})(211.9 \text{ g}) \\ &= (133.03 + 4388.10 + 103.49) \text{ cal.} \\ &= 4624.62 \text{ cal.}\end{aligned}$$

or  $\Delta H (\text{solidification})/\text{g}$  of cement/resin sample = 21.8 cal/g.

Using the higher heat capacity value of 0.312 cal/g/K for the cement-solidified resin results in a heat of solidification of 22.02 cal/g for Test #9. Similar values are obtained for the other resin solidification tests.

APPENDIX F  
SIMULATED DEWATERING TESTS

CASK DEWATERING PARAMETERS AND STANDARDS

The following information concerning actual resin cask dewatering parameters and standards was provided to Battelle-Northwest by Arkansas Power and Light Company and should be considered proprietary information until permission for further dissemination is given by AP&L. This information provided the basis of the simulated dewatering tests performed by Battelle-Northwest.

Cask Dimensions

Cask A ~ 103 cubic feet liner

External diameter	=	60 in.
Height	=	72 in.
Inner diameter	≅	58 in.
Inner height	≅	67 in.

Dewatering Cycle and Cask Disposal Criteria

Dewatering Cycle: 8 hours pumping, 16 hours of no pumping.

During dewatering, the pump rate is set when pumping water. If the pump quits pumping water, it pumps air and the pump rate increases when pumping air. Normally, the pump is readjusted when it is pumping air to the same pump rate used for pumping water. However, if no one was present to readjust the pump rate, it could have pumped air at a greater rate than that used for water.

Water Standard for Liner Burial: <2 L of free water at end of an 8-hour pump cycle.

### Pump Parameters

Pump Capacity  $\cong$  1.5 gallon of water per second.

Average Displacement per Stroke = 0.34 gal. (1.3 L)

Minimum Chem-Nuclear Specifications = Pump rate of 15-20 strokes per minute (minimum).

Pump Rate Set by AP&L: 2 strokes per second when pumping water. Possible pump rate is 3-5 strokes per second (information from Chem-Nuclear representative at ANO).

### CALCULATIONS/ASSUMPTIONS USED FOR LABORATORY-SCALE SIMULATED DEWATERING TESTS

The following gives the complete calculations and assumptions used by Battelle-Northwest to conduct the laboratory-scale simulated dewatering tests.

#### Air Flow Through Cask Resin Bed

Pump rate: Minimum = 2 strokes/sec.

Maximum = 5 strokes/sec.

Air Flow through Resin Bed:

Minimum = (2 strokes/sec)(1.3 L/stroke)  
= 2.6 L/sec.

Maximum = (5 strokes/sec) (1.3 L/stroke)  
= 6.5 L/sec.

#### Cask and Resin Bed Volume

Cask Volume: Volume =  $\pi r^2 h$   
=  $(\pi)(29 \text{ in})^2(67 \text{ in})$   
= 176,929 in<sup>3</sup>

1 in<sup>3</sup> = (2.54 cm)<sup>3</sup> = 16.39 cm<sup>3</sup>

Volume = 2,899,875 cm<sup>3</sup>  
= 2,899 L

$$\begin{aligned}
 \text{Check: Stated volume} &\cong 103 \text{ ft}^3 \\
 (103 \text{ ft}^3)(12 \text{ in/ft})^3 &= 177,984 \text{ in}^3 \\
 &= 2,917,158 \text{ cm}^3 \\
 &= 2,917 \text{ L}
 \end{aligned}$$

Check is close enough - use volume based on estimated inner dimensions (~2900 L).

Cross-Sectional Area of Resin Bed:

$$\begin{aligned}
 \text{Area} &= \pi r^2 \\
 &= \pi (29 \text{ in})^2 \\
 &= 2,640 \text{ in}^2 \\
 &= 17,037 \text{ cm}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Resin Volume} &= (\text{Cross-Sectional Area}) \\
 &\quad (\text{Resin bed depth}) \\
 &= (2,640 \text{ in}^2) (42 \text{ in}) \\
 &= 110880 \text{ in}^3 \\
 &= 1817 \text{ L}
 \end{aligned}$$

#### Exit Velocity

$$\begin{aligned}
 \text{Exit Velocity} &= \text{Flow rate/cross-sectional area.} \\
 \text{Minimum} &= (2,600 \text{ cm}^3/\text{sec}) / (17,037 \text{ cm}^2) \\
 &= 0.15 \text{ cm/sec.} \\
 \text{Maximum} &= (6,500 \text{ cm}^3/\text{sec}) / (17,037 \text{ cm}^2) \\
 &= 0.38 \text{ cm/sec.}
 \end{aligned}$$

A 300 mL volume of resin bed was used in the experimental dewatering tests; the air flow rates needed to duplicate the AP&L dewatering conditions are:

Minimum Air Flow:

$$\frac{300 \text{ mL}}{1.8 \times 10^6 \text{ mL}} = \frac{x}{2.6 \times 10^3 \text{ mL/sec.}}$$

$$x = \frac{(3 \times 10^2 \text{ mL})(2.6 \times 10^3 \text{ mL/sec.})}{1.8 \times 10^6 \text{ mL}}$$

$$x = 0.433 \text{ mL/sec.}$$

$$x = 26.0 \text{ mL/min.}$$

Maximum Air Flow:

$$\frac{300 \text{ mL}}{1.8 \times 10^6 \text{ mL}} = \frac{x}{6.5 \times 10^3 \text{ mL/sec.}}$$

$$x = \frac{(3 \times 10^2 \text{ mL})(6.5 \times 10^3 \text{ mL/sec.})}{1.8 \times 10^6 \text{ mL}}$$

$$x = 1.083 \text{ mL/sec.}$$

$$x = 65.0 \text{ mL/min.}$$

Dewatering Test Air Flow Rates:

For 300 mL resin: Minimum  $\cong$  26 mL/min.

Maximum  $\cong$  65 mL/min.

#### Predicted Maximum Temperature Increase for Dewatering Tests

The thermodynamic calculations discussed under Phase III used an estimated resin composition in Cask A of ARA-9371, ARC-9358, IRA-200C and IRA-900C, present in equal volumes. The same assumed composition is used in the following calculations.

Assume 300 mL of resin:

Composition = 38.8 g H<sub>2</sub>O/100 mL = 116.4 g H<sub>2</sub>O/300 mL  
36.6 g Exchanger/100 mL = 109.8 g Exchanger/300 mL  
(24.6% void space).

Assume the heat capacity of the exchanger = 0.3 cal/g/deg.

Airflow through resin bed: Minimum = 1,560 mL/h.  
Maximum = 3,900 mL/h.

Oxygen flow through resin bed (air = 20.95% O<sub>2</sub>):

Minimum = 326.8 mL/h.  
=  $1.5 \times 10^{-2}$  mole O<sub>2</sub>/h.  
Maximum = 817.0 mL/h.  
=  $3.6 \times 10^{-2}$  mole O<sub>2</sub>/h.

$\Delta H_{\text{combustion}}$  for resin (using ethyl benzene as a representative "stand-in") from thermodynamic calculations is:

$\Delta H_{\text{comb}} = -114.4$  kcal/mole O<sub>2</sub> to form carbon and water (liq.).

Assuming 100% utilization (reaction) of the oxygen passing through the resin gives heat of combustion rates.

$\Delta H_{\text{comb}}$  (minimum O<sub>2</sub> flow) = -1.72 kcal/hr.

$\Delta H_{\text{comb}}$  (maximum O<sub>2</sub> flow) = -4.12 kcal/hr.

Heat Available to Raise Temperature of Resin Bed:

$\Delta H_{\text{comb}}$  - Heat Loss to Dewar - Heat loss to air being passed through bed.

The heat loss to the air being passed through the bed is estimated as follows:

Heat capacity of O<sub>2</sub> = 7.017 cal/deg/mole  
Heat capacity of N<sub>2</sub> = 6.960 cal/deg/mole.

If it is assumed all the  $O_2$  reacted, only the heat capacity of  $N_2$  should be considered (the difference in the heat capacity of  $O_2$  and  $N_2$  is insignificant for the present purpose even if the assumption is not correct).

$$\begin{aligned}\text{Minimum } N_2 \text{ flow through 300 mL experimental resin bed} &= 1233 \text{ mL/h} \\ &= 5.5 \times 10^{-2} \text{ mole } N_2/\text{h}\end{aligned}$$

$$\begin{aligned}\text{Maximum } N_2 \text{ flow through 300 mL experimental resin bed} &= 3083 \text{ mL/h} \\ &= 1.4 \times 10^{-1} \text{ mole } N_2/\text{h}\end{aligned}$$

The maximum heat absorbed by the  $N_2$  in 300 mL experimental resin bed is:

$$\begin{aligned}\text{Minimum flow} &= (6.960 \times 10^{-3} \text{ kcal/deg/mole})(5.5 \times 10^{-2} \text{ mole/h}) \\ &= 3.8 \times 10^{-4} \text{ kcal/deg/h}\end{aligned}$$

$$\begin{aligned}\text{Maximum flow} &= (6.960 \times 10^{-3} \text{ kcal/deg/mole})(1.4 \times 10^{-1} \text{ mole/h}) \\ &= 9.7 \times 10^{-4} \text{ kcal/deg/h}\end{aligned}$$

Thus, we concluded that the heat loss to the  $N_2$  exiting the system was negligible in comparison to the heat of combustion and to the other heat sinks in the system (dewar plus (resin + water)) and could be neglected.

The heat rate loss from the dewars used in the experimental dewatering tests was estimated from the data obtained in Test 4 (see Table 6) in which heated resin was used; the 6 hour time period was used for these calculations.

$$\begin{aligned}300 \text{ mL resin bed} &\cong 226.2 \text{ g} \\ \text{Initial Temperature} &= 54^\circ \text{ C} \\ \text{Final Temperature} &= 28^\circ \text{ C} \\ \text{Heat Loss Rate} &= \Delta H/\Delta t = C_p \Delta T/\Delta t \\ &= (1.5 \times 10^{-1} \text{ kcal/deg})(26 \text{ deg})/6 \text{ h} \\ &= 6.5 \times 10^{-1} \text{ kcal/h}\end{aligned}$$

The heat absorbed by the water and exchanger material present in the experimental system (300 mL resin bed) was calculated as shown below:

$$\begin{aligned}\text{Heat Absorbed by Water Present in the Resin:} & \\ &= (116.4 \text{ g } H_2O)(1 \times 10^{-3} \text{ kcal/deg/g } H_2O) \\ &\cong 1.2 \times 10^{-1} \text{ kcal/deg}\end{aligned}$$

Heat Absorbed by Exchanger:

$$\begin{aligned} &= (109.8 \text{ g exchanger})(3 \times 10^{-4} \text{ kcal/deg/g exchanger}) \\ &\cong 3.3 \times 10^{-2} \text{ kcal/deg} \end{aligned}$$

Heat Absorbed by 300 mL Resin Bed  $\cong 1.5 \times 10^{-1}$  kcal/deg

Therefore, the heat available to raise the temperature of the resin bed is:

$$\Delta H_{\text{comb}} - \text{Heat Loss Rate of Dewar}$$

At the minimum flow rate:

$$\begin{aligned} \text{Heat available} &= -1.72 \text{ kcal/h} + 0.65 \text{ kcal/h} \\ &= -1.07 \text{ kcal/h} \end{aligned}$$

At the maximum flow rate:

$$\begin{aligned} \text{Heat available} &= -4.12 \text{ kcal/h} + 0.65 \text{ kcal/h} \\ &= -3.47 \text{ kcal/h} \end{aligned}$$

The expected temperature increase in the experimental system (300 mL resin bed), assuming 100% utilization of the oxygen in the air passing through the bed would be:

$$\Delta T(\text{increase}) = (\text{Heat Available})/(\text{Heat Absorbed by Resin Bed})$$

At the minimum flow rate,

$$\begin{aligned} \Delta T &= (1.07 \text{ kcal/h})/(0.15 \text{ kcal/deg}) \\ &\cong 7 \text{ deg/h} \end{aligned}$$

At the maximum flow rate

$$\begin{aligned} \Delta T &= (3.47 \text{ kcal/h})/(0.15 \text{ kcal/deg}) \\ &\cong 23 \text{ deg/h} \end{aligned}$$

During the early stages of the dewatering process, one would not expect 100% oxygen utilization for oxidation. In reality, to approach 100% oxygen utilization, the heat loss rate through the system and to the air flowing through the system must be slower than the rate of heat increase caused by the oxidation process.

The experimental dewatering tests and the simulated dewatering test calculations do reemphasize, however, that even if all available oxygen were used, the temperature increase would be relatively slow in a bed of resin undergoing air oxidation at the air flow rates used in cask dewatering.