

February 15, 1983

Docket No. 50-298

Mr. J. M. Pilant, Director  
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Nebraska Public Power District  
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Dear Mr. Pilant:

SUBJECT: REVIEW OF POST-ACCIDENT SAMPLING SYSTEM, NUREG-0737, ITEM II.B.3

Re: Cooper Nuclear Station

We have reviewed your Post-Accident Sampling System based on your September 1, and December 28, 1982 submittals for compliance with criteria in NUREG-0737, Item II.B.3. We have determined that the additional information identified in Enclosure 1 is needed for us to complete our review.

It is requested that you provide a response to this Request For Additional Information within 60 days of receipt of this letter. If you wish to discuss or have clarified any of these issues identified, contact your Project Manager and he will arrange a conference call with the appropriate technical review branch personnel.

This request for information was approved by the Office of Management and Budget under Clearance No. 3150-0065 which expires May 31, 1983.

Sincerely,

ORIGINAL SIGNED BY

Domenic B. Vassallo, Chief  
Operating Reactors Branch #2  
Division of Licensing

**Enclosures**

Request for Additional  
Information  
W/Attachments 1 thru 4

cc: See next page

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REQUEST FOR ADDITIONAL INFORMATION

NUREG-0737, ITEM II.B.3

POST-ACCIDENT SAMPLING SYSTEM (PASS)

COOPER NUCLEAR STATION

- 1) We have determined, based on your submittals, that you partially meet Criterion 2 of Item II.B.3 by establishing an on-site radiological and chemical analysis capability. However, provide a procedure to estimate the extent of core damage based on radionuclide concentrations that takes into consideration other physical parameters, such as core temperature data and sample location. In addition, please describe the accuracy of your chloride analysis.

Attachment 1 contains a guide that can be used to aid you in the preparation of a procedure to estimate core damage to satisfy Criterion 2 of Item II.B.3. If you propose a procedure based on these guidelines NRC Staff review will still be required. Attachment 2 contains a procedure that we have approved for estimating core damage and if you agree to adopt this procedure NRC Staff review is not required.

- 2) We have determined that your submittals only partially satisfy Criterion 4 of Item II.B.3. To totally satisfy Criterion 4 please commit to include the capability to verify that dissolved oxygen in the reactor coolant is less than 0.1 ppm when the chloride concentration exceeds 0.15 ppm or provide justification for an alternate approach.
- 3) Criterion 6 of Item II.B.3. pertains to radiation exposures to individuals obtaining and analyzing reactor coolant and containment atmosphere samples. We have determined that you partially meet Criterion 6. To fully satisfy this criterion, please provide an analysis to demonstrate that the radiation exposure during post-accident sampling will be less than 75 rem for extremities.
- 4) Criterion 10 of Item II.B.3 states that the accuracy, range, and sensitivity shall be adequate to provide pertinent data to the operator in order to describe radiological and chemical status of the reactor coolant systems.

We find that you partially meet Criterion 10 in that only the lower limit of detectability was provided for boron analysis. Please provide information on the range, accuracy, and sensitivity of the procedure to demonstrate that the selected procedures and instrumentation will achieve the analytical accuracies. In addition information demonstrating their applicability in the post accident water chemistry and radiation environment should be provided. This can be accomplished by performing tests utilizing the standard test matrix provided below or by providing evidence that the selected procedure or instrument has been used successfully in a similar environment.

STANDARD TEST MATRIX  
FOR  
UNDILUTED REACTOR COOLANT SAMPLES IN A POST-ACCIDENT ENVIRONMENT

<u>Constituent</u>	<u>Nominal Concentration (ppm)</u>	<u>Added as (chemical salt)</u>
I-	40	Potassium Iodide
Cs+	250	Cesium Nitrate
Ba+2	10	Barium Nitrate
La+3	5	Lanthanum Chloride
Ce+4	5	Ammonium Cerium Nitrate
Cl-	10	
B	2000	Boric Acid
Li+	2	Lithium Hydroxide
NO <sub>3</sub> <sup>-</sup>	150	
NH <sub>4</sub> <sup>+</sup>	5	
K+	20	
Gamma Radiation (Induced Field)	10 <sup>4</sup> Rad/gm of Reactor Coolant	Adsorbed Dose

NOTES:

- 1) Instrumentation and procedures which are applicable to diluted samples only, should be tested with an equally diluted chemical test matrix. The induced radiation environment should be adjusted commensurate with the weight of actual reactor coolant in the sample being tested.
- 2) Procedures which may be affected by containment spray additive chemicals must be tested in both the standard test matrix plus appropriate spray additives. Both procedures (with and without spray additives) are required to be available.
- 3) In lieu of conducting tests utilizing the standard test matrix for instruments and procedures, provide evidence that the selected instrument or procedure has been used successfully in a similar environment.



Also please provide information to assure the following: all equipment and procedures which are used for post accident sampling and analysis will be calibrated or tested at a frequency which will ensure, to a high degree of reliability, that it will be available when required; and operators will receive initial and refresher training in post accident sampling, analysis and transport. A minimum frequency for the above efforts is considered to be every six months if indicated by testing.

Attachment 3 contains a report on the evaluation of Sentry Equipment Corporation and General Electric Company analytical chemical procedures for post accident analysis. An acceptable position to satisfy Criterion 10 would be to reference the procedures in this report or propose alternate procedures which would be subject to our review and approval.

- 5) Criterion II of Item II.B.3 states that in the design of the post accident sampling and analysis capability, consideration should be given to the following items:
- a) Provisions for purging sample lines, for reducing plateout in sample lines, for minimizing the sample loss or distortion, for preventing blockage of sample lines by loose material in the RCS or containment, for appropriate disposal of the samples, and for flow restrictions to limit reactor coolant loss from a rupture of the sample line. The post accident reactor coolant and containment atmosphere samples should be representative of the reactor coolant in the core area and the containment atmosphere following a transient or accident. The sample lines should be as short as possible to minimize the volume of fluid to be taken from containment. The residues of sample collection should be returned to containment or to a closed system.
  - b) The ventilation exhaust from the sampling station should be filtered with charcoal adsorbers and high-efficiency particulate air (HEPA) filters.

Your PASS sample lines are quarter-inch outside diameter stainless steel tubing, which minimizes purge volumes, maintains turbulent flow through the sample line, and provides a flow restriction to minimize reactor coolant loss from a ruptured sample line. Purge volumes are returned to the drywell equipment drain sump and diluted samples are discarded in the radioactive waste system. The containment atmosphere sample line is insulated and heat tracted from the drywell wall to the PASS. The sample lines do not contain flow restrictors. Reactor coolant and RHR samples are taken through the normal sample points which are automatically isolated on containment isolation and/or safety injection signals. Containment atmosphere samples can be taken from three

different representative drywell elevations.

The system is located inside the Reactor Building which has exhaust ventilation through charcoal adsorbers and HEPA filters.

We have determined that these provisions partially meet Criterion II. However, we have concerns about the capability to obtain representative samples from the reactor vessel and suppression pool under accident conditions. Therefore, provide sufficient information to demonstrate that representative samples can be obtained from the reactor coolant inside the reactor vessel and from the suppression pool water. Attachment 4 contains a copy of the Light-Water Reactor Review Group position paper (LRG-11) on reactor coolant sampling. An acceptable position to satisfy Criterion II would be to reference LRG-11 or provide an alternative procedure which would be subject to our review and approval.

Attachments.

1. Guide
2. Sample Approval  
Plant Procedure
3. Evaluation of GE and  
SEC Procedures
4. LRG-11

POST-ACCIDENT SAMPLING  
GUIDE FOR PREPARATION OF A PROCEDURE  
TO ESTIMATE CORE DAMAGE

The major issue remaining to complete our evaluation of NTOL's for compliance with the post-accident sampling criteria of NUREG-0737 is preparation of procedures for relating radionuclide concentrations to core damage. To date, none of the applicants has been successful in providing an acceptable procedure. As a consequence, each NTOL has a license condition which may restrict power operations. One of the contributing factors in the applicant's slow responses to this item is their confusion on exactly what to prepare. The attachment is intended to provide informal guidance to each NTOL applicant so that their procedures, when prepared, will address the core damage estimation in a manner acceptable to us.

We anticipate that preparation of a final procedure for estimating core damage may take approximately 12 months. Therefore, we are willing to accept an interim procedure which focuses on fewer radionuclides than are indicated in the attachment. The interim procedure in conjunction with a firm date for the final procedure would be used to remove the power restricting license condition.

The primary purpose in preparing a procedure for relating radionuclide concentrations to core damage is to be able to provide a realistic estimate of core damage. We are primarily interested in being able to differentiate between four major fuel conditions; no damage, cladding failures, fuel overheating and core melt. Estimates of core damage should be as realistic as possible. If a core actually has one percent cladding failures, we do not want a prediction of fifty percent core melt or vice versa; extremes in either direction could significantly alter the actions taken to recover from an accident. Therefore, the procedure for estimating core damage should include not only the measurement of specific radionuclides but a weighted assessment of their meaning based on all available plant indicators. The following discussion is intended to provide general guidance pertaining to the factors which should be considered in preparing a procedure for estimating core damage but is not intended to provide an all inclusive plant specific list.

The rationale for selecting specific radionuclides to perform "core damage estimates from fission product release" is included in the Rogovin Report (page 524 through 527, attached). Basically, the Rogovin Report states that three major factors must be considered when attempting to estimate core damage based on radionuclide concentrations.

1. For the measured radionuclides, what percent of the total available activity is released (i.e. is only gap activity released, is sufficient activity released to predict fuel overheating or is the quantity of activity released, only available through core melt?)

2. What radionuclides are not present (i.e. some radionuclides will, in all probability, not be released unless fuel overheating or melt occurs). The absence of these species bounds the maximum extent of fuel damage.
3. What are the ratios of various radionuclide species (i.e. the gap activity ratio for various radionuclides may differ from the ratio in the pellet). The measurement of a specific ratio will then indicate whether the activity released came from the gap or fuel overheating/melt.

In addition to the radionuclide measurements, other plant indicators may be available which can aid in estimating core damage. These include incore temperature indicators, total quantity of hydrogen released from zirconium degradation and containment radiation monitors. When providing an estimate of core damage the information available from all indications should be factored into the final estimate (i.e. if the incore temperature indicators show fuel overheat and the radionuclide concentrations indicate no damage, then a recheck of both indications should be performed).

Consistent with the categorization of fuel damage in the Rogovin Report, the four major categories of fuel damage can be further broken down, similar to the following list, consistent with state-of-the-art technology. The suggested categories of fuel damage are intended solely to address fuel integrity for post-accident sampling and do not pertain to meeting normal off-site doses as a consequence of fuel failures.

1. No fuel damage.
2. Cladding failures (<10%).
3. Intermediate cladding failures (10% - 50%).
4. Major cladding failures (>50%).
5. Fuel pellet overheating (<10%).
6. Intermediate fuel pellet overheating (10% - 50%).
7. Major fuel pellet overheating (>50%).
8. Fuel pellet melting (<10%).
9. Intermediate fuel pellet melting (10% - 50%).
10. Major fuel pellet melting (>50%).



Because core degradation will in all probability not take place uniformly, the final categories will not be clear cut, as are the ten listed above. Therefore, the preparation of a core damage estimate should be an iterative process where the first determination is to find which of the four major categories is indicated (for illustrative purposes, only radionuclide concentrations will be considered in the following example, but as indicated above, the plant specific procedure should include input from other plant indicators). Then proceed to narrow down the estimate based on all available data and knowledge of how the plant systems function.

#### Example

In a given accident condition, there is 70% clad failure, significant fuel overheating and one fuel bundle melted. Utilizing the iterative process

First calculate the maximum fuel melted by arbitrarily attributing all activity to fuel melt (under these conditions, five to ten melted bundles may be predicted). Therefore, the worst possible condition is fuel pellet melting."

Second, calculate the maximum fuel overheated, by arbitrarily attributing all activity to fuel pellet overheating (under these conditions, major fuel pellet overheating is predicted).

Third, calculate the maximum cladding failures, by arbitrarily attributing all activity to cladding failures (under these conditions, greater than 100% fuel cladding damage is predicted).

At this point it is obvious that major cladding damage is present and that a large amount of fuel pellet overheating has occurred with the potential for some minor fuel pellet melting.

Fourth, check for the presence of radionuclides which are indicators of fuel pellet melting and overheating. In this instance, obvious indicators of overheating will exist along with trace indicators of potential pellet melt.

Fifth, based on the radionuclide indicators of fuel pellet overheating damage (confirmed by incore temperature) make an estimate of how much fuel overheated. This result will in all probability indicate major fuel pellet overheating.

Sixth, subtract the activity estimated from fuel pellet overheating, plus the activity attributable to 100% gap release from the total activity found. This will result in a negative number because the contributions from overestimating cladding damage (100% versus 70%) and fuel overheating (major versus intermediate) will exceed the activity contribution from one melted bundle.

At this point, knowledgeable judgment must be employed to establish the best estimate of core damage. Although all damage could be attributable to cladding damage and fuel pellet overheating, the trace of radionuclide indicators of fuel pellet melt indicate the possibility of some fuel melting. Based on knowledge of core temperature variations, it is highly unlikely that 100% cladding damage would exist without significant fuel melting. Also, some of the activity attributed to fuel pellet overheating must be associated with the amount of fuel pellet melting which is indicated. Therefore, the best estimate of fuel damage would be that "intermediate fuel overheating had occurred, with major cladding damage and the possibility of minor fuel pellet melting in one or two fuel bundles out of 150 fuel bundles."

The above example is obviously ideal and makes the major assumptions that:

- A. The radionuclide/s monitored are at equal concentrations in all fuel rods.

In actuality, at no time will all radionuclides be at equal concentrations in all fuel rods. Because the time to reach equilibrium for each radionuclide is different, due to their highly variable production and different decay rates. Some isotopes will approach equilibrium quickly, while others never reach equilibrium. Therefore, it is necessary to factor in reactor power history when determining which radionuclide is optimum for monitoring in a given accident condition. Probably the optimum radionuclides for estimating core damage will vary as a function of time after refueling and based on power history.

- B. Equilibrated samples are readily available from all sample locations at the instant of sampling. Considering the large volumes of liquid and vapor spaces that a leakage source migrates to and mixes with, for other than very large leaks, it will take many hours or even days to approach equilibrium conditions at all sample locations.

- C. Maximum core degradation occurred prior to initiation of sampling. Unless total cooling is lost, core degradation can be anticipated to progress over a period of hours. Thus, there is not a given instant when sampling can be conducted with positive assurance that maximum degradation has occurred.

Considering that ideal conditions will not exist, then procedure for estimating core damage should be prepared in a manner that the effects of variables such as time in core life and type of accident are accounted for. Therefore, the procedure for estimating core damage should include the determination of both short and long lived gaseous and non-volatile radionuclides along with ratios for appropriate species. Each separate radionuclide analyzed, along with predicted ratios of selected radionuclides would be used to estimate core damage. This process will result in four separate estimates of core damage, (short and long-lived, gaseous and non-volatile species) which can be weighed, based on power history, to determine the best estimate of core damage.

The post-accident sampling system locations for liquid and gaseous samples varies for each plant. To obtain the most accurate assessment of core damage, it is necessary to sample and analyze radionuclides from each of these locations (reactor coolant, containment atmosphere, containment sumps and suppression pool), then relate the measured concentrations to the total curies for each radionuclide at each sample location. These measured radionuclide concentrations need to be decay corrected to the estimated time of core damage (to). Their relationship to core damage can be obtained by comparing the total quantity and ratios of the radionuclides released with the predetermined radionuclide concentrations and ratios which are available in the core based on power history. Assuming one hour per sample location to recirculate, obtain and analyze a sample from each location it would take \_\_\_\_\_ hours to perform each of those analyses.

Based on the above rationale, the final procedure for estimating core damage using measured radionuclide concentrations will probably rely only on one or two sample locations during the initial phases of an accident. The optimum radionuclides for estimating core damage will also, in the short term, be based on recent power history. When equilibrium conditions are established at all sample locations, radionuclide analysis can be performed to obtain a better estimate of core damage. The specific radionuclides to be analyzed under equilibrium conditions may be different than those initially analyzed because of initial abundances and different decay rates.

The specific sample locations to be used during the initial phases of an accident should be selected based on the type of accident in progress (i.e. for a BWR, a small liquid line break in the primary containment would release only small quantities of volatile species to the dry well. Therefore, sampling the dry well first would not indicate the true magnitude of core damage). For the same small break accident, if pressure is reduced by venting safety valves to the suppression pool, then the suppression chamber vapor space would contain the majority of gaseous activity. In the case of a small steam line break, without venting safety valves to the suppression pool, the dry well may be the best sample location.

To account for the variations in prime sample locations, based on type of accident, the procedure should include a list of primary sample locations. This list should include both a prime liquid and gaseous location and state the reasoning used to determine that these locations are best. Additionally, the procedure should address other plant indications which can be used to verify that the sample locations selected are best for the specified accident condition.

Finally, the procedure should incorporate plant specific examples which show estimates of core damage based on predicted radionuclide concentrations. Methodology for this step is provided by letter of May 4, 1981, from McGuire Nuclear Station, Docket No. 50-369.



## Part 2, Vol II - Rogovin Report

- at 2 hours 54 minutes, although additional slumping occurred at 3 hours 45 minutes.
7. All of the fuel rods in the core burst, during an approximately 30-minute (center bundle) to 40-minute (lowest power peripheral bundles) period after the top of the core was uncovered at depths ranging from 1½ feet (center bundle) to 2 feet (peripheral bundle) from the top of the fuel rods.
  8. Temperatures at which liquefied fuel ( $\text{UO}_2$  dissolved in the zirconium metal-zirconium dioxide liquid eutectic at about 3500 to 3600°F) could be formed were calculated to have first been reached at 6 inches from the top of the fuel in the fuel rods in the central fuel bundle about 33 minutes after the top of the core was uncovered and were reached as low as 36 inches from the top of the fuel. Such temperatures were calculated to have been reached in the peripheral bundles at a depth of about 14 inches from the top of the fuel in about 46 minutes after the core was uncovered and at a depth of about 41 inches in 57 minutes.
  9. The peak temperatures calculated for the fuel rods ranged from 4370°F in about 52 minutes for the highest powered bundle to a maximum of 4412°F for a medium powered bundle at 58 minutes to about 4358°F for a lower powered peripheral bundle at about 78 minutes.
  10. The amount of hydrogen formed by oxidation of solid Zircaloy cladding during the temperature excursion was calculated to be about 308 pounds, and that formed from all of the damaged Zircaloy, including that contained in the liquefied fuel present at 3 hours, was calculated to be about 720 pounds. This is the minimum amount of hydrogen estimated to have been formed. The maximum could be as high as 820 pounds.
  11. The major releases of hydrogen to the containment occurred before 4 hours accident time and during the long depressurization around 8 hours. No significant amount of hydrogen was produced after about 4 hours.
  12. The minimum water level occurring in the core up to 3 hours is estimated to have been  $4 \pm \frac{1}{2}$  ft from the bottom of the fuel in the fuel rods on the basis of the amount of hydrogen produced, the amount of radioactivity released, the time at which significant levels of radioactivity were detected, and the structural damage estimated in the core.
  13. The total amount of Zircaloy oxidized is calculated to be not less than 16 400 pounds and may have been as high as 18 700 pounds; i.e.,

between about 10% and 20% of the total Zircaloy in the core.

14. The damage in the core extends from the top downward at least 7 feet, and probably 8 feet, over most of the core and consists of oxygen embrittled Zircaloy cladding topped by a bed of debris that probably consists of fuel pellet fragments, partially dissolved fuel pellets, shells of Zircaloy oxide, and segments of embrittled Zircaloy cladding with outer skins of Zircaloy oxide, all glued together with liquefied fuel into a relatively tight and compact mass extending entirely across the core from wall to wall and penetrated by only a few vertical passageways, at most. In addition, fingers of liquefied fuel extend downward from the debris bed in several continuous subchannels between fuel rods, encompassing the neighboring fuel rods, to a depth of about 1 foot above the bottom of the fuel stack in the fuel rods. Not less than 32% of the fuel assemblies have such fingers of liquefied fuel.

### c. Core Damage Estimates from Fission Product Release

At shutdown the reactor core contained fission products, activation products, and actinides. Some of these, notably krypton and xenon, are gaseous and can diffuse through the fuel pellet to collect in the gap between the fuel and the cladding. To a lesser extent, the halogens (iodine and bromine) can also diffuse into the fuel-clad gap. Any perforation of the cladding can release these fission products into the reactor coolant.

If the fuel temperatures are higher than operating temperatures, but well below melting, other radioactive materials are volatilized and can diffuse out. Also, diffusion of the noble gases and halogens increases so that a larger fraction of these can be released. The release of cesium is quite variable and could be caused by compound formation. Because of this variability and what is now known about cesium, it is not possible to determine precisely the temperature at which a reasonably large fraction of the cesium would be released; however, it is believed temperatures would not be lower than 1300°C (2370°F).<sup>187,188</sup>

At higher temperatures that cause the liquefaction or melting of fuel, some fraction of other fission products such as tellurium can be released. Data reported show that the escape of tellurium depends on many factors other than temperature.<sup>189</sup> Under oxidizing conditions some ruthenium may be



released before melting. In general, rather large fractions of both tellurium and ruthenium are released in melting; but under some conditions, these materials can also be released before melt. The presence of ruthenium and tellurium does not prove that melt has occurred, but the absence of them is a good indicator that melt has not occurred. More recent experimental work,<sup>187,190</sup> while tending to confirm previous data, has not resolved all the questions regarding conditions—especially temperature conditions—under which fission products would be released.

Many of the fission products and most of the actinides occur as refractory oxides and are released only in relatively small amounts even at elevated temperatures. However, if damaged fuel pellets are rewetted, some of the more refractory radioactive material can be leached out. This process is slow and only small fractions of these materials find their way into the coolant by leaching. The longer damaged fuel is in contact with water, the more materials are released.

#### Categories of Fission Product Releases and Their Relation to TMI-2

Fission products and actinides can be divided into typical release groups, based on the ease with which they are volatilized. One such grouping (from Ref. 191) is in order of decreasing volatility.

- I Noble gases (Kr, Xe)
- II Halogens (I, Br)
- III Alkali metals (Cs, Rb)
- IV Tellurium (Te)
- V Alkaline earths (Sr, Ba)
- VI Noble metals (Ru, Rh, Pd, Mo, Tc)
- VII Rare earths and actinides
- VIII Refractory oxides of Zr and Nb

The fraction of gaseous and volatile fission products released depends on the temperature and the size of the fuel fragments. If the temperature is high or if the fuel is highly fragmented, nearly complete release of the volatile materials can be assumed.

Under the conditions that have been calculated for the accident at TMI-2,<sup>188</sup> nearly complete release of groups I and II can be assumed from all fuel that was severely damaged, plus some additional fraction from fuel rods whose cladding was perforated without damage to the fuel. This additional amount from perforated but otherwise undamaged rods is, probably partly balanced by the amount not released from severely damaged fuel.

A major fraction of group III and a much smaller fraction of group IV could have been released from

the most severely damaged fuel. Small fractions, approximately 10% or less, could have been released from perforated but otherwise undamaged rods, but this cannot be well estimated.

#### Leaching from Irradiated Fuel

Very small fractions of the remaining groups may have been released from the very hottest fuel. The principal mechanism for release of these refractory materials is probably leaching. Leaching from irradiated  $UO_2$  has not been thoroughly studied. However, the work of Katayama<sup>192,193</sup> and of Forsyth and Eklund<sup>194</sup> has shown that the leaching rates are slow, comparable to those from glass. Quantitative data, especially for the temperatures and conditions existing in TMI-2, are too sparse for a reliable calculation of the rate of leaching, especially when one considers that the condition of the damaged fuel is completely unknown.

An additional complication is presented because the effective surface area of irradiated fuel presented to the water is almost impossible to estimate because of cracking and porosity. The most that can be done with the available data is to form an "educated guess" as to whether the fuel appears to be mainly in the form of very large pieces or in the form of very fine fragments. Without additional data it is not possible to estimate the actual size distribution of the fragments. However, a small fraction of the most refractory material can be expected to have found its way into the reactor coolant. An approximate leaching calculation is presented in Appendix II.7. On the basis of this approximate calculation, it is possible to state, with very low confidence, that a large fraction of the fuel can presently be fragmented and that the size of the fragments is more likely to be a few millimeters than dustlike. A similar calculation has been carried out by Powers.<sup>191</sup> His conclusions, although not identical with these, indicate that the observed activity may have been caused either by leaching from large-sized fragments or by distribution of particle sizes no more than a few percent smaller than 2 millimeters in diameter and none smaller than 0.6 millimeter in diameter.

#### Expected Dispersion of the Fission Products from the Reactor

Principal fuel damage probably started before 3 hours after turbine trip. There was probably only minor damage before 2 hours. The calculated total inventory<sup>195</sup> of fission products, activation products,

TABLE II-56. Activity in release groups\*

Group	Activity
I	$2.97 \times 10^3$ Ci
II	$4.47 \times 10^8$ Ci
III	$4.6 \times 10^7$ Ci
IV	$1.61 \times 10^8$ Ci
V	$3.85 \times 10^8$ Ci
VI	$6.34 \times 10^8$ Ci
VII	$2.69 \times 10^9$ Ci
VIII	$4.80 \times 10^8$ Ci
Total	$5.11 \times 10^9$ Ci**

\*A few elements of low total activity, notably Fe, Cu, As, and Sb, have been arbitrarily located on the basis of melting point.

\*\*Total does not quite agree with calculated total activity because of rounding.

and actinides is given in Table II-56 for 3 hours after shutdown.

A detailed discussion of the fission product-release pathways begins in Section II.B of this report where a short summary is included. Radioactive material released to the reactor coolant may have been partially flushed to the containment through the open PORV (RC-R2). Some of the material may have been flushed to the containment prior to the containment isolation and then pumped to the auxiliary building. However, the coolant may have contained only a minute fraction of the total activity at this time; it is highly improbable that a significant fraction of the coolant was released before the reactor building sump pumps were shutdown. There is an unsubstantiated possibility<sup>196</sup> that more water leaked to the auxiliary building after pump shutdown. This leakage would have terminated when the reactor building was isolated after 3 hours 56 minutes.

Most of the material flushed out of the RCS probably remained in the reactor building. Some additional material may have volatilized from the makeup tank. Aside from these losses, which are not expected to be very large, estimates of the total activity released from the fuel can be made by analyzing the reactor building air and water samples, the reactor coolant, and the auxiliary building tanks.

Iodine is quite volatile, and it may be supposed that a significant fraction is found in the air. However,

the very high solubility of iodine in water and the strong tendency of atmospheric iodine to plate out on surface quickly reduces the amount of iodine in the air. Cesium, less volatile, is not expected to be present in the air in a significant quantity. On the other hand, the solubility of xenon and krypton is very low; these gases will be found almost entirely in the air.

To summarize, nearly complete release of noble gases, iodine, and cesium from damaged fuel is expected, even if the temperature is below the melting point. Significant releases of tellurium, ruthenium, and more refractory materials will occur only if the temperature approaches the melting point. Most of the noble gases will be found in air, and most of the other fission products will be found in water.

#### Distribution of Fission Products at the TMI Site

Analyses of samples of containment air, reactor coolant water, and auxiliary building tank water are summarized in Ref. 197. Reactor coolant analyses show between 7% and 15% of the calculated inventory of iodine and cesium isotopes to be in the coolant. If these measurements are corrected for dilution by water from the borated water storage tank, the fractions will be a factor of 3 higher. Results for refractory materials show great variation. A sample taken on April 10 was analyzed by four laboratories. There was a large variation from laboratory to laboratory, indicating low confidence in the results. Analyses of krypton and xenon isotopes in the containment atmosphere also showed considerable variation. However, based on the most abundant isotopes (<sup>85</sup>Kr and <sup>133</sup>Xe), there seemed to be 29% to 62% of the core inventory of noble gases in the containment air. Only 2% to 3% of the iodine and cesium was found in the auxiliary building tanks.

On August 28, 1979, a hole was drilled into the reactor building and samples of sump water were removed. Analyses of these samples showed 22% to 48% of the core inventory of iodine and cesium to be in the reactor building sump water.<sup>198</sup> In addition to iodine and cesium, very small amounts of Ru, Zr, Nb, Sb, La, and Ag were found. As expected, little <sup>90</sup>Sr was found. At most, the amounts corresponded to a few millionths of the core inventory. About 0.02% of the core inventory of <sup>129m</sup>Te was found.

All of these sample analyses were corrected for decay of the radionuclides to the time of analysis. This correction process is certainly more accurate than the analyses themselves; i.e., the accuracy of the estimates does not depend on the accuracy of

the daily calculation. Table II-57 is a recapitulation of the release of volatiles.

#### Findings

From these results, one can cautiously conclude that between 40% and 60% of the core inventory of release groups I-III was released to the coolant; that only a small fraction of group IV was released; and that only minute amounts of the remaining groups were released. The amount of refractory isotopes released is consistent with leaching (see Appendix B.7).

These data tend to confirm other analyses of core damage. The data on radioactivity released are too sparse and variable for a precise conclusion to be made on the amount of core damage; however, the following conclusions appear to be supported.

1. About 50% of the reactor core was damaged sufficiently to release the most volatile fission products.
2. The low fractions of tellurium, ruthenium, and strontium indicate that no significant quantity of fuel reached the melting point of  $\text{UO}_2$  (5200°F).
3. The amount of refractory isotopes in the reactor coolant is consistent with leaching.

#### d. Hydrogen Production, Removal, and Hazard

##### Introduction

One of the surprises of TMI-2 was the formation of large amounts of hydrogen from the reaction of

the cladding reacting with the steam generated by the boiling water. In this section several aspects of the hydrogen "problem" are discussed. The following subjects are treated in this section:

1. hydrogen production,
2. hydrogen accounting,
3. calculation of bubble size,
4. removal of the hydrogen bubble, and
5. the hazard from the hydrogen bubble.

##### Hydrogen Production

Two possible sources of hydrogen are considered: metal-water reactions and radiolysis. Other conceivable sources include oxidation of  $\text{UO}_2$ , which has not been investigated. The production of hydrogen from metal-water reactions is known to have been large; therefore any hydrogen from other mechanisms is expected to be small in comparison. Radiolysis is not expected to produce large amounts of hydrogen. It is investigated because the possibility of oxygen production was considered at the time of the accident. If oxygen had been released, the hydrogen that was trapped in the reactor coolant system could have become flammable.

##### Metal-Water Reaction

Many metals are oxidized by water. The reaction is very slow at low temperatures for most metals. Both steel and zirconium are oxidized at an increasing rate as the temperature rises. The oxidation of zirconium, the major constituent of the cladding, oc-

TABLE II-57. Total volatile isotopes released from core

Released To	Isotope (fraction of core inventory)				
	$^{133}\text{Xe}$	$^{131}\text{I}$	$^{137}\text{Cs}$	$^{134}\text{Cs}$	
Environment	0.01 <sup>1</sup>	— <sup>2</sup>	—	—	
RB Atmosphere	0.46 <sup>3</sup>	—	—	—	X
RB Water	—	0.22 <sup>4</sup>	0.48 <sup>4</sup>	0.34 <sup>4</sup>	X
RC Water	—	0.14 <sup>4</sup>	0.12 <sup>4</sup>	0.08 <sup>4</sup>	X
Aux. Bldg. Tanks	—	0.03	0.03	0.02	
Totals	0.46	0.39	0.63	0.44	

<sup>1</sup> See Ref. 199

<sup>2</sup> Dashes indicate low values (generally less than 1%)

<sup>3</sup> Best estimate from data in Ref. 197.

<sup>4</sup> Average of observations.



## SAMPLE APPROVED PLANT PROCEDURE

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## 1.0 OBJECTIVE AND SCOPE

The purpose of this procedure is to determine the degree of reactor core damage from the measured fission product concentrations in either the water or gas samples taken from the primary system under accident conditions. The procedure involves calculations of fission product inventories in the core and the release of inventories into the primary system under postulated loss-of-coolant accident (LOCA) conditions. The fuel gap fission products are assumed to be released upon the rupture of fuel cladding, and the majority of fission product inventories in a fuel rod would be released if fuel melting were to occur in that rod. A BWR-6/238 with a Mark III containment is used as a reference plant in the demonstration of this procedure. Application of the procedure for any other type or size of boiling water reactor (BWR) is described.

## 2.0 PROCEDURES FOR DETERMINATIONS OF CORE DAMAGE

### 2.1 Reference Plant (BWR-6/238, Mark III)

#### 2.1.1 Reference Plant Parameters

The pertinent plant parameters for the reference plant are given below:

Rated reactor thermal power	3579 MWt
Number of fuel bundles	748 bundles
Total primary coolant mass (reactor water plus suppression pool water)	$3.92 \times 10^9$ g
Total containment and drywell gas space volume	$4.0 \times 10^{10}$ cc

The fission product inventories in the core are calculated based on three years (1095 days) of continuous operation at 3651 MWt, or 102% of rated power, by using a computer code developed at Los Alamos and adapted to the GE computer system.<sup>(1)</sup> The inventories of some major fission products in the core at the time of reactor shutdown are given in Table 1.

#### 2.1.2 Procedure

Either the gas or water samples taken from the post accident sampling system are analyzed for major fission product concentrations by gamma ray spectrometry. If the concentration of a fission product in reactor water or drywell, corrected for decay from the time of reactor shutdown, is measured to be higher than the baseline concentration shown in Table 2 (see Section 3.1 for details), the extent of fuel or cladding damage can be determined directly from Figures 1-4 based on isotopes I-131, Cs-137, Xe-133, and Kr-85. Measurements of Cs-137 and Kr-85 activities are not very likely until the reactor has been shut down for longer than a few weeks and most of the shorter-lived isotopes have decayed.

If the concentration falls into the range where release of the fission product from the fuel gap or the molten fuel cannot be definitively determined, additional data may be needed to determine the source of fission product release (see below).

It is recommended that both the water and gas phase samples be measured in order to reduce the uncertainty in core damage estimations.

### 2.1.3 Supplementary Data

In addition to the longer-lived isotopes, some shorter-lived isotope concentrations may be measured in the sample. The ratios of isotopes released from either the fuel gap or the molten fuel are significantly different as shown in Table 3 (see Section 3.3 for detail), thus the source (fuel or gap) of release may be identified. Furthermore, some less volatile elements in the core may also start to release as the fuel starts to melt. If the less volatile fission products, such as isotopes of Sr, Ba, La, and Ru (either soluble or insoluble), are found to have unusually high concentrations in the water sample, some degree of fuel melting may be inferred. In a mixture of fission products 2.7h Sr-92 (1.385 MeV) and 40 h La-140 (1.597 MeV) should be relatively easy to identify and measure from a gamma ray spectrum. More work, however, is needed to establish the baseline concentrations for those isotopes.

## 2.2 Specific Plant Application

### 2.2.1 Plant Parameters

The pertinent reactor parameters for selected plants currently being retrofitted with the post accident sampling system are tabulated in Table 4. (2)

### 2.2.2 Procedure

The extent of core damage in an operating BWR can be determined by comparing the measured concentrations of major fission products in either the gas or water samples, after appropriate normalization, with the reference plant data. The following procedure is recommended.

- (1) Obtain the samples from the post accident sampling system, and the concentration of a fission product  $i$  ( $C_{wi}$  in water or  $C_{gi}$  in gas) is determined.
- (2) Correct the measured concentration for decay from the time of reactor shutdown.
- (3) Correct the measured gaseous activity concentration for temperature and pressure difference in the sample vial and the containment (torus) gas phase (see footnote on p. 3).

- (4) Calculate the fission product inventory correction factor (Section 2.2.2.2).
- (5) Calculate the plant parameter correction factor (section 2.2.2.3).
- (6) By using the correction factors, calculate the normalized concentration,  $C_{wi}^{Ref}$  or  $C_{gi}^{Ref}$  (section 2.2.2.1).
- (7) Use Figures 1 through 4 to estimate the extent of fuel or cladding damage.

#### 2.2.2.1 Comparison with Reference Plant Data

The extent of core damage can be estimated from the measured fission product concentrations in either the gas or water samples, as described for the reference plant. However, the measured concentration must be corrected for the differences in operation power level, time of operation, primary coolant mass and containment gas volume.

$$C_{wi}^{Ref} = C_{wi} e^{\lambda_i t} \times F_{Ii} \times F_w \quad \text{or}$$

$$C_{gi}^{Ref} = C_{gi} e^{\lambda_i t} \times F_{Ii} \times F_g$$

where  $C_{wi}^{Ref}$  = concentration of isotope i in the reference plant coolant (Ci/g)

$C_{gi}^{Ref}$  = concentration of isotope i in the reference plant containment gas (Ci/cc)

$C_{wi}$  = measured concentration of isotope i in the operating coolant at time, t (Ci/g)

$C_{gi}$  = measured concentration of isotope  $i$  in the operating containment gas at time,  $t$  (Ci/cc)\*\*

$e^{-\lambda_i t}$  = decay correction to the time of reactor shutdown

$\lambda_i$  = decay constant of isotope  $i$  (day)

$t$  = time between the reactor shutdown and the sample time (day)

$F_{Ii}$  = inventory correction factor for isotope  $i$  (see Section 2.2.2.2)

$F_g$  = containment gas volume correction factor (see Section 2.2.2.3)

$F_w$  = primary coolant mass correction factor (see Section 2.2.2.3)

#### 2.2.2.2 Inventory Correction Factor

$F_{Ii} = \frac{\text{Inventory in reference plant}}{\text{Inventory in operating plant}}$

$$= \frac{3651 (1 - e^{-1095 \lambda_i})}{\sum_j [P_j (1 - e^{-\lambda_i T_j}) e^{-\lambda_i T_j^0}]}$$

where  $P_j$  = steady reactor power operated in period  $j$  (MWt)\*

$T_j$  = duration of operating period  $j$  (day)\*

$T_j^0$  = time between the end of operating period  $j$  and time of reactor shutdown (day)

For a particular short-lived isotope,  $i$ , a calculation for only a period of ~6 half-lives of reactor operation time before reactor shutdown should be accurate enough. It should be pointed out that the computer calculation of core inventory takes into account the fuel burnup, plutonium fission and neutron capture reactions. The correction factor calculated from this equation may not be entirely accurate, but the error is insignificant in comparison to the uncertainties in the fission product release fractions (Table 5) and other assumptions (Section 3.2).

\*In each period, the variation of steady power should be limited to  $\pm 20\%$ .

\*\*The following correction for the measured concentration is needed if the temperature and pressure in the sample vial ( $T_1, P_1$ ) are different from that in the containment ( $T_2, P_2$ ):

$$C_{gi} = C_{gi(\text{vial})} \times \frac{P_2 T_1}{P_1 T_2}$$



### 2.2.2.3 Plant Parameter Correction Factors

$$F_w = \frac{\text{operating plant coolant mass (g)}}{\text{reference plant coolant mass (3.92x10}^9 \text{ g)}}$$

$$F_g = \frac{\text{operating plant containment gas volume (cc)}}{\text{reference plant containment gas vol. (4x10}^{10} \text{ cc)}}$$

In case the fission product concentrations are measured separately for the reactor water and suppression pool water or the drywell gas and the torus gas, the measured concentrations  $C_{wi}$  or  $C_{gi}$  would be averaged from the separate measurements:

$$C_{wi} = \frac{(\text{Conc. in Rx water}) \times (\text{Rx water mass}) + (\text{conc. in pool}) \times (\text{pool water mass})}{\text{Reactor water mass} + \text{pool water}}$$

$$C_{gi} = \frac{(\text{conc. in drywell}) \times (\text{drywell gas vol}) + (\text{conc. in torus}) \times (\text{torus gas vol})}{\text{drywell gas volume} + \text{torus gas volume}}$$

## 3.0 TECHNICAL BASIS

### 3.1 Fission Product Concentrations in the Primary System During Reactor Shutdown Under Normal Operation Conditions

#### 3.1.1 Fission Product Concentrations in Reactor Water

It is well known that some volatile and water soluble fission products, mainly iodine and cesium isotopes, will be released (called spiking) from defect fuel rods when the reactor is shut down and depressurized. Based on Pasadag of NRC, (4) the maximum I-131 release would be 10 Ci per each  $\mu\text{Ci/sec}$  release rate during normal power operation. According to the GE design basis of I-131 release rate at 700  $\mu\text{Ci/sec}$  (5) a maximum of 7000 Ci of I-131 may be released during reactor shutdown, and the concentration in reactor water would be 29  $\mu\text{Ci/g}$ .

An analytical model to predict the magnitude of I-131 spiking following reactor shutdown in operating BWRs has been reported by Brutschy et al (3). The "best estimate" concentration for I-131 has to be calculated based on the analytical model (3) for the individual reactor according to its fuel condition. However, if one adopts a standard I-131 concentration of  $5 \times 10^{-3}$   $\mu\text{Ci/g}$  or  $\sim 18$   $\mu\text{Ci/sec}$  as proposed by ANS (6), the nominal I-131 spiking is estimated to be  $\sim 0.7$   $\mu\text{Ci/g}$  in the reference plant water. This concentration is consistent with an average spiking concentration observed experimentally. (3) The results of these estimations, including the Cs-137 concentration, have been summarized in Table 2.

Potential future research in this area will be discussed in Section 4.

### 3.1.2 Noble Gas Concentrations in Drywell and Torus Gas Phase

Similar to the spiking magnitude, the noble gas activities in the drywell and the torus gas may vary significantly from reactor to reactor, mainly depending on the fuel condition and the steam leakage rate. In one operating BWR when the Xe-133 release rate measured at the steam jet air ejector (SJAE) was  $1.5 \times 10^4$   $\mu\text{Ci/sec}$ \* (compared to design basis release rate of 8200  $\mu\text{Ci/sec}$ ), the noble gas concentrations in the drywell were determined to be  $\sim 10^{-4}$   $\mu\text{Ci/cc}$  for Xe-133 and  $\sim 4 \times 10^{-5}$   $\mu\text{Ci/cc}$  for Kr-85. These data may be considered as upper limit values, at the time of measurement was the worst ever observed at an operating BWR.

### 3.2 Fission Product Release Source Terms Under Accident Conditions

The source terms for the damaged core under accident conditions have been proposed by several investigators.(7,8) The "best estimate" release source terms for different chemical groups of fission products are summarized in Table 5.

The release of fission products from the damaged core has been estimated to be a function of temperature,(9) and time after the loss-of-coolant accident.(7) In the present procedure, the fraction of fission product release from the core is assumed to be proportional to the fraction of core damage as suggested by Malinauskas, et.al.(9) It is further assumed that the core is homogeneous so that each fuel rod has an identical exposure history. ~~It is assumed that~~ <sup>that</sup> cladding rupture would occur over the temperature range from about 780° to 1100°C, and the entire fission product noble gas inventory in the fuel gap would be released. All other fission products in the fuel gap, which may be present in a condensed phase, or as vapor in equilibrium with a condensed phase, will not be released as quickly as noble gases until the temperature is further increased. According to a model calculation,(7) portions of the fuel may start to melt before the cladding is totally destroyed.

### 3.3 Isotopic Distribution in Fuel Gap

Diffusion equations predict that the fractional release of radioactive isotopes from the fuel to the plenum and void spaces should be inversely proportional to the square root of the decay constant for isotope reaching production-decay equilibrium.(10,11) This prediction has been substantiated by experimental data reported by several investigators.(12-17) A comparison of isotopic distributions in the total fuel inventory and the predicted distribution for some major fission products has been shown in Table 3. Thus, by measuring the ratios of fission product activities in either the gas or water samples, the source of fission product release may be semi-quantitatively determined (see more discussion in Section 4).

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\* The fission product release pattern was found to be mostly "recoil."

### 3.4 Anticipated Chemical Behavior of Iodine and Coolant Chemistry Under Accident Conditions

The results of measurements of Three Mile Island-2 (TMI-2) (18,19) indicate that the airborne radioiodine release was much lower when compared to the noble gas activity release (by a factor of  $\sim 10^4$ ). Extensive investigations at the Oak Ridge National Laboratory (ORNL) on the nature and quantity of fission product release from the over-heated fuel have concluded that cesium iodide CsI (B.P. = 1280°C) is the primary volatile species released from the fuel at elevated temperatures. (19) The behavior of iodine under loss-of-coolant accident (LOCA) conditions has been evaluated by Lin (21) and Campbell et al. (22)

For iodine at a concentration of a few ppm in aqueous solutions, the redox reactions should be more predictable and formations of anomalous or organic species should be much smaller than that at very low concentrations as generally assumed for radioiodine release. If iodine is released as CsI, it should stay in water as the  $I^-$  ion in a slightly basic solution (mainly due to Cs ions which may be released as elemental Cs or Cs oxides in addition to CsI). Air oxidation (23) or radiation-induced oxidation of  $I^-$  to  $I_2$  (24) is not very likely to occur in a basic solution. In addition to the reducing nature of zirconium and iron metals in the core, the production of hydrogen from Zr-steam reactions should make the chemistry environment in the primary system favorable to reducing reactions for iodine.

There are three known volatile forms of iodine,  $I_2$ , HIO, and organic iodine. The formation of  $I_2$  from  $I^-$  is not very likely in basic solutions. The existence of HIO has never been chemically identified due to its low stable concentration. The airborne species called HIO is one which behaves differently from  $I_2$  and organic iodine determined by using the iodine species sampling method developed by Keller, et al. (25) However, some convincing evidence has been given by Lin (26) that HIO, a product of  $I_2$  hydrolysis, is the second volatile inorganic species in the gas phase when  $I_2$  was initially added to water in equilibrium partitioning studies. The partition coefficient increases with decreasing iodine concentration; at very low iodine concentrations, the total iodine partition coefficients have been determined to be  $\sim 8000$  at 21°C and  $\sim 1600$  at 72°C. (26) It must be pointed out that since both  $I_2$  and HIO are very reactive species, any reducing impurities in water or on construction material surfaces would reduce  $I_2$  or HIO to  $I^-$  and significantly reduce the airborne iodine concentration.



The mechanisms of converting inorganic iodine to organic iodine, which is generally observed in gas<sup>air</sup> phase at very low concentrations, are largely unknown. However, at least more than a stoichiometric amount of organic species (or carbon-containing compounds) should be readily available for reaction with iodine. As such organic species are limited, the results of several experiments (27) indicate that the yield of organic iodine decreases with increasing iodine concentration in the gas phase. Less than 0.1% conversion is expected when the airborne iodine concentration is 1 g/m<sup>3</sup> or larger. (27) The total iodine concentration could be ~3 g/m<sup>3</sup> in the containment free air space if all iodine is assumed to become airborne. It is also important to realize that the organic iodine, e.g., CH<sub>3</sub>I is readily hydrolyzed in water (28) and basic solutions (29) at higher temperatures. The half-time of hydrolysis is ~20 min in water at 100°C and ~3 sec at 200°C, based on Heppollette and Robertson's data. (28)

Thus, the very low release of iodine activities to the atmosphere in the TMI-2 accident can be explained in terms of the nature of iodine released from the fuel and the subsequent stabilization in water. Water plays an important role in preventing iodine from release to the atmosphere. In the present procedure, all the iodine activities are assumed to stay in water, and the airborne activities are dominated by the noble gas fission products.

The chemistry in the primary coolant may be significantly changed under accident conditions. Mainly due to the release of cesium, the water pH may increase to ~10.5 (21) and the water conductivity may increase from ~10 µS/cm (torus water quality specification) to as high as ~170 µS/cm.

#### 4.0 DISCUSSION AND SUGGESTIONS FOR FUTURE WORK

It is evident that the uncertainty of gas release fractions for iodine and cesium are too large for an accurate calculation of the extent of core damage. While additional experimental work in fuel gap measurements is apparently needed, the lower limit release fraction for iodine<sup>in water</sup> may be re-evaluated by examining the iodine spiking release data from defective fuel rods following normal operation shutdowns.

Although the I-131 spiking data has been well documented previously (3), the analytical model may be refined to reflect more recent experimental data. The maximum spiking release of I-131 estimated by Pasadag (4), based on pre-1973 data, is too high, particularly when the improved fuels which are currently used in most of the operating BWRs are considered.

The accuracy of core damage estimation may be significantly improved by measuring more than iodine, cesium, and noble gas activities. Some less volatile but easy to measure isotopes of Sr, Ba, La, and Ru may be determined in the water sample. More work, however, is needed to establish the release fractions as well as the baseline (shutdown spiking) concentrations for those isotopes.

As mentioned in Section 3.3, it is possible to determine the source of fission product release by measuring the activity ratios of noble gases or iodine isotopes. It must be cautioned, however, each isotope should be accurately measured. Particular care must be exercised when the Xe-133 activity is determined in a mixture of other fission products with high concentration because of its low gamma ray energy (81 keV). Additional work is required to perfect this procedure.

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TABLE 1  
CORE INVENTORY OF MAJOR FISSION PRODUCTS IN A  
REFERENCE PLANT OPERATED AT 3651 MWt FOR THREE YEARS

CHEMICAL GROUP	ISOTOPE*	HALF-LIFE	INVENTORY** 10 <sup>6</sup> Ci	MAJOR GAMMA RAY ENERGY (INTENSITY)
				KeV ( $\gamma/d$ )
Noble gases	Kr-85m	4.48h	24.6	151(0.755)
	Kr-85	10.72y	1.1	514(0.0043)
	Kr-87	76. m	47.1	403(0.494)
	Kr-88	2.84h	66.8	196(0.203), 1530(0.109)
	Xe-133	5.25d	202.	81(0.371)
	Xe-135	9.09h	26.1	250(0.906)
Halogens	I-131	8.04d	96.	364(0.824)
	I-132	2.29h	140	668(0.99), 773(0.762)
	I-133	20.8 h	201	530(0.87)
	I-134	52.6 m	221	847(0.954), 824(0.653)
	I-135	6.59h	189	1132(0.231), 1260(0.293)
Alkali Metals	Cs-134	2.06y	19.6	605(0.98), 796(0.88)
	Cs-137	30.17y	12.1	662(0.85)
	Cs-138	32.2 m	178.	463(0.267), 1436(0.75)
				228(0.88)
Tellurium Group	Te-132	78. h	138	740(0.138)
				497(0.9)
Noble Metals	Mo-99	66.02h	183	750(0.24)
	Ru-103	39.4 d	155	1385(0.9)
Alkaline Earths	Sr-91	9.52h	115	537(0.238)
	Sr-92	2.71h	123	934(0.137)
	Ba-140	12.8 d	173	487(0.453), 1597(0.953)
				145(0.49)
Rare Earths	Y-92	58.6 d	118	134(0.108)
	La-140	40.2 h	184	724(0.435), 757(0.543)
	Ce-141	32.5 d	161	743(0.933)
	Ce-144	284.4 d	129	
Refractories	Zr-95	46. d	161	
	Zr-97	16.8 h	166	

\*Only the representative isotopes which have relatively large inventory and considered to be easy to measure are listed here.

\*\*At the time of reactor shutdown.

TABLE 2  
FISSION PRODUCT CONCENTRATIONS IN REACTOR WATER  
AND DRYWELL GAS SPACE DURING REACTOR SHUTDOWN UNDER NORMAL CONDITIONS

ISOTOPE	REACTOR WATER, $\mu\text{Ci/g}$		DRYWELL GAS ( $\mu\text{Ci/cc}$ )	
	UPPER LIMIT	NOMINAL	UPPER LIMIT	NOMINAL
I-131	29	0.7	—	—
Cs-137	0.3*	0.03**	—	—
Xe-133	—	—	$10^{-4}$ *	$10^{-5}$ **
Kr-85	—	—	$4 \times 10^{-5}$ *	$4 \times 10^{-6}$ **

\* Observed experimentally, in an operating BWR-3 with MK I containment, data obtained from GE unpublished document.

\*\* Assuming 10% of the upper limit values



TABLE 3  
RATIOS OF ISOTOPES IN CORE INVENTORY AND FUEL GAP

<u>ISOTOPE</u>	<u>HALF-LIFE</u>	<u>ACTIVITY* RATIO IN CORE INVENTORY</u>	<u>ACTIVITY RATIO* IN FUEL GAP</u>
Kr-87	76 m	0.233	0.0234
Kr-88	2.84h	0.33	0.0495
Kr-85m	4.48h	0.122	0.023
Xe-133	5.25d	1.0*	1.0*
I-134	52.6 m	2.3	0.155
I-132	2.28h	1.46	0.127
I-135	6.59h	1.97	0.364
I-133	20.8 h	2.09	0.685
I-131	8.04d	1.0*	1.0*

---

\*Ratio =  $\frac{\text{noble gas isotope concentration}}{\text{Xe-133 concentration}}$  for noble gases

"  $\frac{\text{Iodine isotope concentration}}{\text{I-131 concentration}}$  for iodines

TABLE 4  
PLANT PARAMETERS (REF. 2)

PLANT	REACTOR TYPE/CONTAINMENT DESIGN	RATED POWER (MWt)	PRIMARY COOLANT*		CONTAINMENT GAS*	
			REACTOR WATER MASS (10 <sup>8</sup> g)	SUPPRESSION POOL WATER (10 <sup>8</sup> g)	DRYWELL GAS VOL. (10 <sup>8</sup> cc)	TORUS/CONTAINMENT GAS VOLUME (10 <sup>8</sup> cc)
Standard	BWR 6/III	3579	2.46	3.67	7.77	32.5
Brunswick-1/2	BWR 4/I	2436	2.14	2.48	4.65	3.46
Chinshan-1/2	BWR 4/I	1775	1.76	1.93	3.68	2.69
Cofrentes	BWR 6/III	2894	2.04	3.14	6.91	32.43
Cooper	BWR 4/I	2380	2.00	2.48	3.75	3.03
Dresden-2/3	BWR 3/I	2527	2.61	3.18	4.48	3.30
Duane Arnold	BWR 4/I	1593	1.45	1.67	2.67	2.67
Fermi-2	BWR 4/I	3293	2.77	3.23	4.64	3.71
Fitzpatrick	BWR 4/I	2436	2.14	3.00	4.37	3.20
Hanford-2	BWR 5/II	3323	2.74	3.17	5.75	4.08
Hatch-1	BWR 4/I	2436	2.00	2.47	4.07	3.20
Hatch-2	BWR 4/I	2436	2.00	2.47	4.12	3.11
Hope Creek-1/2	BWR 4/I	3293	2.93	3.34	4.79	3.78
Kuo sheng-1/2	BWR 6/III	2894	2.04	3.74	6.74	40.50
Limerick-1/2	BWR 4/II	3293	2.93	3.63	6.66	4.23
Millstone-1	BWR 3/I	2011	2.05	2.78	4.16	3.06
Monticello	BWR 3/I	1670	1.75	1.93	3.80	2.76
NPP-1	BWR 2/I	1850	2.17	2.34	5.10	3.33
Oyster Creek	BWR 2/I	1933	2.05	2.32	5.10	3.58
Peach Bottom-2/3	BWR 4/I	3293	2.67	3.48	4.98	3.62
Pilgrim	BWR 3/I	1990	2.05	2.38	4.16	3.18
Susquehanna-1/2	BWR 4/II	3293	2.92	3.60	6.79	4.36
Vermont Yankee	BWR 4/I	1593	1.77	1.93	3.79	3.18

\*Total Primary Coolant Mass = Reactor Water + Suppression Pool Water

Total Containment Gas Volume = Drywell Gas + Torus (or Primary Containment in MKIII) gas

TABLE 5. BEST-ESTIMATE FISSION PRODUCT RELEASE FRACTIONS(Ref. 7,8)

	Gap Release <sup>a</sup>			Meltdown Release			Oxidation Release			Vaporization Release		
	Nominal	Lower Limit	Upper Limit	Nominal	Lower Limit	Upper Limit	Nominal	Lower Limit	Upper Limit	Nominal	Lower Limit	Upper Limit
Noble Gases (Xe, Kr)	0.030	0.010	0.12	0.873	0.485	0.970	0.087	0.078	0.097	0.010	0.010	0.010
Halogens (I, Br)	0.017	0.001	0.20	0.883	0.492	0.983	0.088	0.078	0.098	0.010	0.010	0.010
Alkali Metals (Cs, Rb)	0.050	0.004	0.30	0.760	0.380	0.855	---	---	---	0.010	0.010	0.010
Tellurium Group (Te, Se, Sn)	0.0001	$3 \times 10^{-7}$	0.04	0.150	0.05	0.250	0.310	0.340	0.680	0.340	0.340	0.340
Noble Metals (Ru,Rh,Pd,Mo,Tc)	---	---	---	0.030	0.01	0.10	0.873	0.776	0.970	0.003	0.001	0.024
Alkaline Earths (Sr, Ba)	$1 \times 10^{-6}$	$3 \times 10^{-9}$	0.0004	0.100	0.02	0.20	---	---	---	0.009	0.002	0.045
Rare Earths (Y,La,Ce,Nd,Pr, Eu,Pm,Sm,Np,Pu)	---	---	---	0.003	0.001	0.01	---	---	---	0.010	0.002	0.050
Refractories (Zr, Hf)	---	---	---	0.003	0.001	0.01	---	---	---	---	---	---

<sup>a</sup>Notes: Recent values of the gap release measured at Oak Ridge National Laboratory (Ref 30) are significantly lower. For the stable and long-lived members of the chemical groups they report 0.0127 for the noble gases, 0.00033 for the halogens, and 0.00025 for the alkali metals.



FIGURE 1. Relationship between I-131 Concentration in the Primary Coolant (Reactor Water + Pool Water) and the Extent of Core Damage in Reference Plant

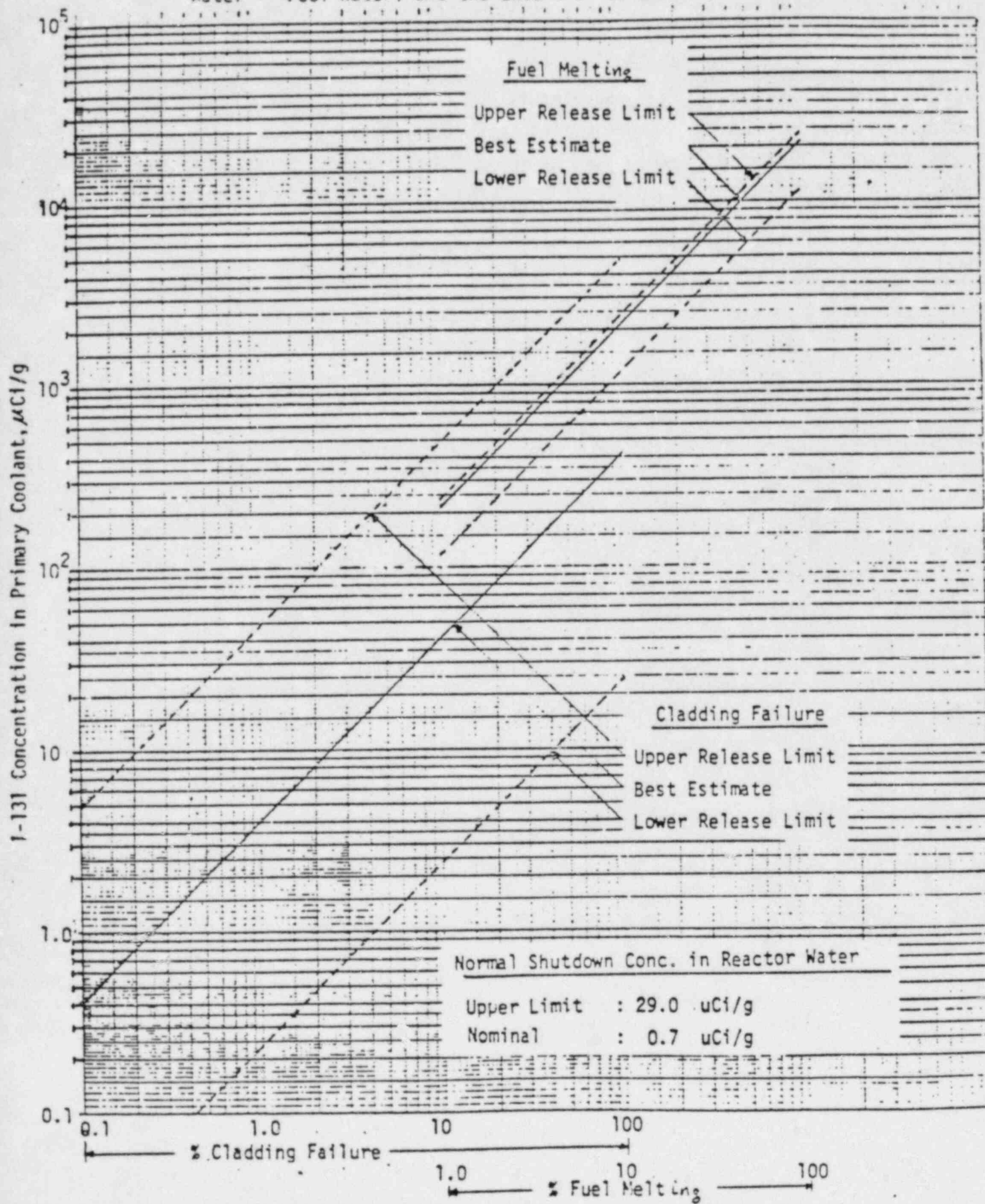


FIGURE 2. Relationship between Cs-137 Concentration in the Primary Coolant (Reactor Water + Pool Water) and the Extent of Core Damage in Reference Plant.

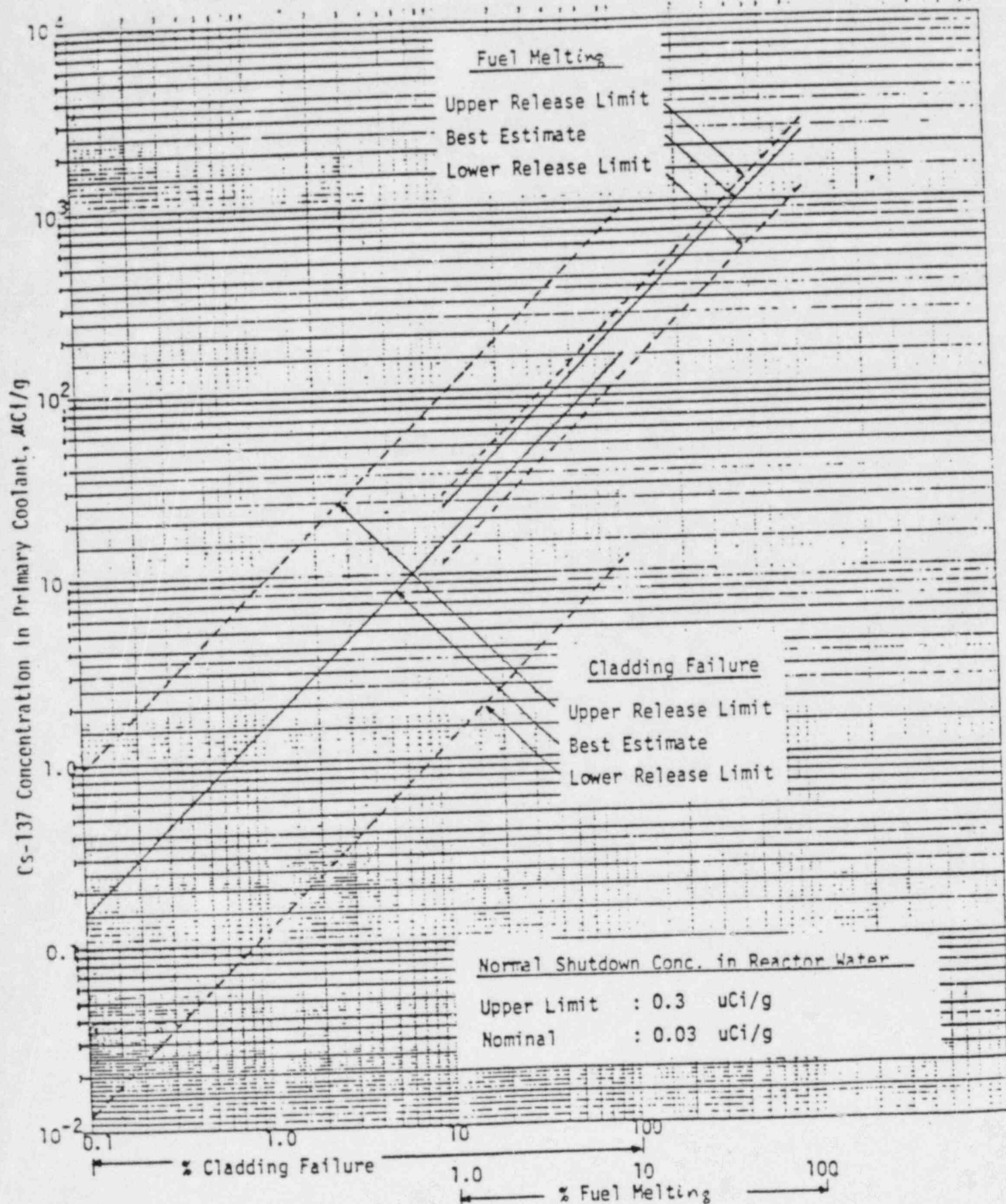


FIGURE 3. Relationship between Xe-133 Concentration in the Containment Gas (Drywell + Torus Gas) and the Extent of Core Damage in Reference Plant

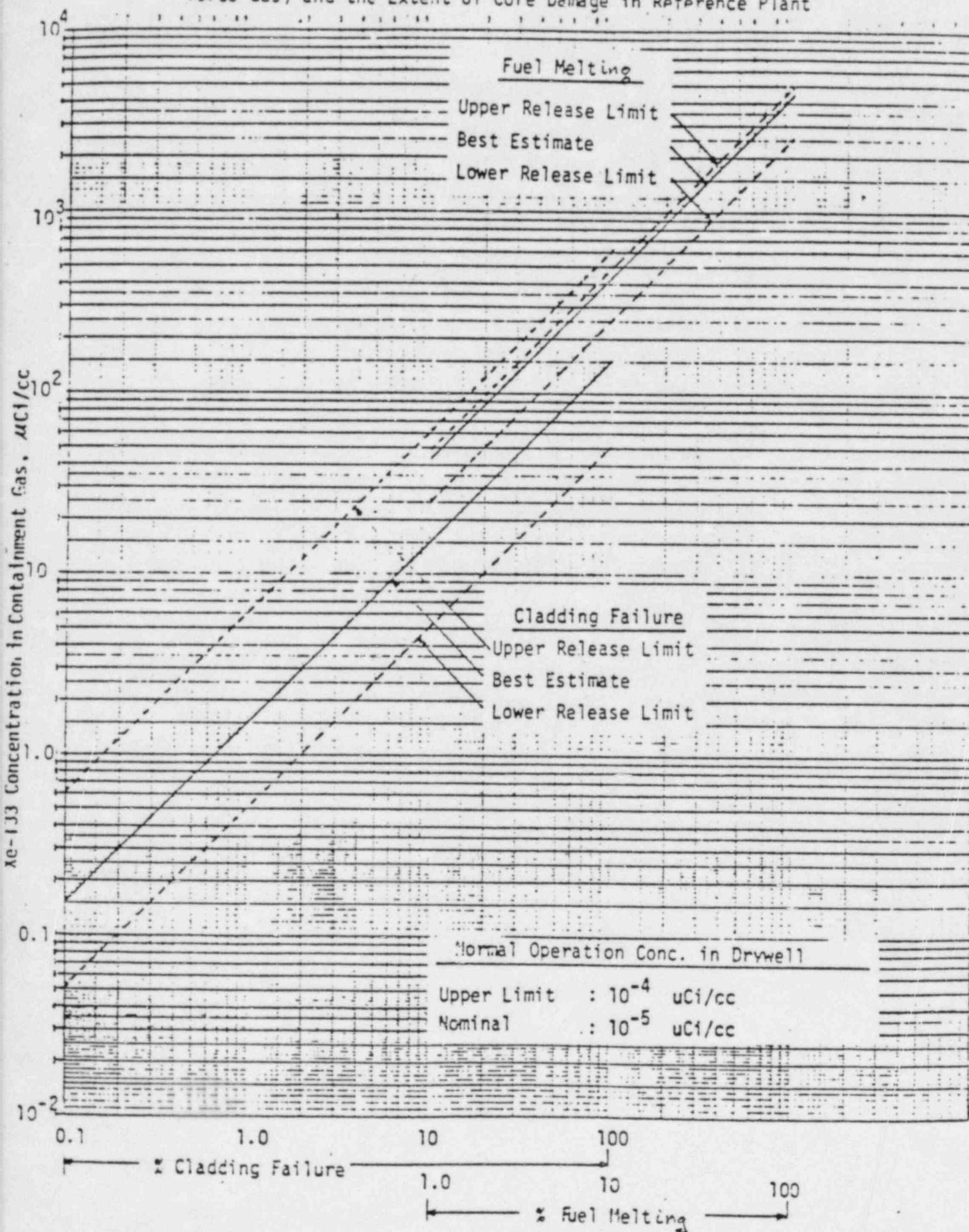
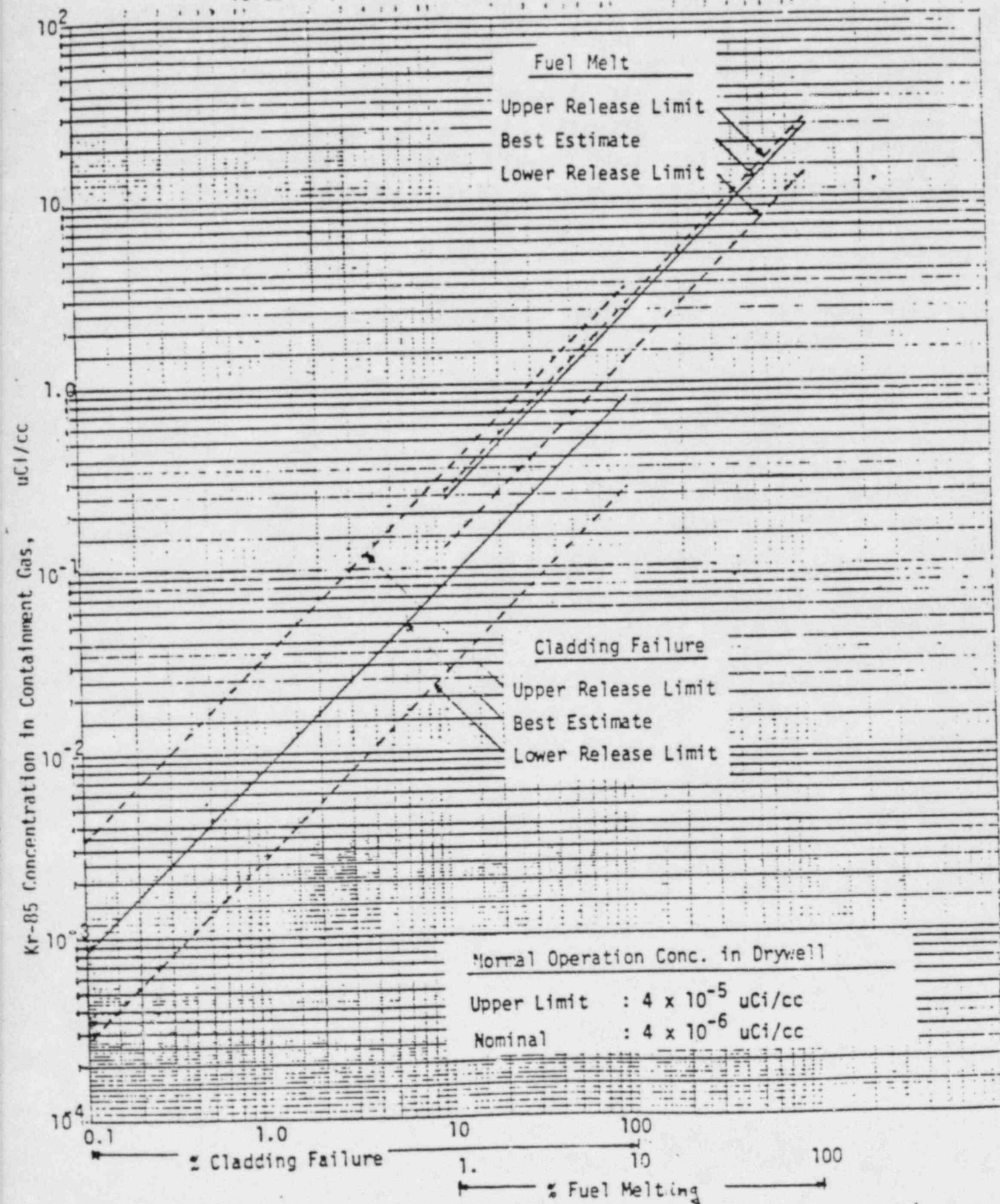




FIGURE 4. Relationship between Kr-85 Concentration in the Containment Gas (Drywell + Torus Gas) and the Extent of Core Damage in Reference Plant.





EVALUATION OF GE AND SEC CHEMICAL PROCEDURES FOR POSTACCIDENT  
ANALYSIS OF REACTOR COOLANT SAMPLES

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for

The Nuclear Regulatory Commission

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# EVALUATION OF SEC AND GE ANALYTICAL CHEMICAL PROCEDURES FOR POSTACCIDENT ANALYSIS OF REACTOR COOLANT SAMPLES

## 1.0 SUMMARY AND CONCLUSIONS

### Summary

As a result of the Three Mile Island Unit 2 incident, the Nuclear Regulatory Commission (NRC) required licensees of nuclear power plants to implement, by January 1, 1982, the capability to collect and analyze reactor coolant samples following an accident. A number of licensees have proposed the use of postaccident sampling and analysis systems supplied by Sentry Equipment Corporation (SEC) or General Electric Company (GE).

Under a technical assistance contract to the NRC, Exxon Nuclear Idaho Company, Inc. (ENICO) evaluated the sample collection and chemical analysis procedures associated with the two systems. The objective of the evaluation was to determine applicable procedures and to identify the most appropriate method. The study involved a review of the NRC requirements, the establishment of review criteria, and the evaluation of the proposed analysis methods and test data against the requirements and evaluation criteria.

The most appropriate methods selected by ENICO for the required chemical analysis of postaccident reactor coolant samples are shown below. Detailed descriptions, advantages, disadvantages, and/or deficiencies of the selected procedures are summarized in section 4.2. Also in section 4.2 is the same information for other procedures proposed by SEC and GE. It is worthy of note that a number of the other procedures proposed are also appropriate, as indicated; included below are only those deemed most appropriate.

1. Boron - Fluoroborate Selective Ion Electrode
2. Chloride - Ion Chromatography
3. Dissolved Hydrogen - Gas Chromatography
4. Dissolved Oxygen - Oxygen Probe
5. Conductivity - Conductivity Cell
6. pH - pH Probe

Although ENICO did not conduct tests to evaluate the suitability of any of the procedures; in ENICO's judgement, the laboratory tests performed by SEC and GE are sufficient to provide a high degree of assurance of the suitability of the selected and the noted alternate procedures for analysis of accident reactor coolant samples.

For suitability testing of additional analytical procedures, ENICO recommends that standard test matrix samples be utilized to demonstrate their acceptability. Standard matrix solutions similar to test solutions employed by SEC are recommended as they contain the most significant core degradation products in concentrations equal to or greater than those projected from an accident with a Regulatory Guide 1.3 or 1.4 source term. Test solutions used by SEC consider the effects of chemicals which might be added to the reactor coolant following an accident.

For chemical procedures that are to be used for the analysis of undiluted reactor coolant samples, the following standard test matrix containing nonradioactive species is recommended.

<u>Constituent</u>	<u>Concentration (ppm)</u>
I <sup>-</sup>	40
Cs <sup>+</sup>	250
Ba <sup>+2</sup>	10
La <sup>+3</sup>	5
Ce <sup>+4</sup>	5
Cl <sup>-</sup>	10
B	2000
Li <sup>+</sup>	2
NO <sub>3</sub> <sup>+</sup> -	150
NH <sub>4</sub> <sup>+</sup>	5
K <sup>+</sup>	20



For chemical procedures that are to be used for analysis of diluted reactor coolant samples, testing should be performed with a standard matrix diluted by a volume equal to the dilution to be used in the procedure to be tested. It is also recommended that the procedures and associated instrumentation be tested in an induced gamma radiation field which will yield a total absorbed dose of  $10^4$  rads per gram of reactor coolant.

*also for diluted samples?*

## 2.0 BACKGROUND

From studies of the incident at Three Mile Island Unit 2 (TMI-2), the need for improvement of the capability of licensees of nuclear power plants to determine plant conditions in a more timely manner was identified. Subsequently, the NRC issued,<sup>1-5</sup> for implementation by the licensees, specific requirements in several areas for improvement of the capability. In addition to the development and implementation of the upgraded capabilities, the requirements specified that the licensees should prepare and have available documentation of the capabilities for a post-implementation evaluation of compliance.

Exxon Nuclear Idaho Company, Inc. (ENICO) was contracted by the NRC's Division of Licensing to provide technical assistance for the evaluation of the post-implementation documentation in a number of areas. One area was "Postaccident Sampling Capability", Item II.B.3 of NUREG-0737.<sup>6</sup> It pertains to the ability of the licensees to obtain reactor coolant and containment atmosphere samples and to analyze the samples for selected radionuclides and chemical species under accident conditions.

In order to facilitate the evaluation of the post-implementation documentation, ENICO was requested<sup>7</sup> to evaluate the applicability of the chemical and radiological analysis capabilities associated with two postaccident sampling systems proposed<sup>8</sup> for use by several power plants (Table 1). The two system vendors are Sentry Equipment Corporation (SEC) and General Electric Company (GE).

The initial plan<sup>9</sup> called for ENICO to evaluate the SEC system only and to perform the evaluation in two phases. As it was believed that current technology was suitable for radiological analysis, the two phases were to be a brief summary report on the chemical analysis procedures and a more detailed report on both the chemical and radiological analysis procedures. However, due to manpower shortage at ENICO and an NRC request to incorporate the GE system into the evaluation, an alternate approach was taken. The alternate approach is to: 1) evaluate and prepare a detailed report of the chemical procedures for both the SEC

TABLE 1  
STATIONS WITH PROPOSED USAGE OF SEC  
AND GE POSTACCIDENT SAMPLING SYSTEM

---

<u>GENERAL ELECTRIC</u>	<u>SENTRY</u>
Brunswick 1/2	Dresden 1/2
Nine Mile Point 1	Quad Cities 1/2
Fitzpatrick	Zion 1/2
Oyster Creek	Browns Ferry 1/2/3
Pilgrim 1	Salem 1
Duane Arnold	Kewaunee
Monticello	Indian Point 2
Peach Bottom 2/3	Surry 1/2
	North Anna 1/2
	Palisades

---

and GE system and 2) evaluate and document the radiochemical analysis procedures associated with both sampling systems later. The detailed evaluation of the chemical analysis procedures is the topic of this report, which is limited to the analysis of reactor coolant samples.

### 3.0 REQUIREMENTS AND EVALUATION CRITERIA FOR THE CHEMICAL ANALYSIS OF REACTOR COOLANT SAMPLES

#### 3.1 Requirements

To provide information for the assessment of core integrity, shutdown neutron adsorber concentration, and reactor coolant corrosion potential; licensees or applicants for licenses of nuclear power plants are required to establish a capability for the timely collection and chemical analysis of reactor coolant samples under accident conditions. Per NUREG-0737 the required chemical analyses for reactor coolant samples are boron (PWR only), chloride, and either total dissolved gases or hydrogen; the measurement of dissolved oxygen is recommended in NUREG-0737 but not required. Per Regulatory Guide 1.97<sup>10</sup> the measurement of dissolved oxygen, pH, and boron in all plants is required. NUREG-0737 also specified that the analysis could be performed by employing a combination of pressurized/unpressurized, diluted/undiluted grab samples or inline monitoring methods. However, for analyses performed by inline methods, a capability to collect backup grab samples and to provide procedures for their analysis is required. In all cases, the collection of grab samples for analysis and the inline analysis must be able to be performed with or without the operation of an auxiliary reactor coolant system, e.g., letdown.

With the exception of the chloride analysis, the time allotted for sampling and on site analysis of the samples is three (3) hours or less. Time allotted for the chloride analysis, which can be performed offsite, depends on the type of reactor coolant water and the number of barriers between the reactor coolant water and the primary containment system. For plants with seawater or brackish reactor coolant water or with a single-barrier, primary coolant containment system, chloride analyses are required within twenty-four (24) hours. For other plants the chloride analysis is required within ninety-six (96) hours.

In addition, the licensees or applicants are required to consider the radiological hazards associated with the sample collection and analyses. The assumptions of a Regulatory Guide 1.3<sup>11</sup> or 1.4<sup>12</sup> source term and radiation exposure limits<sup>13</sup> of five (5) rem to the whole body



or seventy-five (75) rem to the extremities of any individual are to be used in system design and selection of chemical analysis methods.

Last, the licensees or applicants are to provide provisions for restricting background radiation levels in the chemical analysis facility and for insuring the validity and accuracy of the sample analyses. These provisions include such things as sample shielding, adequate ventilation air and filtration, proper sample disposal, sample line purging, reduction of plate-out in sample lines, etc.

The requirements for post accident chemical analysis of reactor coolant samples are presented in Table 2.

### 3.2 Evaluation Criteria

The objective of the present evaluation of potential methods for the chemical analysis of reactor coolant samples under postulated accident conditions is to determine applicable procedures and to identify the most appropriate procedure for each of the required analyses.

Many factors were considered in the evaluation of the proposed methods. Obviously, compliance with the requirements of sensitivity, accuracy, range, analysis time, radiological dose limitations, and sample collection methods were evaluated. This included comparisons of the advantages (lower radiological exposures) and disadvantages (reduced sensitivity and accuracy) of utilizing diluted or very small reactor coolant samples versus larger undiluted reactor coolant samples. It also involved an estimation of the significance of chemical and radiologically-induced interferences. Other factors which were considered are the complexity of the procedures and the applicability of the technique to both accident and normal condition usage.

Due to the unavailability of information in a number of instances, factors not considered were specific design features of the two sampling systems. Examples are sampling locations, shielding, sample line purging, sample validity, ventilation, etc.

TABLE 2

SUMMARY OF REQUIREMENTS FOR POSTACCIDENT CHEMICAL ANALYSIS  
OF REACTOR COOLANT SAMPLES

Analysis Capability Units	Boron (ppm)	Chloride (ppm)	Total scc/kg	Dissolved Gases <sup>(1)</sup> Hydrogen scc/kg
<u>Requirement</u>				
Range	0-1000 <sup>(3)</sup> 0-6000 <sup>(4)</sup>	0-20	0-2000	0-2000
Accuracy <sup>(6)</sup> Percent Units	+5 if >1000 +50 if <1000	+10 if >0.5 +0.05 if <0.5	+10 if >50 +5 if <50	+10 if >50 +5 if <50
Sampling Method <sup>(7)</sup> Inline Grab Sample	Optional Required	Optional Required	Optional Required	Optional Required
Analysis Location Onsite Offsite	Required Optional	Optional <sup>(8)</sup> Optional	Required Optional	Required Optional
Sample Collection and Analysis Time (hours)	3	24 <sup>(8)</sup> 96	3	3
Radiological Exposure Limits	(9)	(9)	(9)	(9)

## Notes:

- 1) A pressurized reactor coolant sample is not required if the dissolved gases can be determined with an unpressurized sample.
- 2) The measurement of conductivity is not required in NUREG-0737 or Reg. Guide 1.97, Revision 2; however, methods to measure conductivity are proposed by SEC and GE. Accordingly, the measurement of conductivity has been included in this study.

TABLE 2 (Continued)

SUMMARY OF REQUIREMENTS FOR POSTACCIDENT CHEMICAL ANALYSIS  
OF REACTOR COOLANT SAMPLES

Analysis Capability Units	Oxygen (ppm)	pH (pH units)	Conductivity(2) μS/cm
<u>Requirement</u>			
Range	0-20	1-13	1-1000(5)
Accuracy(6) Percent Units	+10 if >0.5 +0.05 if <0.5	Not applicable + 0.3 if 5 >pH<9 + 0.5 if 5 <pH>9	+ 20 Not Applicable
Sampling Method(7) Inline Grab Sample	Optional Required	Optional Required	Optional Required
Analysis Location Onsite Offsite	Required Optional	Required Optional	Optional Required Optional
Sample Collection and Analysis Time (hours)	3	3	3
Radiological Exposure Limits	(9)	(9)	(9)

Notes: (Continued)

3) Boiling Water Reactors

4) Pressurized Water Reactors

5) The required range for measurement of conductivity was taken  
from reference 14.

- 6) The designation of percent accuracy as  $\pm 5$  if  $>1000$  indicates the required accuracy is  $\pm 5$  percent if the required measurement is greater than 1000 units. The designation of units accuracy as  $\pm 50$  if  $<1000$  indicates that the required accuracy is  $\pm 50$  measurement units if the required measurement is less than 1000 units. The required accuracies were taken from reference 7.
- 7) Analysis may be performed with either grab sampling or inline monitoring methods. However, for inline analysis methods the capability to collect and analyze backup grab samples is required. The capability to collect and analyze at least one sample per day for seven (7) days following the onset of the accident and at least one sample per week until the accident no longer exists is also required.
- 8) For nuclear power plants which utilize seawater or brackish water as a source of reactor coolant water or which have a single-barrier, reactor coolant containment system, the chloride analysis must be performed within 24 hours; for other nuclear power plants, the required chloride analysis time is 96 hours. The chloride analysis may be performed offsite.
- 9) The radiation exposures to any individual involved in the collection and analysis of reactor coolant samples under accident conditions may not exceed 5 rem to the whole body or 75 rem to the extremities.



The evaluation criteria used in the study were:

1. Analysis Time - As the time required for sample collection was not specified by SEC or GE, it was assumed sample collection could be performed within one hour. Accordingly, an upper limit of two hours was allotted for sample analysis; chemical analysis procedures which required two hours or less for analysis were satisfactory.
2. Sensitivity, Range, Accuracy - Chemical procedures which encompassed the entire measurement range with the required accuracy were considered adequate. To cover the full range of measurement as required, sample dilution methods were considered satisfactory.
3. Radiological Exposure Limits, Sample Size - Radiological exposure to any individual is limited to 5 rem to the whole body and 75 rem to the extremities during the collection and analysis of reactor coolant samples. Under the assumption of Regulatory Guides 1.3 or 1.4 releases of fission products to the reactor coolant, calculated<sup>14</sup> dose rates from reactor coolant samples are nominally 140 R/h/g at 10 cm with a one hour decay. Maintenance of radiological exposures within acceptable limits requires the usage of safety factors such as: shielding, distance, exposure time, sample dilution, very small undiluted sample, and/or inline monitoring.

The chemical analysis procedures, including dissolved gases, proposed by GE and SEC make use of inline monitoring, very small undiluted samples, and remote dilutions of the initial reactor coolant sample. The diluted reactor coolant samples are used for subsequent "hands-on" analysis. With the exception of the subsequent hands-on analysis, this study did not evaluate the radiological hazards associated with the above methods. It was assumed that adequate shielding and/or remote operation would minimize radiological exposures to personnel. In regard to the subsequent analysis of diluted reactor coolant samples; only estimates of radiological exposures could be made as they are

not only a function of the amount of reactor coolant in the sample, but also depend on the techniques of the analyst and the design of the analytical facility.

The method which was established to lessen exposure is to limit the amount of reactor coolant in the sample taken for analysis to 0.1 ml. The basis for this criterion is the knowledge that doses to the extremities will be the limiting factor for hands on chemical procedures. For example, calculated exposures to the extremities, using the above value of 140 R/h/g of reactor coolant at 10 cm, will exceed the 75 rem limit by a factor of almost two for a two hour exposure to a 1. ml sample. It would require approximately five hours of continuous exposure to exceed the dose limits for a 0.1 ml sample. It is realized that the limitation to a 0.1 ml reactor coolant sample size is conservative as exposure time will, in reality, be less than two hours and techniques to reduce the exposures will probably be employed. However, to allow a sufficient margin of safety, a 0.1 ml reactor coolant sample was considered an acceptable size sample in this study. In a final evaluation of acceptable sample sizes, larger samples may be permissible, but all factors must be considered.

4. Complexity, Routine/Accident Usage - Two other criteria which were used are the complexity of performance of the procedures and the applicability of the procedures to both routine and accident condition usage. The procedures were assigned low, medium, or high levels of complexity based primarily on the number and nature of manipulations involved in the procedure. Procedures with applicability to both routine and accident conditions were considered more satisfactory than procedures applicable to accident conditions as the use of nonroutine procedures can create confusion and cause errors under accident conditions.
5. Chemical and Radiologically-Induced Interferences - The release of large quantities of both radioactive and nonradioactive fission products will result in high radiation fields and chemical-

ly significant levels of various ionic species in the reactor coolant. Both the radiation and ionic species can interfere with the accuracy of chemical procedures used to analyze reactor coolant samples. In the selection of an appropriate chemical analysis method, these matrix effects should be considered. In this study a chemical procedure was considered unsatisfactory if the interferences cause the accuracy of the procedure to exceed the required limits. The evaluation included a review of available test data and professional judgements based on past experiences of personnel involved in the review.

#### 4.0 EVALUATION OF CHEMICAL PROCUDURES FOR ANALYSIS OF POSTACCIDENT REACTOR COOLANT SAMPLES

In the evaluation of the applicability of chemical procedures for analysis of postaccident reactor coolant samples, ENICO studied the chemistry of the procedures, compared their capabilities with NUREG-0737 requirements and the established evaluation criteria, and ranked the procedures in order of appropriateness. Some of the procedures are similar to ones used at the Idaho National Engineering Laboratory (INEL); this experience added to the data base.

Presented below in Section 4.1 is a summary of the sample collection and chemical analysis procedures proposed by SEC and GE and a general outline of the testing program conducted by SEC and GE. This is followed by a presentation of ENICO's evaluation of the procedures. Included are brief descriptions of the procedure methodology and the advantages and/or disadvantages of each procedure. Last, the overall evaluation of the individual procedures are summarized for a given type analysis.

##### 4.1 SEC and GE Sample Collection, Recommended Analysis Methodology and Chemical Procedure Evaluation Program

Methods for analysis of postaccident reactor coolant samples proposed by SEC<sup>15</sup> and GE<sup>16-19</sup> include inline monitoring and laboratory analysis of grab samples. For inline monitoring, sample streams are diverted either continuously or intermittently through inline sensors. For laboratory analysis, the reactor coolant grab samples are diluted inline before transfer to the laboratory or directly to an analytical instrument. Either diluted liquid or dissolved gas grab samples can be obtained. To obtain liquid samples, 1:100 dilutions of 0.1 ml reactor coolant samples are typically performed; larger initial dilutions or secondary dilutions of the initial dilution can also be performed. To obtain a dissolved gas grab sample; thirty (30) to seventy (70) milliliters of pressurized reactor coolant are isolated, the sample is depressurized, and the dissolved gases are purged into a gas holding chamber with an inert gas. One milliliter or larger aliquots of the diluted sample are analyzed following dilution with the inert gas to a known pressure.



The chemical procedures associated with the proposed methods are either conventional or modifications of conventional chemical analysis procedures. A summary of the methodology, including chemical analysis procedures, recommended by SEC and suggested by GE is presented in Table 3. Not included in Table 3 are other methods detailed by SEC and GE; this information is included in section 4.2.

TABLE 3  
SEC AND GE REACTOR COOLANT ANALYSIS METHODOLOGY

<u>ANALYSIS</u>	<u>SYSTEM VENDOR</u>	<u>SAMPLE TYPE</u>	<u>ANALYSIS METHOD</u>
Boron	SEC	Grab	Fluoroborate
	GE		Electrode
		Grab	Spectrophotometric (carminic acid)
Chloride	SEC	Inline, grab	Ion Chromatography
	GE		Turbidimetric
Dissolved Hydrogen	SEC	Inline, grab	Gas Chromatography
	GE	Grab	Gas Chromatography
Dissolved Oxygen	SEC	Inline	YSI Oxygen Analyzer
	GE	Grab	Gas Chromatography
pH	SEC	Inline	pH probe
	GE	Grab	pH paper
Conductivity	SEC	Inline	Conductivity Cell
	GE	Inline	Conductivity Cell

Chemical procedures recommended by SEC are the result of a development and testing program conducted by Nuclear Utility Services (NUS) for SEC. In the study the recommended methods and several other chemical analysis methods were evaluated in the laboratory to identify chemical interferences due to sample matrices, to determine operational characteristics of instrumentation, and to measure the sensitivities, ranges, and accuracies of methods. Employed in the study were simulated post-accident reactor coolant test samples. They contained, in addition to the chemical species of interest, high-yield, stable fission products and appropriate concentrations of chemical additives anticipated to be present in the reactor coolant following an accident. The study did not include actual measurements of possible effects of high radiation fields on the procedures; however, it did include the results of a survey of personnel with prior experience in the analysis of samples with high radiation fields and a literature review of effects of high irradiation on different materials.

Chemical procedures suggested by GE, except those coincidental to the SEC tested methods, are not the result of detailed laboratory testing. The only testing of the procedures is related to the effects of high irradiation of the samples. The suggested procedures were selected primarily on the basis of simplicity, stability and availability of reagents, minimum radiation exposure, and likelihood of causing contamination problems.<sup>18</sup>

#### 4.2 Chemical Procedure Descriptions, Advantages/Disadvantages and Evaluation Summaries

In the selection, recommendation, and/or suggestion of chemical procedures for analysis of postaccident reactor coolant, SEC and GE considered a total of twenty-seven (27) procedures. The chemical procedures considered by the two vendors are shown in Table 4; also noted in the table are known procedures in use at the INEL. As many of the procedures are similar or identical, they have been grouped together, as appropriate, in ENICO's evaluation of the procedures. Presented in order below are the evaluations of the boron, chloride, hydrogen, oxygen pH and conductivity measurement procedures.

TABLE 4

## CHEMICAL ANALYSIS PROCEDURES CONSIDERED BY SEC AND GE

CHEMICAL ANALYSIS	VENDOR	PROCEDURE
Boron	SEC	Fluoroborate selective ion electrode
	SEC	Curcumin Spectrophotometric
	SEC	Plasma Spectroscopy
	SEC	Boronmetry*
	SEC	Digi Chem Analyzer Mannitol Titration
	SEC, GE	Carminic acid Spectrophotometric
	SEC	Ion chromatography*
	SEC	Manual Mannitol Titration*
	GE	Conductivity of Boron Solutions
Chloride	SEC	Ion Chromatography*
	SEC	Selective Ion Electrode.
	SEC	Mecuric Nitrate Titration
	SEC, GE	Thiocyanate Spectrophotometric
	GE	Silver Chloride Colormetric
	GE	Conductivity of Chloride Solutions
Hydrogen	GE, SEC	Gas Chromatography
Oxygen	GE	Gas Chromatography
	SEC	YSI Oxygen Probe
pH	GE	pH Paper
	GE	Conductivity
	SEC	pH Probe*
Conductivity	SEC, GE	Conductivity Cell*

\* Indicates a procedure that is in use at the Idaho Chemical Processing Plant (ICPP) or the Loss of Fluid Test Facility (LOFT) at the INEL.

#### 4.2.1 Boron Analysis Procedures

4.2.1.1 Fluoroborate Selective Ion Electrode (FSIE). In the FSIE chemical analysis procedure, the boron content of a sample is determined by the measurement of the concentration of the tetrafluoroborate ion. In addition to the sensing electrode, which contains a membrane with a selective tetrafluoroborate ion exchanger, a single junction reference electrode (KCl/saturated AgCl) and a conventional millivolt meter with a relative millivolt mode are required.

The procedure requires precise laboratory techniques; care must be exercised to add the reagents to the standards or samples in sequence and to perform measurements at prescribed times. In the analysis procedure a standard and a sample are analyzed simultaneously. Initially, 1.0 ml of saturated sodium fluoride is added to 5.0 ml of the standard, and then 0.5 ml 10 N sulfuric acid is added (the sodium fluoride and sulfuric acid converts boric acid to the tetrafluoroborate ion). With the addition of the acid to the standard, a timer is started; five minutes later the same reagents are added to 5.0 ml of a previously diluted sample. At eight minutes the electrodes are inserted into the standard solution which is being stirred; at ten minutes the millivolt response is adjusted to correspond to a specific value on a pre-established calibration curve.

The millivolt response for the sample is recorded at fifteen minutes and related to the ppm boron from the calibration curve.

To minimize radiological hazards 1.0 ml samples and standards can be analyzed by the above procedure with the use of correspondingly less sodium fluoride and sulfuric acid. In addition, the analysis can be performed by using only 0.3 ml of the original 5.0 ml or 1.0 ml of sample taken for analysis. The analysis using 0.3 ml is performed statically in microdishes.

There are two types of calibration curves. One for the 5.0 ml and/or 1.0 ml samples analyzed by immersion of the electrodes into a stirring solution, and one for the 0.3 ml samples analyzed by immersion of the electrodes in the microdishes. The calibration curves are established using the same techniques employed for the samples; the calibration curves are valid only for the pair of electrodes used to establish them. Calibration curves are estimated to be valid for six months; however, frequent use of the electrodes shortens their life. Accordingly, routine checks of the calibration curves are recommended to maintain their currentness. Approximately a total of one hour is required, to generate new calibration curves for both large and small samples.



Numerous laboratory tests were carried out with simulated postaccident matrix samples to identify chemical interferences to the FSIE procedure. No sample matrix effects were observed when the procedure described above was followed.

The advantages of the procedure are its wide measurement range and accuracy, the small sample sizes required, the lack of chemical interferences, its adaptability to routine and accident condition usage, and the short analysis time required.

The main disadvantage of the procedure is its relative complexity, which will necessitate well-trained analysts and frequent usage of the procedure by the analysts in order to retain their familiarity with it. Another limitation of the procedure, under the assumption of a minimum initial sample dilution of 1:100, is the inability of the procedure to measure boron levels in highly radioactive reactor coolant below fifty ppm. However, in ENICO's opinion, this is not a serious limitation as under accident conditions the concentration of boron in the reactor coolant should be much higher than fifty ppm; and, if it isn't, confirmation that boron levels are fifty ppm or above is sufficient information to determine the need for subsequent corrective actions.

The FSIE analysis procedure has not been tested with high radiation field samples; however, ENICO does not believe irradiation associated with highly radioactive samples will significantly alter the applicability of the method.

4.2.1-2 Curcumin Spectrophotometric. The curcumin spectrophotometric boron method is based on the measurement of a red-colored product, rosocyanine, formed by the reaction of boron and curcumin. To perform the measurement the 1.0 ml diluted sample and standards, which are analyzed concurrently with the samples, are mixed with 4.0 ml of curcumin; evaporated to dryness; dissolved in 95 percent isopropyl alcohol to a total volume of 25 ml; and transferred to a 1.0 cm spectrophotometer cell. In the spectrophotometer, a Bausch and Lomb Spectronic 20 or equivalent, the percent transmittance of the sample and

standard are measured at 540 nm. A calibration chart is prepared from the standards, and the concentration of the boron in the sample is determined from the calibration chart.

The curcumin spectrophotometric procedure was laboratory tested by SEC/NUS. In addition to sample matrix effect studies using samples containing selected nonradioactive fission products and chemicals anticipated to be present after an accident, experiments were performed to optimize the precision, accuracy, and required analysis time.

The advantages of the procedure are its wide measurement range, its accuracy, the small sample size required, the lack of chemical interferences, its utility under accident and routine conditions, and its relative simplicity. The disadvantages of the procedure are the long analysis times required and the necessity to generate calibration curves at the same time sample analyses are performed. The latter is considered a disadvantage as a significant amount of time could be wasted if a satisfactory calibration can not be obtained the first time. Another limitation of the procedure is the inability to measure levels of boron levels in reactor water below twenty ppm. However, as noted above, ENICO does not consider this a major limitation as required corrective action can be made based on the knowledge of boron concentrations of twenty ppm or more. *below 1000 ppm*

The effects of high radiation fields on the procedure have not been determined. In ENICO's judgement, the accuracy or sensitivity of the procedure would not be compromised; but this needs to be confirmed before the procedure is used.

4.2.1.3 Plasma Spectroscopy. The analysis of boron by plasma spectroscopy is achieved by vaporization of the sample in a plasma jet and analysis of the atomic emission spectra which is generated. The boron resonance wavelength of either 249.7 or 249.8 nm is used. Readout of the unknown is compared to standards. Five milliliters of a diluted reactor coolant sample is required. One milliliter of the sample and associated radioactivity is completely vaporized and released; the other

four milliliters are collected in a waste container as condensed spray droplets. The required analysis time is fifteen to thirty minutes.

No specific laboratory testing details were provided; however, it was indicated that limited tests were performed on simulated reactor matrix solutions with satisfactory reproducibility and accuracy. The measurement range associated with the procedure also was not provided; however, a lower detection limit of less than 1 ppm boron is reported. With this sensitivity and appropriate sample dilution, it appears the measurement range would be sufficient to cover the measurement range required.

*measurement range*

The advantages of the procedure are its apparent simplicity, time required for analysis, and small sample sizes.

The disadvantages of the procedure are the lack of sufficient laboratory testing and the radioactivity releases associated with it. It is assumed that appropriate design modifications could be incorporated to circumvent this latter deficiency; but the design must include features to collect all the radioactive releases, not merely to contain them in a fumehood, as is done with the existing design. High radiation fields will not affect the applicability of the procedure.

4.2.1.4 Boronometry. The analysis of boron by boronometry is based on the attenuation of a collimated neutron beam by a solution of boron between the source of neutrons and the detector. The neutron count rate from the detector tube is converted directly to boron concentration on the readout electrometer or pulse counter. Californium-252 or plutonium-beryllium are typically used as sources of neutrons. Boron trifluoride ( $\text{BF}_3$ ) tubes or fission chambers are two types of detectors. Although  $\text{BF}_3$  tubes have been reported to operate satisfactorily in gamma-ray fields up to 100 R/hr, later boronmeters use fission chambers as they are virtually insensitive to gamma-ray fields.

Boronometers typically employ relatively large volume samples, 1-2 liters or more. Accordingly, massive shielding of the sample station and separation of the sample station and readout instrumentation is required for accident condition usage. As the detectors are sensitive to other sources of neutrons, location of the detectors within the plant should be considered, and the detectors should be located away from these sources.

The sensitivity of boronometers is on the order of 1 ppm boron with a useful range of 5000 ppm or more.

Calibration of boronometers can be performed statically or by flowing standards with a variety of boron concentrations past the detector.

Although no laboratory testing was performed on the effects of sample matrices, no chemical interferences are anticipated.

The advantages of boron analysis by boronometry are the continuous readout of the boron concentration, the wide measurement range with or without sample dilutions, the applicability of the method to routine and accident use, and existence of proven boronometers.

The disadvantage of the method is the use of large volume samples, which could create maintenance problems should a failure occur during an accident. However, the impact of such an occurrence could be minimized as a backup boron analysis capability using grab samples is required for inline monitoring methods.

As noted above, high radiation fields will not affect the performance of boron analysis performed by boronometry.

#### 4.2.1.5 DigiChem Analyzer of Manual Mannitol Titrations.

The procedure for boron analysis using either the DigiChem Analyzer or manual titrimetry methods is, in principle, the same. Mannitol is added to the sample to form a boron mannitol complex; hydrochloric acid is added to initially adjust the pH of the solution to 4.4; and the sample



is titrated to the end point (pH 8.5) with sodium hydroxide. The boron content of the sample is derived from the volume of sodium hydroxide titrant used and comparison to standards data.

The difference in the two procedures is obvious; one employs hands-on techniques and the other employs remote analysis. The remote analysis is performed automatically with the DigiChem Analyzer. It makes use of a microprocessor for sample and reagent dispensing, solution mixing, and concentration measurements. The analyzer automatically calculates the boron content and outputs it on a computer-compatible tape. Analysis by the analyzer can be performed continuously, semicontinuously, or in the batch mode. Separation of the sensing element and the readout device is required to eliminate radiation effects on the system electronics; the sensor and electronics can be separated by at least twenty-five feet without degradation of the signal. The analysis times are seven minutes with the automatic analyzer and twenty minutes for the hands-on methods.

A total of two hundred micrograms of boron is required for analysis with either the automatic or manual procedure. Accordingly, the required sample sizes depend on the concentration in the sample. For example, under the assumption that 0.1 ml of reactor coolant is an upper limit for the reactor coolant sample size, the initial concentration of boron in the reactor coolant would have to be two thousand ppm or greater to provide sufficient boron for analysis. The two thousand ppm represents the lower limit of detection for 0.1 ml samples and, as a result, precludes the usage of the hands-on mannitol titration procedure usage on accident condition samples. However, it does not preclude the use of the DigiChem Analyzer for accident conditions as larger samples can be collected and analyzed remotely.

In fact, the DigiChem Analyzer has been laboratory tested on standards, with and without the presence of potential interferences; accurate, precise, interference free results were obtained. The measurement range of the procedure for a 4.0 ml sample is 50-6000 ppm boron, which could be extended downward by the use of larger samples.

The advantage of the automatic mannitol titration procedure is its relative simplicity, remote operational characteristics, utility under routine and accident conditions, and wide measurement range.

The only apparent disadvantage of the procedure is the potential maintenance difficulty which might occur during replacement of sensing elements under accident conditions or rapid repair of the microprocessor. However, as backup capabilities to analyze boron samples are required for inline sample methods, the DigiChem analyzer should meet all measurement requirements.

The effects of high radiation fields have not been tested. ENICO feels that the effects probably will not be significant; however, this should be confirmed.

4.2.1.6 Ion Chromatography (IC). An ion chromatograph operates on the principle of selective retention and elution of ionic species on and from ion exchange media. It basically consists of a separator column and eluent, a suppressor column, a conductimetric detector, and a readout device. To perform an analysis for anions, such as borates or chlorides, the sample is first passed through the separator column - an anion exchange medium which retains the anions and replaces them with another anion from the exchange medium. The retained anions are then selectively removed from the separator column with the eluent, normally a dilute salt solution, and passed through the suppressor column. In the suppressor column - a cation exchange medium - the anions are converted to their acid forms which pass unretarded to the conductimetric detector. The conductivity of these dilute acid solutions is a function of the anion concentrations in the sample.

The time between sample injection and the appearance of conductivity peak for a particular anion depends on the sample size, the physical size of the columns, the types of exchange media, and the types, concentrations, and flow rate of the eluent. As a result different anions in a single sample can be separated and analyzed by proper selection of parameters.

In the development of an ion chromatographic procedure for the analysis of boron and/or chloride; SEC/NUS studied various combinations of eluents, separator columns, suppressor columns, and sample injection loop sizes. Initial testing resulted in a method which used a sodium tetraborate eluent and was applicable for chloride analysis of postaccident reactor coolant samples (cf Section 4.2.2.1). However, the analysis of boric acid solutions with the procedure showed inconsistent results.

Additional development and testing by Dionex, the manufacturer of the ion chromatograph used, resulted in a procedure for the simultaneous analysis of boron and chloride using a single sample.

In the test program a modified Dionex Model 10 Ion Chromatograph was used. The modifications included two 4 x 250 mm separator columns, a 3 x 250 mm suppressor column, a twenty cm (0.043 ml) sample injection loop, and a sodium carbonate/sodium hydroxide/mannitol eluent. An additional requirement identified was the need of a cation pre-column to remove excess base and convert borates to boric acid prior to loading highly basic samples into the injection loop. With a twenty-five percent pump stroke, the necessary times for the boron and chloride peaks to appear following injection to the sampling loop are respectively 5-6 and 9-10 minutes.

To consistently obtain satisfactory results, periodic washing and/or regeneration of the suppressor and pre-columns is necessary. The pre-column requires regeneration after the analysis of every two to three samples containing 0.4 M sodium hydroxide. The required frequency for washing and regeneration of the suppressor columns was not stated. However, based on the frequency noted in the initial chloride analysis development work, estimated frequency for regeneration is every four hours of continuous operation. The need for this is indicated by an erratic baseline on the readout device. The required frequency for washing the suppressor is once daily or prior to each regeneration.

If column washing and regeneration are not required, the analysis time is forty minutes. If column washing and regeneration are required prior to analysis, the sample analysis time is approximately two hours. Neither case includes system calibration time, which is fifteen minutes.

The IC procedure for simultaneous chloride and boron analysis has been laboratory tested using simulated postaccident reactor coolant samples, stable fission products, caustic, cooling water impurities, and normal reactor coolant chemical additives. No sample matrix effects were observed within the specified measurement range.

The advantages of the procedure are its adaptability to remote operation, the large chloride measurement range, the simplicity of operation, small sample sizes, potentially short sample analysis time, and the lack of chemical interferences.

The disadvantages of the procedure are the lack of a sufficient measurement range for boron, the need of a pre-column for basic samples, and the need for column washes and regeneration which might lead to long analysis times.

The effects of large irradiations associated with highly radioactive samples have not been evaluated. However, based on a literature study of radiation effects on the components of the IC and on limited laboratory tests used to determine the effects of 0-200 ppm hydrogen peroxide in samples, no radiological effects are anticipated. The literature showed that cation resins begin to degrade at approximately  $10^8$  rads and that the electronic components are resistant to exposure well above  $10^5$  rads. Both levels are well above those anticipated to be encountered by the IC during analysis of samples.

4.2.1.7 Carminic Acid Spectrophotometry. Two procedures were presented for boron analysis with carminic acid, one by SEC and one by GE. The one presented by GE was detailed; it was developed by HACH Chemical Company<sup>20</sup> and closely follows an ASTM procedure.<sup>21</sup> The



procedure presented by SEC was only an outline. Since both methods were similar and the HACH procedure had a slightly larger measurement range, only the HACH procedure is discussed.

The HACH procedure is very simple. First the carminic acid in preweighed tablet form is added to 75 ml of sulfuric acid and mixed; then, 35 ml of the prepared solution is added to 2.0 ml of the sample, blank, and/or standard. After the development of the color, 20-30 minutes, 25 ml of the solution(s) is transferred to spectrophotometric cells and the percent transmittance is measured at 605 nm with a Bausch and Lomb Spectronic 20 spectrophotometer, or equivalent. The measurement range is 0-15 ppm boron without sample dilution and 0 - several thousand ppm boron with sample dilution. The total analysis time is approximately 40 minutes.

The procedure has not been tested for postaccident reactor coolant sample chemical matrix effects; it has been tested for effects of high sample radiation fields. At the maximum anticipated source term,  $8 \times 10^3$  rad/h for a 0.1 ml reactor coolant sample diluted to 25.0 ml the effects of irradiation should be equivalent to no more than 5 ppm boron. This would result in negligible error when compared to levels of boron in postaccident samples.

The advantages of the procedure are the small sample sizes required, the wide measurement range, the adaptability to routine and accident conditions, and the simplicity.

The disadvantage is lack of laboratory testing with postaccident chemical matrix samples.

4.2.1.8 Conductivity of Boron Solutions. A GE specification requires the Standby Liquid Control System (SLCS) at BWR's to be filled with a solution of borax and boric acid at a ratio of 1.028. GE proposed that, in the event the SLCS were actuated, the boron concentration in the reactor coolant could be estimated from conductivity. GE tested the

hypothesis with a 1.028 borax to boric acid solution by varying the boron concentration between 5.4 and 201 ppm boron. The calibration curve was linear between 10.8 and 201 ppm boron.

This suggests that, with sample dilution, the boron concentration of reactor coolant can be determined by conductimetric measurements. However, ENICO believes that under accident condition there are too many other variables which could affect the conductivity of the reactor coolant and cause erroneous measurement. Accordingly, the approach is not considered to be applicable for measurement of boron concentration in reactor coolant.

#### 4.2.1.9 Summary and Conclusions for Boron Analysis

Procedures. The results of ENICO's evaluation of potential chemical analysis procedures and methods for postaccident reactor coolant sample boron analysis are summarized in Table 5. Included are the measurement ranges, sensitivities, accuracies, analysis times, sample sizes, and analysis methods. Also noted are the complexity of the procedures and the existence, based on actual testing and/or professional judgements, of known or anticipated chemical or radiological interferences. Finally, the applicability of the procedure to routine and accident condition use is indicated.

As all but one of the procedures met or exceeded the criteria for required sample size, radiological exposures, measurement range and accuracy, and analysis times; the selection and ranking of the procedures in order of applicability were based to a degree on the complexity of the procedure and the laboratory testing which had been performed. If two procedures had similar complexities or amounts of laboratory testing; other factors, like time of analysis, were considered. Inline analysis procedures were ranked lower than grab sampling procedures with similar qualifications as the capability to analyze backup grab samples is required for inline methods. Last, anticipated maintenance problems or potential contamination were considered.

TABLE 5  
FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR BORON

Method Feature	Fluoroborate Electrode	Curcumin Spectrophotometric	Plasma Spectroscopy
RANGE (ppm)			
Direct Analysis	0.5 - 6.0	0.2 - 2.0	0-<1.0
With 1:100 Dilution	50-600	20-200	0-<100
With 1:1000 Dilution	500-6000	200-2000	0-<1000
With Other Dilutions >1:100 (2)	50-6000	20-6000	0-6000
Accuracy (%)	$\pm 30$ if B = 50	$\pm 13$	$\pm 20$ (3)
(B in ppm)	$\pm 10$ if B > 300		
Sample and/or Analysis Method?			
Inline	No	No	No
Grab	Yes	Yes	Yes
Analytical Backup Required?	No	No	No
Sample Collection Method	--	--	--
Sample Analysis Method	--	--	--
Sample Size (ml)			
Diluted Analysis Sample	1.0-5.0	1.0	0.25
Actual RC(4)	0.01-0.05	0.01	~0.006
Analysis Time (min)	20	120	30
Procedure Complexity	Medium	Medium	Low
Chemical Interferences?	No	No	Unknown
Tested	Yes	Yes	Limited
Anticipated	--	--	No
Radiological Effects?	Unknown	Unknown	Unknown
Tested	No	No	No
Anticipated	No	No	No
Application			
Routine	Yes	Yes	Yes
Accident	Yes	Yes	Yes

TABLE 5 (Continued)  
FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR BORON

Method Feature	Cerminic Acid Spectrophotometric	Mannitol Titrimetry (Manual or Digi- Chem. Analyzer)	Boronometer	Ion Chromatography
RANGE (ppm)				
Direct Analysis	0-10.0	50-6000	0-5000(1)	500-6000
With 1:100 Dilution	10-100	Not appropriate	0-500,000	Not appropriate
With 1:1000 Dilution	100-1000	due to lack	0-5,000,000	due to lack of
With Other Dilutions	0-6000	of sensitivity	0-6000	sensitivity
>1:100 (2)				
Accuracy (%)	<u>+15</u> (3)	<u>+5</u>	<u>+8</u>	<u>+8</u>
B in ppm)				
(Sample and/or				
Analysis Method?				
Inline	No	Yes	Yes	Yes
Grab	Yes	No	No	No
Analytical Backup				
Required?	No	Yes, For Inline	Yes, For	No
Sample Collection Method	--	Available	Inline	--
Sample Analysis Method	--	Not Specified	Available	--
			Not Specified	--
Sample Size (ml)	2.0	4.3(5)	1000-2000	0.04
Diluted Analysis Sample	0.02	1-2	10-20	0.04(5)
Actual RC(4)				
Analysis Time (min)	40(6)	5-30	continuous	40-120(7)
Procedure Complexity	Low	Low	--	Medium
Chemical Interferences?	Unknown	No	Unknown	No
Tested	No	Yes	No	Yes
Anticipated	No	--	No	--
Radiological Effects?	No	Unknown	No	Unknown
Tested	Yes	No	yes	No
Anticipated	--	No	--	No
Application	Yes	Yes(8)	Yes	No(9)
Routine	Yes	Yes	Yes	No
Accident				

Notes:

- 1) The range of measurements using neutron adsorption is based on boron densitometers used at the Idaho National Engineering Laboratory.



- 2) With dilutions greater than 1:100 the upper limit of the measurement range can be extended to ten-of-thousands of ppm. However an upper limit of 6000 ppm is noted as measurements above 6000 ppm are not required.
- 3) In the procedure presented the uncertainty of the method was not included; based on professional judgement the uncertainty has been estimated at  $\pm 20$  percent.
- 4) The actual volume of reactor coolant used in the analysis was determined from a 100-fold dilution of 0.1 ml of reactor coolant and the volume of diluted sample required for the analysis.
- 5) Due to a lack of sensitivity for boron, typical sample dilution of 1:100 of 0.1 ml reactor coolant samples is not appropriate. Consequently, boron analysis of grab samples can not be made with the procedure. However, the procedure has sufficient sensitivity to analyze chloride in diluted grab samples (see sections 4.2.2.1 and 4.2.2.5).
- 6) Two procedures were presented for boron analysis with carminic acid, one by SEC and one by GE. The analysis time specified by GE and SEC were 40 and 90 minutes, respectively. The difference in times is the number of minutes required for cooling following carminic acid addition and for color development. As GE had tested the procedure and SEC had not, 40 minutes is assumed to be correct.
- 7) The actual boron analysis time is forty (40) minutes. However, during continuous operation a column wash/regeneration/equilibration cycle is required every four hours. Accordingly, an analysis could require approximately two hours.
- 8) The manual mannitol titrimetry is appropriate for routine use only as the method lacks sensitivity to analyze small reactor coolant samples; the manual method is commonly used at PWR's under normal conditions. The DigiChem Analyzer method is applicable to routine or accident condition usage as the method uses remote analysis of larger reactor coolant samples.
- 9) The ion chromatographic procedure is not appropriate for routine or accident condition usage due to insufficient sensitivity. If the lower detection of 500 ppm boron were deemed to be sufficiently sensitive, the procedure would be appropriate for accident condition use only.

Listed in order of appropriateness is the result of ENICO's evaluation of the boron analysis procedures:

1. Fluoroborate Electrode
2. DigiChem Analyzer Mannitol Titrimetry
3. Curcumin Spectrophotometric
4. Boronometer
5. Carminic Acid Spectrophotometric
6. Plasma Spectroscopy
7. Ion Chromatography

It should be emphasized that the order of ranking is based on presently available information only. With additional testing the order could change. For example, with confirmation that there are no chemical interferences to the carminic acid spectrophotometric method, it would be ranked at or near the top due to ease of use. Likewise, modifications to the plasma spectroscopy instrument, which would insure containment of volatilized radioactivity, would improve its rating. Last, confirmation of the existence or nonexistence of radiological interferences could alter the order of ranking.

#### 4.2.2 Chloride Analysis Methods

4.2.2.1 Ion Chromatography (IC). Described in Section 4.2.1.6 was an ion chromatographic procedure for the simultaneous analysis of boron and chloride. Included in the description were the columns, sample sizes, eluent, and operational characteristics required for satisfactory analysis of boron and chloride in a single sample.

The measurement range, accuracy, sample size, and analysis time for chloride analysis with the procedure are respectively 0.1-2000 ppm,  $\pm 10$  percent, 0.04 ml of undiluted reactor coolant, and 40-120 minutes. The procedure, which has been laboratory tested, is applicable for routine and accident condition use. It can also be used as an inline monitor or for analysis of grab samples.

The advantages of the procedure are the measurement range for chloride, normal and accident usage, small sample size, the lack of chemical interferences, remote operability, simplicity of operation, and potentially short analysis time.

The disadvantages of the procedure are the lack of a sufficient measurement range for boron, the required column washes/regenerations, which increase the analysis times, and the need of a pre-column for basic samples. Another unknown is the lack of data on the potential effects of highly radioactive samples.

Sentry Equipment Corporation also developed and tested another ion chromatographic procedure for chloride analysis. The procedure can not be used for boron analysis; however, it is very similar to the boron-chloride analysis described previously. The procedure uses a 3 x 250 mm separator column, a 6 x 250 mm suppressor column, a sodium tetraborate eluent, and a 0.04 ml sample. The procedure does not use a pre-column. To obtain satisfactory results the columns must be washed and regenerated. Washing frequency is once daily or prior to each regeneration.

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Regeneration frequency is one every four hours of continuous operation. A high erratic baseline, a change in the time of the appearance of the chloride peak (normally six minutes), and/or a change in the peak height for the standard indicate a need for regeneration.

The tetraborate IC procedure has been tested in the laboratory with simulated samples of fission products and chemical additives. Special laboratory tests were performed to determine the effects of morpholine, hydrazine, ammonia, and natural and synthetic oils. The only effect observed was due to oils, which caused a progressive 10-30 percent increase in the chloride response and a memory effect. However, as the memory effect can be eliminated with column washing and regeneration and as the increase in chloride peak height is associated with longer elution times, the effect is not considered significant as it can be detected and corrected.

Laboratory tests were also performed with the tetraborate IC procedure to determine its ability to measure fluoride and iodide. The data indicated that the fluoride elution time was 1.5 minutes and that measurement of fluoride is possible down to 25 ppm ( $\pm 10$  percent) in the presence of fewer than 100 ppm boron. Attempts to measure fluoride in the presence of higher concentrations of boron were unsuccessful due to peak overlap. The iodide measurements indicate that iodide could not be detected at low concentrations (0.5 ppm), and at high concentrations (up to 100 ppm) small responses were observed. The iodide data indicates that iodide will not interfere with the tetraborate IC chloride analysis method.

The advantages and disadvantages of the tetraborate IC procedure are essentially the same as the ones presented above for the boron-chloride IC procedure.

4.2.2.2 Specific Ion Electrode (SIE). The procedure for chloride analysis by SIE is very simple and rapid. The pH of the solution is adjusted to 2-4 and the SIE and a reference electrode are immersed in the solution and the millivolt response is related to the chloride concentration.

The investigative studies performed by SEC/NUS employed a Graphic Controls Ultra-Sensitive Solid State Chloride Electrode (Model PHI 91100) and a Graphic Controls double-junction reference electrode (No. GC 54473). In the procedure 1.0 ml of nitric acid was added to 100 ml of sample to adjust the pH. The measurement range determined with standard chloride solutions was 0.01 to 35,000 ppm chloride.

With the above measurement range, the SIE is applicable to routine use only as approximately 10.0 ml of reactor coolant sample, diluted to the 100 ml sample analysis size, would be required to detect 0.1 ppm chloride. Furthermore, the method suffers from interference of other halogens. The interference problem possibly can be solved by a combination of selective oxidation and solvent extractions; however, at present the SIE is not applicable to postaccident chloride analysis due to the relatively large sample size required.



Conceivably, the SIE could be adapted to remote operation; but, as noted, the chemical interference problem must be solved. Overall, the method is not a good candidate.

#### 4.2.2.3 Turbidimetric, Colorimetric, Titrimetric and

Spectrophotmetric. General Electric and SEC/NUS evaluated or suggested a number of other candidate procedures for chloride analysis. All are basically hands-on methods; however, one (titrimetry) could be adapted to remote inline analysis. There has been limited or no laboratory testing of the procedures by SEC/NUS or GE in regard to their applicability to analysis of reactor coolant samples with potential fission product or chemical interferences. However, based on the judgement of personnel at ICPP who have prior experience with the same problems on similar procedures, it is anticipated that iodides and/or other halogens will interfere with all the procedures presented in this section. Furthermore, due to the relatively large size reactor coolant samples required for analysis, 2-50 ml, use of the procedures for hands-on analysis is prohibited under accident conditions. Accordingly, the procedures are not applicable to analysis of postaccident samples without further testing, modification, and development, or without remote use.

For informational purposes, each procedure is briefly outlined below.

#### Turbidimetric and Colorimetric

The turbidimetric and colorimetric procedures are very similar. Six drops of concentrated nitric acid are added to the sample, 12 ml for colorimetric and 25 ml for turbidimetric; the percent transmittance is recorded; seven drops of 1 N silver nitrate are added; and the percent transmittance is recorded again. The difference between the two recorded measurements is related to the concentration of chloride by the use of calibration standards. For turbidimetry a HACH Turbiditymeter or equivalent is recommended, and for colorimetry a Coleman Nephrocolorimeter, or equivalent, is recommended.

### Spectrophotometric

The spectrophotometric procedure presented is also simple and commonly used for chloride analysis. It involves the mixing of 10 ml of ferric ammonium sulfate solution, 5.0 ml of mercuric thiocyanate methanol solution, and 25 ml of sample. This is followed by the measurement of the percent transmittance at 463 nm in a 10 cm spectrophotometric cell.

### Titrimetry

The titrimetry method is based on the formation of a mercury complex, diphenylcarbozone-bromphenol blue, and mercurous chloride. The end-point color development occurs when mercurous ions are in excess of the chloride. In the procedure 25 ml of sample, 1-2 ml of diphenyl-carbozone, and a few drops of the bromphenol blue indicator are mixed. This is followed by the addition of mercuric nitrate. The quantity of mercuric nitrate added is a function of the chloride concentration.

4.2.2.4 Conductivity of Chloride Solutions. For a dilute solution of an ionic species the specific conductance,  $K$ , in  $\mu\text{S}/\text{cm}$  is given by:

$$K = 10^3 \Lambda C \quad (4-1)$$

where  $\Lambda$  is the equivalent conductivity and  $C$  is the concentration of the ionic species in solution in electrolytic equivalents. When the conductivity of a solution is due to several ionic species, the specific conductance of the solution can be expressed as the summation of the conductances of each of the separate ionic species:

$$K = 10^3 \sum (\lambda_i C_i) \quad (4-2)$$

where  $\lambda_i$  and  $C_i$  are respectively the limiting equivalent ionic conductance and concentration of the individual species in solution. Values, which are available in handbooks, of the equivalent conductance of different ionic species can be used to calculate the conductivity or, alternately, the concentration of the ionic species provided the ionic species concentrations are known or the conductivity of the solution is known.

The proposed procedure utilizes the above technique for estimation of upper limits of chloride concentration in postaccident reactor coolant samples. ENICO agrees such a technique is applicable for estimation of upper limits of chloride or other ionic species in solution, but does not believe the technique meets the intent of the NRC requirement for chloride analysis. For example, chloride concentrations calculated from the conductivity of postaccident solution will, in all probability, be in excess of the 0.1 ppm limitation due to the presence of fission products, high radiation fields, and/or other chemicals. As a result, corrective actions will be taken or, more likely, accurate analysis of chloride concentrations will be made. Initial accurate determinations will preclude undue concern and/or unnecessary actions.

#### 4.2.2.5 Summary and Conclusion of Chloride Analysis

Procedures. At present there is only one applicable method for chloride analysis of postaccident chloride analysis: ion chromatography. The other procedures evaluated are not appropriate due to the large sample sizes required and known or anticipated chemical interferences to the procedures. The results and features of the procedures evaluated are shown in Table 6.

The chemical procedures have not been ranked in order of applicability. Of the methods not presently applicable, the specific ion electrode and the titrimetry methods appear to have the most potential due to adaptability to remote use, i.e., reduction of radiological exposures. Their use, however, will depend on elimination of chemical interferences, such as other halogens. Limited investigative work was performed by SEC/NUS to eliminate the chemical interferences. Their technique, which ENICO believes has good potential, was selective oxidation - solvent extraction. Consequently, with additional testing and development one or more of these procedures could be adapted for postaccident use. Specific procedures proposed in the future will require evaluation as they become available.

#### 4.2.3 Dissolved Hydrogen and Oxygen

4.2.3.1 Gas Chromatography (GC) - Hydrogen Analysis. A gas chromatograph consists of a sample injection loop, a chromatographic

column containing a media such as charcoal or molecular sieves, a thermal conductivity cell, and a meter-readout device. The thermal conductivity cell, or detector, has two, matched hot wire filaments. Two streams of carrier gas, e.g., argon, are supplied to the GC from a common source. One stream flows directly past one of the filaments; the other stream flows through the GC column then to the second hot wire filament. In the absence of a sample, the two filaments reach thermal equilibrium (constant resistance) and no detector output is observed. Upon injection of a sample into the GC column, non-equilibrium between the two filaments is created due to the different thermal conductivities of the gases eluted from the GC column to the sample stream filament. The thermal conductivity imbalance generates a detector output.

As the different constituents of a sample are eluted from the GC column at different and specific times, the observed detector outputs can be attributed to the individual component of the gas sample. The magnitude of the outputs are proportional to the concentrations of the different gases in the sample. Quantification of the concentrations is achieved by comparison of the detector output of samples and standards.

The GC suggested by GE is a Baseline Model 1030, or equivalent. The Model 1030 is a microprocessor controlled instrument with thermal conductivity detectors. It is equipped with a gas conditioner, an automatic retention time indicator, and thermal conductivity peak integrator. The suggested GC column is ten feet of 1/8 to 3/16 inch tubing with 5A molecular sieves. The carrier gas (helium) flowrate and pressure are 30 cm<sup>3</sup>/minute and 15-30 psig; the suggested column temperature was 30-50°C.

Although a Fisher Model 1200 Gas Chromatograph was used in the SEC/NUS development and testing program, SEC/NUS also suggests Baseline GC, or equivalent, for plant applications due to its larger measurement range. Specific GC columns and operational parameters were not given by SEC/NUS. It is assumed the specifications will be similar to those noted by GE. Many combinations of columns, carrier gas flowrates, and temperatures have been used successfully in the past.



TABLE 6

## FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR CHLORIDE

Method Feature	Ion Chromatography	Specific Ion Electrode	Turbidimetric
RANGE (ppm)			
Direct Analysis	0.1 - 100	0.010 - 35,000	0.02 - 10
With 1:100 Dilution	10 - 10,000	Not Applicable	Not Applicable
Overall Range	0.1 - 10,000	due to lack of sensitivity	due to lack of sensitivity
Accuracy (%) (Cl in ppm)	$\pm 15(1)$	$\pm 20$	$\pm 30(2)$
Sample and/or Analysis Method			
Inline	Yes	Yes	No
Grab	Yes	Yes	Yes
Analytical Backup Required?	Yes, For	Yes, For	No
Sample Collection Method	Inline Available	Inline <sup>(4)</sup> Available	-- --
Sample Analysis Method	Not Specified	Not Specified	
Sample Size (ml)			
Diluted Analysis Sample	$\sim 0.04(6)$	100	25
Actual RC	$\sim 0.04$	10 <sup>(7)</sup>	5 <sup>(7)</sup>
Analysis Time (min)	40 - 120 <sup>(8)</sup>	15	20
Procedure Complexity	Medium	Low	Low
Chemical Interferences?	No	Unknown	Unknown
Tested	Yes	Limited	No
Anticipated	--	Yes	Yes
Radiological Effects?	Unknown	Unknown	Yes
Tested	No	No	Yes <sup>(9)</sup>
Anticipated	No	No	--
Application			
Routine	Yes	Yes	Yes
Accident	Yes	No	No

TABLE 6 (Continued)

## FEATURES OF PROPOSED ANALYTICAL PROCEDURES FOR CHLORIDE

	Colorimetric	Titrimetric	Spectrophotometric
RANGE (ppm)			
Direct Analysis	0.04 - 10	0.1 - 10	0.02 -10.0
With 1:100 Dilution	Not Applicable	Not Applicable	Not Applicable
Overall Range	due to lack of sensitivity	due to lack of sensitivity	due to lack of sensitivity
Accuracy (%)			
(Cl in ppm)	$\pm 25(2)$	$\pm 20(3)$	$\pm 20(3)$
Sample and/or	No	Yes	No
Analysis Method	Yes	Yes	Yes
Inline			
Grab			
Analytical Backup	No	Yes, For	No
Required?	--	Inline <sup>(5)</sup>	--
Sample Collection		Available	--
Method		Not Specified	
Sample Analysis Method			
Sample Size (ml)	12	100 <sup>(8)</sup>	25
Diluted Analysis Sample	2.4 <sup>(7)</sup>	50	5 <sup>(7)</sup>
Actual RC			
Analysis Time (min)	30	20	20
Procedure Complexity	Low	Low	Low
Chemical Interferences?	Unknown	Unknown	Unknown
Tested	No	No	No
Anticipated	Yes	Yes	No
Radiological Effects?	Unknown	Unknown	Unknown
Tested	No	No	No
Anticipated	Yes	No	Yes
Application	Yes	No	Yes
Routine	No	No	No
Accident			

## Notes:

- 1) The accuracy of the IC measurements is  $\pm 15\%$  in the 0.1 to 1.0 ppm chloride range and is  $\pm 25\%$  for higher concentrations. By calibration at higher concentrations, the accuracy can be maintained at  $\pm 15\%$ .

- 2) The uncertainties were estimated from calibration curve data presented in the associated documentation.
- 3) The uncertainties are based on professional judgement.
- 4) The SIE method could be adapted for inline use.
- 5) The titrimetry procedure could be used as the inline method by employment of a technique similar to the DigiChem Analyzer method for boron analysis.
- 6) The ion chromatographic procedure uses small ( $\sim 0.4$  ml) undiluted reactor coolant samples.
- 7) Due to insufficient sensitivity, smaller reactor coolant samples are inappropriate for these methods.
- 8) The titrimetry procedure has sufficient sensitivity to measure 0.1 ppm chloride; however, 50 ml of reactor coolant is required. The method is now in use at LOFT at INEL.
- 9) Limited radiological effect testing was performed by GE on the turbidimetric procedure. At the maximum anticipated dose rate,  $8 \times 10^3$  rad/h in a diluted 25 ml sample (0.1 ml diluted to 25 ml), an equivalent response of 1.8 ppm of chloride was calculated from measurement data.

The sample collection procedures for dissolved gases proposed by SEC/NUS and GE are similar. The GE procedure involves the isolation of 70 ml of pressurized reactor water, the depressurization of the sample into a 20 ml gas holding container, and the transferral of aliquots from the gas holding container to 15 ml septum bottles. The 15 ml septum bottles are transferred to the laboratory for GC analysis and/or further dilution. In the laboratory, gas tight syringes are used to take 1.0 ml aliquots from the septum bottles for injection into the GC. The procedure employs Henry's Law and a tracer gas, which is injected into the sample prior to depressurization, to determine sample yield.

The sample collection procedure of SEC/NUS involves the isolation of a 30 ml pressurized reactor water sample, depressurization of the sample, the quantitative transferral of the dissolved gases into a 300 ml gas holding cylinder via an argon gas purge, and the pressurization of the 300 ml cylinder to atmospheric pressure with the argon purge gas. From the 300 ml gas holding cylinder small samples, 0.25 or 1.0 ml are injected remotely into the GC for analysis.

Following collection of the dissolved gas samples the time required for GC analysis is less than ten minutes.

The measurement range reported by SEC/NUS is based on extensive laboratory studies and is applicable for 25-25,000 ppm hydrogen for a 1.0 ml dissolved gas sample. The dilutions associated with the sample collection procedure and the 30 ml sample used for depressurization create a range of 0.5 - 2000 cm<sup>3</sup> of dissolved hydrogen per kilogram of reactor coolant. The accuracy of the measurements is  $\pm$  10 percent.

General Electric did not report a measurement range; however, an estimate of the lower limit of detection was mentioned. Their estimate of the lower detection limit, based on limited laboratory studies, is 0.1 volume percent or 1000 ppm for a 1.0 ml dissolved gas sample. ENICO believes this detection limit is a factor of ten or more high and that the actual detection limit will be similar to the one measured by SEC/NUS, i.e., 100 ppm or lower. If such a detection limit is verified by GE, ENICO estimates the measurement range of the GE gas



chromatograph method for dissolved hydrogen in reactor water will be  $\sqrt{0.1-2000}$  cm<sup>3</sup> per kilogram of water. The estimate is based on the relative size of reactor water samples taken for analysis and the relative volumes of the gas holding cylinders of the SEC/NUS and GE sample collection systems.

The advantages of the GC methods proposed by the two vendors are sufficient measurement ranges, the application to routine and accident usage, the simplicity of operation, and the selective measurement of hydrogen, not total gases. The advantages of the SEC/NUS method over the GE method are the extensiveness of laboratory testing performed by SEC/NUS and the remote analysis capability of the SEC/NUS system. The latter advantage is quite significant as calculated<sup>14</sup> dose rates due to noble gases associated with the dissolved gases in unit volumes of reactor water are in excess of  $10^4$  R/h at one centimeter. As a result the dose rates associated with the GC samples, even with dilution, are potentially a few R/h and will require more caution for hands-on analysis than remote analysis.

The disadvantage of the GC method in general is related to maintenance of the instrument; however, this is not considered significant as GC's are generally very dependable. Another limitation of the method is the lack of laboratory tests on the effects of high radiation field on the procedure; however, there are no anticipated effects.

#### 4.2.3.2 Gas Chromatography, Yellow Springs Analyzer -

Dissolved Oxygen Analysis. As described in the previous section, different constituents in a gas sample are separated in a GC column due to their characteristic diffusion rates through a medium such as charcoal, molecular sieve, etc. As a result GC lends itself to the simultaneous determination of oxygen and hydrogen from the analysis of a single sample.

General electric proposed to use this technique for dissolved oxygen analysis, i.e., simultaneous measurement of hydrogen and oxygen in a single sample. The sample collection procedure, instrumentation, and associated equipment proposed are identical to the ones described above. Specific measurement ranges were not provided by GE.

ENICO's estimate of the measurement range is 51 to 400 ppm in the reactor coolant. The basis of the estimate are the relative thermal conductivities<sup>22</sup> (detector responses) of oxygen and hydrogen and the hydrogen measurement range estimated for the GE system in the above section. This estimated oxygen is inadequate for postaccident analysis of reactor coolant samples as the sensitivity of the procedure is insufficient to measure below 1 ppm dissolved oxygen. However, before the GC procedure is precluded from postaccident application, it should be experimentally verified that the sensitivity of the GC method is inadequate.

Sentry Equipment Corporation proposed an inline monitor for postaccident determinations of dissolved oxygen in reactor coolant. The instrument selected and laboratory tested was a Yellow Springs Instrument (YSI) Model 54 Oxygen Analyzer. The sensing probe, which contains a semipermeable membrane, is remotely located from the meter and output device. The probe holder was redesigned to minimize fluid volume and associated radiation exposure. Calibration of the system is achieved with an oxygen saturated demineralized water source. The actual oxygen content of the standard solution is determined from the temperatures of the water and a solubility chart relating dissolved oxygen to water temperature.

Laboratory tests verified that there were no interferences due to hydrogen in solution or variations in sample flowrate. One problem observed during the tests was a pin hole in one of the probe membranes. This resulted in erratic results. Replacement of the membrane corrected the problem.

Laboratory testing also verified that the accuracy ( $\pm 5\%$ ) was sufficient to measure 0.1 ppm dissolved oxygen. The measurement range was linear between 0.1-7.85 ppm oxygen. Concentrations above 7.85 ppm oxygen were not laboratory tested. It is anticipated the measurement range will be valid up to 20 ppm oxygen; however, this needs verification.

Provided the measurement range can be demonstrated to be 0.1-20 ppm, the YSI Analyzer is applicable to postaccident

applications. The Model 54 Analyzer lacks sufficient sensitivity for routine use. SEC/NUS proposed a Rexnord Analyzer for routine use (sensitivity-ppb) or alternately a Model 56 YSI Analyzer with reported higher sensitivity. The routine condition monitor will be installed in parallel with the accident condition monitor.

The advantages of the YSI oxygen monitors are the remote operability, simplicity, and potentially adequate measurement range.

The disadvantage of the systems is the time, 1-4 hours, required for the system to reach equilibrium after the internal portions of the sensing probe are exposed to air. Based on a review of the literature on the effects of irradiation on the components of the sensing probe, no radiological effects are anticipated. The maximum dose anticipated to the different materials of construction in the probe is  $10^4$  rads; the minimum doses causing damage to the materials was reported at  $10^6$  rads.

4.2.3.3 Evaluation Summary of Dissolved Oxygen and Hydrogen Analysis. The gas chromatographic methods proposed by SEC/NUS for dissolved hydrogen analysis is applicable to postaccident sample analysis. It has sufficient sensitivity, accuracy, and range of measurement ( $0.5-2000 \text{ cm}^3$  hydrogen per kilogram of reactor coolant,  $\pm 10 \%$ ). The measurement range associated with the GE method needs to be verified. After completing collection of the dissolved gas sample, the analysis time is ten minutes or less. The SEC/NUS sample handling has an advantage over the GE procedure due to its remote mode of sample handling. Precautions should be taken when manually handling the dissolved gas samples due to the potentially high radiological fields. The GC method is applicable to routine conditions also. Radiological interferences to the GC method are not anticipated.

The GC method proposed by GE for dissolved oxygen analysis appears to lack sufficient sensitivity for required measurement of low ( $<0.1 \text{ ppm}$ ) concentrations of oxygen. Without further testing to demonstrate the capability of the method to measure the low concentration, the GC method for oxygen analysis is not applicable to post accident sample analysis.

The inline oxygen monitor proposed by SEC is applicable to postaccident analysis provided information is available to verify its ability to measure dissolved oxygen over the entire range of 0.1-20 ppm. At present the measurement range has been demonstrated to be valid between 0.1 and 7.85 ppm only.

In ENICO's opinion, the proven measurement range is sufficient as the intent is to measure the absence of oxygen, not necessarily the presence. If NRC does not agree, additional laboratory studies need to be performed to extend the measurement range.

To meet all NUREG-0737 requirements, licensees which use inline method for analysis must have a backup capability to obtain grab samples and to perform analysis performed by the inline monitor. Dissolved oxygen analysis by hands-on techniques will require diluted, pressurized samples or techniques to collect the gases (oxygen) from a liquid sample. Conventional methods, eg., Winkler, of hands-on analysis can not be used due to the large sample sizes required and/or a lack of sensitivity. Alternative methods must be identified.

#### 4.2.4 Conductivity and pH

4.2.4.1 Conductivity. Both SEC/NUS and GE propose the use of inline monitors for measurement of conductivity. Their proposed conductivity meters have measurement ranges of 0-500  $\mu\text{S}/\text{cm}$  and 0-100  $\mu\text{S}/\text{cm}$ , respectively. The proposed probes have conductivity cells with 0.1 cm cell constants; they are located remote to the meters. The inline probe tested by GE was a standard, commercially available one, and the probe tested by NUS used a modified probe holder designed to minimize fluid volume. The actual cell volumes were not specified. The accuracy associated with the measurements was not specified either; however, high accuracy for 0-2  $\mu\text{S}/\text{cm}$  and decreasing accuracy for higher conductivities was noted.

Laboratory tests were performed by both GE and SEC/NUS. The GE tests involved measurements of the conductivity of water flowing first through a conductivity cell under irradiation and then through a second in-series conductivity cell not under irradiation. The irradiation fields were varied between  $1.3 \times 10^4$  rads/h to  $9.8 \times 10^5$



rads/h. GE also made static (no flow) measurements with the above arrangement. Finally, GE performed conductivity measurements on a 10 ppm chloride solution with ( $9.8 \times 10^5$  rads/h) and without irradiation and with and without flow through the cells. The SEC/NUS laboratory testing was limited to establishing the operability with a flowing sample stream, the effects air bubbles in the air stream, and the effects of hydrogen peroxide on conductivity measurements. SEC/NUS also conducted a literature review for potential radiation effects to the components of the sensing probe.

The results of GE tests on the two in-series cells indicated that the cell under irradiation and the one not under irradiation gave the same results and that the conductivity of the solution increased from 0.1  $\mu\text{S}/\text{cm}$  to 0.65  $\mu\text{S}/\text{cm}$  as the irradiation intensity was increased. The cause for the increase in conductivity is unknown; however, it obviously is due to the generation of an unknown conductive species. The hypothesis that the unknown species is hydrogen peroxide is not supported by the chloride solution tests performed by GE and the hydrogen peroxide tests performed by SEC/NUS; i.e., the conductivity did not change with the addition of chloride - added to decrease the generated species - or with the addition of hydrogen peroxide directly to the flowing stream.

Further results of the SEC/NUS tests show that the monitor is applicable to a flowing sample stream and that the presence of air bubbles at five percent of the water volume does not alter the accuracy of the measurements.

The literature review indicates that the resistance of the probe components to radiation exposure exceeds the anticipated radiation does by a factor of one hundred or more.

The advantages of the method are its utility under accident and normal condition, its resistance to radiation damage, the remote operational mode, and its simplicity.

There are no apparent disadvantages even though the conductivity of water solutions increased with increasing radiation doses. This observation only implies that the monitor was operating

properly as its response increased with an increase in the conductivity of the solution.

A backup method for measurement of conductivity of grab samples was not noted. However, there are commercially available portable conductivity meters which are appropriate for this purpose.

4.2.4.2 pH. To investigate methods of determining pH under postaccident conditions, SEC/NUS evaluated an industrial grade inline pH probe and a sealed, permanently-filled reference electrode. The vertical probe holder, modified to minimize fluid volume, prevents entrapment of air bubbles. A double O-ring seal is used to prevent leakage. The probe can be calibrated in place by injection of buffer solutions (pH 7 and 10) into the sample loop. The probe output is recorded on an industrial grade meter mounted in a remotely located instrument panel.

Testing of the pH monitor was performed to determine its applicability to a flowing sample stream and to evaluate the effects of air bubbles in the liquid. Data indicated the pH monitor is not affected by variations in flow or by the presence of air bubbles.

The optimum operating temperature range of the pH probe is 75-90°F; the maximum temperature and pressure are 125°F and 100 psig. With constant control of the pH probe at a given temperature within the optimum operational range, the accuracy and measurement range will comply with NRC requirements,  $1-13 \pm 0.3$  pH units.

As inline pH monitors have been used reliably for a number of years in the chemical and nuclear industries, there are no apparent disadvantages. The advantages are the application to accident and routine use, the remote operability, the simplicity, and the sufficient measurement range and accuracy.

To fulfill all NUREG-0737 requirements, however, a backup capability to measure the pH of grab sample must be provided. With the proposed grab sample collection systems, this will require pH measurements of diluted reactor coolant samples. ENICO anticipates that pH's measured in diluted samples cannot be used to accurately determine

the actual pH of the reactor water. For example, based on a 1:100 dilution of a 0.1 ml reactor coolant sample with deionized water (pH 7.0), the estimated pH of the reactor coolant water determined from the analysis of the diluted sample could be in error by 2-7 pH units. This takes into account the results of dilution only and not the presence of other constituents which can affect the pH. Accordingly, ENICO does not recommend the use of diluted grab samples for measurement of reactor coolant pH.

General Electric Company suggested the use of pH paper for measurement of pH in reactor water. In conjunction with this idea, a series of laboratory tests were performed to determine the effects of high irradiations on the accuracy of the method. The pH paper was immersed in solutions with pH 3.8 and 10.0 and irradiated for ten minutes ( $1.6 \times 10^5$  rads) in one study and one minute ( $1.6 \times 10^4$  rads) in another study. The colors of the solutions were completely destroyed in the ten minute test and significantly altered in the one minute test (0.5 pH unit shift).

To compensate for this effect, GE suggested that the procedure be modified to decrease the exposures to the pH paper. The suggestion was to moisten the paper with a drop or two of sample instead of total immersion of the pH paper in the sample solution. The proposed modified procedure was not demonstrated to be successful.

ENICO does not believe the pH paper method is satisfactory at present due to the irradiation effects observed. Its future applicability will depend on the additional testing and the development of a technique to collect a small, undiluted reactor coolant sample and to perform the measurement in a radiologically safe manner.

General Electric also suggested that the conductivity of a solution is a potential method to ensure that the pH of the reactor coolant is within certain acceptable ranges, i.e. 5.6 to 8.6. ENICO does not believe this technique meets the NRC intent as the conductivity of the reactor coolant can possibly vary over a large range under accident conditions and cannot be used as an indication of pH with the required accuracy.

#### 4.2.4.3 Summary of Conductivity and pH Analysis Methods.

The method proposed by SEC/NUS and GE is applicable for measurement of the conductivity of reactor coolant water. It includes an inline conductivity cell with a remote readout meter. A backup capability to measure the conductivity of grab samples was not noted by SEC or GE. This backup capability can be provided with commercially available, portable conductivity meters for analysis of grab samples. Alternately, a backup capability, with NRC's concurrence, would be a second, independent inline monitor which could be put into service upon the failure of the first monitor. The monitors are applicable to accident and normal conditions.

Although there was an increase in conductivity of test solutions with an increase in radiation exposures, the effect was not due to monitor component failure. It was a result of an increase of the conductivity of the test solution. It is unknown if the increase in conductivity of the test solutions was inherent to the experimental conditions or whether one should anticipate the generation of a conductive species in postaccident reactor coolant water.

At present the only proven methods which has satisfactory accuracy and is applicable to measurement of pH under accident conditions are inline monitors. The use of pH paper is not applicable due to inaccuracies caused by high radiation fields. The pH paper method may be applicable with further testing; however, the method will require the development of techniques for the remote addition of small reactor coolant samples to the pH paper and for the remote comparison of the pH paper colors with standards.

The pH analysis of diluted reactor coolant samples is not recommended due to the potential inaccuracies of the measurements. The only alternative for a backup analysis capability is the use of two independent inline monitors; one in service and one in standby.

The pH inline monitors are applicable to both accident and routine use. There are no anticipated radiological effects.



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16 February 1982

GE/SEC Chemical Procedures  
Moe-3-82

Mr. C. E. McCracken  
U. S. Nuclear Regulatory Commission  
Phillips Bldg. Room P-302  
Bethesda, MD 20014

Reference: B. G. Motes, "Evaluation of GE and SEC Chemical Procedures for Post-  
accident Analysis of Reactor Coolant Samples", November 1981

Dear Conrad:

In ENICO's evaluation of proposed chemical procedures for postaccident analysis of reactor coolant samples, referenced above, the presence or absence of radiologically induced interferences (effects) were noted for chemical procedures with available test data. For chemical procedures without available test data, it was noted whether radiologically induced interferences were anticipated or not. In the report a general statement was included which indicated that the basis for determining whether radiological effects were anticipated or not was past experiences of personnel involved in the evaluation.

In response to your recent request for a brief amplification of the basis used to determine whether or not radiological effects on the individual procedures are anticipated or not, I have included in the enclosed table a list of the procedures and the respective basis used. Again it should be emphasized that the evaluation for these procedures are professional judgements; they have not been confirmed with laboratory testing. As recommended in the report the procedures should be laboratory tested to confirm the existence or nonexistence of radiologically induced effects.

If you require additional information please call (FTS 583-3577).

Sincerely,

*B. G. Motes*  
B. G. Motes  
Radiochemistry

BGM:aer

Enclosure

cc: B. Barnhart, NRC  
G.L. Vivian, DOE-ID

~~8212130402~~

3pp.

TABLE I  
BASIS FOR RADIOLOGICAL EFFECTS ON SEC/GE CHEMICAL PROCEDURES

Method/Analysis	Radiological Effects	Anticipated	Basis
Fluoroborate SIE/Boron	Unknown	No	Chemistry of the procedure and SEC literature review of radiological effects on similar materials used in construction of the SIE.
Curcumin Spectrophotometric/Boron	Unknown	No	Chemistry of the procedure.
Plasma Spectroscopy/Boron	Unknown	No	Independence of procedure chemistry.
Carminic Acid Spectrophotometric/Boron	No	--	Chemistry of the procedure.
Mannitol Titrimetry/Boron	Unknown	No	Chemistry of the procedure, SEC literature review of radiological effects on pH probes, and prior use of the procedure to analyze relatively high activity samples.
Boronometry/Boron	No	--	Independence of procedure chemistry and prior usage of boronometers in high radiation fields.
Ion Chromatography/Boron	Unknown	No	Chemistry of the method and prior use of a similar method to analyze relatively high activity ( $\sim 1R$ ) samples, including a diluted postaccident TMI-2 sample ( $\sim 0.5R$ ).
Ion Chromatography/Chloride	Unknown	No	Chemistry of the method and prior use of a similar method to analyze relatively high activity samples, including a diluted postaccident TMI-2 sample ( $\sim 0.5R$ ).
Specific Ion Electrode/Chloride	Unknown	No	SEC literature review of radiological effects on similar materials used to construct the electrode.
Turbidimetric/Chloride	Yes	--	Laboratory tests by SEC/NUS.
Colorimetric/Chloride	Unknown	Yes	Laboratory test by SEC/NUS on the turbidimetric method, which is essentially the same as the colorimetric method.



TABLE I

BASIS FOR RADIOLOGICAL EFFECTS ON SEC/GE CHEMICAL PROCEDURES

Method/Analysis	Radiological Effects	Anticipated	Basis
Titrimetric/Chloride	Unknown	No	Chemistry of the procedure and SEC literature review of radiological effects on pH probes.
Spectrophotometric/Chloride	Unknown	Yes	Chemistry of the procedure.
Gas Chromatography/Hydrogen	Unknown	No	Nature of measurement method and prior use of GC to analyze relatively high activity samples ( $\sim 0.5R$ )
Gas Chromatograph/Oxygen	Unknown	No	Nature of measurement method and prior use of GC to analyze relatively high activity samples ( $\sim 0.5R$ )
Yellow Spings Analyzer/Oxygen	Unknown	No	SEC literature review of the radiological effects on the materials of construction of the sample probe.
Conductivity Meter/Conductivity	No	--	Laboratory tests by GE, the SEC literature review of the radiological effects on materials of probe construction and the SEC personnel interviews of individuals with prior experience with similar measurements.
pH Paper/pH	Yes	--	Laboratory tests performed by GE.
pH Probe/pH	No	--	Literature review by SEC of the radiological effects on the materials of probe construction, SEC personnel interviews with individuals with prior experience with similar measurements, and common use of pH probes in high radiation fields.

# LRG-II POSITION PAPERS

## VOLUME IV

TECHNICAL DISCUSSIONS AND RESOLUTION OF 11 LRG-II ISSUES. THE POSITIONS TAKEN IN THESE PAPERS WILL BE REFERENCED IN LRG-II PLANT OL APPLICATIONS.

NOTE: ADDITIONAL ISSUES WILL BE ADDRESSED IN SUBSEQUENT POSITION PAPER VOLUMES. THIS VOLUME ALSO CONTAINS A REVISED LRG-II POSITION FOR ISSUE 4-CPB.

March 12, 1982

1-CHEB  
REACTOR COOLANT SYSTEM

ISSUE

In response to the requirement of EGG-0737, Item II.B.3, "Post Accident Sampling Capability", LRG-II is required to demonstrate that the reactor coolant system sampling locations will provide coolant samples that are representative of core conditions. Of specific concern is the potential for significant dilution of the sample by makeup water which can result in the samples being analyzed at lower concentrations of soluble species (chlorine, boron, iodine, etc) than are actually present in the core.

LRG-II RESPONSE

The LRG-II position is that reactor coolant samples obtained from a tap off the jet pump pressure instrument system will provide representative core coolant samples for accident conditions and that samples be taken from this location.

In order to assure that this sample location provides a representative sample, sufficient core flow is needed to circulate water from the core to the jet pump intake. After a small break or non-break accident, the reactor water level is maintained at or near normal water level by the operator using emergency procedures. For decay power above 1% of rated power the core flow is estimated to be greater than 10% rated flow due to natural circulation. The entire reactor water inventory would be circulated through the jet pumps in about 3 to 4 minutes, thus assuring that representative samples of core coolant will be available at the jet pumps.

At power levels of less than 1% rated, a sample that is representative of core conditions would be obtained by increasing the reactor water level by 18 in. This will fully flood the moisture separators and will provide a thermally induced recirculation flow path for mixing.

Makeup water does not significantly dilute the sample. Makeup water flow amounts to approximately 2% of the core flow for small steam line breaks or non-break accidents. For small liquid line breaks, the makeup water flow rate is estimated to be less than 18% of the core flow. Thus, no significant dilution occurs and the water circulating through the jet pump is representative of reactor coolant inventory for small break or non-break accidents.

Further, sample lines in the RHR system provide for a reactor coolant sample when the reactor is depressurized and at least one of the RHR loops is operating in the shutdown cooling mode.

Finally, for larger line breaks where reactor water level cannot be maintained, reverse flow through the core to the suppression pool is provided. Suppression pool samples are obtained from the RHR pump discharge as discussed in the LRG-II position paper 2-CHEB "Suppression Pool Sampling".



2-CHEB  
SUPPRESSION POOL SAMPLING

ISSUE

In response to the requirements of NUREG-0737, Item II.B.3, "Post Accident Sampling Capability," LRG-II plants are required to demonstrate that the suppression pool sample locations will provide samples that are representative of pool inventory.

LRG-II RESPONSE

The LRG-II position is that suppression pool samples, obtained from the Residual Heat Removal pump discharge with the RHR loop lined up in the suppression pool cooling mode, will be representative of the pool inventory and that samples will be taken from this location.

The sample lines will be installed on the discharge side of the RHR pumps downstream of the pump check valve. Representative samples will be assured by operating the selected RHR loop for approximately 30 minutes prior to taking a sample. Since no SRV's discharge directly into the RHR suction and the SRV discharge locations in the pool facilitate mixing, the suppression pool sample location will provide adequately mixed samples that will be representative of pool inventory.