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Technical Considerations Affecting Preparation of Ion-Exchange Resins for Disposal

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Brookhaven National Laboratory

Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

Three incidents involving low-level waste (LLW) from separate nuclear power plants, i.e., dewatered ion-exchange resins or dewatered filter media, occurred during 1983 and 1984. This report summarizes and reviews the investigations into the causes of each incident. Factors unique to each incident are discussed and recommendations are given on the basis of these factors which may help limit such occurrences in the future.

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TECHNICAL CONSIDERATIONS AFFECTING PREPARATION OF ION-EXCHANGE RESINS FOR DISPOSAL

EXECUTIVE SUMMARY

Three unusual incidents involving low-level radioactive waste (LLW) from separate nuclear power plants occurred during 1983 and 1984. Brookhaven National Laboratory (BNL), under contract with the U.S. Nuclear Regulatory Commission (NRC), has evaluated the available technical information regarding each event, along with data collected regarding the handling and behavior of organic ion-exchange media, in order to determine the probable causes of the incidents.

The first took place at Arkansas Nuclear One (ANO) on January 15, 1983 during the final stages of dewatering ion-exchange resin wastes in a high integrity container (HIC). An exothermic reaction apparently occurred, heating up the resin wastes and causing them to give off smoke and/or steam. The exothermic reaction was stopped by adding water to the HIC.

The other two events were detected during the unloading of containerized wastes at the Barnwell, SC, disposal site. The LLW consisted of dewatered filter media from Millstone Nuclear Station (MNS) and from the James A. Fitzpatrick Nuclear Power Plant (FNPP). One HIC from each of these two power plants had pressurized during transport.

The apparent cause of each incident was different; however, these could not be determined unequivocably. Factors or concerns which could cause similar incidents to occur in the future were categorized as follows: resin dewatering, waste characteristics, and waste storage.

Nuclear power plants and vendors have established a performance baseline for dewatering processes. If abnormalities are observed during dewatering, it is recommended that processing be stopped or at least monitored closely.

The presence of biological activity was identified as a cause of pressurization in the FNPP incident, and as a significant contributing factor in the ANO incident. The effects of biological activity in terms of resin degradation are uncertain, but might include loss of exchange capacity with release of sorbed ions or radionuclides, and release of the more tightly bound water in resin beads. Two effects which appear to be significant are agglomeration or clumping in bead resins, and gas generation.

Chemical contamination was the apparent cause for the MNS pressurization incident. A dry cleaning solvent had been dumped down a drain and ended up in the filter media waste. The pressurization presumably was a consequence of the fact that the solvent, although fairly inert, has a high vapor pressure at room temperature.

This study has found that the use and handling of chemicals at nuclear power plants may not always be monitored closely. Spills may not be reported, and the amounts and identities of chemicals used in restricted access areas may not be known. This may not necessarily be a problem provided the chemicals are disposed of properly.

Chemical testing of resins or filter media waste from holding tanks prior to processing for disposal could help to detect potential problems in waste processing. Chemical tests of the resin waste directly would be most desirable. Chemical tests of the liquids associated with the resins may not provide an accurate measure of the species absorbed on the resins, but in general are easier for routine monitoring purposes. Several chemical tests were discussed, and it was recommended that the adequacy of these tests for establishing a baseline of waste characteristics should be evaluated.

Several administrative procedures were discussed. Practices in the use, handling, and disposal of chemical agents and solvents should be reviewed for adequacy. Controls, if not already in place, should be instituted so that inadvertent or improper disposal of chemicals is minimized. Records or inventories of chemicals brought in, used or disposed of in restricted access areas would be one means of maintaining control.

It was recommended that storage of resins or filter media wastes in holding tanks be limited in order to minimize the potential for biological activity in the wastes. An arbitrary one-year limit was suggested, but if longer storage times are needed, then the wastes should be monitored during transfer, processing and disposal operations. On-site storage of waste containers for three to five days before shipment was recommended as a conservative approach to detecting future pressurization incidents. Since the long-term effects of biological activity in resin and filter media wastes cannot be stated with certainty, it was recommended that the following be investigated:

- the factors which influence and encourage microorganism growth in ion-exchange resins and filter-media wastes,
- the by-products of microbial activity in resins and filter media wastes and changes in the characteristics of the wastes as a result of this activity,
- the effects on the wastes of using biocides or chemical agents to prevent microbial growth,
- the extent to which pressurization can occur in sealed containers,
- the consequences of using vented containers or containers with pressure relief mechanisms, e.g., identities and amounts of gases released,
- the potential for microbial growth and its by-products to degrade or corrode container materials.

1. INTRODUCTION

Three unusual incidents involving low-level waste (LLW) from separate nuclear power plants occurred during 1983 and 1984. Brookhaven National Laboratory (BNL), under contract with the U.S. Nuclear Regulatory Commission (NRC), has evaluated the available technical information regarding each event along with data collected regarding the handling and behavior of organic ion-exchange media in order to determine the probable causes of the incidents.

The first took place at Arkansas Nuclear One (ANO) on January 15, 1983 during the final stages of dewatering ion-exchange resin wastes in a high integrity container (HIC). An exothermic reaction apparently occurred, heating up the resin wastes and causing them to give off smoke and/or steam. The temperature measured along the center line near the top of the HIC was 365°F (185°C). The radiation level at the opening in the top of the HIC was measured and found to be 400 mrem/h. The exothermic reaction was stopped (or supressed) by adding 150 gallons of water to the HIC.

The other two events were detected during the unloading of containerized wastes at the Barnwell, SC, disposal site. The LLW involved in these two incidents consisted of dewatered filter media from Millstone Nuclear Station (MNS) and from the James A. Fitzpatrick Nuclear Power Plant (FNPP). One waste container from each of these two power plants was found to have become pressurized during transport in September 1983 and September 1984, respectively, to the extent that the high integrity containers made of high-density polyethylene had deformed.

A telephone survey of selected nuclear power plants was conducted in order to gather information on the use and handling of ion-exchange resins and chemicals at nuclear power plants. A literature review provided data regarding the conditions which could cause ion-exchange resins to undergo an exothermic reaction. These topics are covered in Section 2. Section 3 describes the events surrounding the incident at ANO in more detail. In Section 4, a review of reports prepared for ANO by Battelle Pacific Northwest Laboratory (BPNL) is given. The reports contain data related to analyses of samples of the resins which exhibited the exotherm. Section 4 also describes the confirmatory testing of ANO resin samples conducted at BNL.

An account of the two incidents involving pressurization of HICs during transport to the Barnwell, SC, disposal site is given in Sections 5 and 6. Section 5 deals with the incident involving wastes from MNS. Section 6 describes the FNPP resin liner incident, and includes the results of biodegradation experiments conducted at BNL.

A comparison of the factors involved in the three incidents is given in Section 7. Recommendations are given which may help limit the occurrence of future incidents similar to those described in this study.

2. SELECTED SURVEY OF NUCLEAR POWER PLANTS AND LITERATURE REVIEW

2.1 Ion-Exchange Resins Used in Nuclear Power Plants

A review of published surveys of nuclear power plant use of ion-exchange resins showed that resins having a polystyrene-divinylbenzene (PS-DVB) matrix are most often used for water treatment. Further, the resins are either the strong acid type with a nuclear sulfonic functional group or the strong base type with a quaternary ammonium functional group. Few plants deviate from the use of gel-type resins having a PS-DVB matrix. The survey by Lin (Lin, K. H.) showed that macroreticular resins were used at Humbolt Bay 3 (conden-sate demineralizer) and at Nine Mile Point (demineralizers for reactor coolant, condensate and equipment drains). No details of resin manufacture were given. In an informal survey of several nuclear plants, it was learned that the Calvert Cliffs Nuclear Power Plant uses macroreticular resins for treatment of the secondary system water. Also the Maine Yankee Atomic Plant uses macro-reticular resins as an organic filter for their makeup water treatment. How ever, since these do not contact in-plant water, they need not be disposed of as radioactive wastes. Clark's survey (Clark, W. E.) indicated that San Onofre, Unit 1 (PWR) used Rohm and Haas Amberlite IRN-300 for fuel pool and radwaste water treatment. This resin designation is for a mixed bed material containing IRN-77, a common cation exchanger, and IRA-60 a weak base resin having an acrylic matrix. The Fort Calhoun Station (PWR) power plant responded to the survey by Piciulo (Piciulo, P. L.) and indicated the use of Duolite ARM-390 or Amberlite IRN-300 resins for the fuel pool demineralizer. The Duolite ARM-390 is a mixed bed resin containing a strong acid, PS-DVB backbone cation exchanger and A-340 weak base anion exchanger having an epoxy-polyamine backbone. Duolite A-340 is the standard resin used to prepare the analytical grade material ARA-9371 which is used at ANO. Although the surveys reviewed do not include all of the operating nuclear plants, they do suggest that epoxy-polyamine and acrylic resins are used by a small number of plants. Except for an incident at the research reactor at Brookhaven National Laboratory (see Section 2.3) there have been no difficulties reported or associated with these types of resins.

Duolite ARC-9358, which is used at ANO, corresponds to a strong-acid cation-exchange resin having a nuclear sulfonic acid functional group on a PS-DVB matrix. This particular resin has a high specification for conversion to the H+ ionic form (i.e., 98%).

Duolite ARA 9371 is a weak base anion exchange resin. The functional group is a polyfunctional amine, and the resin is composed of an epoxypoly-amine matrix. This resin was said to have an exchange capacity of >2 eq/L (2.5 meq/mL minimum capacity is given in Duolite Data Leaflet No. 3), higher than the typical polystyrene matrix equivalent of ≈1 eq/L. Further, the resin is designed to be used in low pH systems. The Duolite Data Leaflet No. 3, 1979 indicates the following feature for this resin: "Iodine-131 removal from borated reactor shims."

Regarding chemical stability of the epoxy-polyamine resins, organics can cause physical fouling of the resins, but they are believed to be as resistant to strong oxidants as the PS-DVB based resins.* The maximum operating temperature indicated in Duolite Data Leaflet No. 3 for ARA-9371 is 80°C (180°F). This compares to 60°C for a strong-base quaternary ammonium Type 1 resin having a polystyrene matrix and to 150°C for the cation exchange resin ARC-9358.

2.2 Some Power Plant Practices for Handling Chemicals and Ion-Exchange Resin Waste

Chemicals, solvents, and reagents are used in different aspects of nuclear plant operations. Based on an informal survey of several nuclear power plants, it is usually the responsibility of the plant chemist to determine the compatibility of the various chemical materials with the nuclear plant components. The chemist relies on experience, the literature, and information supplied by vendors to determine compatibility. For example, an "approved chemicals" list is used at Calvert Cliffs Nuclear Power Plant (CCN) (a PWR) to check materials such as lubricants, sealants, and paints which contact the primary system. Other chemicals generally present in a plant laboratory, e.g., acids, bases, solvents, and reagents are reviewed by the chemist before use in the plant and to establish a disposal method. This includes determining what can be put down drains which ultimately end up in the radwaste cleanup system. In plants using ion-exchange resins to treat radwaste, there is concern for the presence of organics in the waste cleanup system. Soaps and detergents can foul ion-exchange resins; thus non-ionic detergents are pre-ferred since they pass through the resin with minimal fouling. In all the plants surveyed, the major method of controlling what goes into waste treatment is the training of plant personnel with respect to the use of acceptable materials.

Bulk chemicals used in plant operations may pass through ion-exchange resin demineralizers. Pressurized water reactors at St. Lucie Plant (SLP) and at Millstone Nuclear Power Station, Unit 2 use hydrogen peroxide (H_2O_2), to inhibit corrosion during reactor shutdown, and they add hydrazine (N_2H_4) to the primary system to consume oxygen during reactor start-up. Morpholine (tetrahydro-1,4-oxazine; C_4H_8ONH) or ammonium hydroxide (NH_4OH) can be added to increase the pH of the water. These chemicals in the proper concentration are compatible with the reactor components, and no problems have occurred when contacted with ion-exchange resins.

Chemicals used in a plant laboratory are generally in small quantities (i.e., 1 L of solvent or 1 lb of reagent may be used over several months) and are likely to be disposed of down sink drains. Waste is passed to a liquid waste holdup tank, where it can then be handled in different ways. The miscellaneous waste at CCN may be discharged from the plant with or without

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*Telephone conversation between Mr. Jan Griggs (Diamond Shamrock Corporation) and P. L. Piciulo (BNL) on June 17, 1983.

dilution depending on the concentration of the chemical species. It may also be processed by ion exchange. At the Maine Yankee Atomic Power Plant (a PWR), the radwaste is processed by evaporation, and the evaporator bottoms are solidified for disposal. Millstone, Units 1 (a BWR) and 2 (a PWR) have a common chemistry laboratory, and the laboratory waste is processed by evaporation with the condensate then treated by ion exchange. The evaporator bottoms are solidified prior to disposal, and the resins are dewatered.

None of the plants surveyed have carried out any chemical decontaminations. In general, a plant would contract a vendor for such an operation. However, it would be the responsibility of the plant chemist to review the compatibility of chemicals with the system being treated and with any ion-exchange resins that may be involved.

Small quantities of chemicals processed through a radwaste ion-exchange demineralizer are not likely to cause a problem with the resin waste. However, it is not clear what effect there can be, if any, from the long-term storage of resins in holding tanks prior to processing for disposal. In the case of ANO, some resins in the dewatering liner exhibiting the exotherm may have been four years old (see Section 3). Other plants, such as Yankee Rowe Nuclear Power Station, with relatively small amounts of resin waste can have the capacity to accumulate the resins in a larger holding tank for possibly 5 years.

All of the plants surveyed have some general methodology for determining the compatibility of chemicals in use with plant components. It is intended that the procedures extend to control what chemicals contact ion-exchange resins. However, there are still possibilities of unwanted materials entering a water treatment system and the resins. Millstone requires personnel to obtain supervisor permission for the use of certain chemicals and solvents. The Yankee Rowe radwaste supervisor pointed out that during shutdown operations, an outside vendor and personnel may be present at the plant for an extended period. This in turn can lead to confusion and uncertainty as to what has entered the water treatment systems.

The survey has indicated that there is considerable uncertainty as to the chemical makeup of a resin waste stream from a plant. A test for radionuclides is generally the only test performed on the resin during preparation for disposal. Perhaps more attention should be given to the chemistry of a resin waste stream as well as improved control of chemicals within a plant.

Most of the plants surveyed dewater either all or part of their resin waste and use high-integrity containers for disposal. Fort Calhoun Station (a PWR) is presently solidifying resin waste in cement but previously dewatered resins in steel liners before HICs were available. CCN uses resin activity as a basis for determining the disposal method. Resins with a high level of activity (generally from the primary system treatment) may be disposed of in a HIC, and a steel liner could be used for disposal of low-activity resins (secondary system resins). Alternate strategies are to mix resins from different water treatment systems, thereby diluting the total activity on the resins, or resins from a given demineralizer can be handled separately. For example, at SLP the primary coolant resins are disposed of separately, and all other resins are mixed in a holding tank prior to disposal. At the Turkey Point Nuclear Plant (a PWR), which is the sister plant of SLP (both plants are operated by Florida Power and Light Company), resins from the radwaste demineralizer are disposed of separately from all other resins which are mixed in a holding tank. Obviously, resin waste from a single demineralizer can be better characterized than resins from a holding tank which can be from different water treatment systems and of largely different ages.

It was learned from the survey that the occurrence of the exotherm during resin dewatering at ANO was the reason that monitoring the temperature of the resin liner has been added to the dewatering procedure at CCN and SLP. These plants are taking this precaution as a means of detecting an exothermic reaction at an early stage. CCN measures the surface temperature at the side of the container and claims that it remains ambient, but no exact temperature was given. A more involved effort was made to monitor a liner temperature during dewatering at SLP. What was described as a strip thermocouple is placed inside the liner prior to filling with resins. The temperature of resins in the liner is then measured during the dewatering process. The strip is disconnected from the instrumentation when dewatering is completed and is left in the liner for disposal, thus avoiding problems with removal for re-use. Unfortunately, no temperature values were quoted, but the resins were said to have remained at ambient temperature during dewatering. CNSI, the vendor of the dewatering HIC, does not require temperature monitoring in their dewatering procedure and did not provide any values of what a typical temperature range of the resins would be during dewatering except to say they remain at ambient temperature. Monitoring resin liner temperature may indeed help detect a potential problem situation. However, it would be necessary to have a thorough understanding of the baseline temperature to be expected during resin dewatering if this is to be used to detect potential exothermic behavior.

Another means of detecting a possible problem in a liner may be in the dewatering procedure itself. Three dewatering cycles (pumping followed by static draining) seem to be the usual number necessary to meet the free liquid limit in a liner. Both CCN and SLP use the CNSI HICs and reported that the three cycles were in fact sufficient to dewater their liners. In the case of the ANO incident, the liner had been through six dewatering cycles when the exotherm occurred (see Section 3). Perhaps additional precautions should be taken after an upper limit of dewatering cycles have failed to dewater the resin. For example, if a liner is not dewatered after four cycles, this may be indicative of other than normal resin waste in the liner. Data as to what is a typical dewatering process and what may be off normal should be easily supplied by a vendor since there is a log kept of each liner dewatering procedure performed.

2.3 Literature Review of Chemical Interactions Involving Ion-Exchange Resins

A review of the literature was made in an attempt to identify chemicals which could have deleterious effects on the ion-exchange resins used in nuclear power plants. The literature was searched with the intent that possible causes of the exothermic reaction at ANO could be identified, using the following guidelines:

- reactions involving strong oxidizing agents
- autoxidation reactions
- resin degradation products
- interactions with biodegradation by-products.

2.3.1 Reactions Involving Strong Oxidizing Agents

It is generally known that resins based on a PS-DVB matrix are more resistant to oxidizing agents than phenolic condensation-type resins, and cation-exchange resins are more resistant compared to anion-exchange resins having the same polymeric backbone. The latter point can be attributed to the amine functional groups on the resins (Moody, G. J., 1972a). Weak-acid and weak-base resins are generally more stable to oxidants than strong-acid and strong-base resins composed of the same polymeric matrix. No documentation of the comparative oxidative resistance of epoxy-polyamine-based resins could be found in the literature search.

It should be pointed out that studies of the chemical, thermal, and radiolytic stabilities of ion-exchange resins are limited to the extent that the majority involve investigations of cation and anion resins separately, and the resin characteristic of concern is for the most part long-term exchange capacity. Investigations of resin stability are also generally more concerned with resin behavior while submerged in water; consequently, information on the stability of dewatered or dry resins is also very limited. Oxidation reactions in the presence of water are relatively slow, and the heat released from these reactions has not been studied in detail.

Chemical resistance of resins to oxidizing agents can depend on a number of factors. One factor of importance is the strength of the oxidant in question. Examples of relatively harmless species are the mild oxidizing agents oxygen (O_2) and sulfuric acid (H_2SO_4). However, over the long term, anion exchangers show better exchange characteristics if the water being processed is de-aerated first (Moody, G. J., 1972a).

Vendors of ion-exchange resins specify that the resins not be exposed to highly concentrated solutions of strong oxidants. Included in the list of strong oxidants are chlorine (Cl_2), bromine (Br_2), dichromate ($Cr_2O_2^{-2}$), permanganate (MnO_4^-), and nitric acid (HNO_3) above concentrations of 2.5 moles per liter of solution. Most often cited is HNO_3, which in a concentrated form can result in explosive reactions with anion exchange resins.

Miles (Miles, F. W.) discusses seven incidents in which explosions or fires involving anion exchange resins occurred. These incidents shared several common factors: all involved nitrate-form anion resins in strong (>7 N) nitric acid solutions, some source of heat was present, and the resin beds all had a low thermal conductivity. Although these incidents do not correspond directly to the incident at ANO, several aspects may be relevant to the exothermic reaction.

Of particular interest was an explosion of an anion-exchange vessel during the re-nitrating operation of a weak base anion exchange resin. The demineralizer, which was part of the Brookhaven High Flux Beam Reactor, was filled with Duolite A-30B ion-exchange resins. (This Duolite resin is now supplied under the designate A-340 or in the nuclear grade, ARA-9371, which is one of the resins used by ANO.) The explosion occurred during regeneration using 2N HNO_3 and was attributed to a pressure buildup resulting from a reaction between HNO_3 and the resin. The large-scale nitration of an aliphatic-based anion-exchange resin and possible catalyzing effects of iron and chromium ions were cited as factors contributing to the problem.

Subsequent to the accident at BNL, an investigation took place (Tichler, P. L.). Laboratory tests were made on both fresh resin samples and resins withdrawn from the vessel after the explosion. Experiments showed no reactions of the resins with 2N HNO_3 but both samples reacted with 16N HNO_3 above 60°C. Further, the resins from the accident vessel were found to be more reactive than the fresh resins. Although the accidents at BNL and ANO involved the same resins the associated chemical environments were different.

The BNL report describes some characteristics of the Duolite A-30B resins. They are made up of a poly (ethylene diamine) matrix cured with epichlorohydrin which is a reactive epoxide. The resins are likely to have the following reactive groups: tertiary (aliphatic) amines, secondary (aliphatic) amines, secondary alcohols, quaternary ammonium nitrogen, unreacted epoxy groups, and aliphatic chloride. After consideration of the reactivity of the various species with nitric acid the following possibilities were offered to explain the explosion (Tichler, P. L.):

(1) esterification of the alcohol functions with attendant formation of nitrous acid through oxidation of the alcohol, caused by the use of relatively concentrated nitric acid;

(2) the accumulation of a concentration of nitrate esters by previous nitric acid treatment by the vendor which, when augmented by further nitration at BNL, yielded a thermally unstable polynitrate.

The BNL report describes the variety of reactive sites on the Duolite resin some of which may have contributed to the ANO incident. However, there is the question of an oxidizing agent. Concentrated nitric acid is believed responsible for the BNL accident but an oxidizing species is not clearly evident in the ANO accident.

Thermal stability studies of several resins, i.e., Dowex 1, IRA-401, and Permutit SK in an open system revealed that nitrate-form resins undergo a thermal excursion after being heated above a certain temperature. Various factors apparently influence this "self-ignition temperature" (Miles, F. W.). Only nitrate-form resins exhibited exothermic behavior, whereas chloride, sulfate and hydroxide forms became charred, and the self-ignition temperature varied greatly for the different resin brands. The following factors all contributed to a lower self-ignition temperature: more rapid heating rate, increased resin cross-linkage, higher loading with nitrate-containing Pu and Th complexes, and larger resin volumes. The lowest ignition temperature found in these tests was 135°C. It is noteworthy that fresh resins showed lower self-ignition temperatures than used resins.

Also cited by Miles, another follow-up investigation to an explosion at Rocky Flats postulated that the mechanism of the chemical reaction of resins in concentrated HNO_3 involved the exothermic reaction of nitrite ion with the quaternary ammonium exchange sites on the resin. This reaction produced gaseous trimethylamine $[N(CH_3)_3]$ and methyl nitrate (CH_3NO_3). Thermal stability studies of Dowex 1-X4 in a closed system with 7 N HNO_3 showed that pyrolytic decomposition occurred with ignition on heating. In these experiments, when the liquid content of the sample was less than 50%, the resins would ignite at less than 200°C, and decreasing the liquid content of the resins decreased further the temperature and pressure at which ignition occurred. The postulated initiator in this study, the nitrite ion, could have been present as an impurity in HNO_3 or as a decomposition product from the reaction of HNO_3 with the resin.

Obviously, some of the conditions reviewed above, i.e., nitrate-form resins exposed to concentrated nitric acid solutions, do not apply to the ANO incident. However, some of the factors, such as liquid content, and the presence of possible catalytic initiators such as the nitrite ion (see Section 4), may be relevant. The review articles by Moody and Thomas (Moody, G. J., 1972a,b) also discuss anion resin stability in the presence of 7 N nitric acid. Static tests resulted in severe damage to Dowex 1 and Permutit SK "due apparently to the auto catalytic build-up of nitrite." However, anion resins in flowing nitric acid up to 60°C are more stable "provided nitrite is absent" (Moody, G. J., 1972a). The last example is indicative of how difficult it is to predict the effects of any particular oxidant since these are so dependent on experimental conditions.

2.3.2 Autoxidation Reactions

Another route to oxidative decomposition of ion-exchange resins is by autoxidation, or the direct reaction of the resins with atmospheric oxygen. In general, autoxidation of hydrocarbons occurs via a free-radical chain mechanism and is usually a slow process. Direct reaction of most hydrocarbons with O_2 is not favorable thermodynamically and kinetically. However, it "can be favorable when it involves compounds in which hydrogen is bonded to elements other than carbon, as illustrated by the facile air oxidation of thiols, phosphines, and a variety of organo-metallic compounds" (Sheldon, R. A.). In particular, PS-DVB-based ion-exchange resins can first form hydro-peroxides at the methine hydrogen adjacent to the benzene ring on the poly-styrene backbone. The chain process can then occur as follows:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}\cdot \qquad (1)$$

$$\mathrm{RO}\cdot + \mathrm{R'H} \rightarrow \mathrm{ROH} + \mathrm{R'}\cdot \qquad (2)$$

$$\mathrm{OH}\cdot + \mathrm{R'H} \rightarrow \mathrm{H_2O} + \mathrm{R'}\cdot \qquad (3)$$

where R and R' represent different sites on the resin (Moody, G. J., 1972a). Initiating the chain process requires the presence of oxygen, and there is often an initial induction period. Regarding the initiation of autoxidation in hydrocarbons, the induction period can be shortened or eliminated by transition metal ions or substances which are autoxidized very easily (Davies, 1961).

The free-radical chain process is catalyzed by copper, manganese and iron (Frisch, N. W.) as well as some amino acids (Moody and Thomas, 1972a).

The impact of autoxidation on anion-exchange resins was investigated (Frisch, N. W.) because of concerns with the long-term stability of resin exchange capacity. Only PS-DVB resins were investigated, and a different point of attack was postulated for anion resins as opposed to cation resins. In cation resins, the polymeric backbone is degraded by autoxidation, while in strongly basic anion resins the functional amine group is affected. A low oxygen concentration (in the process water stream) effects a reduction in the initial degradation rate only. However, once the initiation step is started, i.e. the formation of a sufficient concentration of hydroperoxide, the rate can accelerate even in the absence of oxygen (Frisch, N. W.).

No information could be found dealing with autoxidation in dewatered ion-exchange resins. The process of dewatering involves pumping air through resin waste, and the possibility of autoxidation occurring should be considered. Autoxidation could well have been a factor in the ANO incident since an above-average number of dewatering cycles were performed.

The consequences of potential organic contamination on the resin waste at ANO were also considered. The concern discussed most in the literature is loss of exchange capacity due to "fouling" by organic materials which can block exchange sites on the resins. Anion resins appear to be more susceptible to fouling than cation resins. A discussion in one paper (Frisch, N. W.) stated that various factors must be considered when determining why a loss in anion exchange capacity occurs. Particular mention was made that "the presence of organic matter susceptible to autoxidation itself and the presence of metallic catalysts can confuse the overall degradation..." (Frisch, N. W.). It is worth noting here that chemical reactions between organic materials and ion-exchange resins can occur. A reference was made in one paper (Davies, 1956) that strong-base anion resins catalytically decompose acetone.

2.3.3 Resin Degradation Products

The possibility that degradation products of the resins due to aging and/or radiolytic processes may have contributed to the exotherm at ANO was also reviewed. There is a dearth of information available on the radiolysis of mixed anion and cation resins. The two studies found (Baumann, E.W.; Swyler, K.J.) indicate that in general H^+ and OH^- forms of strong-acid and strong-base resins are less stable than salt forms. The same conclusions can be drawn from thermal stability tests (Hall, G. R.). Degradation of resins by radiolysis and by thermal methods primarily results in loss of exchange capacity through destruction of the exchange sites. Strong-acid cation resins yield a mixture of sulfite (SO_3^{-2}) and sulfate (SO_4^{-2}) ions on heating while the main water-soluble product of radiolysis is sulfate ion. Strong-base anion resins, on the other hand, release trimethylamine ($N(CH_3)_3$) and, to a lesser extent, methanol (CH_3OH). In anion resins strongly-basic groups can be converted to weakly-basic ones by thermal and radiolytic degradation and anion resins also lose their capacity to retain water.

The degradation products of ion-exchange resins are not expected to be very reactive with the exception of trimethylamine. In fact, reabsorption of the products can occur in mixed bed resins, although in one radiolysis study (Swyler, K. J.), the reabsorption of sulfate ion by irradiated anion resins in a mixed resin system was not complete. Trimethylamine can be reabsorbed by cation exchange resins.

It is worth noting that trimethylamine is a volatile compound which can be explosive. The flash point for the gas is ≈3°C, and the explosive limit in air is 2.0% to 11.6% (Bretherick, L.). In connection with this, it is also worth noting that ammonium and substituted-ammonium nitrite salts can display a wide range of instability. "Ammonium nitrite will decompose explosively either as a solid, or in concentrated aqueous solution when heated to 60-70°C. Presence of traces of acid lowers the decomposition temperature markedly" (Bretherick, L.). Although the conditions for an explosion were not present in the ANO resin waste, it may be that the interstitial water in the resin beads that remains after dewatering constitutes a micro-environment in which the decomposition of ammonium nitrite generates enough heat to initiate an exotherm. A related concern is the possibility of forming nitrite salts of amine-metal complexes, e.g., tetraamine copper(II) nitrite, which is known to be explosive (Brethrick, L.). The latter compound becomes more of a concern if one considers that copper(II) ion can be sorbed by ARA-9371 anion resin in spite of its positive charge.

2.3.4 Interactions With Biodegradation By-Products

One last area which was surveyed in the literature was that regarding biodegradation. This was considered because of the sewage smell observed coming from the Cask A resins at ANO (see Section 3). While the heat generated by biodegradation cannot be considered an important factor in the exothermic incident, reactions between the chemical by-products of biodegradation and either the ion-exchange resins or ion species present on the resins may be significant. Biodegradation can produce a wide variety of chemicals depending on available oxygen, nutrients, and the microbes present. Assuming that primarily anoxic conditions prevailed in the holding tank, then low-molecular weight carbon compounds including organic acids, alcohols, and esters could be produced. Substances which could have caused the sewage smell are sulfur- and/or nitrogen-based compounds,* and these include dimethyl sulfide, hydrogen sulfide, methanethiol, and various amines. The presence of thiols and hydrogen sulfide could be most significant. As mentioned above, thiols are easily autoxidized. This process is catalyzed by aqueous base or by olefins, i.e., unsaturated hydrocarbons (Oswald, A. A.), and proceeds by a free-radical chain mechanism also.

There is a significant lack of data available indicating the extent to which biodegradation of ion-exchange resins can occur. In a recent survey (Piciulo, P. L.) on the use of high integrity containers for packaging dewatered resins for disposal, a power plant reported that gas-generation occurred in 55-gallon drums containing dewatered resins which were stored on-site for approximately one month. The buildup of gas was stopped or prevented by the addition of small amounts of formaldehyde to each drum. Because formaldehyde stopped the gas buildup, biodegradation was believed to be the cause.

2.3.5 Summary of Literature Review

This literature survey section can be summarized as follows:

1. There is a limited amount of information available on exothermic reactions involving ion-exchange resins. Studies of oxidative attack on resins are in general more interested in exchange capacity losses in water process streams. In this case oxidative attack is relatively slow, and the self-heating of the resins is not of much concern.

2. The only reported incidents of explosions or fires involved anion resins in nitrate form exposed to concentrated nitric acid. Conditions in some of these incidents which may relate to the ANO exotherm were the poor thermal conductivity of resin beds, large resin containers, contamination with nitrite ion, and dryness of resins, i.e., exposure to air.

3. The degradation products of resins are relatively innocuous and in mixed resin systems are probably reabsorbed provided anion and cation resin capacity is not fully expended.

4. Autoxidation can occur in ion-exchange resins. This is also generally a slow process, but can be catalyzed by the presence of a more

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*Telephone conversation between A. J. Francis, BNL and B. S. Bowerman, BNL, August 1983.

easily autoxidized material and iron, manganese, and copper. Some of the products of biodegradation, e.g., thiols, are easily autoxidized.

5. Studies of the stability of ion-exchange resins generally involve those with a PS-DVB matrix. No information on the stability of epoxy-polyamine based resins, the type used at ANO, could be found.

6. No information on biodegradation of ion-exchange resins would be found, particularly data identifying the conditions under which biodegradation can occur, or the characteristics of ion-exchange resins in which biodegradation has occurred.

3. BACKGROUND AND DESCRIPTION OF ANO INCIDENT

The information contained in this section was obtained primarily during a meeting held at the Arkansas Nuclear One (ANO) site on June 28, 1983. Additional information was made available by ANO in subsequent telephone contacts and correspondence.

The incident was first discovered on January 15, 1983 when smoke or steam was observed coming from the high integrity container (HIC) in which the resin wastes were being dewatered. The gas was described as having a strong chemical smell. The resins had undergone an extended dewatering procedure compared to the time normally required. The temperature of the resins measured at that time was 365°F (185°C), and the radiation level was 400 mrem/h. The exothermic reaction was stopped or suppressed by the addition of water to the HIC.

Another HIC containing resins from the same holding tank (2T13) in the initial stages of dewatering was refilled with water as a precautionary measure. All the contents of tank 2T13 were later transferred to HICs and stored for some months. Following tests conducted by Battelle Pacific Northwest Laboratory for ANO (see Section 4.4), the resin wastes were solidified in cement and disposed of at Barnwell, SC.

3.1 Events Leading up to the Incident

Holding tank 2T13, constructed of stainless steel, is normally used for the storage of spent resin waste from the liquid radwaste cleanup system and from the demineralizer used to process water from the spent fuel storage pool (see Section 3.2).

The holding tank 2T13 had been drained in December, 1982. The transfer of resins had been carried out until only water appeared to be coming from the tank. It was believed at the time that 2T13 was empty. However, according to ANO, subsequent transfers of resin waste to 2T13 indicated that the holding tank was nearly full. It was concluded that caking of the resins had occurred or that a clog in the piping was present. A transfer of spent resins was attempted in January, 1983 and was completed on January 9, 1983. A HIC, later labelled Cask A, was filled and dewatering operations begun. About 3 hours after dewatering had begun, an overwhelming smell of sewage was observed. In the words of ANO personnel, it was as if a septic tank had been vented into the bay where the HIC was located. The dewatering of Cask A proceeded through six cycles, which is an abnormally long dewatering time. A second HIC, labelled Cask B, was also filled with resin waste from 2T13 a day or two later and dewatering was initiated, but no sewage smell was observed. After the sixth dewatering cycle of Cask A, the incident occurred as described in the Record of Events, reproduced in Appendix A with additional comments and details.

3.2 Follow-up Investigations by ANO

Follow-up investigation of the incident by ANO was divided into three phases. Phase 1 consisted primarily of contracting with Battelle Pacific Northwest Laboratories (BPNL) to analyse resin samples from Casks A and B obtained before, during and after the incident as well as other resins from holding tank 2T13. A review of the report on this initial analytical study is given in Section 4.2.

Tank 2T13 was emptied completely, and all the resin waste was stored on-site in five HICs. No more dewatering of these particular resins was attempted. After 2T13 was emptied, an inspection of the interior revealed that several inches of resin remained. The top of this resin layer had a crusty covering. No corrosion was evident in the tank after the resins were removed. This was the first time the tank had ever been emptied and inspected. Sampling of resins in the holding tank before transferral to HICs is not possible at this time, but ANO is investigating procedures that will make this option available in the future. In addition, ANO planned to monitor resin temperatures during dewatering operations since the incident in order to establish a data base for a "normal" dewatering procedure.

Phase 2 and Phase 3 of ANO's follow-up also included subcontracting with BPNL for further studies of the resin waste. Under Phase 2, solidification of the resins in cement was studied. More extensive (and presumably more representative) samples of resins from Cask A as well as from the other HICs containing waste from 2T13 were sent to BPNL for the Phase 2 study.

Following successful solidification tests, all the resins from 2T13 stored in HICs on-site at ANO were solidified and shipped to Barnwell, SC, for disposal in December 1983. The solidification tests are discussed in more detail in Section 4.4.

The work conducted at PNL under Phase 3 of ANO's follow-up program continued into 1984. The final results of the Phase 3 study are discussed in Section 4.4.

3.3 Description of Relevant Plant Systems and Operations

The generating plant at the ANO site consists of two pressurized water reactors (PWR). Unit 1, built by Babcock and Wilcox Co., generates 850 MW and has been in operation since 1974. Unit 2 with a capacity of 912 MW was built by Combustion Engineering and started up in 1978.

The low-level ion-exchange resin waste at ANO comes from two sources: the primary demineralizer system and the radwaste system. In the primary demineralizer system, there are two beds available for each generating unit at ANO. Each unit has only one demineralizer bed in service, while the other bed containing expended ion-exchange resins is used as a holding tank until the bed in service as a demineralizer is nearly expended. Then expended resins from the bed being used as a storage tank are sluiced directly to a liner for shipment and disposal. Generally, the primary demineralizer beds are changed over once every six months. The criterion for determining when to change over to a fresh demineralizer bed is based on the decontamination factor (DF). Consequently, some exchange capacity may remain available on the resins. The primary demineralizer system uses only IRN-150 LC mixed bed ion-exchange resins from Rohm and Haas, Inc.

Entirely separate from the primary demineralizer system is the liquid radwaste cleanup system (LRWCS). The LRWCS processes water from equipment and floor drains in the primary or restricted access areas of the reactor. Water from specialized cleanup jobs, e.g., decontamination, is also processed by the LRWCS.

There are two separate LRWCSs, one each for Units 1 and 2; however, waste water from one unit can be processed by the LRWCS in the other unit if necessary. ANO claimed that for the most part, ion-exchange resins for the LRWCS are obtained from Diamond Shamrock Corporation. The resins used were described as gel-type resins having a polystyrene backbone with divinylbenzene cross-linking. The Diamond Shamrock resins used are Duolite ARA-9371 and ARC-9358; however, it should be mentioned that ARA-9371 has an expoxy-polyamine backbone. These are anion and cation exchange resins, respectively, and are mixed at ANO to make mixed bed demineralizers. The relative amounts of anion and cation resins used in preparing the mixed beds are tailored to the particular cleanup application although generally a 50:50 mix is used. Some stratification of the resins probably occurs when they are mixed, because a barrel of each type of resin is added alternately to the radwaste system demineralizers. Extra cation resins are used at the top of the demineralizer beds in the LRWCS to reduce the pH of the liquid waste stream, thereby enhancing the mechanical filtering capability of the mixed resins for Co-60.

Water from the spent fuel storage pool is processed in a separate demineralizer in which Rohm and Haas IRN-150 LC resins are used. Boric acid is the only chemical added to the spent fuel pool. When the resins used to process the spent fuel pool are replaced, the waste resins are sluiced to holding tank 2T13, the same holding tank used for LRWCS waste resins.

DF is used as a criterion for determining when to replace LRWCS ion-exchange resins. Waste resins from the LRWCS are slurry pumped into stainless steel holding tanks for storage before being disposed of. There is one holding tank for each unit. These are designated T13 for Unit 1 and 2T13 for Unit 2. (Holding Tank 2T13 is a cylindrical tank with convex end caps. It is constructed of stainless steel and is approximately five feet in diameter and 12 feet high.) LRWCS resin waste is accumulated in the holding tanks. Stratification of the resin wastes probably occurs in the holding tanks because the resins are sluiced in through a pipe inlet at the top of the tank. However, some mixing also takes place during transfers into and out of the tank, due to gas sparging which serves to break up to some extent any resin agglomeration.

When the storage tanks have reached their capacity, resin wastes are sluiced into high integrity containers (HICs) for dewatering and disposal.

The HICs are supplied by Chem-Nuclear Systems, Inc. (CNSI). Transfers take place usually once a month, although during the month of the exothermic incident two transfers were carried out. The resins involved in the incident had been stored in 2T13. It is noteworthy that resin transfers do not necessarily completely empty the holding tanks. Consequently some of the contents of the holding tanks could be rather old. It was estimated that the maximum age of the resins in the tanks could be as much as 4-5 years. (See Section 3.5 for a further discussion of the possible age of the resin wastes involved in the exotherm.) The resin transfers are carried out at 90°F (32°C) using deionized water as a carrier, and four resin samples are obtained for each HIC during transfer operations. The samples are obtained using a bypass pipeline at different stages of the liner filling operations, mixed, and then analysed for radioisotopes and total activity.

After the resins have been transferred to the HICs, dewatering operations commence. The resin transfer and dewatering operations are supervised by a representative from CNSI who works full-time at the ANO site. The dewatering procedure consists of cycles of eight hours of active pumping followed by 16 hours of static draining of the HIC. After the third cycle, following the static drainage period, liquid effluent from the HIC is collected and measured. If the volume of this liquid exceeds 2,000 mL, the cycle is repeated until less than 2,000 mL of drainable free liquid is collected. Usually three cycles are sufficient in routine dewatering operations, although it was stated that the necessity for four dewatering cycles is common. Further details of the dewatering procedure were not provided by ANO personnel, since these were described as proprietary.

Some of the floor drains which lead to the LRWCS are located in the Auxiliary Extension Building which houses the Unit 2 secondary system startup and blow-down demineralizer. Thus any spillage of water or resins in this building would be washed down the drain system and subsequently to the LRWCS. ANO noted that spills are not normally experienced, but that minor spills may occur during resin regeneration.

Macroporous (macroreticular) resins are used in the secondary condensate polishing deionizers for the routine processing of the service water. The resins used in this application were identified as Amberlite-200C, a strongly acidic cation exchange resin with sulfonic acid functionality, and IRA-900C, a strong-base anion exchanger with quaternary ammonium functional groups. Both are polystyrene-based macroporous resins with divinylbenzene (DVB) cross-linking and are obtained from Rohm and Haas. The letter C in each name designates special bead size designed for high flow deionization.

The Unit 2 Auxiliary Building, which houses equipment associated with the primary system, experiences groundwater seepage through the concrete. The seepage enters the floor drain system and is subsequently processed in the LRWCS.

3.4 Potential Chemical Contamination of Resin Waste at ANO

There was some concern regarding whether chemical contamination of the ion-exchange resin wastes involved in the exotherm could have occurred. From discussion with ANO personnel, the following information was obtained.

Some concerns were expressed by ANO personnel at the June meeting regarding a spill which had occurred during a chemical cleaning of the service water system (SWS). The chemical cleaning had taken place about one month before the exothermic incident and involved the use of a 5-8% solution of citric acid ($3 < pH < 5$) with 1000-2000 ppm sodium nitrite ($NaNO_2$). This was flushed through the SWS, followed by the addition of ammonium hydroxide (NH_4OH) solution to raise the pH. During the cleaning, a spill of approximately 10,000 gallons of the cleaning solution went to the floor-drain system. It was later learned* that this solution was processed through a vendor-supplied portable demineralizer and not through the LWRCS.

The possibility of resin contamination by oils and organic solvents exists. This is particularly true of the LRWCS which includes floor drains and sump systems. ANO indicated that drain water, etc. is pumped into a sump tank which is then processed. This tank can only be pumped down to 6-8% of the tank's volume due to a pump shut-off, thus the tank is never completely emptied. As a result it is not probable that significant quantities of oil contamination can be attributed to this source. Furthermore, no oil sheen by visual observation of the resin water slurries after being sluiced into HICs has been seen.

The presence of oxidizing agents in the LRWCS is believed to be minimal. Detergents from floor drains are also present, but the use of bleaches or other cleansing agents was not confirmed. It should be mentioned that chemical spills which ultimately end up in the floor drain system are not necessarily always monitored or logged if they are discovered. One example mentioned was a sodium hydroxide (NaOH) spill which occurred after the January incident. ANO has indicated that "it is not possible to provide regular use quantities since records are not maintained for the use of chemicals, solvents, detergents, etc. inside radiologically controlled areas."*

Another source of chemical contamination which might be of some concern is small-scale decontamination operations. The amounts of liquid generated during decontaminations are limited as much as possible, and for the most part water only is used to clean contaminated surfaces. There is some use of Nutek DC 13 in the ultrasonic cleaning of smaller components.

3.5 Comments and Discussion

At the June, 1983 meeting, one of the ANO representatives expressed the opinion that by the time the exotherm was discovered, it had run its course

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*Letter from D. Snellings, AP&L to B. S. Bowerman, BNL, August 27, 1984.

and was nearly over. This was based on the fact that Cask A appeared to have cooled to some extent as evidenced by the fact that when water was added, no sound of boiling was heard. It should be noted that the resins in Cask A may have undergone some mixing during the time that the water added after the exotherm was being recirculated.

The large quantities of air pumped through the resins during the extended dewatering operations might have been a contributing factor to the exotherm, since oxygen is a relatively good oxidizing agent. Also, the sewage smell observed may have indicated the presence of mercaptans or related sulfur compounds on the resins. It also suggests the possibility of other by-products of biodegradation.

The fact that more extensive temperature measurements were not made at the time is regrettable, since it is not clear from the available information that the 100 ft^3 of resins in Cask A heated up uniformly. The exothermic reaction may have been confined to one small section of the HIC. If one assumes that the resin waste density was 45 lb/ft^3, the water content of the dewatered resins is 40% by weight, and that the heat capacity of the resins was approximately equal to that for polystyrene, i.e., 0.3 BTU/lb-°F, then it can be shown that a heat requirement of 783,000 BTUs is necessary to heat 100 ft^3 of resins uniformly from 50°F to 350°F. A similar calculation in reverse based on the 37,500 BTUs which heated the water added to stop the exotherm (see Appendix A) indicates that the average temperature of the resins before the water was added was ≈95°F. This indicates that either the exotherm had indeed run its course as was suggested above, or that it was confined to a localized "hot-spot" in the liner. The above calculations should be considered as only approximate since the exact water content and heat capacity of the resins are not known.

An additional and relevant point concerns the age and characteristics of the resins from holding tank 2T13. As noted earlier, ANO estimated that some of the resins present in 2T13 might be as old as 4 years because the tank was never completely emptied when resins were transferred from 2T13 for disposal. However, according to a U. S. NRC Inspection and Enforcement notice obtained by BNL (U.S. NRC, 1983), the spent resin was caked around the side of the tank for several years. The available capacity of the 350 ft^3 tank was said to have been ≈160 ft^3 since commercial power operation began in 1980. Consequently, ≈190 ft^3 of resins had been in the tank for approximately 3 years. The notice also stated that the caked resins had been used prior to commercial operation, and hence, may have been "exposed to chemicals and contaminants not normally associated with power operation."

The agglomerated state of the resins would be indicative of some deterioration in them, although the original cause for this may not be identifiable. The presence of the strong odor of sewage which appeared shortly after dewatering started suggests that biodegradation had occurred to some extent in the resin wastes.

4. ANALYSES OF ANO RESIN SAMPLES

4.1 ANO Resin Samples

BNL received samples of resins from APL on June 15, 1983. These samples were the remainder of those analyzed by BPNL. Included in the samples were specimens of resins from Cask A collected prior to the exotherm, resins collected during the exotherm, and resins collected 24 days after the exotherm. Specimens of resins and liquids from Cask B and of Unit 1 T13 resins were also received. A listing of the sample identifications is given in Table 4.1. With the exception of the AII samples, all were stored in water continuously. The AII samples obtained during the exotherm were kept dry until February 8, 1983, at which time water was added and they were shipped to BPNL.

Table 4.1

Arkansas Nuclear One Resin Samples Sent From
Battelle to Brookhaven National Laboratory

			mR/h
AI	Initial sample from Cask A on Jan. 8, 1983 (prior to exothermic reaction.		≈5
AII	Resin samples form Cask A obtained during the exothermic reaction.		
	AII-1	Surface	<1
	AII-2	≈8 in. below surface	<1
	AII-3	≈16 in. below surface	<1
	AII-4	≈24 in. below surface	5
	AII-5	Mixture of samples AII1, AII2, AII3, and AII4	<1
AIII	Resin samples from Cask A taken on Feb. 8, 1983		
	AIII-1	Surface	15
	AIII-2	≈8 in. below surface	20
	AIII-3	≈16 in. below surface	25
	AIII-4	Liquid sample from Cask A	<1
B	Samples taken from Cask B on Feb. 8, 1983		
	B-1	Resin from Cask B	40
	B-2	Water from Cask B	<1
C	Unit I T13 resin sample taken on Feb. 8, 1983		400

4.2 Review of BPNL Analytical Report

An initial analysis of resins which had undergone the exotherm was performed by BPNL as Phase 1 of ANO's follow-up investigation of the incident. Since ANO considered the information contained in the report proprietary, the review given here does not include the details of the BPNL analyses. However, the results and conclusions drawn from the BPNL report and discussed in this section were either transmitted verbally to BNL by ANO or confirmed during analytical work done at BNL, and therefore, is considered in the public domain.

The work carried out by BPNL under Phases 2 and 3 of ANO's follow-up investigation is reviewed in Section 4.4 and 4.5. ANO intends to publish a summary report on these phases of its investigation eventually. At this writing, ANO's summary report was not available for review.

The analyses performed at BPNL consisted of the following: a thorough physical (visual) examination of the various resin samples from ANO, a chemical analysis of the resin solids and associated liquid solutions for ionic content, extraction and determination of non-ionic organic chemical content, thermal stability tests, and tests to determine the presence of oxidizing agents. The general conclusion of the report was that no single specific cause for the exothermic incident could be determined.

Several specific results from the BPNL report are worthy of comment. First, in the visual examination of the resins, a reddish precipitate was observed. This was seen only in AII samples which were obtained from Cask A during the exotherm. The AII samples were stored dry for several weeks at which time they were covered in water prior to shipment to BPNL for analysis. The red solids in some cases were fine enough to give the associated liquids a red coloring, but in all cases, the solutions became clear after filtering. In addition, the physical examination of the resins revealed the presence of a significant amount of macroporous resins in the samples obtained from Cask A. As mentioned in Section 3, macroporous resins are not used in the LRWCS and should not have been mixed in with resin waste from holding tank 2T13 which is used exclusively for storage of spent LRWCS resins.

The source of the macroporous resins is unknown, although they may have been part of the resin wastes which had been sticking to the sides of Tank 2T13 since commercial power operation began in 1980.

The BPNL study of ANO resin samples included tests for organic chemicals and solvents. No significant quantities of organic chemicals or solvents were detected in the samples sent to BPNL.

The only unusual aspect of the chemical analyses of the resin samples was that rather high levels of iron, copper, zinc, and ammonium cations and chloride and sulfate anions were detected. Some nitrite (NO_2^-) and nitrate (NO_3^-)were detected, but the total amount of both was not enough to account for the heat generated if a reaction between these and the resins were the cause of the exotherm.

The thermal stability tests carried out at BPNL consisted of differential scanning calorimetry (DSC) experiments and thermogravimetric analyses (TGA). The latter measures sample weight loss during heating, while in DSC experiments, the heat generated (or absorbed) by exothermic (or endothermic) reactions as a sample is being heated is measured. Different atmospheric environments can be imposed on the sample, and the BPNL experiments for the most part examined the effect of heating samples while purging them with air.

BPNL examined several samples obtained from Casks A and B and found no exotherms appearing below 300°C. New Duolite ARA-9371 and ARC-9358 resins, both as-received and loaded with suspected exotherm initiators, were also tested separately. The lowest temperature at which an exotherm appeared was at ≈210°C in new ARA-9371 anion resin loaded with copper ions (Cu^{2+}). In all tests except one, there was a pronounced endotherm up to ≈120°C which could be attributed to the loss of water in the resin samples. The one exception which showed no endotherm below 100°C was a vacuum-dried sample of otherwise untreated ARA-9371, but this also showed no exothermic behavior below ≈300°C.

The tests for oxidants carried out at BPNL consisted of potentiometric titrations of the associated liquid samples and of solutions obtained by eluting the resin samples with potassium perchlorate ($KClO_4$). Insufficient quantities of oxidizing agents which could account for the exotherm were detected, but the presence of unidentified oxidizing species was indicated in all the samples tested.

4.3 Anlayses of Samples at BNL

4.3.1 Visual Examination of ANO Resin Samples

Small aliquots of each of the ANO samples were examined visually and by photomicroscopy in order to document some of the effects of the exothermic reaction. The photomicrographs of the samples are reproduced in Appendix B.

Sample AI, which was collected during resin transfer to the HIC prior to the exothermic excursion, contained mostly translucent amber beads and some opaque black beads and white beads. Also evident in the photomicrographs were broken beads and some irregularly-shaped translucent white particles. In general, the translucent beads are gel-type resins while opaque beads are macroreticular beads and can appear white, gray, brown, or black. Resins in sample AI were quite different from those in samples AII and AIII which were collected during and after the exothermic excursion, respectively. Resins in samples B-1 taken from Cask B were similar in appearance to those in sample AI.

The series of samples labelled AII were collected during the exothermic reaction from different depths in the resin bed in Cask A. They show a variation of bead appearances from a mixture of opaque white, gray, brown, and black beads collected at the surface of the bed to predominately opaque black-beads with some translucent amber beads and a few white beads in the sample collected at ≈24 inches below the bed surface. It is likely that the opaque beads are macroreticular resins, and they may be predominant in these samples simply because they are more stable at high temperatures than the gel-type beads which may have undergone more destruction during the exotherm. Photomicrographs of the samples revealed both smooth-surfaced and textured-surfaced black beads. The fractured beads indicate that some are black throughout, whereas others have only a discolored surface and a white interior. The bicolored beads suggest damage to the beads resulting from the exotherm. Sample AII-5 was claimed to be a mixture of samples AII-1 through -4. Based on comparison of bead sizes (ranging from ≈0.4 mm to 1.5 mm) and color, it is likely that sample AII-5 was a mixture of the others but was not composed of equal fractions since there were few gel-type resins visible. The liquid present in each of the AII samples appeared colored and varied from a red-orange to brown. The liquid was colorless after filtering indicating that the color was due to particulates. The photomicrographs of sample AII-5 showed a much larger amount of fine particulate material than any other sample. It was only the liquids of AII samples which were distinctly colored. The liquids associated with the other samples had only a slight gray tinge.

The AIII samples, collected 24 days after the exotherm and rewatering of the liner, appear much different from the AII samples even though the sampling locations were similar. Beads in the AIII samples appeared similar in color and size to those in the AII samples. However, there were in general significantly more translucent amber beads (gel-type resins). Since the liner had been rewatered and the water circulated through the liner, the presence of more gel-type resins in the AIII samples suggests some disturbance of at least the top 16 inch layer of the resin bed. (It is possible that mixing took place to a greater depth than 16 inches, but this is the deepest sampling point into the bed.)

A sample of resins from Unit I T13 was supplied and appeared to be all gel-type resins with no macroreticular beads observed.

4.3.2 Confirmatory Testing

A chemical characterization of the resin samples from APL was carried out by BPNL. It was not the intention of the present study to duplicate the BPNL effort but rather to review the reported analysis and perform some confirmatory tests to more fully understand the BPNL results. The confirmatory testing included the analysis of liquids from the samples for the concentrations of some selected ions, and the digestion of some solids with subsequent quantitative analysis for selected ions. Additionally, the thermal analysis of resin samples was performed.

Liquids from each of the APL samples received were collected after filtering approximately 8-mL aliquot through a Millex-HA 0.45-μm filter (Millipore Corporation). A 2-mL volume of solids from sample AII-5 was placed in a plastic syringe packed with some glass wool and the excess water removed by flushing the syringe several times with air. This material was considered "dried". A 0.2250-g sample of solids (mostly resins) was digested in 5 mL of hot concentrated sulfuric acid with 30% hydrogen peroxide as co-oxidant. There was a small amount of black particles remaining when the sample was diluted for analysis. If these particles were resins, it was believed that the severe conditions of the digestion would exchange all the ions from the resin into solution. A blank (no solids) of the digestion reagents was prepared and analyzed for comparison. Also a 1-mL aliquot of liquid and suspended red solids was mixed with 5 mL of sulfuric acid and heated prior to dilution to 100 mL.

The solutions were analyzed by atomic absorption spectroscopy for iron, zinc, and copper content. Standards were prepared by dissolving the pure metal in acid and diluting. Analysis was performed on an Instrumentation Laboratory AA/AE Spectrophotometer 951 using an air acetylene flame.

The concentration of Fe, Zn, and Cu measured in the aqueous solutions associated with each of the samples are listed in Table 4.2. Results of the zinc and copper determinations agree with those from BPNL to within a factor of two for all the samples except those of the AIII series. For the zinc analysis, BNL results are more than a factor of two lower than the BPNL values for samples AIII-1, 2, and 3, which contain resins; the liquid from Cask A showed comparable zinc concentrations. Similarly, copper detected in samples AIII- 1, 2, and 3 was less than that reported by BPNL. The liquid from Cask A showed more copper than the other AIII samples and the BNL value was a factor of 3 greater than the BPNL value. The measurements of iron concentration in the samples showed the greatest differences. Iron concentrations in samples other than B1 were lower in this study than the BPNL analysis. One sample, AII-5, was also analyzed by the method of standard additions in an attempt to detect effects on the measurement from other species in the solution. It was concluded that matrix effects cannot account for the low measures of iron in solution. Colloidal iron oxide can precipitate from aqueous solution even in acidic solution (Cotton, F. A.). Thus, some of the iron may have precipitated during the period between the analysis by BPNL and this work. Based on the analysis of the sample containing suspended red solids which were dissolved in hot sulfuric acid, the iron concentration was 1200 ppm. The red precipitate was concluded to be an iron precipitate. It is noteworthy that the Cu content of this sample was 70 ppm which is larger than that of the filtered solutions.

The results of the analysis of the resins and solids taken from sample AII-5 were as follows: Fe, 9 ± 2 mg/g; Zn, 2.1 ± 0.1 mg/g, and Cu, 0.9 ± 0.4 mg/g. The concentration of Zn detected showed good agreement with the BPNL results. However, this study measured lower concentrations of iron and copper than BPNL. It was possible that the portion of solids other than resins may have differed in the two tests. It was stated previously that the red precipitate contains both iron and copper.

Based on these analyses, it was assumed that the BPNL results are a reasonable measure of the content of the various chemical species in the samples. However, it appears that some of the chemical species may have been present in a different phase (solution, solids, or resins) at the time of the exotherm than at the time of the analysis.

Table 4.2

Concentrations of Some Metals in Liquids From the ANO Samples[a] (ppm)

	Fe	Zn	Cu
AI	ND	0.08±0.01	ND
AII-1	0.38±0.06	0.25±0.02	0.03±0.02
AII-2	0.80±0.07	0.57±0.01	0.12±0.02
AII-3	ND	1.41±0.01	ND
AII-4	0.05±0.04	1.41±0.02	0.04±0.02
AII-5	37 ±12	104 ±3	42 ±2
AIII-1	0.06±0.05	0.07±0.01	ND
AIII-2	0.14±0.05	0.08±0.01	ND
AIII-3	ND	0.17±0.01	0.02±0.01
AIII-4	0.17±0.06	0.27±0.01	0.05±0.02
B-1	1.01±0.05	0.05±0.01	0.05±0.02
B-2	ND	ND	ND
C	ND	ND	ND

[a] ND = not detected.

Thermal stability tests similar to those done by BPNL were carried out at BNL. The method used was differential thermal analysis (DTA) in which a sample is heated and its temperature measured and compared to that of an inert material heated at the same rate. An air purge was used in all cases. DTA experiments are more difficult to interpret quantitatively than DSC experiments in which heat is supplied to the sample or reference material so that the two maintain equal temperatures while being heated. In other words DSC provides a more direct measurement of the energy generated or absorbed by reactions which occur while the sample is being heated. DTA is more useful as a qualitative indicator of the presence of a reaction and whether it is endothermic or exothermic. Factors such as sample particle size, moisture content, sample packing, and sample frothing or creeping while heating can influence the reproducibility of either type of thermal analysis. Heating rate, atmosphere flow characteristics, and sample holder geometry can also affect the position of DTA and DSC peaks, i.e., the temperature at which exotherms or endotherms appear (Vogel, A. I.). TGA experiments were not performed due to the limited time available.

The DTA experiments reported here were performed using a Perkin-Elmer DTA 1700 controlled by a Perkin Elmer 7/4 Thermal Analysis Controller. One limitation of the apparatus which should be considered is that it is primarily designed for high-temperature (500°C to 1500°C) studies. Therefore, results obtained at lower temperatures may be questionable with respect to the magnitude of the differential temperatures measured. In addition, the thermal characteristics of the furnace and the tube containing the samples in the DTA 1700 are such that the baseline indicating zero temperature difference between sample and reference material can shift if the sample tube is not positioned exactly the same as in the previous run.

Confirmatory thermal stability tests were run on several samples from Casks A and B, as well as on new resins of the type used in the LRWCS at ANO. The results were essentially the same as those found at BPNL. For resin samples AI, BI, and AII-2, no evidence of exothermic behavior on heating in air was seen below 300°C. (Endotherms, i.e., processes which absorb heat, are indicated by dips in the DTA curve toward the bottom of the figure, while exotherms, or energy-releasing processes, are characterized by peaks in the DTA curve above the baseline.) One point worth noting is that these samples were dried to the extent that no surface moisture remained on the resin beads. Consequently, the endotherm below ≈100°C corresponding to the loss of water from the resins is reduced. Figure 4.1 illustrates the DTA curve for sample AII-2 up to 320°C.

It was realized that the thermal stability experiments by BPNL were somewhat limited, at least with respect to the tests on new resins. BPNL's DSC tests of new resins involved heating cation and anion resins separately; however, the resin wastes in which the exotherm occurred probably consisted of mixed anion and cation resins. BPNL's approach to the problem apparently was based on the assumption that one particular factor could be singled out as the cause of the exotherm, rather than a combination of factors. Because the BPNL study indicated that the presence of Cu^{2+} on ARA-9371, resin resulted in the appearance of an exotherm at ≈210°C compared to 300°C for untreated ARA-9371, it was decided to try to simulate the Cask A resins as closely as possible to determine whether a mixture of ARA-9358 and ARA-9371 loaded with all the anions and cations found in the Cask A resin waste would lower even further the temperature at which an exotherm could occur. It was also realized that the moisture content of the resin samples could significantly influence the thermal behavior of the resins. This is illustrated in Figures 4.2 and 4.3, in which new anion (ARA-9371) and cation (ARC-9358) resins were mixed one-to-one by weight, slurried in deionized water, and dewatered by vacuum filtration prior to the DTA analysis. Figure 4.2 shows the behavior of damp resins immediately after dewatering for ≈5 minutes, while in Figure 4.3, the same resin mixture after 24 hours drying in air, is markedly different, particularly in the neighborhood of the exotherm near 300°C and in the range less than 100°C. The latter endothermic peak is significantly reduced.

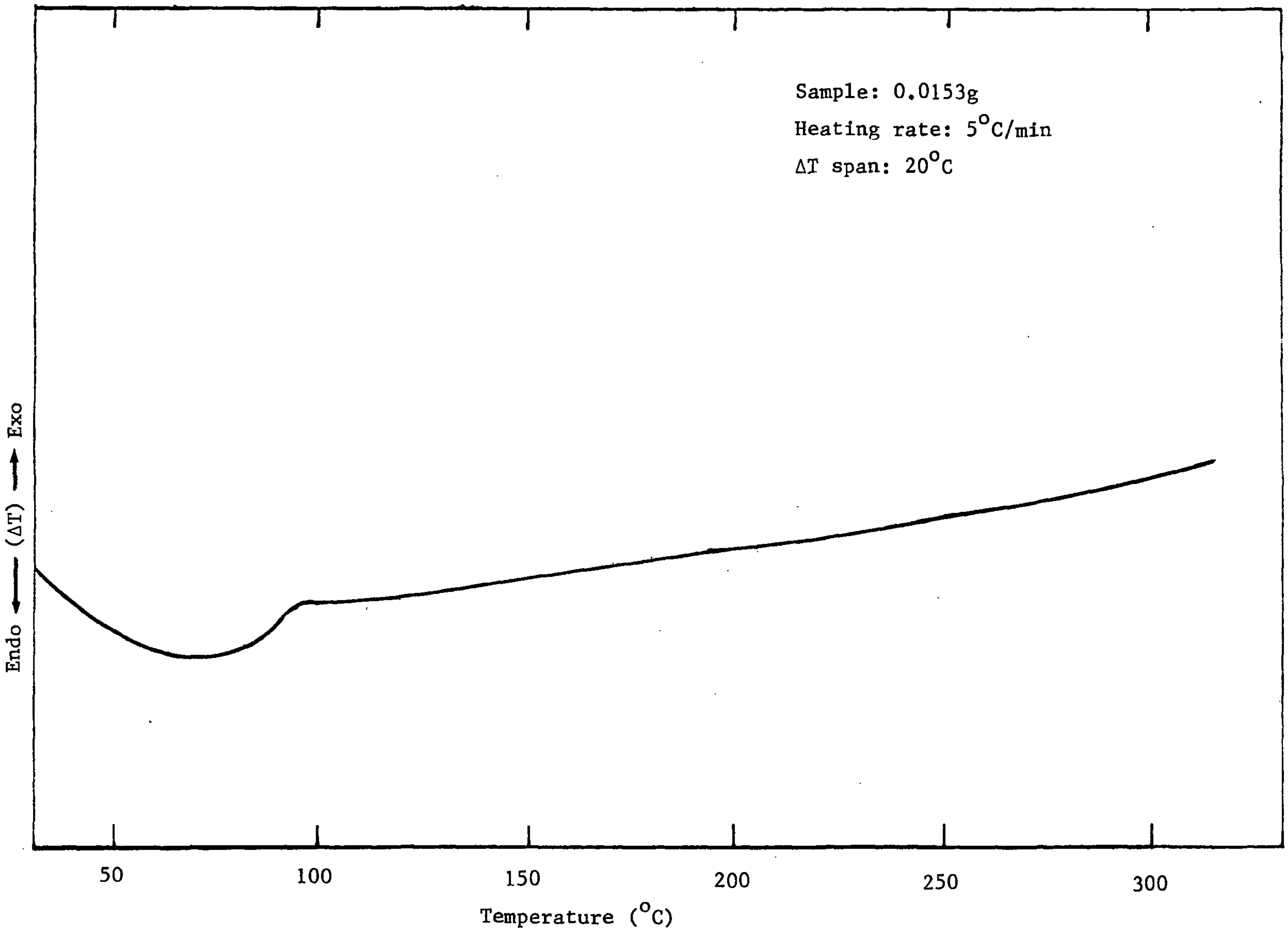

Figure 4.1 DTA curve for ANO sample AII-2.

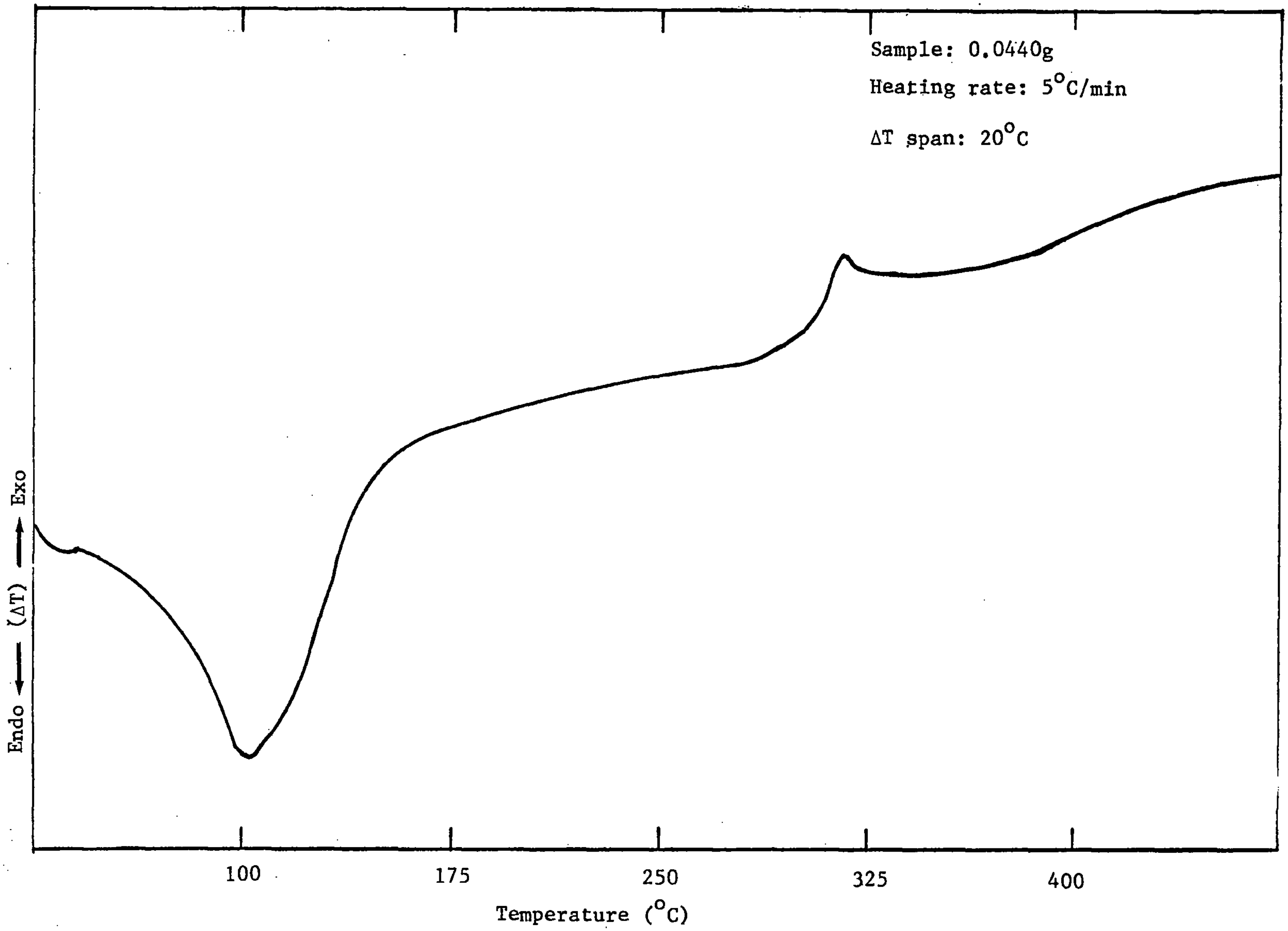

Figure 4.2 DTA curve for damp resins: Duolite ARC-9358 and AR A-9371 resins mixed 1:1 by weight in deionized water and dewatered by vacuum filtration for ≈5 minutes.

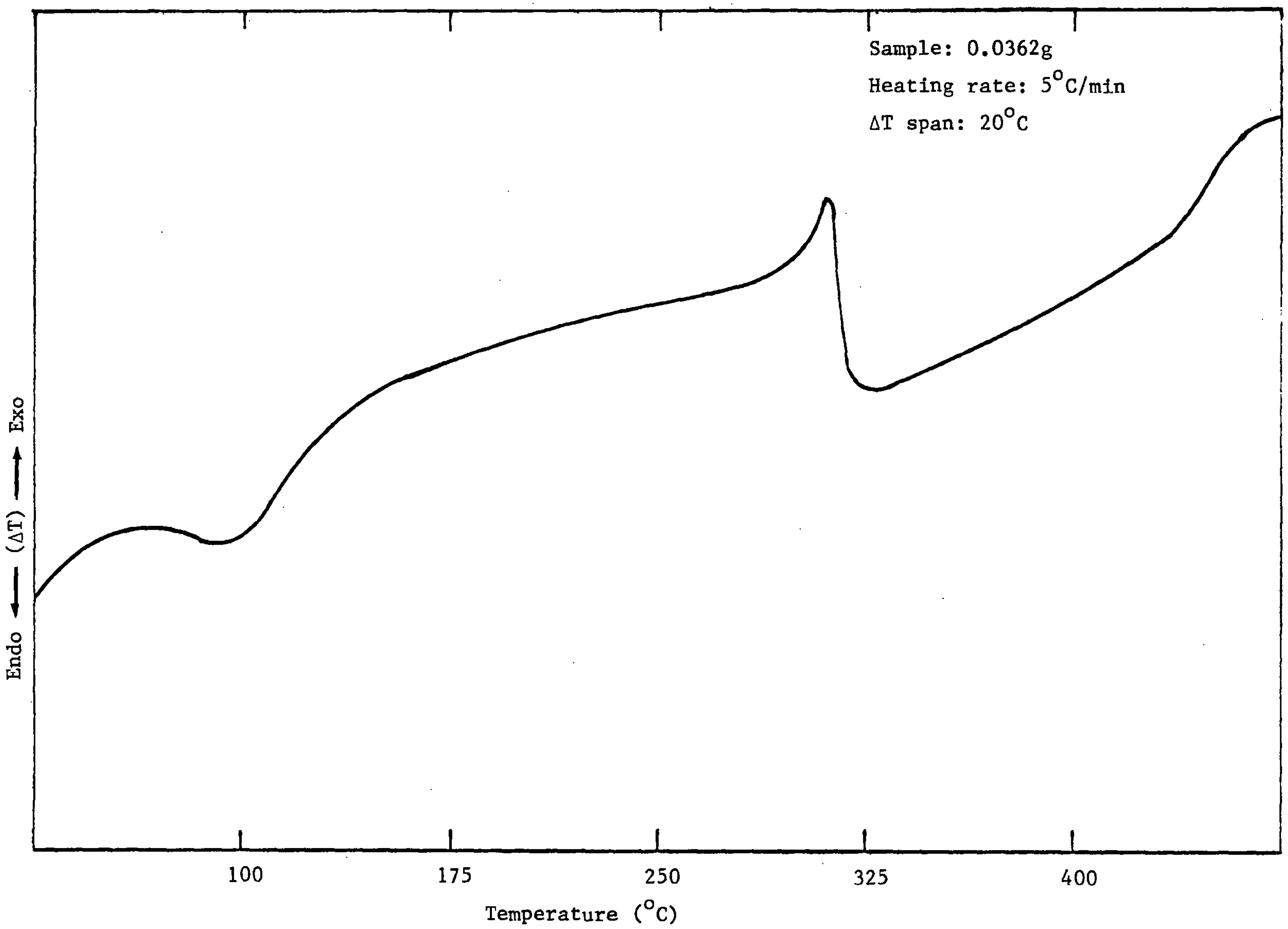

Figure 4.3 DTA curve for damp resins: Duolite ARC-9358 and ARA-9371 resins mixed 1:1 by weight in deionized water, dewatered for ≈5 minutes and dried in air for 24 hours.

Samples of new ARA-9371 and ARA-9358 resins were mixed one-to-one by weight and equilibrated with a solution containing a mixture of cations and anions reported in the BPNL study as being present in the Cask A resins. The equilibrium period was five days, and the conductivity of the liquid-resin mixture dropped from 3,300 μmho to <10 μmho; final pH was 4.6. The mixture included iron, copper, zinc, manganese, ammonium, calcium and sodium cations and chloride, bromide, sulfate, nitrite, nitrate, and borate anions. The results of several DTA tests on these samples are shown in Figures 4.4 to 4.6. The resins were dewatered approximately 30 minutes prior to the test corresponding to the DTA shown in Figure 4.4. One hour of vacuum filtration followed by three hours of standing in air gave the results depicted in Figure 4.5 in which it appears that a small exotherm begins at 100°C and continues up to ≈300°C. Comparison with Figure 4.3 indicates that what appears to be the baseline from 30°C to ≈80°C or just before the appearance of the exotherm at ≈100°C could well be a smaller water loss endotherm. A test of the same dewatered and air-dried resins utilizing the "scanning autozero" function on the DTA apparatus seems to confirm that there is a small endotherm extending up to ≈140°C. (See Figure 4.6.) Above this point, at ≈170°C, the DTA curve begins to increase slowly. This could be an indication of a small and continuous release of heat up to ≈300°C, at which point a strong exothermic peak occurs. Attributing the small and slow increase in the DTA curve to an exotherm must be based on the assumption that the scanning autozero function used in this test provides a straight flat baseline. From the discussion given earlier on the limitations of the DTA apparatus used, this assumption may not be valid.

No conclusion can be drawn from these experiments regarding what caused the exotherm in the ANO resins. However, they do indicate that the moisture content of the resins can influence their thermal behavior.

Further testing to obtain a quantitative correlation between moisture content and the thermal behavior of the resins was beyond the scope of the work done here. However, it appears that this aspect of the properties of ion-exchange resin waste may bear more investigation.

4.4 Review of BPNL Solidification Report

The study by BPNL conducted as Phase 2 of ANO's follow-up investigation of the exothermic incident was concerned primarily with determining whether solidfication of the resins stored in Casks A, B, C, D, and E would cause the resins to undergo excessive temperature increases. BPNL utilized the proprietary solidifcation method marketed by Chem-Nuclear Systems, Incorporated (CNSI). The report describing BPNL's work was released to BNL only after BNL agreed to treat as proprietary all details of CNSI's solidification procedure. The BPNL Phase 2 report contains details regarding the samples which were used to evaluate the solidification process and other information which, it is felt, are not proprietary. This information is discussed in this section.

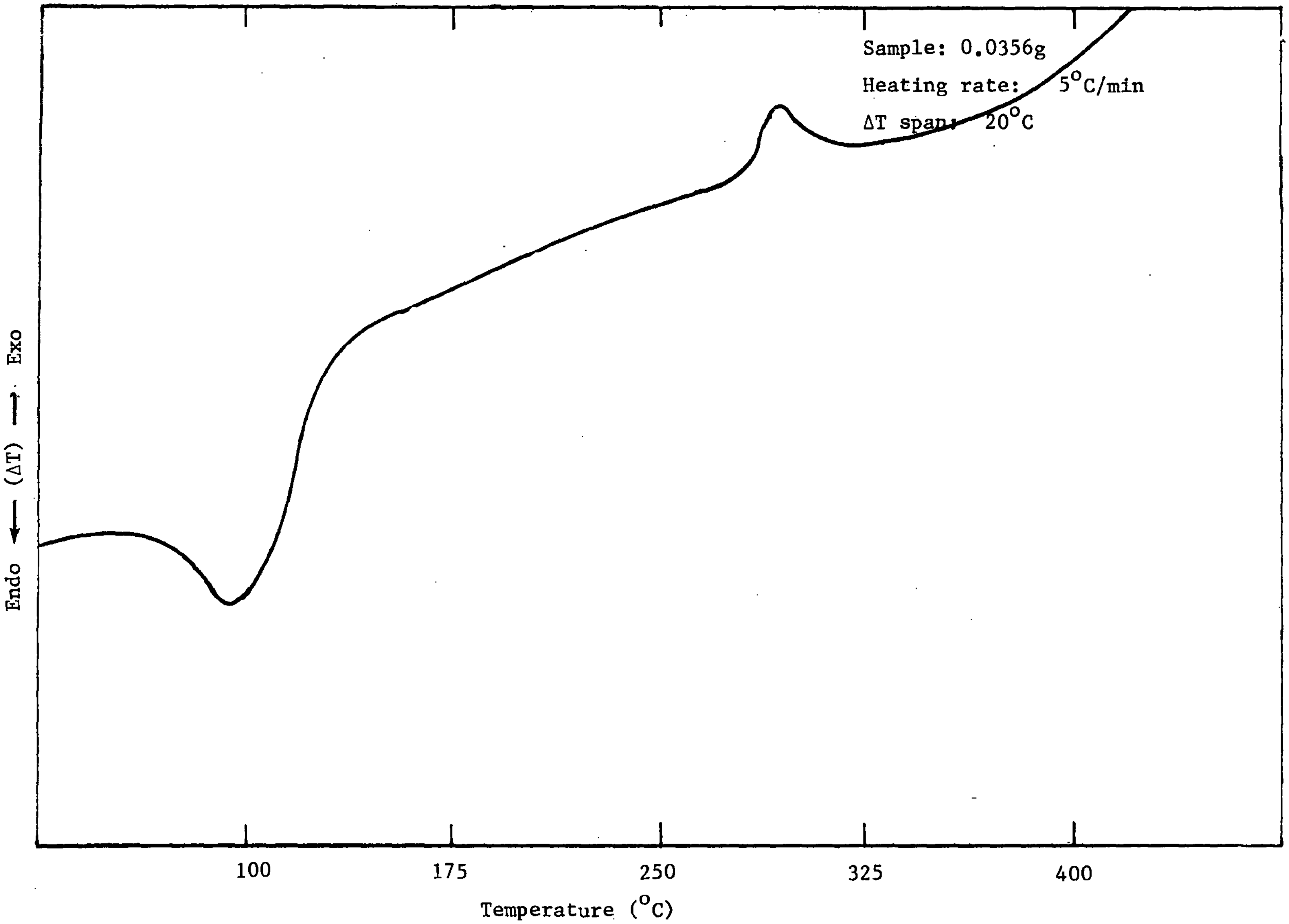

Figure 4.4 DTA curve for damp resins: Duolite ARC-9358 and ARA-9371 mixed 1:1 by weight, equilibrated with mixed-ion solution as described in text, and dewatered ~30 minutes.

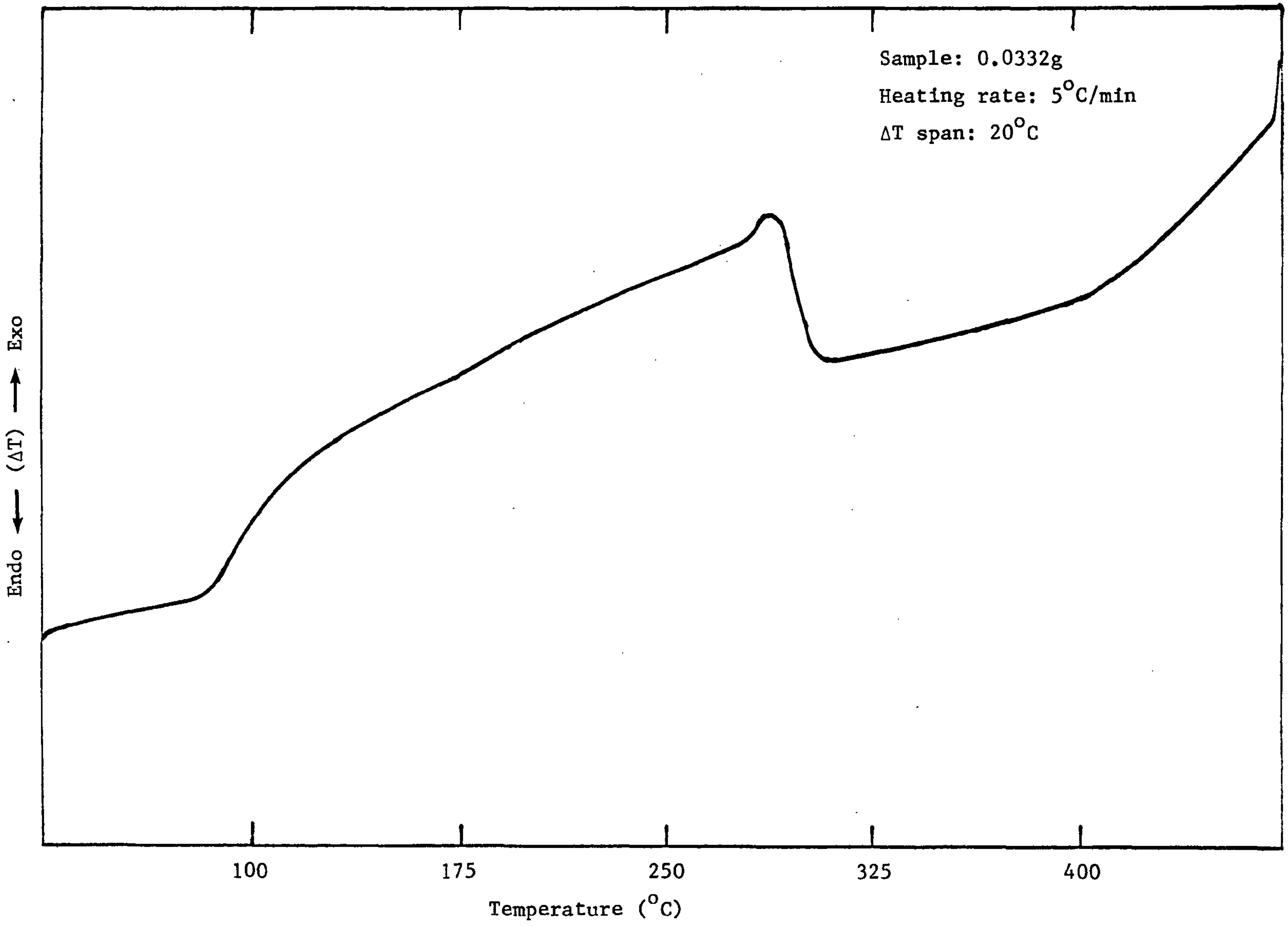

Figure 4.5 DTA curve for dried resins: Duolite ARC-9358 and ARA-9371 mixed 1:1 by weight, equilibrated with mixed-ion solution as described in text, dewatered for ~1 h and dried in air for 3 h.

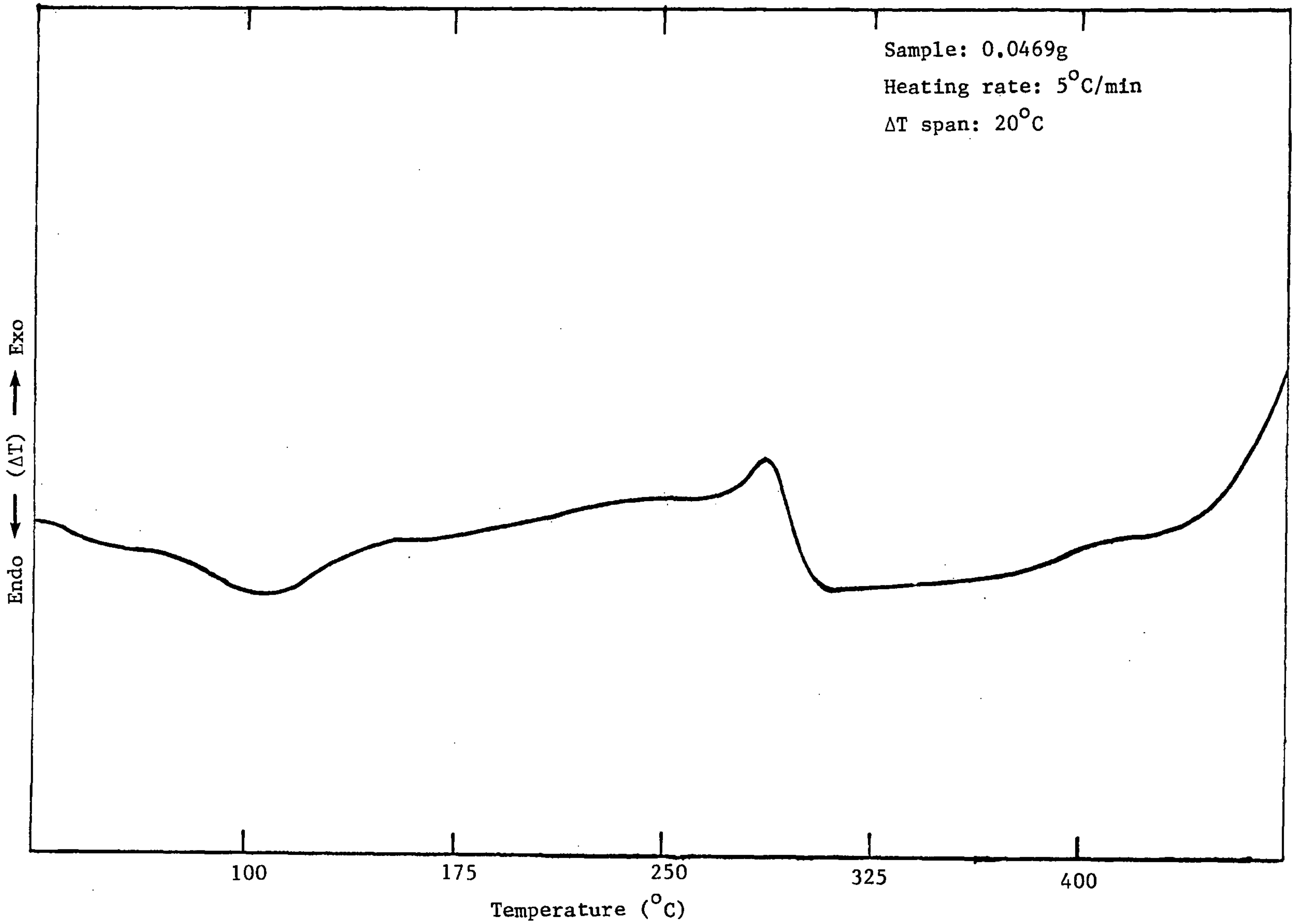

Figure 4.6 DTA curve for dried resins: Duolite ARC-9358 and ARA-9371 mixed 1:1 by weight, equilibrated with mixed-ion solution as described in text, dewatered for ≈1 h, and dried in air for 24 h, run with "scanning autozero".

4.4.1 Description of Samples Used for Solidification Studies

New, unused resin samples, as well as samples from each cask, were obtained from ANO for the solidification studies. The resin samples obtained for the solidification studies were apparently divided into portions for both Phase 2 and Phase 3 studies, since the same samples are described in the report summarizing the results of the Phase 3 study. (See Section 4.5.)

The new resins were identified according to type as indicated in Table 4.3. These represent all the ion-exchange resin types used at the ANO plant, although they are not necessarily those that are routinely used in the liquid radwaste cleanup system. Because the exact identities of the resins which experienced the exotherm were unknown, BPNL conducted solidification tests with all the new resin samples.

Table 4.3

New Resin Samples Used in BPNL Solidification Studies

Designation[a]	Manufacturer	Type[b]	Function
IRA-200C	Rohm and Haas	macroreticular, PS-DVB	strong acid cation
IRA-900C	Rohm and Haas	macroreticular, PS-DVB	strong base anion
A-101D	Diamond Shamrock	gel, PS	strong base anion
ARC-9358 (C20H)	Diamond Shamrock	gel, PS-DVB	strong acid cation
ARA-9371	Diamond Shamrock	gel, EP	weak base anion
RWA-78 (IRN-78)	Rohm & Haas	gel, PS-DVB	strong base anion
IRN-150	Rohm & Haas	gel, PS-DVB	mixed (strong acid cation and strong base anion)

[a] As given by ANO, the designations in parentheses are identities of the resins assigned by BPNL.

[b] PS = polystyrene, DVB = divinylbenzene cross-linking, EP = epoxy-polyamine.

Samples of the resins in Casks A through E were obtained in August 1983 by BPNL personnel using a core sampler which was designed and constructed at BPNL. According to the Phase 2 report, the spent resin holding tank 2T13 had had more resins added to it after Casks A and B were filled. After the exothermic incident, Tank 2T13 was emptied out completely into Casks C and D. Inspection of 2T13 revealed more "caked" resins in the tank whose removal required the use of high-pressure water streams. The latter resins were transferred to Cask E.

The approximate volume of the "newer" resin added to the holding tank after Casks A and B had been filled was 270 ft^3, and it was noted that ≈170 ft^3 of "older" resin of indeterminate age remained in Tank 2T13 before the "newer" resin was added.

Casks A and B were stored unsealed in a makeshift plastic greenhouse, while Casks C, D, and E were sealed and stored outside. Casks A and B had approximate internal volumes of 103 ft^3, while Casks C, D, and E were larger, with internal volumes of ≈164 ft^3.

Two core samples were obtained from Cask A and Cask E, while one core sample was obtained from Casks B, C, and D. The cores from Casks A, D, and E were divided into portions. A summary and description of all the samples are given in Table 4.4.

During the collection of the core samples from the casks, several observations were noted. Bubbles were seen during sampling of Casks A, B, and E. An odor described as "sewer-like", or similar to the odor from an opened septic tank, was observed during the sampling of Cask A. A rotten smell, different from that associated with Cask A, was detected in Casks C, D, and E when they were initially opened. A growth of "pond-scum" was apparent on the surface of the liquid in Cask B, which was stored alongside Cask A without being sealed or directly covered. There was an oily scum on the surface of the liquid in Cask E, with some clear oil in globules. The thickness of the scum layer was measured and found to be between 3/8- to 1/2-in. thick.

The amount of resins in each of the casks varied somewhat. In particular, the depths of resin in each of the casks as measured from the core samples were as follows: Casks A and B, 3.5 ft.; Cask C, 4.5 ft.; Cask D, 4 ft., 4 in; Cask E, 10 in.

Table 4.4

Spent Resin Samples Obtained From ANO Storage Casks

Sampling Location	Description
Cask A, Sample I,	vertical core near center line
Portion 1	bottom 6 in., black color
Portion 2	no description given
Portion 3	"chunk" of resin 7 in. above bottom
Portion 4	material from 1.5 ft. above bottom to top of core
Cask A, Sample II,	core from center top to bottom sidewall
Portion 1	bottom 6 in., one chunk excluded, black but not as dark as Portion 1, Sample I
Portion 2	material from 6 inches above bottom to top of core, brown/black mixture
Portion 3	crust from top of core and a chunk from ≈8 in. below top
Portion 4	a thin (≈ 3/4 in.) layer ≈ 8 in. above core bottom, "different" visual appearance not described further
Cask B,	vertical core near center line
	entire core, brown resins, excluded bottom 1 in. containing white macroreticular resins and top 1 in.
Cask C,	vertical core near center line
	entire core, resins appeared "new", i.e., yellowish, not brown or black
Cask D,	vertical core near center line
Portion 1	bottom 6 in. of core, dark brown resins
Portion 2	material from 8 in. above bottom to top of core, clear and amber gel resins mixed with black and red beads
Cask E,	surface of liquid
	oily scum, globules floating on top (≈1/2 in. thick)
Cask E, Sample I,	vertical core near center line (10 in. deep)
Portion 1	bottom 3 in. of core, gel-type resins
Portion 2	remaining upper 6 in., mostly macroreticular resin
Cask E, Sample II,	core near bottom sidewall (10 in. deep)
Portion 1	sludge and resins from very bottom of core
Portion 2	red resin beads from near bottom of core
Portion 3	material from ≈3 in. above bottom to top of core, sludge at top of core excluded, mostly macroreticular resins

4.4.2 Evaluation of Solidification Tests

Details of CNSI's proprietary cement solidification procedure can not be given here. However, BPNL modified the procedure by conducting the solidification tests in insulated dewar flasks, and monitored the temperature of the forms during solidification. Small-scale tests of the cask resin samples mentioned above indicated a maximum temperature increase of 3°C for Cask A resins, 2.8°C for Cask E resins, and smaller increases for resins from Casks B, C, and D. Somewhat larger temperature increases were observed in the tests involving new resin samples.

There were no descriptions given of the final waste forms, e.g., whether the forms dried completely, exhibited cracks, or were free standing solids.

The report stated that no significant temperature differences were expected between lab-scale and full-scale tests and predicted that no excessive temperature increases would be experienced in solidification of the resins. However, no calculations extrapolating the small-scale temperature results to large-scale solidification were presented. Such an extrapolation would require, as a minimum, some estimate of the heat of solidification, as well as the heat capacity of the resin/cement mixtures.

It was noted that the solidification process excluded oxygen from the resin, and that further exothermic behavior in the resins would not be expected because oxygen was believed to be the oxidant necessary for the exotherm to occur originally.

4.5 Review of Final BPNL Report

The copy of the BPNL report entitled, "Chemical Characterization of Organic Ion-Exchange Resins Supplied by Arkansas Power and Light Company" was received stamped with the legend "Proprietary Information Per 10 CFR 2.790 Withold From Public Disclosure." Consequently, the material in this section is considered confidential and should not be released to the general public.

4.5.1 Summary of Phase 1 and Phase 2 Studies

The final BPNL report (referred to here as the Phase 3 report) contains summaries of the Phase 1 and Phase 2 reports as well as additional studies conducted to determine whether the presence of biodegradation in the resins could have caused the exotherm.

The summary of the Phase 1 studies concludes that a chemical reaction could not have been the cause of the exotherm because no strong oxidants were detected in "sufficient quantity to cause the resin destruction observed in Cask A." However, this does not take into account the fact that strong oxidants would have been consumed during the exotherm and may not have been detectable at all afterward other than in trace quantities. Therefore, on this basis, the possibility of a specific chemical oxidant cannot be ruled out as a possible cause for the incident.

The summary of Phase 2 studies contained some information that was not included in the Phase 2 solidification report (reviewed in Section 4.4). Two items are noteworthy.

First, the role of supplied air from the dewatering process as the oxidant necessary for the exothermic event was discussed. It was pointed out that oxides of nitrogen would have been present in the gases evolving from Cask A if nitric acid, nitrates, or nitrite had been the oxidant responsible for causing the exotherm, and that no oxides of nitrogen were noted by ANO personnel when the exotherm was detected. Presumably, this alludes to the fact that nitrogen dioxide (NO_2) would have been noticeable as a brown gas. However, it is not clear how long the resins had been experiencing the exotherm before it was detected. Nitrogen oxides might have been given off in the early stages of the exotherm. Discussions with ANO personnel (see Section 3) indicate that the exotherm could have been going on for several hours.

The second item to note concerns the presence of oily organic matter. The organic material was found as a coating on some samples of resin beads from Cask A and on the surface of the liquid phase in Cask E. The organic material was examined by gas chromatography and infrared spectroscopy and described as having a "high boiling point" and consisting of mainly aliphatic hydrocarbons. Traces of aromatic materials were detected, and it was stated that organic acids and esters were probably present as well.

It was concluded that there were no significant differences between the organic material from Cask A and that from Cask E. The organic material was considered stable, i.e., not easily oxidized, because some was still present in Cask A after the exotherm. It was suggested that the organic material may have contributed to the difficulties encountered in transferring the resins from holding tank 2T13, by acting as a "binder to form an aggregated resin mass." The source of the organic material (possibly a lubricating oil) was unknown.

4.5.2 Phase 3 Studies

The Phase 3 studies included thermal stability tests of new ion-exchange resins. New resins were heated in an oven in open glass vials to observe changes in appearance. Differential scanning calorimetry (DSC) was employed to identify the exact temperatures at which exothermic reactions would occur in new and used resins. New resins in general began to show visible changes in appearance by 150°C. The DSC studies showed no obvious exothermic behavior below 200°C. BPNL concluded on the basis of the studies and the visual appearance of resins from Cask A after the exotherm that all the resins in the cask reached a minimum temperature of 300°C during the exothermic event.

BPNL conducted tests to evaluate the significance of microorganism growth in the resins and its potential for initiating the exotherm. These involved two types of studies:

1. Determine whether indicators of microbial growth were present in Casks A to E, and

2. Demonstrate that the spent resin waste, as well as new "as-received" resins were capable of supporting microbial growth.

Small samples of resins from each cask and small samples of new resins were divided into four portions according to the scheme shown in Table 4.5. There were five samples representing Casks A through E and eight samples of new as-received resins corresponding to those mentioned in Section 4.4. After 7 days incubation in an anaerobic environment at 30°C, the tubes containing the sample portions were examined for growth and gram stains were prepared.

Table 4.5

Experimental Scheme: Microbe Growth in Resins[a]

	Lactate[b]		Inoculated[c]	
Portion	Added	Not Added	Yes	No
1	x		x	
2		x	x	
3	x			x
4		x		x

[a] Each resin type (new or from Casks A through E) was mixed with reduced Postgate medium.

[b] Lactate added as readily available carbon source.

[c] Inoculated from a culture of Desulfovibrio desulfuricans, a sulfate-reducing bacterium.

Cask A and B samples exhibited growth and H_2S production (indicative of the presence of anaerobic sulfate-reducing microorganisms) in all cases. Cask C, D, and E resins had evidence of microbial growth in all cases and gas generation (not H_2S) in the uninoculated specimens. Casks C, D, and E inoculated specimens exhibited H_2S production.

The staining tests showed gram-positive rods with spores and gram-negative long rods and short curved rods in Casks C, D, and E. Results of the gram stain tests were not reported for samples from Casks A and B.

The new resins all showed growth and H_2S production in the inoculated samples except for the C20-H and ARC-9358 resins. All uninoculated new resins showed no growth except for RWA-78 resin which had a mold-like growth on the surface of the resin.

Further studies to isolate and identify the different micro-organisms found in the casks yielded the following information.

1. A gram-negative rod which was oxidase positive and a member of the *Psuedomonas* species was found in resins from all of the casks. These organisms are normally aerobes, but were said to be able to respire anaerobically using nitrate.

2. Resin samples from all of the casks except those from Cask B contained a gram-positive spore-forming anaerobe of the *Clostridium* species. This organism was said to be "capable of producing copious amounts of gas (not H_2S)."

3. Resins from Casks C, D, and E contained a medium-sized gram-positive rod able to grow under both aerobic and anaerobic conditions. This was said to be of the *Corynebacterium* species, based on the microscopic and colonial morphology of the cultures.

4. Resins from Cask B contained a small vibrioid gram-negative rod. This was described as a strict anaerobe of the *Desulfovibrio* species.

The microbial studies, conducted under Phase 3 demonstrate that microbial growth was present in all of the casks. In addition, given the right conditions, even new resins were shown to be capable of supporting microbial growth.

There was some discussion in the report as to what mechanisms may have been possible for initiating the exotherm. Under the assumption that air (oxygen) was the necessary oxidant and significant quantities (growth) of microbial organisms provided the remaining ingredients, several mechansims were postulated.

1. Heat generation as a by-product of microbial metabolism. Under favorable conditions population growth of micro-organisms can be extremely rapid. The heat generated from this growth can be retained by the bulk material, increasing its temperature. Compost piles are an example of this effect. A sufficient temperature increase can cause autoxidation (reaction with oxygen in the air) of the bulk material, and can result in combustion, as evidenced in "green-hay" fires.

2. The presence of a large number of micro-organisms, both live and dead, is a source of finely divided organic material. The high surface area could be favorable to oxidation of the microbes directly at lower temperatures compared to resins. As the oxidation of the organic material occurs, heat is generated and retained by the bulk material, increasing the temperature to the point at which combustion is initiated.

3. The metabolic by-products of microbial growth may be more easily oxidized compared to the resins.

Small-scale dewatering tests were conducted by BPNL in order "to monitor events potentially leading up to the exotherm observed in Cask A." The simulated dewaterings were conducted on resin samples from each Cask and on a mixture of new resins. Additional samples from Cask E were "spiked" with Desulfovibrio desulfuricans. Each sample consisted of 300 mL of resin, and the dewaterings were conducted in insulated vessels. The air flow was scaled to resin volume rather than cross-sectional area, because the latter flow of 650-1625 mL/min was "not practical for laboratory operation." Details of the resin bed geometry, e.g., resin bed diameter and depth, were not specified. The design of the laboratory vessels used to conduct the dewaterings was not given.

The results of the dewatering tests were summarized in a table which showed air flow rate, initial temperature, temperature range over the duration of the dewatering, and run time. The largest temperature range reported was 20 to 24°C, for a dewatering time of 109 hours. Information regarding the change of temperature with time was not given. This point may be significant, since, for example, the temperature may have increased quickly then slowly decreased over the remainder of the run, or it may have increased slowly throughout the run.

The correlation of small temperature changes in the small-scale laboratory dewatering experiments to a full-scale dewatering was not attempted, primarily because such a prediction would have to include some knowledge of the thermal conductivity properties of both small-scale and large-scale systems. Thus, no temperature change in a small-scale test would not eliminate the possibility of a significant temperature increase in a large-scale dewatering under identical (scaled) conditions of resin make-up, bed geometry, and air-flow.

4.6 Conclusions and Recommendations

4.6.1 Probable Cause of Incident

The cause of the exotherm in the ANO resin waste could not be unequivocally identified from the analyses of resin samples performed at BPNL and BNL. It should be stressed that the resin samples examined under Phase 1 of BPNL's study were not necessarily representative of the entire contents of Cask A since stratification of the resins can occur. ANO's follow-up investigation (Phase 2 and Phase 3) included more extensive sampling of all the resins which had been stored in holding tank 2T13. However, the chemical analysis of the resins conducted under Phase 1 of the investigation was not repeated for the samples obtained later.

There are several factors which suggest that the exotherm was a unique occurrence:

1. The need to dewater the resins through six cycles as compared to a normal three or four;

2. The smell of sewage associated with the resins;

3. The presence of solids and macroreticular resins mixed in with the "normal" gel-type resin waste from the LRWCS at ANO; and

4. The uncertain age of the resins.

Although ANO uses epoxy-polyamine-based anion resins in its LRWCS that are atypical compared to most other nuclear power plants, these cannot be blamed specifically for the exotherm. ANO's experience in dewatering its LRWCS resin waste before the exothermic incident indicates that the epoxy-polyamine type resins are usually as stable as those based on a PS-DVB matrix.

A probable scenario for the cause of the exotherm involves the inclusion of several factors. The low level of radioactivity present in Cask A seems to eliminate direct radiolysis and radiolytic heating effects being the cause. The presence of macroreticular resins in Cask A and the uncertainty as to their source and use before being stored in holding tank 2T13, for as long as three or four years, as well as the uncertainty over whether other resins were present in the holding tank for a comparable amount of time, brings up two possible mechanisms for intitiating the exotherm. These are that:

1. The "older" resins contained a chemical or chemicals that reacted with the resins normally used in the LRWCS or reacted with air during the dewatering process; or

2. The "older" resins were degraded either biologically or by some aging process and as a result contained some reactive chemicals.

Failing the identification of a particular chemical oxidant reactive enough to cause the exotherm, it would appear that the most likely candidate for the cause of the exotherm is autoxidation. This is known to occur to some degree with in-service ion-exchange resins. Extra dewatering cycles would only promote the possibility of it occurring. While autoxidation is recognized as a slow process, the combination of additional dewatering cycles and poor heat transfer characteristics of the resins could have had the cumulative effect of providing the conditions favorable enough for an exotherm to occur. The long time (induction period) of five to six days which passed before the exotherm occurred seems to confirm autoxidation as the cause of the exotherm. However, the material or chemical or combination of these which rendered the resin wastes susceptible to autoxidation are not known.

It is likely that the presence of biological activity in the resin waste, as indicated by the sewage smell, was a significant contributing factor. The investigations by BPNL (Section 4.5) confirmed the presence of microbial activity in samples of the ANO resin wastes. It cannot be determined at present whether the microorganisms were directly autoxidizable, or if metabolic by-products and/or by-products resulting from biological degradation of the resins were the materials which were susceptible to autoxidation.

Additional pumping associated with extended dewatering exposes the resin wastes to excess amounts of air. The requirement to continue dewatering was probably associated with the fact that the resins exhibited some agglomeration, also referred to as bridging, clumping or caking. The cause of this agglomeration is not clear, but may have been a result of the presence of biological activity. Agglomeration can be expected to result in difficulties transferring from holding tanks to disposal liners (Martineit, et al, 1978). Bridging may also be expected to influence the dewatering process, by interfering with the easy drainage of "free" liquids in the waste.

It must be stressed that the above constitutes speculation as to the most probable cause. It is likely that the exact cause of the exothermic reaction may never be known. The characteristics of the resins in Cask A at the time of the incident cannot be determined for a variety of reasons. Among these are:

1. Water added to Cask A to supress the exotherm was recirculated for several hours, which could have had the effects of homogenizing the resins, dissolving water-soluble species, and redistributing the ions loaded on the resins.

2. Assuming that a particular chemical or chemicals initiated the reaction, it is possible that some reaction products were gaseous and lost to the atmosphere. This may be particularly true if nitrate or nitrite ions are the suspected initiators, since these when reacting as oxidizing agents can be reduced to NO, NO_2, N_2O, and N_2.

3. A temperature profile of Cask A at the time of the incident was not obtained. Hence, it is not certain whether the exothermic reaction occurred in one small area of the HIC or involved the entire contents.

In conclusion, the exact cause of the exotherm cannot be unequivably stated.

4.6.2 Disposal of ANO Resins Involved in the Exothermic Incident

The resins involved in the exothermic incident (Cask A) and the other resins from holding tank 2T13 (Casks B, C, D and E) were solidified in cement prior to being shipped for disposal at the commercial site in Barnwell, SC.

In the Phase 2 investigation conducted by BPNL using cask resin samples, there were no indications of temperature increases in the small-scale solidification tests other than those associated with the heat of hydration in cement. It was stated in the BPNL report that large temperature increases would therefore not be expected in large-scale solidification. Although this conclusion may be open to some question, any heat generated, e.g. from the heat of hydration associated with the setting of cement, would not be expected to inititiate further degradation or, more importantly, combustion in the resin wastes because air (oxygen) would be effectively excluded from the resins by the cement matrix. This last point is of prime concern if it is assumed that the cause of the exotherm was autoxidation.

There is no information as to whether the resin wastes were solidified directly in the casks in which they were stored. Details regarding the final solidification procedure were not available. In particular, it is not known if the resins were transferred to other containers for solidifications or if the temperature of the wastes was monitored during the solidification process.

The use of solidification for processing the resin wastes after the exothermic incident was a reasonable and practical alternative compared to attempting further dewatering operations. The failure to find a specific cause for the exotherm would rule out further attempts to dewater the same or similar wastes unless these were monitored very carefully, e.g. by measuring continuously the temperature at several points in the disposal liner during dewatering. The small-scale solidification tests conducted by BPNL (see Section 4.4) appeared to be adequate for demonstrating that exothermic reactions other than those associated with the heat of hydration of cement would not occur during solidification of the resin wastes.

4.6.3 Technical Considerations and Recommendations

It was stated that several circumstances surrounding the exothermic incident at ANO indicated that it was an isolated event. However, the possible initiating mechanism discussed in Section 4.6.1 raises more general concerns regarding the dewatering process. If autoxidation of the resin waste was the operative mechanism, then any conditions which could promote this should be defined. These conditions include resin moisture content, resin type, and age, ionic species absorbed on the resins, radioactivity level, contamination by organic chemicals such as solvents, or oils, and biodegradation.

The operating experience with resin dewatering (with one exception) indicates that this is a convenient means of processing prior to disposal. However, there is a lack of information regarding what constitutes a "normal" dewatering for disposal. The method is tailored to the particular waste involved, e.g., powdered resins and sludge require different treatment compared to bead-type resins. The number of dewatering cycles can vary for different HIC designs, as well as for the waste to be dewatered. Certainly, no information could be found regarding whether some heat generation can be expected during a "normal" dewatering. A possible source of heat could be from the heat of hydration of the resins. This could occur if, for example, some of the resins had more than the easily drainable liquids removed during the dewatering process. Subsequent drainage from other portions of the container or even absorption of moisture from the air might cause hot spots to develop. The magnitude of such heat effects are unknown. Indeed, the potential for resin wastes to become sufficiently dry during dewatering so that such heat effects can occur is not known either.

Some guidelines regarding what constitutes "normal" dewatering should be available so that, in the future, abnormal occurrences, such as the extra dewatering cycles that were required for Cask A at ANO, can be recognized and appropriate measures taken. These measures include closer monitoring of the waste or the use of an alternative processing method. The responsibility for defining these guidelines rests with the vendors of resin dewatering services.

Several practical considerations could prevent incidents similar to the exothermic reaction in the ANO resin wastes from occurring in the future. These considerations are necessarily based on the assumptions that autoxidation was the reaction mechanism responsible for the incident and that the agglomeration and the biological activity present in the resins were significant contributing factors.

1. If bridging or agglomeration of resin wastes is suspected as a result of visual observations or from difficulties during transfer of the resins from holding tanks, then dewatering operations should be monitored carefully. Temperature measurements may not be necessary, if the characteristics of dewatering, e.g. time required or pressure changes during pumping, are well-known and monitored during dewatering.

2. If extended dewatering becomes necessary (compared to normal practices) it should only be continued if there are continuous temperature measurements at several locations in the dewatering liner. A more conservative approach would be to stop dewatering operations, check temperatures, and obtain samples to determine why the extended dewatering is required. If this can be attributed to the presence of biological activity or chemical contamination, alternative methods of processing the wastes should be utilized.

5. MILLSTONE NUCLEAR STATION RESIN LINER INCIDENT

The information in this section was obtained during a meeting at Millstone Nuclear Station (MNS) held November 9, 1983, and during subsequent telephone contacts.

5.1 Description of Incident

On Thursday, September 22, 1983, a HIC was filled with ≈120 cu. ft. of waste sludge consisting of Ecodex filter media. The liner was dewatered using procedures normal to Millstone and shipped out Friday, September 23, 1983. The only unusual aspect of this waste package compared to similar liners shipped by Millstone was the addition of previously dewatered filter media (Ecodex) which had been stored in four 55-gallon drums since the last shipment of filter sludge sometime in February or March. This waste, which had no unusual smell, was added on top of the filter sludge which had been sluiced into the HIC already. The HIC had 6 to 12 inches space between the top of the liner and the surface of the filter sludge. The total radioactivity contained in the HIC was 10.139 curies. A detailed isotopic analysis was provided by Millstone and is included here as Appendix C.

The HIC arrived at Barnwell on Tuesday, September 27, 1983. When the lid of the shipping cask containing the HIC was unbolted, it raised several inches. Closer examination showed that internal pressure in the HIC had caused the HIC to bulge, but there was no change in diameter. The contact temperature of the liner was measured and found to be 90°F. A tap was drilled into the HIC by Barnwell personnel and the pressure released. At the same time, a sample of the gas was taken. This sample was analyzed by Chem-Nuclear Systems, Inc. (CNSI) using gas chromatography. The results of this analysis are shown in Table 5.1.

Table 5.1

Analysis of Gas in Millstone HIC
(Percent by Volume)

Nitrogen	78.57%
Oxygen	18.51%
Methane	1.81%
Argon	0.74%
Carbon Dioxide	0.57%
Water	0.17%

The composition of this gas is much like that of the atmosphere except for a slightly lower percentage of oxygen and higher levels of methane and carbon dioxide. It is worth noting that no hydrogen was detected although this is one of the primary products of radiolysis. The higher than normal concentrations of methane and carbon dioxide may be associated with biological activity.

The waste in the HIC was composed entirely of Ecodex-X-203-H filter media. This material consists of powdered ion-exchange resins and cellulosic material. The ion-exchange resins are mixed cation and anion resins with a composition 2 to 1, respectively. The Ecodex is used as a pre-filter for deep-bed demineralizers in Unit 1 only at Millstone site. (Unit 1 is a 680 MW BWR built by GE. Unit 2 is a 890 MW PWR built by Combustion Engineering. Unit 3, still under construction, is a 1250 MW PWR being built by Westinghouse). There is no chance of contamination from the other units at Millstone since the only common system is that for release of gases. All liquid radwaste is handled separately. Units 1 and 2 share a common chemistry lab but have separate staffs. The liquid waste from the chemistry lab is sent to a single holding tank. The influent to the Ecodex filters is water which comes from a concentrator and equipment drain water. The conductivity of this stream is monitored and, should this increase to >45 μmho, the water is checked more carefully for pH, a back-up conductivity measurement, and then a colorimetric determination of ammonia content. The Ecodex is used primarily as a particulate filter. The chemical exchange capacity is expended quickly, and filter media replacement is based on pressure drop across the bed.

The dewatered sludge in the four 55-gal drums which were added to the HIC was the residue from a cleanout of the sludge storage tank. The tank had been "mucked out" after the last previous sludge shipment in February or March. The four drums had been sealed and stored on-site.

Regarding the dewatering process, there was nothing unusual about this particular HIC compared to other waste sludge shipments. CNSI supervises all dewatering operations, and there is a representative present at the Millstone site on a full-time basis. The only anaylsis is a measurement of the isotopic contents of the waste: these are determined by the CNSI representative at the time of dewatering. Generally the waste is pumped out until a given level of vacuum is obtained. The waste is then allowed to drain for some time without pumping, after which pumping is again started to determine the amount of drainable liquids. A visual inspection of the inside of the HIC is also made after dewatering as part of the QC procedure.

5.2 Probable Cause of Pressurization and Final Disposal

There was some discussion of the possibility of chemical contamination of the sludge waste, especially by solvents. The only solvents used around Unit 1 in any quantity are trichlorotrifluoroethane (Freon 113) for dry cleaning and pentatone 927. The Freon 113 was suspected because some contamination of the concentrator mentioned earlier by this chemical was discovered about the time that the pressurization was detected at Barnwell. The contamination was detected as a result of "burping" in the concentrator and the presence of a strong smell, but it was not known how the solvent had entered the system. Scoping experiments by D. Wilkens, the chemist for Unit 1, revealed that gas pockets appeared in Ecodex sludge wastes treated with 0.1% trichlorotrifluoroethane and dewatered in a test tube by centrifuging. This only confirms the possibility that contamination by this solvent caused the pressure in the HIC.

In the meeting held at Millstone to discuss the incident there was some uncertainty as to how such contamination had entered the filter media waste before it was shipped to Barnwell. At the time it was believed that the waste holding tank had been full and isolated for some time before the filter media waste was transferred to the HIC for shipment to Barnwell. It was later determined that there had been some slurrying between the two holding tanks available for filter media waste, and that this had occurred around the time that the shipment to Barnwell was made and the Freon 113 contamination discovered. Contamination of the waste in the HIC could not have been detected by smell at the time of the transfer because this is carried out remotely due to radiological concerns.

Millstone conducted experiments to demonstrate that the filter media waste would not cause pressurization to occur again in the HIC. The tests were conducted using core samples obtained from the HIC involved in the incident, and the experiments consisted of heating samples in a sealed container immersed in a 90°F water bath. The pressure was monitored, and no sign of pressurization was observed. It was not clear how long the experiments were run.

This HIC which had become pressurized during shipment to Barnwell was finally disposed of by shallow land burial.* Chem-Nuclear was satisfied that this investigation at Millstone into the problem demonstrated that the HIC containing filter media sludge would not become pressurized again.

There was no specific chemical analysis of the filter media samples from the HIC for Freon-113. MNS has not specifically identified how the Freon-113 got into the water system, but their own conclusion was that someone had poured it down a drain. Administrative procedures at MNS for handling chemical and solvents were believed to be adequate to prevent such occurrences.* However, workers for outside contractors might not be as aware as in-plant personnel of these control procedures and the need to follow them carefully. There can be problems controlling outside contractors who on occassion bring in their own chemicals and solvents.

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*Telephone conversation with J. Kangley, Radwaste Supervisor at Millstone Nuclear Station, Connecticut, May 9, 1984.

Unfortunately, the pressure of the Millstone HIC was not measured at Barnwell, so the magnitude of pressure generated was only estimated. From the weight of the cask lid and contact area of the top of the HIC with the lid, it was calculated to be ≈2.5 pounds per square inch (psi) above atmospheric pressure. However, this may not be a reliable estimate, and should perhaps be considered a lower bound, since the amount of pressure required to distort a HIC is not known at present.

It is possible that heating could have caused (or contributed to) the internal pressure generation. At the meeting with Millstone personnel held November 9, 1983, it was stated that process water temperatures are approximately 70°F (21°C). During September, meteorological conditions were such that air temperatures were as high as 95°F (35°C). However, this temperature change results in an increase of only 0.7 psi in a sealed container. In order to account for a pressure increase of 2.5 psi, the temperature of the liner would have had to increase to ≈ 160°F (71°C).

Another explanation of the pressurization in the HIC depends on the presence of trichlorotrifluoroethane. This chemical, also known as Freon-113, has a relatively high vapor pressure. Provided enough Freon-113 is present in a condensed phase, i.e., as a liquid or adsorbed onto a solid, at 70°F in a sealed container, the Freon-113 will evaporate until its vapor pressure is ≈5.5 psi (Perry, 1973). Assuming a six-foot diameter for the HIC and a twelve-inch gap between the top of the HIC and the level of the waste, the total gas volume available is ≈28 ft^3. The amount of Freon-113 required to increase the pressure to 2.5 psi above atmospheric pressure in a volume of this size can be calculated and is ≈14 pounds (≈1.2 gal). Whether the waste in question was contaminated with Freon-113 or any other volatile material is not certain. No odors were reported when the waste was transferred to the HIC, but the contamination found in the filter system after the HIC was shipped was initially detected by the presence of an unusual odor in the plant.

A gas sample taken from the HIC at Barnwell was analyzed by gas chromatography (GC). The reported composition was very similar to air, except for high levels of methane (CH_4) and carbon dioxide (CO_2). No hydrogen or organics were detected. It should be noted that GC is a limited technique in some respects. Experimental variables, particularly the type of column and detector used, limit the range of chemical species which can be detected in a single experiment. Detailed information regarding the analysis of the gas sample is not available, and the possibility exists that other chemicals, e.g., Freon 113, were present which were not detected because of the limitation of the method. A more appropriate method of analysis of gas samples from the Millstone HIC may have been mass spectrometry, or Fourier Transform Infrared (FTIR) spectroscopy. The GC analysis does not rule out the possibility that Freon-113 contamination caused the pressurization in the HIC.

The presence of CH_4 and CO_2 may be indicative of biodegradation and/or gas generation by radiolysis. However, the fact that the pressure appeared after only five days and did not occur again before burial since the HIC was resealed at Barnwell, seems to obviate either of these as the primary cause.

5.3 Changes in Waste Management Procedures

As a result of the pressurization incident, new quality control procedures have been instituted at MNS. They now have a total organic carbon (TOC) analyzer for monitoring water process streams and the water contents of waste holding tanks. Prior to waste transfer from holding tanks for processing and disposal, measurements of TOC are made. Following this, no operations other than transfer for disposal are allowed on the holding tank. In addition, after HICs are ready for shipment, they are stored on-site and monitored for changes in pressure before they are shipped for disposal. The HICs are sealed with a modified lid which incorporates a pressure gauge, and the pressure is monitored for the 3 to 5 days before the HIC is shipped.

6. FITZPATRICK NUCLEAR POWER PLANT RESIN LINER INCIDENT

6.1 Background and Description of the Incident

On September 21, 1984 a shipment of dewatered ion-exchange media from the James A. Fitzpatrick Nuclear Power Plant (FNPP) arrived at the radioactive waste disposal site near Barnwell, SC. When the primary lid of the shipping cask was unbolted, on September 24, 1984, the lid raised approximately three inches, presumably due to pressurization of the high integrity container (HIC) inside the cask.

The cause of the pressurization of the HIC was attributed to gas generation resulting from biodegradation. BNL received a sample of the resins from FNPP and measured a rate of gas generation to determine whether biodegradation could have caused the pressurization. This section of the report provides background regarding the incident and waste involved. The results of laboratory testing are presented and discussed in Section 6.2.

6.1.1 Description of the Resin Waste Shipment

The resin liner contained 60 cubic feet of dewatered powdered resin. This material was transferred to the HIC from the radwaste waste sludge tank. The 11,000 gallon tank receives powdered resins and other wastes from the following sources:

- Reactor water clean-up phase separators (powdered resins).
- Radwaste floor drain filter backwash (powdered resins).
- Radwaste waste filter backwash (powdered resins).
- Fuel pool filter backwash (powdered resins).
- Ultrasonic resin cleaner (solids from bead resin cleaning).
- Drains from cask handling area of the radwaste building.
- Sludge from the Waste Surge Tank.

The powdered resins used are a mixture of cation exchangers and anion exchangers. Additionally, FNPP uses Sulkaflock with the powdered resins in some demineralizers. Sulkaflock is a cellulosic material added to powdered resin beds to increase filtering efficiency. These materials will be present in the sludge waste and subject to possible biodegradation.

The Waste Surge Tank was cleaned just prior to the preparation of the waste for shipment. Material from that tank was considered a possible source of microbial activity. The Waste Surge Tank was described* as a 55,000 gal, flat-bottomed tank that was de-sludged to the waste sludge tank using a fire hose and lake water (Lake Ontario). It was estimated that it had been 3 to 4 years since the tank was last cleaned thus it is possible that some material may have been in the tank for as long a period. This marks a similarity to the waste involved in the ANO incident in that resin waste was stored in a holding tank for an extended period (i.e. 3 to 4 yr at FNPP; 4 to 5 yr. at ANO). No unusual odor which might be indicative of biodegradation (e.g., sewer smell) was observed during the transfer of sludge at FNPP. Other sources of microbes may have been from the lake water used in the cleaning operations and through floor drains. Low concentrations of microbes in the lake water could have been absorbed and concentrated on the resin waste.

The 60 cubic feet (3700 lbs) of dewatered resins had a total activity of 73 curies. Principal radionuclides and activities are listed in Table 6.1. The waste was classified according to 10 CFR Part 61 as Class B. Classification is based on the concentration of Cs-137 (1.8 Ci/m^3) and Sr-90 (0.34 Ci/m^3) which exceed the Class A limits of 1 Ci/m^3 and 0.04 Ci/m^3 for the radionuclides, respectively. The radiation dose rate on contact with the liner was 6 rem/h. Radiolysis (discussed in Section 6.2.1) is not considered a significant source of gas generation.

Table 6.1

Principal Radionuclides and Activities (mCi) in FNPP Resin Shipment[a]

Isotope	Activity	Isotope	Activity	Isotope	Activity
Cr-51	1.1 E+3	Sr-90	5.7 E+2	Np-237	2.4 E-4
Mn-54	2.4 E+3	Tc-99	2.2 E-1	Pu-238	4.7 E-3
Fe-55	3.0 E+4	Cs-134	1.7 E+3	Pu-239/40	5.5 E-3
Co-58	4.3 E+2	Cs-137	3.0 E+3	Pu-241	1.0 E+0
Co-60	2.9 E+4	Ce-141	3.6 E+1	Pu-242	2.4 E-4
Ni-59	3.9 E+2	Ce-144	1.7 E-1	Am-241	1.1 E-3
Ni-63	9.2 E+2	Sr-89	2.1 E+3	Cm-242	2.9 E-2
Zn-65	1.0 E+3	La-140	5.8 E+1	Cm-243/44	9.3 E-4

[a] Data taken from shipping manifest. Activities in mCi were calculated based on the 60 ft^3 shipment.

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*Telephone conversation between P. L. Piciulo (BNL) and D. Robert (FNPP) on January 31, 1985.

6.1.2 Resin Liner Dewatering

The resin waste was transferred on September 17, 1984, from the radwaste waste sludge tank to a L6-80 HIC (Chem-Nuclear Systems, Inc.) equipped with dewatering internals for powdered resins. According to the dewatering record from FNPP the process started on September 17, 1984 and was completed on September 20, 1984 after three dewatering cycles. The first dewatering cycle consisted of pumping the liner for 12 h. The next two cycles consisted of a 16-h period during which the liner stood without pumping followed by eight hours of pumping. During the third pumping period a vacuum of 3 in. Hg was measured at each of three pumping valves in the system. There were no additional comments on the Dewatering Completion Record; thus, it is assumed that this was a typical liner dewatering.

6.1.3 Follow-up Activities

The resin shipment arrived at the disposal site near Barnwell, SC on Friday, September 21, 1984. Unloading operations began the following Monday. The lid on the shipping cask raised after unbolting, and it was assumed that the resin liner pressurized and expanded. When personnel at FNPP were notified they found that the container of a waste sample collected for isotopic analysis had also pressurized. It was assumed that the contents of this sample was representative of waste in the liner and that the gas in the liner and the sample bottle were the same. Some tests were made on the gas in the FNPP sample bottle, but no data were available on the gas inside the resin liner. The pressure of the gas inside the liner at the burial site was not measured, but after venting the liner the internal pressure was monitored for two weeks and no change was observed. The contents of the liner were solidified with vinyl ester-styrene using a Dow Co. in-situ process prior to burial.

The FNPP resin sample for isotopic analysis consisted of approximately 20 mL of waste in a ≈100 mL plastic bottle. A sample of the gas analyzed by gas chromatography (GC) was primarily nitrogen (≈99%) with little oxygen (<1%) or hydrogen (<0.1%). The amount of methane in the gas was believed to be <0.5% based on analysis using a Draeger indicator tube. Carbon dioxide in the gas was analyzed using a Draeger indicator tube, and the concentration was concluded to be greater than 6% of the gas composition. (The discrepancy of 99% N_2 and 6% CO_2 results from applying separate tests to identify the gases present. The GC analysis reflects the composition of detectable gases, and the GC analyzer may not have been capable of measuring CO_2. See discussion at end of Section 5.2.) An aliquot of the gas was diluted with air and then sparked with no subsequent reaction, thus, it was concluded that the gas mixture was not explosive. The large amount of carbon dioxide was believed indicative of biological growth in the waste.

FNPP personnel collected samples of material remaining in the waste sludge tank on September 30, 1984 for additional testing. One sample was dewatered, kept in a sealed plastic container and observed for pressurization due to gas buildup. It was concluded that after about one week there was no gas generation. No gas analysis was made on the contents of the bottle. Other sludge samples collected were used in a solidification Process Control Program. It was concluded that gas generation would not be a problem if this waste were solidified in cement. All the material in the Waste Sludge Tank was transferred to the Concentrated Waste Tank and was to be solidified in cement prior to disposal.

6.2 Analysis of FNPP Waste Sample

BNL received the waste sample collected for isotopic analysis from FNPP on February 25, 1985. The sample was a volume of approximately 20 mL in a 100 mL plastic bottle. The dose rate on contact measured 450 mrem/h. The material looked like a black sludge; however, it was pointed out by FNPP personnel that the physical appearance of the sample had changed since the sample was collected. Initially, the sample looked like powdered resins. The sample taken by FNPP from the sludge tank (on September 30, 1984) was not available for analysis at BNL.

6.2.1 Gas Analysis

A sample of gas from the plastic bottle containing the resin waste sample was obtained by puncturing it with a syringe needle, and an aliquot (≈0.5 cc) of gas withdrawn. A Perkin Elmer Model 3920 Gas Chromatograph was used with a Carbosieve S-II (Supelco Co.) Column for measurement of permanent gases. The analysis was performed three times, and the percents by volume of H_2, O_2, N_2, CO, CH_4, and CO_2 were determined by comparison with the analysis of standard gas mixtures. The composition of the gas sample is given in Table 6.2 together with data supplied by FNPP.

Table 6.2

Composition of Gas in
FNPP Resin Sample Bottle
(% by Volume)

Gas	BNL Analysis	FNPP Analysis
O_2	2.9 ± 0.1	<1
N_2	86. ± 1	99
CH_4	0.54 ± 0.03	<0.5
CO_2	8.2 ± 0.1	>6

The results of the BNL analysis and that of FNPP are similar. They indicated a depletion of oxygen and an increase in the amount of CO_2 present relative to the expected gaseous composition of air. Also present was a small quantity of methane. The BNL analysis showed no detectable hydrogen (<0.1%),as reported also by FNPP.

Work by BNL has indicated that H_2, as well as CO_2 and CO, are generated on irradiation of organic ion-exchange resins (MacKenzie et al.; Swyler et al.). If the pressurization of the FNPP resin container was due to radiolysis of the resins, H_2 gas would be expected to be present. Since H_2 was not detectable, it is unlikely that the pressurization was due to gas generation by radiolysis.

Since the gas analyses indicate relatively large amounts of CO_2 it is likely that gas generation resulted from microbial action in the sample. The small amount of methane may also have been a product of biodegradation.

6.2.2 Measurements of Carbon Dioxide Generation

The production of carbon dioxide by bacteria in the waste sample was measured by a modified procedure of Bartha and Pramer. Details of the method used here are given elsewhere (Bowerman et al.). A temporal measure of CO_2 generation was obtained from which a rate was estimated.

The waste sample (≈18 g) was divided into four aliquots (5.17 g, 3.82 g, 4.72 g, 4.07 g) each in a 10 mL beaker. After some preliminary testing it was concluded that a sufficient amount of CO_2 was produced by each sample that four individual tests could be performed and the results averaged. Each beaker was placed in a 250 mL biometer and the CO_2 production was measured periodically for the four replicate samples. A control sample consisting of an empty 10 ml beaker in the biometer was monitored for CO_2 throughout the experiment. The samples were cultured in an incubator kept at 28 to 30°C for the duration of the experiment. The average amount of carbon dioxide generated by the samples is listed in Table 6.3 and the cumulative gas generation is plotted in Figure 6.1

Table 6.3

Incremental Carbon Dioxide Production
from FNPP Waste Sample

Day	mg CO_2 per gram resin
3	1.12 ± 0.06
7	1.57 ± 0.08
10	0.95 ± 0.06
16	1.9 ± 0.1
23	1.45 ± 0.07
30	1.2 ± 0.1
37	1.7 ± 0.3
44	1.6 ± 0.5
51	2.0 ± 0.6

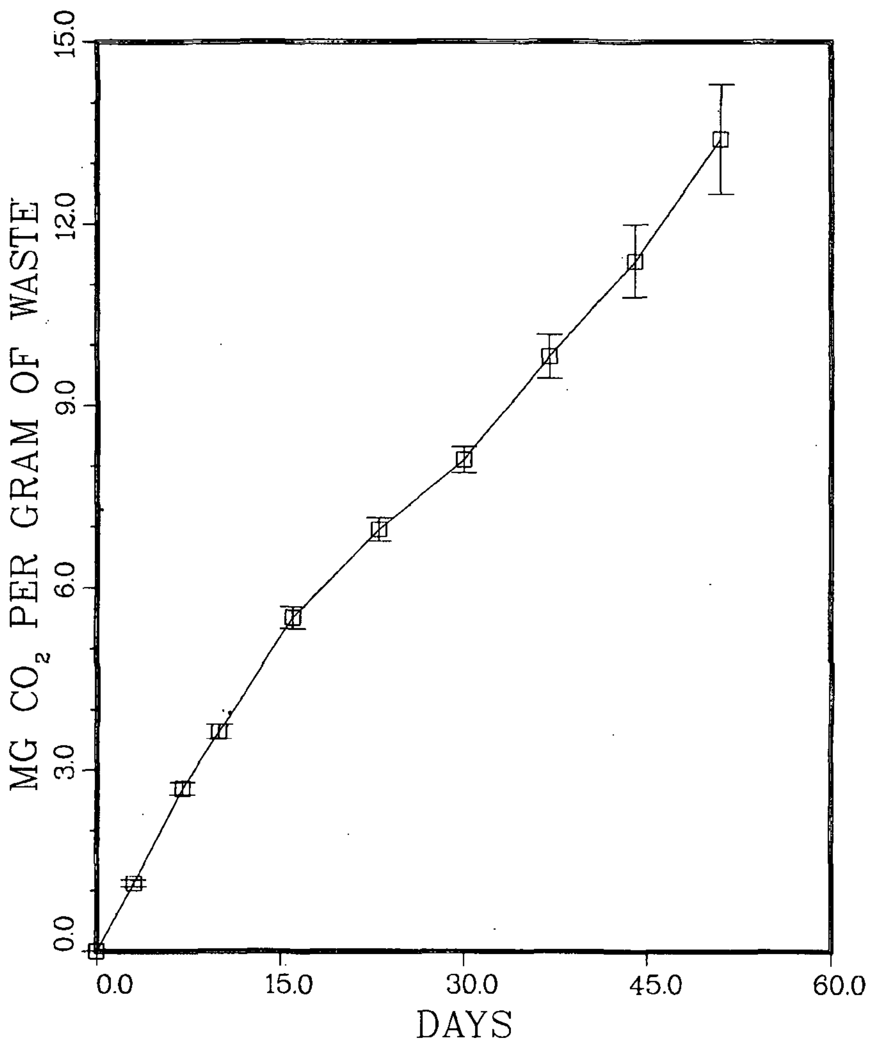

Figure 6.1 Cumulative production of CO_2 from FNPP resin samples.

Carbon dioxide produced by the waste sample indicates that active viable microorganisms are present. A rate of CO_2 gas generation from the resins was estimated based on a linear least squares fit of the data. Listed in Table 6.4 are rates of CO_2 production calculated using different portions of the cumulative gas generation data. The rate was greatest during the first 16 days of the experiments and decreased to about two-thirds the initial rate during the last 5 weeks of testing.

Table 6.4

Rate of CO_2 Generation

Days 3 to 16	0.33+0.01 $mgCO_2/(g$ resin-day)
Days 3 to 51	0.24+0.01 $mgCO_2/(g$ resin-day)
Days 16 to 51	0.22+0.01 $mgCO_2/(g$ resin-day)

There is little data in the open literature regarding biodegradation associated with organic ion-exchange resins used in nuclear reactor systems. Francis measured carbon dioxide production from spent reactor resins due to microbial activity (Francis, 1981). The resin waste consisted of mixed bed bead resins from the reactor at Brookhaven National Laboratory. Resin samples were examined and two types of bacteria were isolated. Growth of the microorganisms was monitored by measuring CO_2 production periodically. In these experiments a mineral salts medium was mixed with the resins and CO_2 was measured. Other samples had a secondary source of carbon (glucose) added before measuring CO_2 production. Results of these tests indicated a greater production of CO_2 than that measured with the FNPP sample. Approximately 490 mg CO_2 per gram resin was produced in a 10 day test compared with 13 mg CO_2 per gram of resin measured in ≈50 days with the FNPP samples. The mineral salts medium provides a more favorable environment for microbial growth and thus may account for the larger gas production.

6.2.3 Pressurization of the High Integrity Container

Based on the results of the CO_2 production measurements and assuming an ideal gas behavior, an internal pressure resulting from biological activity can be estimated for a sealed HIC. Although it is not certain that the CO_2 production rate measured in this study would be the same as that in the resin liner, the rate can be used to provide some indication of the possible pressure that could build up in the HIC.

It was assumed that the gas generation rate was a first-order kinetic process and that the gas (CO_2) production could be calculated as follows:

$$n = CStg$$

where

n = moles of CO_2 produced
C = a conversion factor (2.3×10^{-5} moles CO_2/mg CO_2)
S = rate of CO_2 production (mg CO_2/g resin-day; values in Table 6.4)
t = time (days)
g = total weight of resin in liner (grams).

Substituting C and considering that the liner contained 3700 lbs (1.68×10^6 g) of resin waste, the rate equation becomes:

$$n = 38.6\ St.$$

According to the ideal gas law the internal pressure (psi) can be calculated as follows:

$$P = nRT/V$$

where n is the number of moles of carbon dioxide, T is the absolute temperature (°K), V is the void volume in ft^3 and the gas constant $R = 0.0426\ ft^3\text{-psi}/(°K\text{-mole})$. Combining the two equations gives

$$P = 38.6\ StRT/V$$

The void volume for the L6-80 HIC is estimated to be 15 ft^3. This value is based on an internal volume for the HIC* of 72 ft^3 minus the 60 ft^3 of resins and assuming a 5% settling of the resins. The temperature of the resins may have ranged between ≈50°F to as high as ≈90°F. These values are based on average high and low temperatures during the period of the incident obtained from the weather stations at Oswego (east), NY near FNPP and Aiken, SC near Barnwell, SC. A mid point temperature of 75°F (24°C) is assumed for the present calculation. The time for gas build up due to biodegradation is assumed to start when the container was sealed (September 20, 1984) and can be as long as four days. This would be until the container was discovered pressurized on September 24, 1984. It is possible that gas generation from aerobic microbial action may have stopped at some time during that 4 day period due to the consumption of oxygen in the liner. Recall that after venting the liner there was no pressure build-up observed during the following two weeks. This may have been because there was no oxygen to sustain growth. For the purpose of this calculation the period of gas generation was assumed to be 2 days (t = 2). Based on these assumptions and considering both the slowest and fastest rates given in Table 6.4, the calculated pressure in the HIC would range between 14 and 21 psi. Considering that the oxygen in the liner was consumed results in a pressure drop of ≈3 psi. Thus, the calculated pressures would be lowered accordingly; ≈11 psi to ≈18 psi. This analysis indicates that biodegradation may have indeed pressurized the HIC containing waste from FNPP. The exact pressure would of course depend on the values of the various parameters (i.e., temperature, void volume, gas generation rate and the period of biodegradation) during the period of the incident.

The observed effect of the liner pressurization was the raising of the cask lid when the shipment was being prepared for unloading at the burial site. The L6-80 HIC was shipped in a CNSI 6-80-2 cask. The total weight of the primary and secondary lid of the cask is 8300 lbs. Although the HIC has a

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*Conversation between Mr. Les Poppe (CNSI) and P. Piciulo (BNL), June 4, 1985.

domed top it is packaged with a hard plastic collar such that the container with the collar fill the cask. Since the diameter of the HIC and collar was ≈58 in. having a surface area of ≈2650 in.^{2}, the force of the lid on the top of the cask was ≈3 psi. If a point of the lid rested on the cask thus acting like a fulcrum, there would have been a somewhat smaller force. In order for the HIC to raise the lid of the cask its dimensions would have to distort when pressurized. It is likely that the large flat bottom of the HIC would bulge when the container becomes pressurized. This would move the top of the container up like a piston which in turn could raise the top of the cask. A description of how the HIC distorts under internal pressurization was not available. However, the pressures calculated in this analysis are clearly greater than the three psi needed to raise the lid of the cask and may be sufficient to distort the HIC.

6.3 Summary and Conclusions

The major points concluded from the analysis of the incident involving the Fitzpatrick Nuclear Power Plant resin liner are:

- Carbon dioxide observed in the gas sample and the continued production of CO_2 from the waste sample indicate the presence of viable microorganisms.
- Possible sources of active microbes include floor drain wastes, 3 to 4 year old material from the waste surge tank and lake water used to clean the waste surge tank.
- Based on the rates of CO_2 production it is believed that biodegradation caused the pressurization of the HIC.

7. CONCLUSIONS

7.1 Comparison of Resin Liner Incidents

The three incidents involving dewatered resin and filter media wastes raise several generic concerns regarding the processing, storage and disposal of such wastes. These concerns become apparent after considering the similarities and differences among the three incidents.

Two of the incidents (MNS and FNPP) were detected at the disposal site and involved a pressure build-up in a sealed HIC. The first to occur (ANO) was detected on-site, after the wastes had been dewatered for an extended period of time, i.e. twice as long as normal. The wastes involved in the pressurization incidents were dewatered normally.

All three incidents involved synthetic organic materials which were dewatered for disposal in high density polyethylene HICs. In the exothermic incidents the organic materials consisted of gel-type and macroreticular ion-exchange resin beads. In the pressurization incidents the organic materials were filter media, i.e. a mixture of powdered ion-exchange resins and cellulosics.

In two of the incidents (FNPP and ANO) biological activity was the cause or was a significant contributing factor. In these two incidents at least some of the wastes involved had apparently been stored in holding tanks for several years. In the MNS incident, the pressure buildup in the HIC was attributed to contamination with a volatile chemical, Freon-113. However, the analysis of the gas from the liner showed levels of CO_2 and CH_4 higher than expected for air, which could have been the result of biological activity.

From the above comparison, Table 7.1 was compiled. The apparent cause of each incident is different; however, these were not determined unequivocably, and the evidence in each case points to the stated cause.

The relevant conclusions can be summarized as follows:

- all three incidents involved wastes which had been dewatered,
- there was some evidence in all three cases that biological activity was present,
- the age of the wastes in two of the incidents was uncertain.

These points and recommendations concerning them are discussed in more detail in the next section.

Table 7.1

Comparison of Resin Liner Incidents

	ANO[a]	MNS[a]	FNPP[a]
Incident Type	exothermic reaction	pressure build-up	pressure build-up
Where Detected	at plant	at disposal site	at disposal site
Wastes Involved	ion-exchange resin beads	filter media (powdered resins and cellulosics)	filter media (powdered resins and cellulosics)
Apparent Cause	autoxidation	chemical contamination	biological activity
Dewatering Characteristics	longer than normal time	normal	normal
Age of Wastes Involved	uncertain, some as much as 3-4 years	≈6 months	uncertain, some as much as 3-4 years
Evidence of Biological Activity	odor during dewatering, microscopic examination	gas analysis (CO_2, CH_4)	gas analysis (CO_2)

[a] ANO = Arkansas Nuclear One; MNS = Millstone Nuclear Station; FNPP = Fitzpatrick Nuclear Power Plant.

7.2 Technical Considerations and Recommendations

The comparison of the liner incidents leads to the consideration of what factors could cause similar incidents to occur in the future and what steps can be taken to prevent them from occurring. These factors or concerns can be separated into the following categories: dewatering, waste characteristics, and storage/disposal.

7.2.1 Dewatering

The practice of dewatering ion-exchange resin wastes and filter media wastes prior to disposal is apparently a common one. The significance of these three incidents involving dewatered wastes may be small in terms of the total amount of wastes processed for disposal in this manner.

The incident at ANO is most applicable in voicing concerns regarding dewatering. These were discussed earlier (Section 4.6.3) and can be summarized as follows:

1) Dewatering can be conducted without incident in almost all cases. Nuclear power plants and vendors of dewatering services have established a performance baseline for this process.

2) Abnormalities observed in the wastes to be dewatered or observed during the process should be considered as indicators of a problem.

3) If abnormalities are observed, dewatering should be closely monitored or, more conservatively, stopped and the cause of the abnormality identified.

7.2.2 Waste Characteristics

The investigations of the three liner incidents identified several concerns regarding waste characteristics which may be applicable to other situations. These include the presence and significance of biological activity in the wastes, the potential for chemical contamination, and the sources and identities of wastes present in holding tanks.

The presence of biological activity was identified as a cause of pressurization in the FNPP incident, and as a significant contributing factor in the ANO incident. The extent to which biological activity occurs in ion-exchange resins and filter media under conditions of normal use and disposal is unknown. In addition it is not known what the effects of biological activity are in terms of resin degradation. Such effects might include loss of exchange capacity with release of sorbed ions or radionuclides, and release of the more tightly bound water in resin beads. Two effects which appear to be significant are agglomeration or clumping in bead resins, and gas generation. The impacts of these effects on storage and disposal are discussed in more detail below.

It can only be stated at present that biological activity can occur in both resin beads and powdered resins. Whether this is significant while these materials are in service, while they are accumulated or stored in holding tanks, or when they are dewatered in containers for disposal is not clear. As evidenced by the ANO and FNPP incidents, it appears that longer storage times in holding tanks contributes to the extent of biological activity.

The concern regarding the potential for chemical contamination results from the apparent cause for the MNS pressurization incident. In this incident it was concluded that a dry cleaning solvent, Freon-113, had been dumped down a drain and ended up in the filter media waste. The pressurization presumably was a consequence of the fact that Freon-113, although fairly inert, has a high vapor pressure at room temperature.

This incident and some of the information obtained as a result of the ANO incident indicate that the use and handling of chemicals at nuclear power plants may not always be monitored closely. Spills may in some cases not be logged. More importantly, the amounts and identities of chemicals used in restricted access areas may not be known. This may not necessarily be a problem provided the chemicals are disposed of properly. The control of chemical use can be particularly difficult when workers for outside contractors, who may not be familiar with plant practices in the handling of chemicals, are working in-plant.

The impacts of improper chemical disposal are twofold. First, the behavior and stability of resins or filter media which process drain and sump liquids may be suspect, as evidenced by the MNS incident. Second, the presence of certain chemicals, especially solvents, may raise the question as to whether wastes contaminated with these chemicals should be regarded as mixed wastes.

The last topic of concern regards the identities of wastes accumulated and stored in holding tanks. This is a significant concern when incidents such as those reported here occur. Trying to determine the characteristics of wastes which have exhibited abnormal behavior would be simplified if records were kept as to the identities and quantities of wastes stored in holding tanks, how long they were stored, and when they were removed for disposal. Records of this sort could also be useful in identifying means of minimizing waste generation.

The limitation of keeping records of wastes stored in holding tanks rests in the fact that the tanks may not be completely emptied when wastes are transferred to containers for disposal. However, considering the potential consequences of wastes remaining in holding tanks for long periods of time, e.g., three to four years, the complete removal of wastes from tanks during each transfer operation may be an operating practice worth achieving.

Two approaches are available in formulating recommendations based on the considerations presented above. The first involves testing of wastes, the second consists of administrative practices.

Chemical testing of resins or filter media waste from holding tanks prior to processing for disposal could provide a better characterization of the waste and help to detect potential problems in waste processing.

Identifying which chemical characteristics are most relevant to preventing exothermic behavior or gas generation may require further research. In addition, the chemical properties of waste resins in holding tanks can be expected to show some variability dependent on the application the resins were used for, the age of the resins, and perhaps other factors. Hence, some information about the range of variability which can be expected is required as well. Chemical tests of the resin waste directly would be most desirable, but could be inconvenient and expensive. Chemical tests of the liquids associated with the resins may not provide a completely accurate measure of the species absorbed on the resins, but in general are easier for routine monitoring purposes.

Two water properties appear to be most relevant with respect to monitoring the possibility of contamination which could affect resin behavior: Eh, a measure of the oxidizing potential of a solution, and total organic carbon (TOC). Other measurements which can provide additional information for the purposes of determining baseline waste characteristics are pH, conductivity, total suspended solids (TSS), and chemical oxygen demand (COD).

Eh could be useful for determining whether strong oxidizing or reducing agents are present in the wastes. TOC would be a useful indicator of contamination by organic solvents and could also serve as an indicator of the presence of biological activity. It is worth repeating that these tests of the liquids associated with resin or filter media wastes may not provide an absolute or accurate measure of the amounts of reactive chemical species or microbial activity present in the wastes. Hence, the recommendation is given that the adequacy of these tests for establishing a baseline of waste characteristics should be evaluated. This evaluation would ideally include data from power plants using these methods.

The second recommendation consists of two levels of administrative procedures. Practices in the use and handling control and disposal of chemical agents and solvents should be reviewed for adequacy. Controls, if not already in place, should be instituted so that inadvertent or improper disposal of chemicals is minimized. The latter is particularly important with regard to non-plant personnel or employees of outside contractors who bring in chemicals for non-routine projects. Records or inventories of chemicals brought in, used or disposed of in restricted access areas would be one means of maintaining control.

Specifically with regard to waste management, it is recommended that storage of resins or filter media wastes in holding tanks be limited to one year in order to minimize the potential for biological activity in the wastes. This time limit is an arbitrary one, but it is believed to be conservative and should reduce the possibility of the wastes caking or clumping. If this time limit presents difficulties and longer storage times are needed, then the wastes should be monitored during transfer, processing and disposal operations. Monitoring should consist of obtaining a number of samples of the waste, and observations for evidence of agglomeration or biological activity. If the wastes are to be dewatered, the temperature should be measured during the process. The samples will only be required for further analysis if problems arise prior to final disposal.

7.2.3 Storage and Disposal

Two of three incidents (MNS and FNPP) raise concerns with respect to the storage and disposal of dewatered ion-exchange resin and filter media wastes. These concerns are associated with the presence and potential consequences of biological activity in these wastes. The consequences of biological activity can be separated into short-term and long-term effects.

One short-term effect which is now apparent is pressurization in sealed containers. The approach used at MNS, i.e. on-site storage of waste containers before shipment for three to five days, is a reasonable one for the detection of a pressure build-up. Therefore, this practice is recommended as a conservative approach to detecting future pressurization incidents before shipment to a disposal site.

The long-term effects of biological activity in resin and filter media wastes cannot be stated with certainty. However, the effects potentially include gas generation with subsequent pressure build-up in sealed containers, degradation of the wastes with subsequent release of liquids and/or radioactivity from the wastes within the containers, and corrosion or degradation of container materials. Because so little is known about the long-term consequences of biological activity in these wastes, it is recommended that studies be initiated to identify what the effects are. Specifically, it is recommended that the following be investigated:

- the factors which influence and encourage microorganism growth in ion-exchange resins and filter-media wastes,
- the by-products of microbial activity in resins and filter media wastes and changes in the characteristics of the wastes as a result of this activity,
- the effects on the wastes of using biocides or chemical agents to prevent microbial growth,
- the extent to which pressurization can occur in sealed containers,
- the consequences of using vented containers or containers with pressure relief mechanisms, e.g. identities and amounts of gases released,
- the potential for microbial growth and its by-products to degrade or corrode container materials.

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APPENDIX A

RECORD OF EVENTS DURING THE EXOTHERMIC INCIDENT

This record of events has been edited with comments and details based on discussions between ANO and BNL personnel.

<u>January 15, 1983</u>

0030 - Secured dewatering pump after 6th cycle of dewatering. There was approximately 16 ounces of water collected in the barrel. No abnormal indications were noticed.

0800 - Smoke/steam observed drifting out from under herculite tarp that was placed over cask and liner to provide protection from inclement weather. Vapor was very odorous and sharp (heavy chemical smell).

Ambient temperature at 8:00 AM was ≃30°F. The odorous vapor was described as being sharper and having a head-clearing effect stronger than ammonia (NH_3). The smoke/steam was colorless.

0805 - Notified Fire and Safety, Health Physics, Radiochemistry, Engineering and Technical Support, and Chem-Nuclear at Barnwell, SC.

0820 - Drew a portable air sample under edge of tarp. Results indicated $<1 \times 10^{-9}$ μCi/cc.

0835 - Sampled for toxic gases - results were negative.

The toxic gas sampling was carried out by ANO's Fire and Safety unit. A Gastec Model 400 sample pump and Gastec Analyzer Tubes (Bendix Corp.) were used to test for styrene, carbon monoxide (CO) and amines. A Biomarine Model 902A Combustible Gas/Oxygen monitor (Rexnord Safety Products) for detecting hydrocarbon-based combustible gases was also utililized.

0845 - Performed pH analysis on water collected during dewatering using litmus paper. Results were 3.5 to 4.0. Sent sample to Hot Lab for analysis on pH meter.

0900 - Chem-Nuclear recommended adding 50 gallons of 1/2 molar Sodium Hydroxide to the resin liner, then filling the liner with D.I. water.

0930 - Chemist mixing sodium hydroxide.

RECORD OF EVENTS DURING THE EXOTHERMIC INCIDENT

The sodium hydroxide was never added to the resin liner.

0941 - Drew a core sample of resin with a grain sampler, which caused the smoke/steam to increase. Chemist reported that the resin in the top of the liner had formed a crust.

The samples obtained were limited to a depth of 24 inches.

0955 - Measured temperature of resin in hole left from core sample. Temperature was 365°F (185°C). Measured temperature of the liner material. Temperature was 86°F (30°C).

The temperature was measured with a mercury thermometer. This was obtained along the center line of the HIC near the surface of the resins. No measurement of the temperature at other locations was attempted. The liner material temperature was obtained by contacting the thermometer to the side of the HIC.

1000 - Drew air sample at opening of liner. Results indicated 2 x 10^{-9} μCi/cc, 15% MPC.

The MPC was for a mixture of radionuclides, including Co-60, Y-91, Cs-134, and Cs-137.

1007 - Filled second liner in train bay with DI water as a precaution. This liner had resin in it from the same source and had completed its second day of dewatering. (Designated as Cask B).

1032 - Radiochemistry reported earlier pH sample had read 5.6 by pH meter.

1035 - Added 75 gallons of DI water to resin liner with original problem (designated as Cask A).

1037 - Set up continuous air monitor in general area of Cask A.

1045 - Drew a general area air sample, results were <1 x 10^{-9} μCi/cc.

The continuous air monitor was set up downwind of Cask A and indicated no radioactivity above background. By about 1030 the smoke/steam had stopped evolving.

1046 - Filled liner to hose connection plate in liner with DI water. Placed liner on recirc through sandpiper pump. Total water added

RECORD OF EVENTS DURING THE EXOTHERMIC INCIDENT

was approximately 150 gals. at 50°F. Measured temperature of recirc water. Read 80°F.

The temperature change of the recirculating water corresponds to ≈37,500 BTU's (9,450 kcal or 39,500 kjoules). When the water was added to the resin liner there was no bubbling, hissing or gurgling such as one would expect when adding cold water to a container in which the measured temperature 30-45 minutes earlier was well above the boiling point.

1135 - Established surveillance on Cask B, monitoring temperature of water in liner.

1300 - Moved Cask B from Train Bay to RWB, next to Cask A.

1430 - Began hourly monitoring of temperature and pH to continue until temperature stabilizes.

1900 - Temperatures stabilized, sampling pH and monitoring temperature every three hours.

The stabilized temperature was ≈80°F.

January 17, 1983

1600 - Received word from Dow Chemical that we may have the potential for a bomb if the resin has been exposed to nitrates and we then attempt to dewater the resin. Hot Lab says that it is likely that resin was exposed to nitrates. Requested a nitrate analysis of water in liner.

Saying that there was the potential for a bomb was probably an overstatement given the levels of nitrate which were eventually detected. No information is available concerning what minimum levels of nitrate or other oxidizing agents on resins could be dangerous during dewatering. Those events in which explosions or fires occurred (Section 2) involved resins with high levels of nitrate in concentrated nitric acid.

January 18, 1983

1300 - Installed thermocouples at bottom, middle and top of resin in Cask A, connected to chart recorder.

1315 - Recirculated water in liner until temperature equalized. Middle thermocouple reads 10°F higher than top and bottom due to inaccuracy of system.

APPENDIX A, Continued

RECORD OF EVENTS DURING THE EXOTHERMIC INCIDENT

1700 - Performed oxidation reactions analysis on water from both liners. Results indicate that oxidizing agents are present in Cask A and reducing agents are present in Cask B.

The oxidation reaction analysis was a general chemical test indicating only the presence of oxidizing and/or reducing agents.

<u>January 19, 1983</u>

0700 - Results of nitrate analysis indicated Cask A at 0.575 ppm and Cask B at 0.045 ppm. Notified Chem-Nuclear, they are notifying Dow.

0800 - Chem-Nuclear called, Dow says we could have a problem if we dewatered the resin, but they don't have a solution.

The references to Dow are in the Record of Events because Chem-Nuclear contacted Dow for their expertise on ion-exchange resins. During the meeting, reference was made to a statement by Dow that 50-100 ppm NO_3^- could be dangerous in the presence of ion-exchange resins during dewatering.

APPENDIX B

PHOTOMICROGRAPHS OF RESIN SAMPLES FROM ARKANSAS POWER AND LIGHT COMPANY
(Magnification x 23)

The following photomicrographs are of ion-exchange resin samples from ANO (magnificaion 23x). The locations from which these samples were taken are listed in Table B.1. In the photographs examples of the different kinds of beads present, i.e., macroporous (macroreticular) and gel-type, as well as damaged beads, i.e., cracked and charred beads, are highlighted according to the scheme shown in Table B.2. A more complete description is given in Section 4.3.1. In some cases, it is difficult to distinguish between translucent and opaque beads because of the quality of the copies.

Table B.1

Description of Resin Sampling Locations for Associated Photomicrographs

AI	Initial sample from Cask A on Jan. 8, 1983 (prior to exothermic reaction).	
AII	Resin samples form Cask A obtained during the exothermic reaction.	
	AII-1	Surface
	AII-2	≈8 in. below surface
	AII-3	≈16 in. below surface
	AII-4	≈24 in. below surface
	AII-5	Mixture of samples AII1, AII2, AII3, and AII4
AIII	Resin samples from Cask A taken on Feb. 8, 1983.	
	AIII-1	Surface
	AIII-2	≈8 in. below surface
	AIII-3	≈16 in. below surface
B	Samples taken from Cask B on Feb. 8, 1983.	
	B-1	Resin from Cask B
C	Unit I T13 resin sample taken on Feb. 8, 1983.	

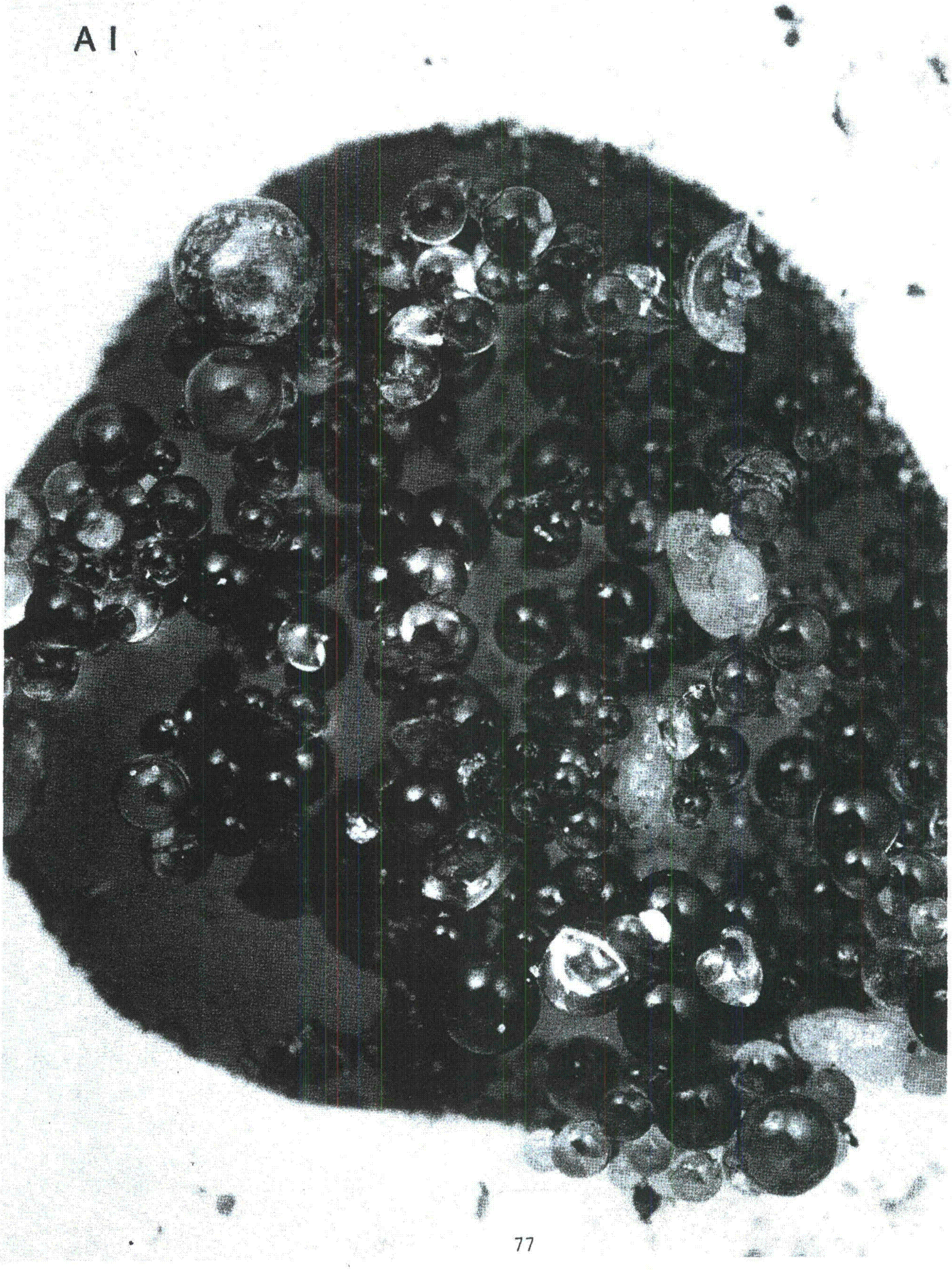
PHOTOMICROGRAPHS OF RESIN SAMPLES FROM ARKANSAS POWER AND LIGHT COMPANY
(Magnification x 23)

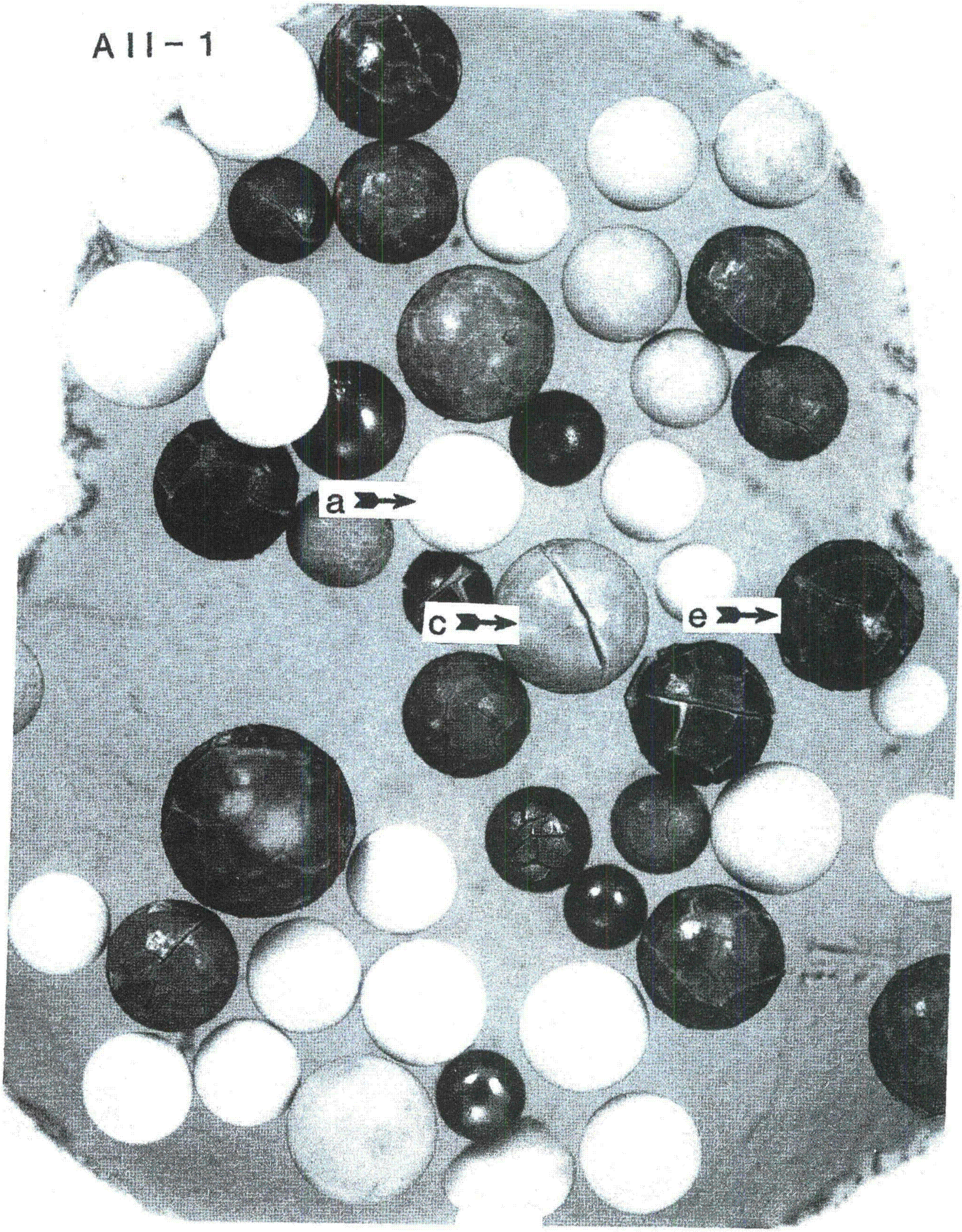
Table B.2

Designations for Highlighted Beads in Photographs

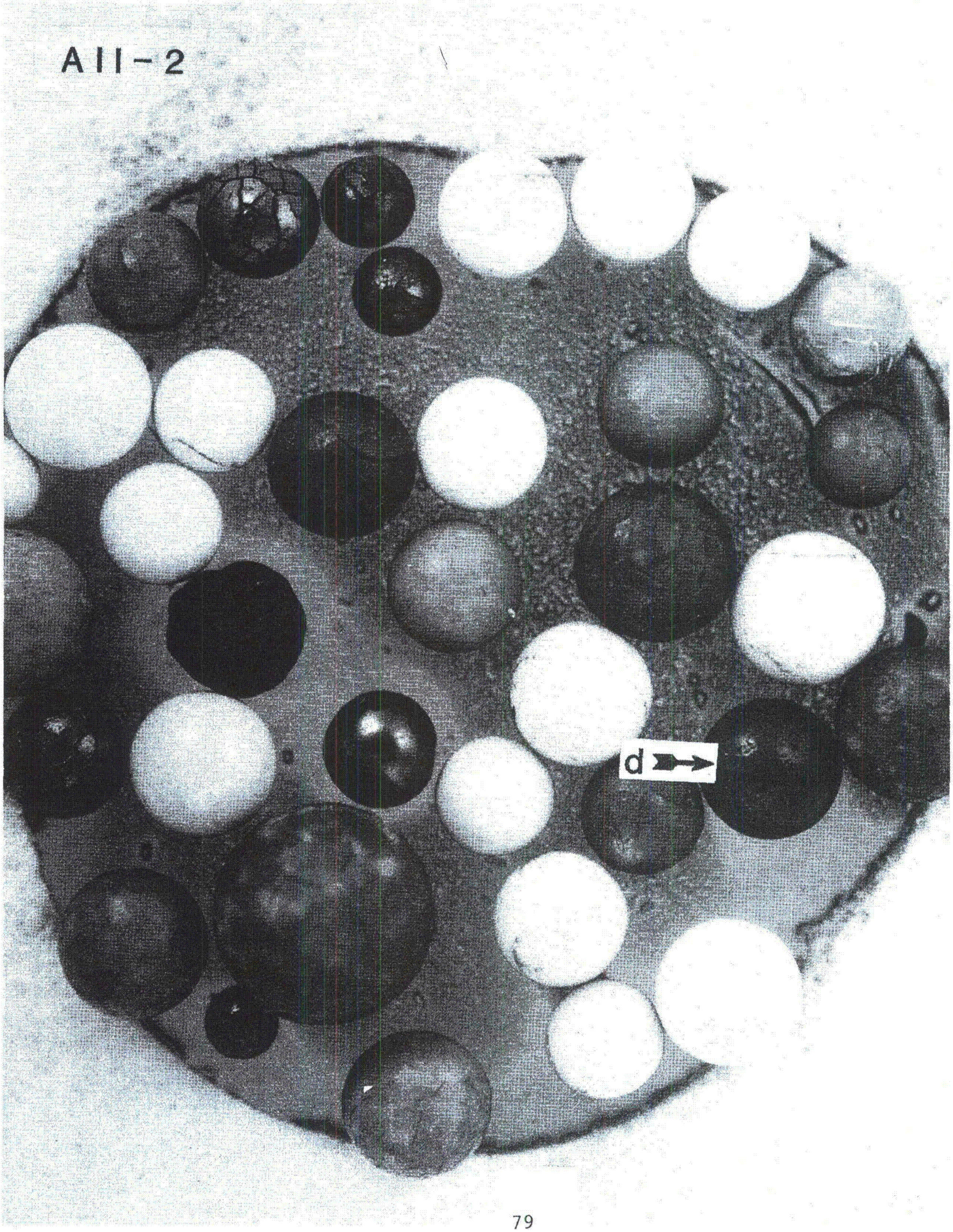
Label	Description	Sampling Location
a	undamaged macroporous (opaque) bead	AII-1
b	undamaged gel-type (translucent) bead	B-1,C
c	cracked macroporous bead	AII-1, AII-3
d	charred macroporous bead	AII-2, AII-3
e	cracked and charred macroporous beads	AII-1, AII-3

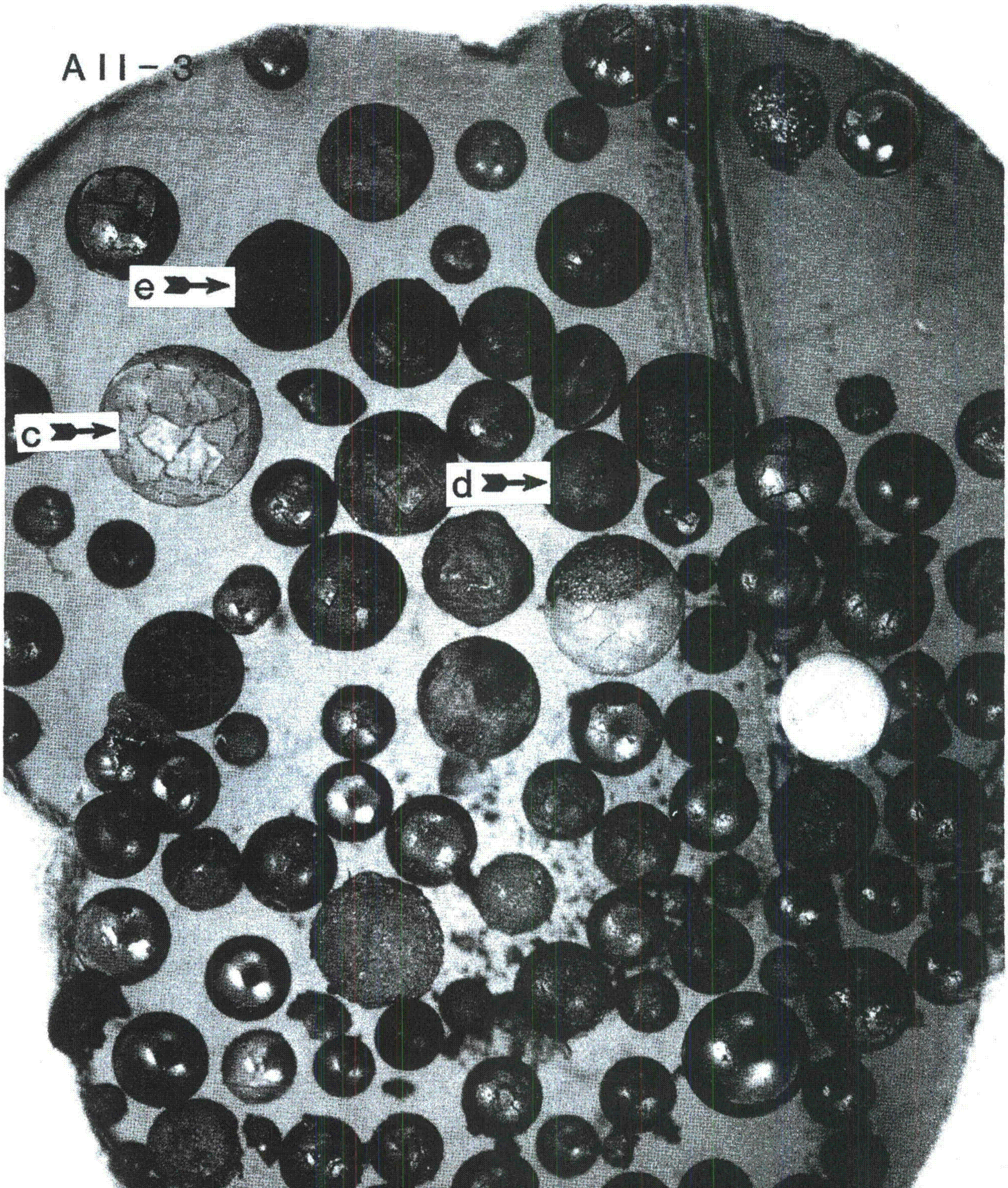
A1




AII-1
a
c
e

AII-2

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c
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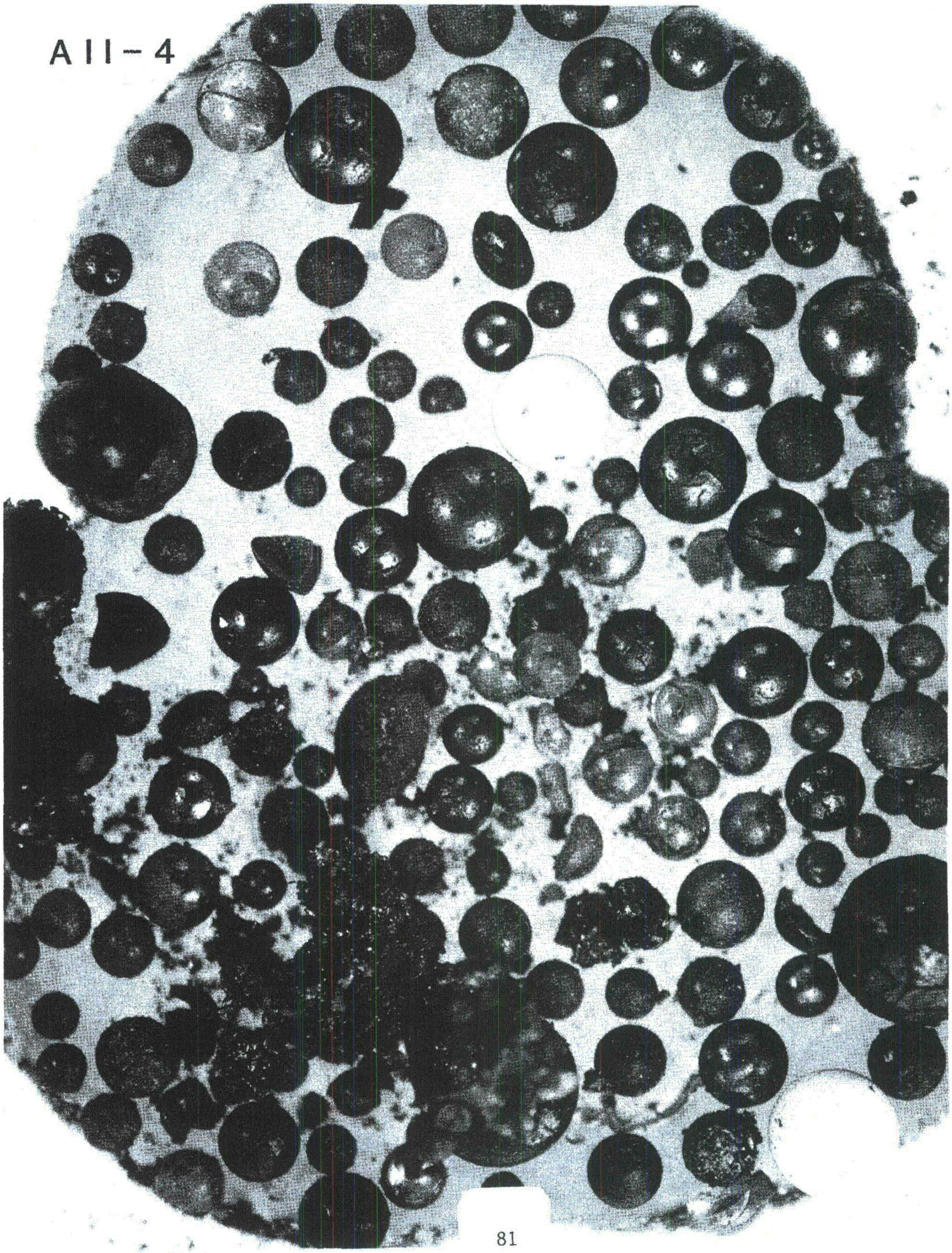

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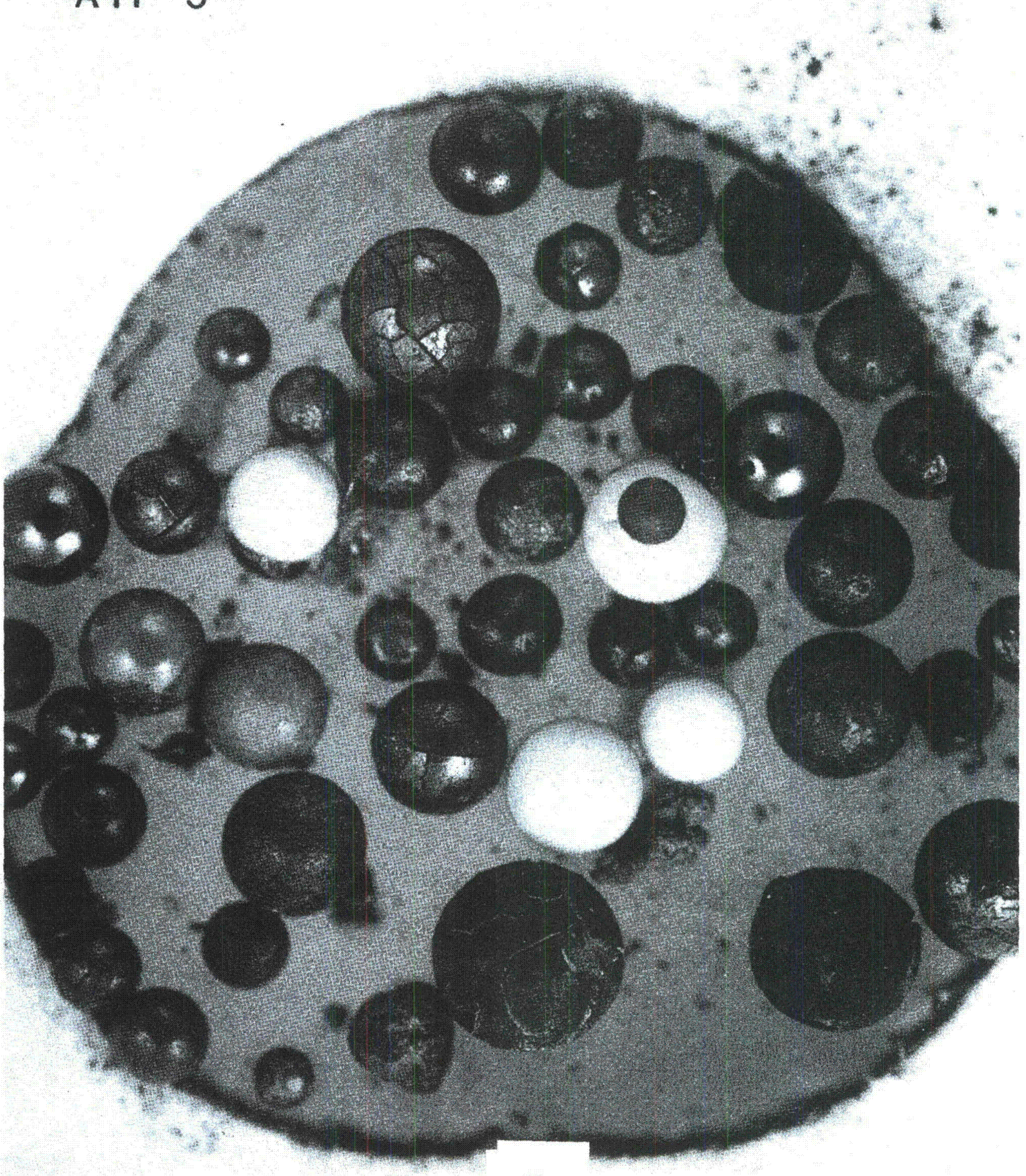

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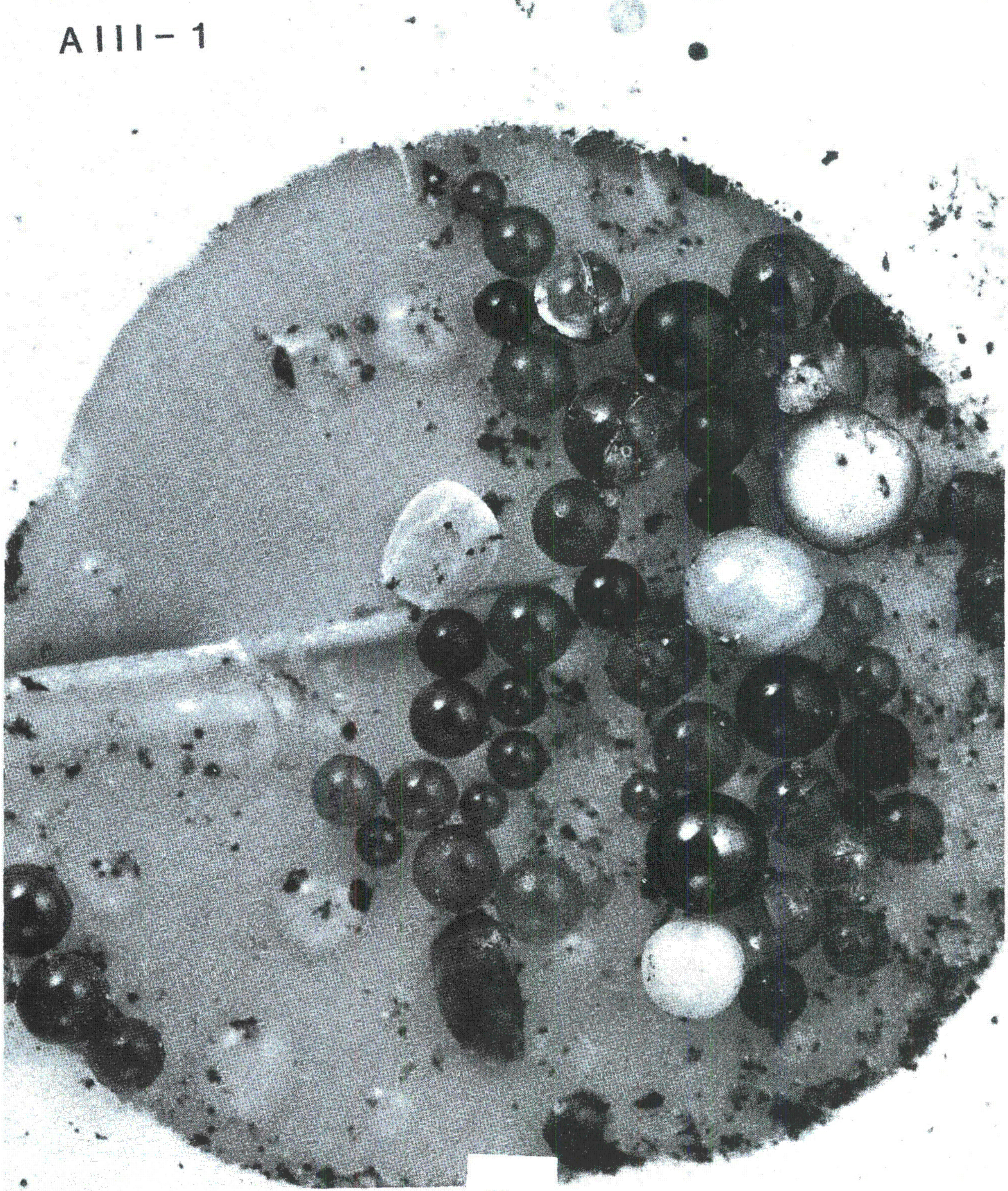

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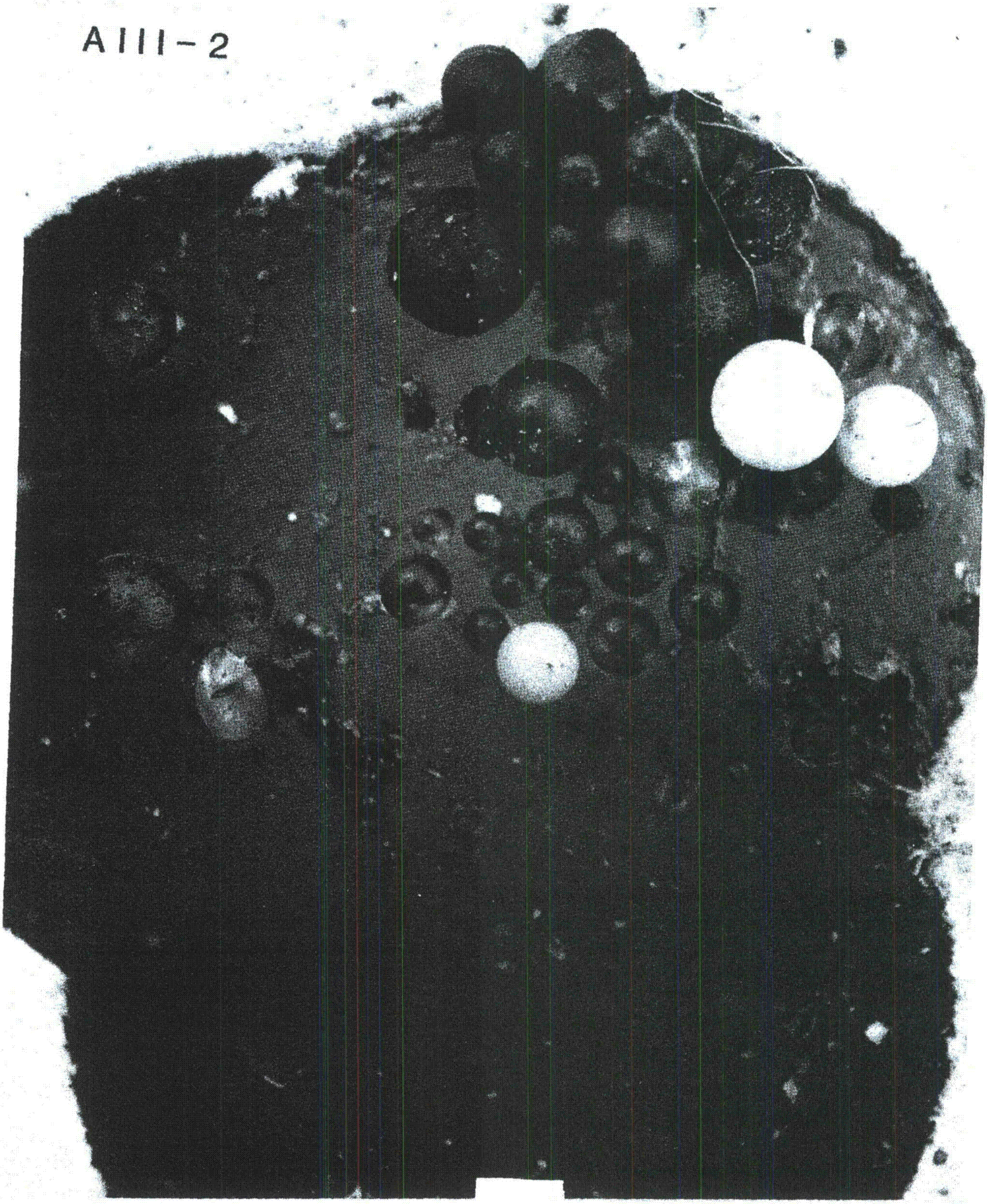

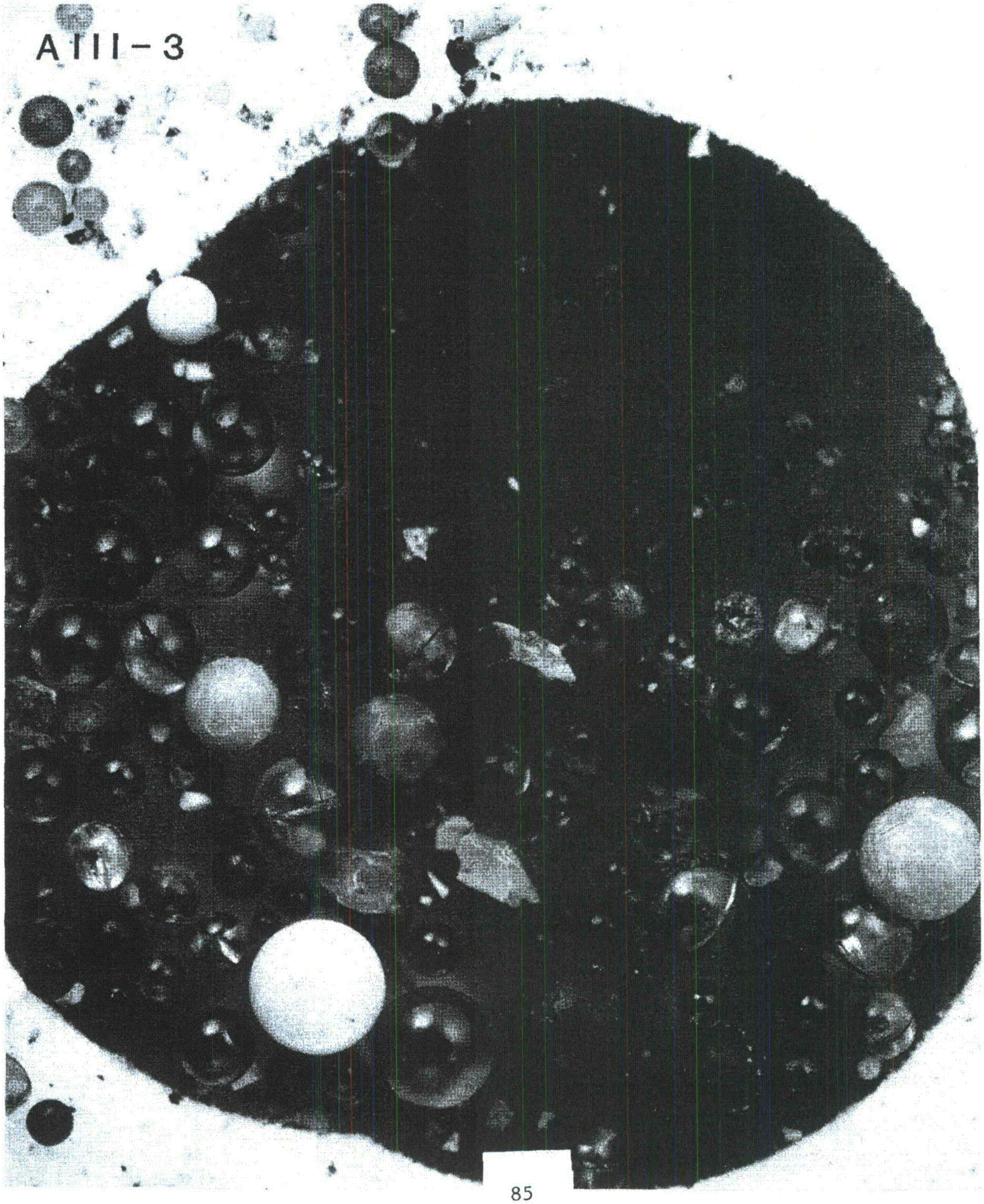

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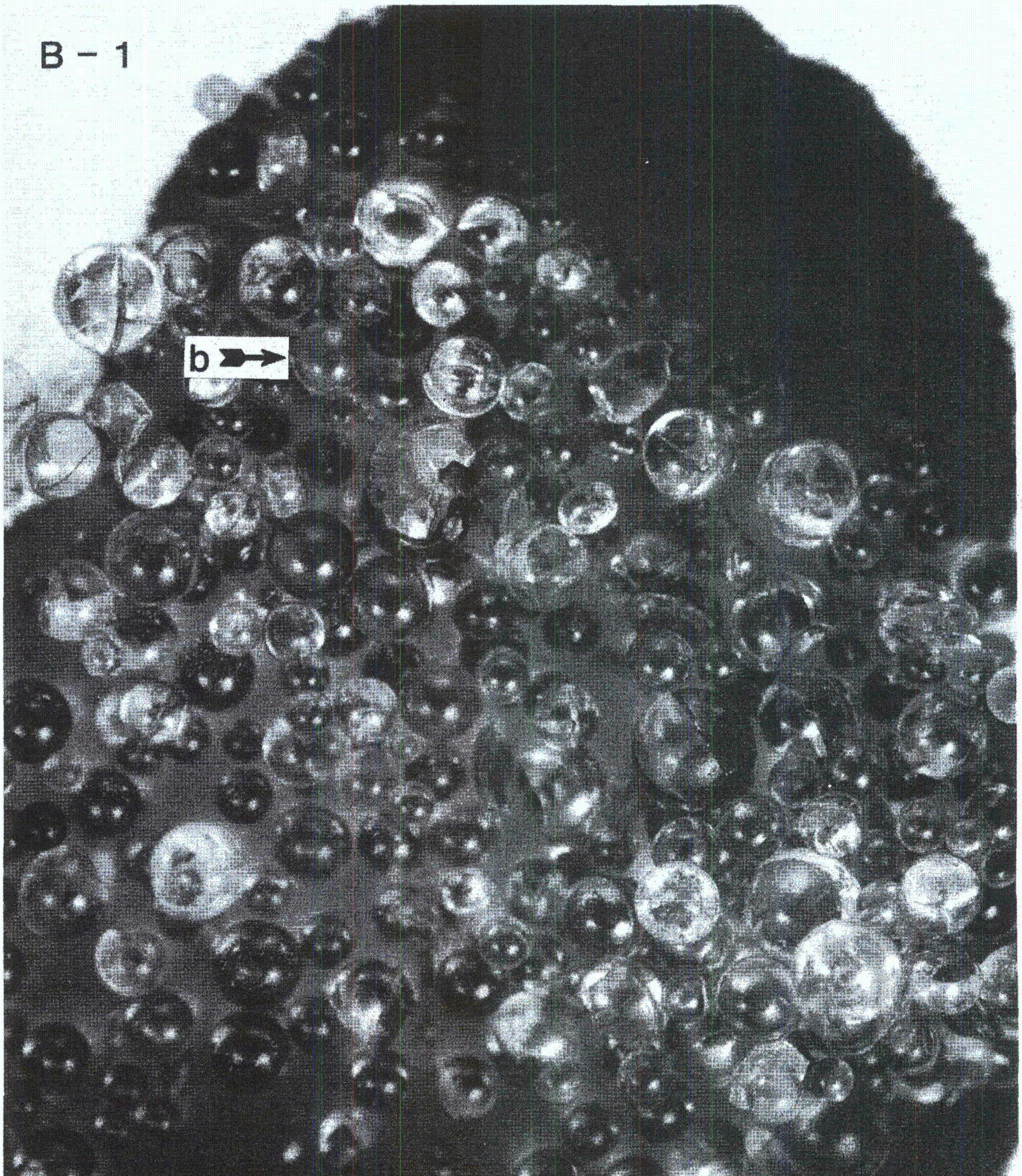
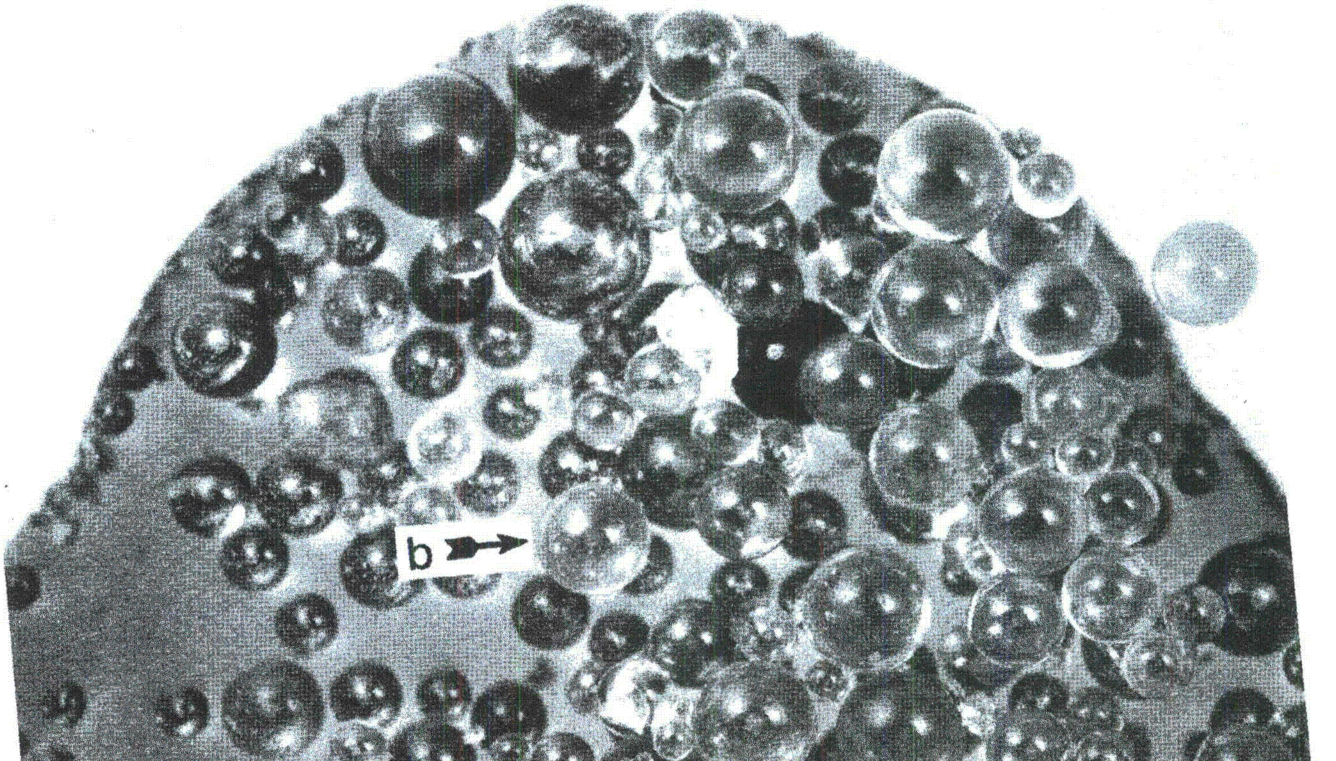


C(T13)



APPENDIX C

RADIOISOTOPE ANALYSIS OF MILLSTONE FILTER MEDIA WASTE

```
MILLSTONE  QUANTITATIVE  RADIOISOTOPIC
              RADWASTE  ANALYSIS
               23 SEP 1983  8:07:27

              DEWATERED  FILTER  MEDIA

SAMPLED BY   ____MP_________

                                         83-046-1

UNIT NUMBER................:          1
DEWATERED WEIGHT (GM/ML)...:      0.849
RADWASTE WEIGHT (LBS)......:  6.348E 03
SHIPMENT VOLUME (CU FT)....:  1.200E 02

* DENOTES CALC VALUE FOR NON-GAMMA EMITTING COMPONENTS
# DENOTES TOTAL ACT (UCI/CC) FOR ISOTOPES WITH HALF LIVES > 5 YR

 ISOTOPE      ACTIVITY      ACTIVITY      SPECIFIC ACT TRANS GROUP  LSA LIMI
              (UCI/CC)      (MCURIES)     (MC/GM)                   (MC/GM)

  MN-54       2.301E-01     7.821E 02     2.711E-04         IV      3.0E-01
  CO-58       2.480E-02     8.426E 01     2.921E-05         IV      3.0E-01
  CO-60       1.839E 00     6.250E 03     2.166E-03         III     3.0E-01
  I-131       1.026E-02     3.485E 01     1.208E-05         III     3.0E-01
  CS-134      3.564E-02     1.211E 02     4.197E-05         III     3.0E-01
  CS-137      4.286E-01     1.457E 03     5.048E-04         III     3.0E-01
* FE-55       1.307E-02     4.443E 01     1.540E-05         IV      3.0E-01
* NI-63       1.230E-03     4.180E 00     1.449E-06         IV      3.0E-01
* SR-89       4.003E-01     1.360E 03     4.715E-04         III     3.0E-0
* SR-90       4.800E-04     1.631E 00     5.654E-07         II      5.0E-0
* ALPHA       1.659E-05     5.637E-02     1.954E-08

  TOTALS.  : # 2.269E 00    1.014E 04     3.514E-03

 SPECIFIC ACTIVITY (UCI/CC) =
  ACTIVITY (MCI) * 1000 (UCI/CI) /  (2.83E4 (CC/FT3) * TOTAL VOLUME (FT3));

  LSA  SHIPMENT

  GREATER  THEN  TYPE  A  SHIPMENT
```

John L Etheridge
Rad. Mat'ls Hand Supv.

NRC FORM 335
(2-84)
NRCM 1102,
3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

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13. ABSTRACT *(200 words or less)*

Three incidents involving low-level waste (LLW) from separate nuclear power plants, i.e., dewatered ion-exchange resins or dewatered filter media, occurred during 1983 and 1984. This report summarizes and reviews the investigations into the causes of each incident. Factors unique to each incident are discussed and recommendations are given on the basis of these factors which may help limit such occurrences in the future.

14. DOCUMENT ANALYSIS – a. KEYWORDS/DESCRIPTORS
ion-exchange resins, filter media, waste processing, dewatering gas generation, exothermic reaction, biodegradation, high integrity container, low-level waste

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