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U.S. NUCLEAR
 REGULATORY COMMISSION

TMI Program Office
 Attn: Mr. L. H. Barrett, Deputy Program Director
 US Nuclear Regulatory Commission
 c/o Three Mile Island Nuclear Station
 Middletown, PA 17057-0191

Dear Sir:

Three Mile Island Nuclear Station, Unit 2 (TMI-2)
 Operating License No. DPR-73
 Docket No. 50-320
 Make Up and Purification Demineralizer Resin Sampling

The next step in GPUNC's Make Up and Purification Demineralizer Resin Characterization Program is resin sampling. This activity is currently scheduled to commence on February 28, 1983, in order to support the commitment made in GPUNC letter 4410-82-L-0052 dated November 18, 1982, from B. K. Kanga to L. H. Barrett, to complete resin analyses by the end of the first quarter of 1983. The purpose of this Program is to develop a technically sound removal and disposition program for the resins. To date the Program activities which have been accomplished include:

- determination of the demineralizers resin operating history,
- remote visual inspection of the cubicles,
- non-destructive assay of the fuel and radiological contents of the demineralizers,
- laboratory scale simulation of resin conditions,
- sampling and purging tank atmosphere,
- analyzing tank gas samples, and
- modifications to support installation of resin sampling equipment

The attached Safety Evaluation for the resin sampling evolution shows that based, in part, on the gas analysis, the hydrogen generation rates are not sufficient to generate explosive hydrogen levels even if allowed to collect for 30 days, and there is insufficient fuel content in the resins to pose a criticality concern.

The resin sampling evolution will be accomplished utilizing

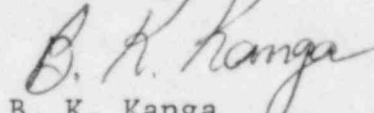
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procedures approved pursuant to Technical Specification 6.8.1 and appropriate radiological procedures and Radiation Work Permits.

If you have any questions, please feel free to contact Mr. J. J. Byrne of my staff.

Sincerely,



B. K. Kanga
Director, TMI-2

BKK/KJH-SDC/jep

Attachment

CC: Dr. B. J. Snyder, Program Director - TMI Program Office

Safety Evaluation for
Sampling Resins in Make Up and Purification Demineralizers

Purpose

The purpose of this evolution is to obtain resin samples from Make Up and Purification Demineralizers MU-K-1A and MU-K-1B as discussed below. Resin samples are required to characterize the present resin conditions for the development of a technically sound resin disposal program. Under the sponsorship of the US Department of Energy, scientists at the Oak Ridge National Laboratory are being asked to characterize the resin sample by analyses and by subjecting the resins to an elution and sluicibility testing program.

Sampling will be accomplished through the resin fill line penetrating the top of each tank. A section of the resin fill line will be removed as it enters the Hays Gas Analyzer Room. A flange and a 3" ball valve are being installed on the resin fill lines. Sample retrieval will be performed by passing the sampling probe through the new ball valve and down through the resin fill line isolation diaphragm valve (MU-V111A(B)), then into the tank and resin bed. Provisions have been made to assist the diaphragm valve open, if required. The sample is then withdrawn into a sample receiver and remotely transferred to a sample bottle located inside a shielded container. Optical fiberoptic examinations of the diaphragm valve and the resin bed are available to assist in sampling

A. Fuel Analyses

Three independent measurements of the fuel content in the Make Up and Purification Demineralizers were performed by scientists from Westinghouse-Hanford Engineering Development Laboratory (WHEDL) and Los Alamos Scientific Laboratory (LASL) using non-destructive assay (NDA) techniques. Two different NDA techniques were employed by the WHEDL group: 1. gamma ray spectrometry using a shielded Si(Li) Compton recoil gamma ray spectrometer; and, 2. neutron dosimetry using Solid State Track Recorders (SSTR). Assay technique number 1 involves the detection of the 2.18 MeV gamma ray emitted in the decay of ^{144}Pr and its radioactive parent ^{144}Ce . The quantity of fuel is then deduced from the ratio of ^{144}Ce to uranium in the fuel assuming no partitioning. The second technique involves a more direct measurement of the fuel by determining the neutron flux arising from spontaneous fission. The LASL group employed a third technique to determine the ^{144}Ce content. A Be (γ, n) detector which is sensitive only to gamma rays above 1.67 MeV was used to estimate the quantity of ^{144}Ce present in the demineralizers and thereby the fuel content. This technique is, however, less sensitive to fuel and less accurate.

The results of these analyses are summarized in the table below:

FUEL CONTENT		
<u>NDA Technique</u>	<u>Demineralizer A</u>	<u>Demineralizer B</u>
Si(Li)	1.3 ± 0.6 kg	
SSTR	1.7 ± 0.6 kg	
Be(γ, n)	11 ± 6 kg	3.9 ± 1.5 kg

Copies of the final reports^{1,2} of the analyses performed by WHEDL are available. Only an informal report³ of the LASL studies has been received to date.

These results indicate that during sampling activities, no criticality concerns are evident. The measurements of the fuel content are well below the estimated 70 kg of fuel of TMI-2 enrichment required for criticality.

B. Present Demineralizer Conditions

Both Make Up and Purification Demineralizers have been safely vented and purged of their trapped gases. Laboratory scale tests of organic ion exchange resins representative of those used in the demineralizers have been performed by WHEDL. These tests were designed to simulate the estimated temperature and radiation conditions experienced by the demineralizers during and since the accident. The resins were heated in excess of 360°F and exposed to integrated gamma dose rates of 2×10^9 rads. Gas, liquid and resin samples were analyzed for degradation products and general characteristics. The analyses of the gas samples from the tests showed high hydrogen content, low oxygen content and varying amounts of organic molecules (CH₄, CO₂, CO, etc.). These results were consistent with those observed during the EPICOR II prefilter venting and gas generation studies⁴. Sampling and analyses of the make up demineralizer gas has confirmed the applicability of these tests.⁵ Samples of the gas from the

demineralizer showed high hydrogen, low oxygen and a considerable quantity of non-diatomic gases. Samples of these gases are being shipped for extensive analyses at WHEDL.

The demineralizers were then purged of their hydrogen content by repeated pressurization and venting using nitrogen. The resulting atmosphere contained less than 2% residual hydrogen. The demineralizers were then allowed to remain in a pressurized condition and then sampled. They will be analyzed periodically for hydrogen build up.

Using the model developed from the EPICOR II prefilter venting studies, an estimate of the hydrogen generation rate can be calculated. The results of the gamma spectrometry on the A-Demineralizer indicate a ^{137}Cs content of 3400 ± 2500 Ci. The hydrogen gas generation constant from the EPICOR work is approximately 6×10^{-6} l/hr per curie of total activity. Using this rate constant and the make up demineralizer activity, a calculated hydrogen generation rate of 0.96 l/day would result. This would yield nearly 3 psi pressure increase per year on MU-K-1A due to hydrogen generation. The total pressure on demin-A at the start of sampling was less than 4 psig. Other evidence suggests that the hydrogen gas generation rate is substantially lower than predicted probably due to the absence of significant quantities of water. The history of the demineralizers which would result in a dried condition is described in the attached summary memos by Dr. J. Sheff of Lowell University (Attachment 1). The absence of significant quantities of water has been confirmed by the WHEDL gamma scans and Compton spectrometry (see report¹). A summary of the present demineralizer conditions is shown in the attached table.

If during the sampling operations, the tank atmospheres are permitted to exchange with the ambient atmosphere, the resulting gases will remain non-explosive (i.e. less than 2% H₂). This would remain true for a period of 34 days even if the EPICOR hydrogen gas generation rate were assumed, and the oxygen content was at 20% (present oxygen levels less than 1%). While there will be momentary openings of the depressurized demineralizers for the purpose of inserting tools, etc. it is not planned to purge the demineralizers with air. Therefore, minimum oxygen will be introduced. The capability of repressurization and venting will exist for the purpose of inerting after sampling.

C. Containment During Sampling

The sampling systems have been designed to eliminate release pathways by suitable containment boxes and filtration devices. For the vacuum sampling method, the vacuum pump exhausts back to the demineralizer and does not discharge directly to the Hays Gas Analyzer Room. For the mechanical sampling method, the release of the resin to the sample bottle is accomplished inside a secondary containment receiver. Suitable bagging and sleeving of probes and tools assure minimum spread of contamination. The use of portable shielding and distance from the loaded sampler are employed to minimize exposures to personnel. The small mechanical probe, while requiring several operations to obtain the necessary sample quantity, will also provide some radiation control for each operation. Estimates of the dose rates expected on the sample bottle shield are 530 mr/hr using a 5000 uCi/gm source term for specific activity of the resin and a 100 gram sample limit.

Summary

Careful NDA of the Make Up and Purification Demineralizers have been performed to evaluate the present resin conditions for fuel and curie content. The gases trapped have been safely vented and inerted down to safe levels of residual hydrogen and ^{85}Kr . Resin sampling hardware and procedures have been developed to eliminate a release pathway and minimize exposures to personnel.

References

1. "Fuel Content of the Three Mile Island Unit 2 Make Up Demineralizers", HEDL Report 7285, December, 1982.
2. "Solid State Track Recorder Neutron Dosimetry Measurements for Fuel Debris Assessment of TMI-2 Demineralizer-A", HEDL Report SA-2834, December, 1982.
3. "NDA Measurement of the Demineralizers at TMI-2" LASL Report in preparation.
4. "Sampling, Purging and Analysis of the 49 EPICOR-II Prefilters in Preparation for Shipment from Three Mile Island", S. P. Queen, GEND Report in preparation.
5. "Gas Sampling, Venting and Purging Make Up and Purification Demineralizers (MU-K-1A and MU-K-1B)", K. J. Hofstetter, informal report, February, 1983.

Estimated Demineralizer Loadings

<u>Resin</u>	<u>Initial</u>	<u>A</u>	<u>B</u>
Volume, ft ³	50	22	22
Weight, lb	2,139	1,025	1,025
¹³⁷ Cs, Ci	0	3,400	7,000
¹³⁴ Cs, Ci	0	270	540
 <u>Liquid</u>			
Volume, ft ³	44	3	3
Weight, lb	2,746	193	193
 <u>Debris</u>			
U, lb		5	1
Core Debris, lb		95	19
¹³⁷ Cs, Ci		177	35
¹³⁴ Cs, Ci		16	3
¹⁰⁶ Ru, Ci		21	4
¹⁴⁴ Ce, Ci		28	5
¹²⁵ Sb, Ci		116	23
 <u>Gas</u>			
Volume, ft ³		63	63
Temp, °F		80	80
Pressure, psig		8	4

Inter-Office Memorandum



Date December 17, 1982
4343-82-0004

Subject Comments on the Demineralizer Bed
in the Unit 2 Primary Loop

To D. R. Buchanan

Location Administration Building
Second Floor

Data from the recent radiation scan on the bed indicates a peak near the top of the tank. The peak would be expected to be near the bed surface which would be near the top of the tank of the resin has neither slumped or become otherwise seriously malfunctioning. Thus the indication is that the bed has remained in place.

The estimate of dose is sufficiently high that there is concern that high temperatures in all or parts of the bed may have occurred. This behavior was recognized as a possibility and reported in Memos #5530-82-0586 dated May 28, 1982, #4343-82-0001 dated September 29, 1982, and draft memo dated July 13, 1982. It is the purpose of this memo to provide improved estimates of the early bed time-temperature history.

The dose history of the demineralizer beds was estimated by Paul Babel. The original reference is unknown to me at this time, but the results are reported in 5530-82-0586. They are repeated here.

Dose history:

1st month	6.5 (10^8) rad.
2nd month	8.4 (10^7) rad.
3rd month	4.4 (10^7) rad.
4th month	3.4 (10^7) rad.

Total dose during three years is 1-5 (10^9) rads.

Without the original calculations, it is impossible to be precise about the first week's dose, but since the data is e-folding in about two weeks, the first two weeks contribution was of order 5 (10^8) rad. The dose in the first week was of order 3 (10^8) rads. Conversion of the dose to conventional energy deposition unit precedes as follows:

$$E \text{ kw/ft}^3 = \frac{3 (10^8) \cdot 100 \text{ erg/gr} \cdot 454 \text{ gr/lb} \cdot 62.4 \text{ lb/ft}^3}{10^{10} \frac{\text{erg/kw}}{\text{sec}} \cdot 7 \text{ day} \cdot 24 \text{ hr/day} \cdot 3600 \text{ sec/hr}}$$

$$= 0.141 \text{ kw/ft}^3$$

The energy deposition rate in the first day could be easily seven times this or about 1 kw/ft.³. An earlier estimate made by Paul Babel was one to four kilowatts, but the details of this estimate are unavailable.

In this memo, it will first be shown that for generation rates available in the tank, the water can be heated and vaporized in a very short time assuming the tank is adiabatic. However, to do so means that water must be heated to at least 212°F and some of it boiled. Clearly, convection should establish itself and the tank surface will approach 212°F providing convection cooling to the room. The cooling will reduce the boil-off rate and the convection effect must be quantified before one can estimate the extent to which voiding was slowed. Below, it will be shown that convection cooling was probably not sufficient, but could have removed perhaps 10% or so of the energy for the 1 kw per cuft case.

Several possible pathways or resin histories could result depending upon how the vessel vents, but it will be shown below that all lead in reasonable time to a water free resin bed. This water free resin bed will warm-up, reaching temperatures within its center which could be quite high. Bed melting and softening to the point of sintering should certainly be expected.* Full scale slumping seems not to have occurred as noted above.

The tank contains 78.6 cuft (2226 liters) of resin and water. The mixture will be assumed to behave thermally as water during heat up. The power generated ranged between 1 and 4 kw per cuft (3413 Btu per hr. cuft). Water will heat up at a rate of $3413 \div 62.4 = 54.7$ °F per hour kw cuft. The tank contents thus would reach the boiling temperature for standard pressure in about four hours. The water content of each cubic foot is 54% and the voids are water filled. This water will boil and only a very small amount is necessary to void the tank. The void volume is about 41.8 cuft which includes the tank ends and about 40% of the resin bed volume. Only 1.74 pound of water must be vaporized to void this volume. At 1 kw per cuft, this will happen in much less than an hour. It is assumed that a vent path at or near atmospheric exists. The obvious vent path is the stop-check valve in the tank outlet. This valve was eventually closed solid, but this was done at an uncertain time point. But until that time, venting could occur at or near one atmosphere. After that time, 150 psig would be required for venting via the relief valve.

As noted above, an estimate of convection from a surface at 212°F must be considered. One square foot will be examined. A typical overall heat transfer coefficient for heat transfer from a surface in contact with air flowing at 10 ft./sec. is 9 Btu per hour/ft.² °F.

*Data from Battelle indicates that the resin does not melt. Cross-linking has apparently caused the resins to be non-thermosetting. (Note added in draft.)

For a 150°F temperature difference, 1350 Btu per hour ft.² could be transferred. This is not adequate to cool the 3413 Btu per hour cuft being generated. Correlations for natural convection give a value of U in the range of perhaps 2 Btu per hour ft.² °F.

The conclusion must be that the bed ejected all loose pore water downward via the outlet check valve. This presumes that the stop valve was open for an adequate time period. An adequate time period is of order five hours at 1 kw per ft.³. At 0.3 kw per ft.³, it would be perhaps 24 to 48 hours.

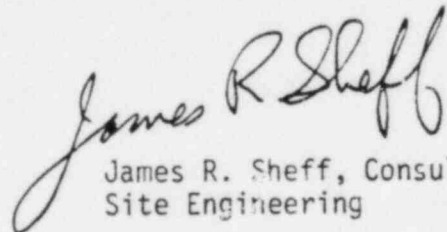
If water were remaining at the time the vessel was solidly closed, the water must be heated to the 150 psig saturation temperature which is about 350°F. At this temperature, steam would again form. The pressure relief vent is apparently near the tank bottom. If this is so, the majority of the water will again be removed by steam through the ejection of a plug of water.

After the water is gone, the resin will continue to heat up. It will start from either 212 or 350°F depending on how the vessel vented itself. The resin is essentially polystyrene and should behave similar to this material. The Handbook of Physics and Chemistry states that polystyrene is injection molded at temperatures between 265 and 600°F.

The conclusion would seem to be that the bed will slump if temperatures of order 600°F are reached. Indeed, it should have done so at a temperature between 265 to 600°F. The slumping could be only in the upper layer if most of the radioactive material were deposited there.

The non-uniform deposition also impacts the energy loss mechanisms and thus may again reduce the effects.

In summary, sufficient evidence seems to exist to conclude the bed was made water free and perhaps saw temperatures high enough to cause local melting and/or sintering in the first week after the accident. Until evidence via sampling confirms or contradicts these estimates, planning for bed removal should be compatible with them.


James R. Sheff, Consultant
Site Engineering

JRS:rr

cc: K. Lionarons

Inter-Office Memorandum



Date December 21, 1982
4343-82-0005

Subject Comments on DOE Reports on the
Demineralizer Bed Studies

To D. R. Buchanan

Location Administration Building
Second Floor

A fairly large stack of information received by TMI-DOE from Battelle has been reviewed. Several relevant facts have surfaced from the work so far. Here, I gather them in a single place so that they do not get lost in the multitude of other paper and details. Dates range from September 15, 1982, to mid November 1982.

- A. The bed now only fills the lower two or three feet of the tank. It has been reduced in size by a combination of high doses and/or high temperatures. Either could do it, probably both combined did.

Evidence is:

- a) The location of the fuel,
- b) Neutron and gamma scans,
- c) Data from several sources along with Battelle's saying 300°F can remove the 54% H₂O from the resin, and
- d) Data from Battelle saying a dose of 2 (10⁹) rad causes all the water to decouple from the resin.

The start of this effect was also observed at Lowell. Although Battelle do not so state, it is the result of increased resin polymer cross-linking as well as polymer chain breakage. The material is becoming a ridged solid rather than an open water filled matrix.

- B. Gas generation is essentially all hydrogen for new wet resin and the quantity agrees within 20% of that made in memo #5530-82-0586 dated May 28, 1982.
- C. At lower doses, about 10⁸ rad, breakdown products from the anion resin were seen. They had disappeared at high doses.
- D. The "cooled" dry resin showed more breakdown products, again mostly from the anion resin. (One sample also may be air contaminated.) Gas generation per gram was only about one third as much.

- E. The resin does not seem to melt. It eventually chars and becomes a solid mass. This happens between 260-538°C. At 260°C (500°F), the resin was still in bead form and apparently not stuck together. At 400°C, the resin was black and had lost substantially more weight than could be rationalized as water.

D.R. Buchanan for
James R. Sheff, Consultant
Site Engineering

JRS:rr

cc: K. J. Hoffstetter
K. Lionarons
J. W. Thiesing
R. P. Warren