

SELECTION OF THE
PERMANENT HYDROGEN MITIGATION SYSTEM
FOR THE
SEQUOYAH NUCLEAR PLANT

TENNESSEE VALLEY AUTHORITY

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1.0 Introduction

In the original operating license for Sequoyah Nuclear Plant unit 1, one of the conditions stated that "for operation of the facility beyond January 31, 1982, the Commission must confirm that an adequate hydrogen control system for the plant is installed and will perform its intended function in a manner that provides adequate safety margins." The present report is submitted to document the selection of controlled combustion using thermal igniters as the Permanent Hydrogen Mitigation System (PHMS) for Sequoyah. The report is being submitted in June 1981 to allow for early review by the NRC staff and timely resolution of all issues before the January 31, 1982, licensing date. However, because of the satisfactory capability of the Interim Distributed Ignition System (IDIS) currently installed in units 1 and 2 at Sequoyah, its similarity with the PHMS, and because of the tremendous expense associated with a forced outage, TVA plans to request approval to complete installation of the PHMS components inside containment during the first refueling outage on each unit.

This report describes the various hydrogen mitigation concepts considered, evaluation criteria, and results of the evaluation. Note that a quantitative cost/benefit assessment, as originally proposed for each of the concepts selected for final evaluation, was not performed because no concept passed the preliminary

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evaluation except controlled ignition. In addition to the selection process, preliminary details of the PHMS design are provided, and ongoing work in support of the system is described.

2.0 Background

In February 1980, the TVA staff was requested by its Board of Directors to undertake a preliminary internal study of potential concepts suitable for mitigation of a degraded core event at Sequoyah Nuclear Plant. A report of the study was completed on April 15, 1980, and submitted to the NRC as Volume I of the Sequoyah Degraded Core Study on September 2, 1980. During the intensive period of the study, several concepts and combinations of concepts were evaluated. These included concepts to prevent or minimize the effects of hydrogen combustion, such as preinerting with nitrogen, postinerting with Halon, or controlled combustion with igniters, and concepts to increase containment capacity for overpressure events such as augmented atmospheric cooling within the containment, venting containment to the atmosphere through a filter, to an additional empty containment, or to another reactor containment. Conceptual designs were developed for each of these mitigations based on best-estimate design criteria. Each of these mitigation strategies was evaluated on their effectiveness, technical feasibility, additional risk, reliability, and cost. In the event that a commitment to incorporate some mitigation of hydrogen effects became necessary, the report recommended controlled combustion with igniters.

In June 1980, a TVA commitment was made to enhance hydrogen mitigation at Sequoyah. At that time, an Interim Distributed Ignition System (IDIS) was developed based on the best information available about postaccident containment

response to a hydrogen release, its distribution, and combustion. A detailed report on the safety evaluation of the IDIS was submitted as Volume II of the Sequoyah Degraded Core Study on September 2, 1980, that included a description of the system, those events for which it was designed, the physical phenomena associated with hydrogen combustion, the pertinent containment processes and design, the expected distribution of hydrogen in the containment, the analysis of containment conditions during controlled combustion of hydrogen, and the resulting environmental impact on containment structures and equipment. Following igniter durability testing at TVA's Singleton Laboratory and igniter hydrogen combustion performance testing at Fenwal, Incorporated, and in response to NRC requests for further information, a revised version of Volume II was submitted on December 15, 1980. Through these submittals, "TVA . . . by testing and analysis show(ed) to the satisfaction of the NRC staff that an interim hydrogen control system will provide with reasonable assurance protection against breach of containment in the event that a substantial quantity of hydrogen is generated" as required by the Sequoyah unit 1 operating license. TVA has continued its research and analysis efforts in the mean time and submitted quarterly reports on the work as required by the operating license. Also in response to a condition in the license, TVA has recently submitted (May 31, 1981) a report resolving all equipment survivability issues related to controlled combustion of hydrogen inside containment.

3.0 Major and Other Concepts Considered

Based on the information we assembled for Volume I of the Sequoyah Degraded Core Study (see section 2.0 above) and current thinking in the industry, four major hydrogen mitigation concepts were selected for evaluation as a Permanent Hydrogen Mitigation System (PHMS). These included controlled combustion using thermal igniters, controlled combustion with thermal igniters enhanced by spray fogging, postaccident inerting using Halon 1301, and controlled combustion using catalytic combustors. Each of these concepts will be described briefly in the following and evaluated in detail in section 5.0. In addition, limited evaluations have been made for an oxygen removal concept using a gas turbine and for a postaccident carbon dioxide inerting concept. Results of these evaluations are also included in section 5.0.

3.1 Major Concepts

3.1.1 Controlled Combustion Using Thermal Igniters

The controlled combustion concept has been explored in detail over the past year since TVA introduced its Interim Distributed Ignition System (IDIS). The concept, as evaluated for the PHMS, is similar in purpose: to ignite hydrogen at concentrations near the lower flammability limit to ensure small stepwise or continuous burning in order that the energy addition rate to the containment may be moderated as much as possible. However, the system evaluated for the PHMS had additional and relocated igniters, potentially different types of thermal igniters,

improved reliability and availability, and operator actuation from the main control room.

3.1.2 Control Combustion Using Thermal Igniters Enhanced by Spray Fogging

Very fine microfogs have been proposed as a means to inert a containment postaccident against hydrogen combustion. However, the concept evaluated by TVA for the PHMS consisted of larger droplet fogs used instead as a heat sink in conjunction with igniters to extend the containment capability to accommodate hydrogen combustion. The spray fog system evaluated for the PHMS consisted of spray headers in both the upper and lower compartments and associated pump controls to provide a continuous, dense fog following degraded core events.

3.1.3 Postaccident Inerting Using Halon 1301

Following a degraded core accident, Halon 1301 could be added to the containment atmosphere in sufficient amounts to inert it against hydrogen combustion. The system considered for the PHMS consisted of discharge headers, supply tanks, accumulators, and controls to allow the rapid postaccident injection of Halon.

3.1.4 Controlled Combustion Using Catalytic Combustors

An alternative method for recombining hydrogen following a degraded core accident uses catalytic action to enhance and accelerate the process. Two catalytic combustor applications were considered for the PHMS. One involved using a combustor on the

discharges of the reactor vessel vent and the pressurizer relief line and the other used combustors in the general open containment volume.

3.2 Other Concepts Considered

3.2.1 Oxygen Removal Using a Gas Turbine

Reducing the overall containment oxygen concentration could prevent the uncontrolled combustion of hydrogen following an accident. Gas turbines have been proposed as a postaccident means to eliminate sufficient oxygen.

3.2.2 Postaccident Inerting Using Carbon Dioxide

Similar to Halon 1301, carbon dioxide could be added in sufficient amounts to the containment atmosphere following a degraded core accident to inert it against hydrogen combustion.

4.0 System Evaluation Criteria

Several criteria were used to compare the suitability of each of the four candidates for the PHMS outlined in section 3.1. The comparisons were qualitative in nature and attempted to arrive at a suitable balance of the factors described in the remainder of this section.

First, the concept selected for the PHMS must satisfy the condition in the Sequoyah operating license that requires that "for operation of the facility beyond January 31, 1982, the Commission must confirm that an adequate hydrogen control system for the plant is installed and will perform its intended function in a manner that provides adequate safety margins." An adequate hydrogen mitigation system would be effective in reducing the risk from reasonable accident scenarios such as proposed in the interim rule on October 2, 1980. Specifically, "the maximum duration for hydrogen generation was specified to be eight hours . . . (and) an upper limit of 75 percent should be used for the percent of fuel clad that reacts to produce hydrogen." In addition, the original plant margins of safety should be maintained, if possible, even for these accidents beyond the design basis.

The concept selected for the PHMS should be flexible in application and suitable for further enhancements should such features become available and are believed to be necessary. In addition, the selection should not irrevocably commit the plant to a system with severe limitations pending the outcome of the

proposed generic rulemaking on the issue of degraded core accident mitigation.

The selected concept should be feasible for immediate implementation without requiring extensive further development. No major unresolved technical issues should remain in the functional or implementational capability of the concept. The concept should be able to be designed, procured, installed, tested, and approved by January 31, 1982.

The concept should have minimal impact on existing plant systems providing support functions or features such as physical layout.

The concept selected for the PHMS should avoid adverse operational impacts. Specifically, life safety, effects of inadvertent operation, potential uncertainty of the operator to manually initiate operation, performance monitoring requirements, preoperational and surveillance testing, maintenance, and reliability should be considered.

Finally, the concept selection should minimize cost associated with design, hardware, construction, downtime, operation, and maintenance.

5.0 Concepts Rejected for PHMS

5.1 Major Concepts Rejected

The four hydrogen mitigation concepts outlined in section 3.1 were evaluated qualitatively based on the PHMS selection criteria discussed in section 4.0. Based on that evaluation, controlled combustion with thermal igniters enhanced by spray fogging, postaccident inerting using Halon 1301, and controlled combustion using catalytic combustors were eliminated from consideration for the PHMS. Details of the evaluations are presented in the rest of section 5.1.

5.1.1 Controlled Combustion Using Thermal Igniters Enhanced by Spray Fogging

As stated in section 3.1.2, spray fogging could be used in conjunction with a controlled combustion system using thermal igniters. Since the fog would serve as an additional heat sink for containment pressure suppression and the resulting turbulence would aid igniter effectiveness, fog addition should accommodate a higher rate of hydrogen combustion. Our conceptual design of the igniter/spray system included redundant spray headers and thermal igniters in all areas of the upper and lower compartment. The spray nozzles in the present containment spray system in the upper compartment could probably be replaced to produce the desired nominal droplet size of 100 microns. The spray system would require additional redundant pumping capacity to maintain a drop density of 0.05 percent by volume. The thermal

igniter system would be identical to that described in sections 3.1.1 and 6.0.

Since TVA believes that a controlled combustion system using thermal igniters would meet the operating license condition of being an "adequate hydrogen control system" (see section 6.0), we believe that an enhancement of that system with spray fogging would also be adequate. Similarly, it would satisfy the interim rule and maintain an adequate margin of safety in the containment pressure capability. An enhanced system should have even more flexibility to mitigate a broad spectrum of hydrogen transients that might result from the degraded core rulemaking. However, there remain enough unanswered questions about the true magnitude of the enhancement and whether a practical system could be installed to maintain the required droplet density against the effects of agglomeration and rainout to have caused TVA to reject igniters enhanced by spray fogging for the PHMS.

The spray fogging concept is not feasible for immediate implementation at Sequoyah. is not known presently how much pressure suppression capability the addition of the spray fog system would contribute. The conceptual design called for 100 micron drops distributed throughout the containment.

This would yield benefits mainly for burns occurring in the lower compartment since the present containment spray system already would produce a spray in the upper compartment with a median drop size of 200-300 microns. The latest theoretical and analytical predictions indicate that controlled combustion would generally occur more often in the ice condenser upper plenum than in the lower compartment. In addition, the loss rates for turbulent containment scale fogs of this droplet size are unknown but may be so large as to make the pumping requirements impractical. Sandia National Laboratories state in NUREG/CR-1762, "Analysis of Hydrogen Mitigation for Degraded Core Accidents in the Sequoyah Nuclear Power Plant," that "the suspension of a large mass of water droplets in the containment atmosphere for an extended time may be the most difficult technical problem with fogging . . . This issue must be settled before fogging systems can be designed." The makeup supply system to maintain a fog of specified density would have to be sized based on the currently unknown loss rate. These issues certainly could not be resolved consistent with the January 31, 1982, license condition.

The addition of a spray fogging system could have a significant impact on the existing plant. System

requirements would include space for pumps, containment penetrations, a system of spray headers and nozzles that could be quite elaborate, and accompanying instruments and controls. The electric power requirements for the additional pumps could be substantial and force additional emergency diesel capacity to be obtained. An analysis of the negative pressure following inadvertent spray would also be required.

The impact on operations of an igniter/spray system should not be severe since the only undesirable effects of inadvertent operation would be containment depressurization which could be avoided through pressure relief modifications. The spray system would have to be activated early enough in the accident to allow the steady-state fog density to be achieved.

Preoperational testing of the system would be of a fairly standard type for a mechanical fluid system except that air instead of water would be used to verify that flow to each nozzle was unobstructed. The surveillance test would consist of powering valves and pumps. Maintenance would consist of routine mechanical servicing of pumps and valves. A small amount of plant downtime might be associated with this testing and maintenance. Reliability of a

redundant spray fogging system should be good and on the order of any other large, electrically-powered mechanical fluid system.

A spray fogging system could be relatively expensive if an extensive nozzle system or large pumps are required and if installation and downtime are considered.

In conclusion, the use of spray fogging to enhance the performance of controlled combustion with thermal igniters was rejected by TVA because of the uncertain magnitude of the improvement and the unknown spray droplet loss rate required to size the system. Efforts underway to help TVA quantify these two parameters are described further in section 8.0.

5.1.2 Postaccident Inerting Using Halon 1301

As stated in section 3.1.3, Halon 1301 could be injected into the containment following a degraded core accident to inert the atmosphere against hydrogen combustion. Halon 1301 (CF_3Br) is a halogenated hydrocarbon that was selected as an inertant because of several favorable qualities. While most gases used for this purpose work by diluting oxygen below the mixture's flammability limits, the Halons work by chemically interrupting the combustion process. This effect results in less Halon 1301 being needed to inert a given volume than

other inertants such as nitrogen or carbon dioxide. In addition, there is considerable experience with Halons since they are widely used in commercial applications for fire suppression. Halon 1301 also has the desirable property that it can be stored as a liquid under pressure but vaporizes rapidly when depressurized.

Based on their prior studies and experiments on reactor containment inerting with Halon 1301, Atlantic Research Corporation (ARC) was selected to perform a conceptual design study for an ice condenser inerting system and to address inadvertent actuation, long-term accident recovery, Halon decomposition, water chemistry, and corrosion potential. Their final report is included as Attachment A. As shown in figure 6 of that report, a conceptual system could consist of four Halon tanks and a backup, each pressurized by individual nitrogen accumulators to maintain the Halon as a liquid and propel it into the containment when necessary. The spray headers and nozzles would be located in upper and lower compartments to ensure that the entire containment would receive enough Halon to inert each region. The system piping and discharge pressure was sized to allow the containment to be inerted within 1000 seconds after injection began.

TVA believes that a Halon postinerting system would, in principle, meet the operating license condition of being an "adequate hydrogen control system." It would also satisfy the requirements proposed in the interim rule and should maintain an adequate margin of safety under the containment ultimate pressure capability. In addition, assuming the Halon could be injected rapidly enough, it should have the flexibility to inert against a broad spectrum of hydrogen transients that might result from the degraded core rulemaking. However, there are fairly severe drawbacks to the actual implementation and use of a Halon system that have caused us to reject it for the PHMS.

The Halon 1301 postinerting concept is not feasible for immediate implementation at Sequoyah. Following its use after an accident, a portion of the injected Halon would dissolve in the sump water inside containment. Enough additional Halon could be initially injected to overcome this loss, but the dissolved Halon would radiolytically decompose to form HF and HBr in low concentrations (1200 ppm and 400 ppm, respectively). In addition to general acidic corrosion, potentially severe stress corrosion cracking of stainless steel piping could occur due to the presence of these halides. From section 6.3 of Attachment A, "without treatment . . . potential exists for the following detrimental effects:

- . Probable stress corrosion cracking of stainless steel of heated surfaces.
- . Possible stress corrosion cracking of stainless steel in water held above 150°F for an extended period.
- . Extensive crevice corrosion, pitting and galvanic corrosion initiated during the period of low pH and high temperature perpetuated by increased conductivity of the water and presence of bromide ion."

However, the report goes on to say, "with treatment . . . Halon decomposition may be avoidable by addition of bromide ion (NaBr, KBr, LiBr); likewise, the pH depression may also be avoided . . . Either of these should mitigate the general corrosion and reduce the potential for stress corrosion cracking. Inhibitors can be added which may prevent localized corrosion."

Despite ARC's statement in section 1.0 of Attachment A that "potential corrosion of metals in the primary and secondary cooling systems . . . is not a safety question but rather an economic matter related to system recovery after a LOCA," TVA believed the issue was definitely one of long-term operability and safety and deserved further study. Therefore, we performed experiments at our Singleton Materials Engineering Laboratory to investigate the

metallurgical effects on SS304 of aqueous bromine and fluorine solutions in the concentrations predicted by ARC. The test reports are included in this report as Attachment B. The test results show these environments to be very aggressive and that the straight unbuffered solution caused heavy, intergranular attack. Even when buffered, as suggested above by ARC, the solutions resulted in heavy pitting. Note that these tests were conducted at 200°F because of the unavailability of an autoclave. In practice, the specimen would see system temperatures of up to 650°F and attack would be expected to be even more severe. Based on the effects on the sensitized samples (representing weld areas), long-term postaccident system integrity would be questionable. An extensive development and testing effort would be required to identify whether a suitable postaccident water chemistry control method existed and to demonstrate its effectiveness. The issue certainly could not be resolved consistent with the January 31, 1982, license conditions.

The addition of a Halon postinerting system would have a fairly sizable impact on the existing plant. Space would have to be allocated for the five Halon tanks and their five nitrogen accumulators, two containment penetrations would have to be added, an extensive system of injection headers would be

required to ensure timely coverage of each compartment, and enough instrumentation and controls to initiate system injection and monitor its performance would be necessary.

The impact on operations of a Halon postinerting system could be severe. Stringent guidelines for system activation would be required to prevent inadvertent actuation during personnel occupancy since only about ten minutes would be available to evacuate before physiological harm results. Inadvertent operation would also dump the relatively expensive Halon and require several days of purge and cleanup. These impacts would naturally cause the operator to be hesitant about manually initiating the system even during an event when it might be needed. Since the effectiveness of Halon inerting depends on complete achievement of the required concentration everywhere in the containment, the partial or local injection that might result from a late actuation could still allow uncontrolled hydrogen combustion to occur. This condition would be compounded by the additional pressure from the presence of Halon and thermal decomposition products from the high combustion temperatures. In addition, it is not certain that for all events leading to hydrogen release, the warning signs available to the operator would be both unmistakable enough to require Halon

injection and early enough to allow it. Operator reluctance and unclear guidelines are major drawbacks to the use of Halon.

Preoperational testing of the system would verify valve operability and obstruction-free flow (of air) to each nozzle. The surveillance test would consist of powering valves and verifying sufficient accumulator pressure. Maintenance would consist of routine mechanical servicing of the valves. Little plant downtime would be required for this testing and maintenance. Reliability of a Halon system with a backup tank and redundant valves should be very good since it is a passive system after valve cycling.

A Halon postinerting system would be relatively expensive when costs of the Halon itself, the system hardware, installation, and downtime are considered.

In conclusion, the use of Halon postaccident inerting for the PHMS was rejected by TVA because of probable long-term corrosion effects and operational uncertainties and is not being considered further.

5.1.3 Controlled Combustion Using Catalytic Combustors

As stated in section 3.1.4, a method of controlled combustion alternate to thermal or spark ignition uses catalytic combustors. The catalytic combustor operates by providing a noble metal substrate to

facilitate the reaction of hydrogen and oxygen to form water vapor. Compared to a thermal recombiner, a catalytic combustor operates at a higher flow rate for a given size and should be effective at lower and higher concentrations of hydrogen.

The conceptual design for the catalytic combustor system consisted of a combination of two distinct applications. One type of combustor would be located in the discharge of each vent from the reactor coolant system (such as reactor vessel head vent and pressurizer relief line) to burn hydrogen before it would be released to the contaminant. Another combustor type would be located in the general containment volume to burn any hydrogen in the atmosphere. A fairly sophisticated mixing system would be required to remove moisture and add air to obtain a fuel/air mixture in the operating range of the vent combustors. A forced-air induction system would be required to achieve a reasonably fast throughput rate in the containment combustors. Either supplemental cooling or an exhaust gas distribution system would probably be required for either type of application to prevent local heating problems.

In theory, the catalytic combustor concept would satisfy the operating license condition of being an

"adequate hydrogen control system." It also would meet the requirements proposed in the interim rule and maintain an adequate margin of safety in the containment pressure capability. However, the concept is not suitably developed to be accepted as the PHMS for Sequoyah.

Under ideal operating conditions, controlled combustion using catalytic combustors may be slightly more flexible in mitigating any hydrogen transients that might result from rulemaking than controlled combustion using thermal igniters. This is because under ideal conditions (in the absence of any catalyst poisons), the catalytic combustor would operate efficiently at lower hydrogen concentrations.

Following a degraded core event, the containment atmosphere could contain some amounts of core fission products. One of these, methyl iodide (CH_3I), was selected as the basis for catalyst poisoning experiments performed for TVA by Acurex Corporation. The studies showed that combustors could remove hydrogen from the inlet stream at high efficiencies and velocities in the absence of methyl iodide. However, at concentrations that could be expected in the postaccident containment atmosphere, the catalyst was easily poisoned and eventually deactivated by the

methyl iodide. This effect was dependent on both methyl iodide and hydrogen concentrations. It was especially pronounced at the low hydrogen concentrations where the prospect of using the catalytic combustor had been proposed as being particularly attractive. Poisoning at low hydrogen concentrations would eliminate the major advantage of catalytic combustors over thermal igniters for controlled combustion.

The design of a practical steam removal and air addition mechanism upstream of the vent combustor would be a difficult obstacle considering the variable water, steam, and hydrogen flows that could be expected in the vent line. Unless the mixing device was able to add sufficient air, unburned hydrogen could pass through the combustor and into the containment. A more serious problem could be the potential for not sufficiently diluting mixtures containing high concentrations of hydrogen before causing ignition.

The poisoning experiments performed by Acurex are bench-scale. Since the poisoning proceeded gradually along the axis of the catalyst bed, it was proposed that merely extending the length of the catalyst as much as necessary to allow for the maximum expected deactivation could overcome the poisoning problem.

However, TVA believes more accurate predictions of maximum atmospheric fission product concentrations and larger scale catalyst tests would be necessary before such basic required information as the number and size of combustors could be reasonably assured.

The impact on plant features could be significant if several containment combustors and an accompanying forced-air induction system were required. Space, power, and cooling or distribution requirements cannot be determined at this time but could be sizable.

The impact on plant operations of a combustor system should not be severe. The containment combustors would have to be activated before hydrogen release to the containment would be expected similar to initiation of controlled combustion using thermal igniters. Inadvertent actuation would not cause any major problems. The vent combustor mixing device should be automatic since the operator could not be expected to provide control under rapidly changing conditions.

Preoperational testing of the system would verify the fan flow rates and the cooling system (if required) heat removal rates. The surveillance test would consist of powering the fans and the vent combustor

mixing device. The maintenance would be of a routine mechanical nature unless the catalyst bed required regeneration or replacement. Some plant downtime would be required to perform this testing and maintenance inside containment. Reliability of a catalytic combustor system should be good unless the catalyst bed performs poorly since the rest of the system is like any other active mechanical system.

The cost of a catalytic combustor system cannot be determined at present since the materials and quantities have not been specified. However, the cost of a number of large, platinum combustors with an extensive forced-air induction system and cooling or distribution system could be fairly sizable. In addition, the research program that would be necessary to develop a practical, proven catalytic combustor would be relatively expensive.

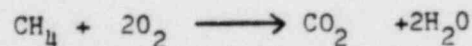
In conclusion, due to the poisoning effects observed at low concentrations of hydrogen, controlled combustion using catalytic combustors does not appear to be superior to controlled combustion using thermal igniters. In addition, not enough information is known about the sizes and numbers of containment combustors or the design of the vent combustor mixing device to judge whether a practical system could eventually be developed. Since these issues

definitely could not be resolved consistent with the January 31, 1982, license condition and since the catalytic combustor system does not appear to be superior to a thermal igniter system, TVA has rejected catalytic combustors for the PHMS for Sequoyah.

5.2 Other Concepts Rejected for PHMS

5.2.1 Oxygen Removal Using a Gas Turbine

A mixture of air and hydrogen can be rendered nonflammable by reducing the oxygen concentration below 5 percent. Gas turbines have been proposed as a means to rapidly inert the containment by reducing the oxygen level following a degraded core accident before hydrogen could be released. Such a system would involve one or more turbines, fuel supply lines, and monitoring instrumentation and controls. It would require an additional forced-air induction system with fans and associated ductwork. It should also include its own supplemental cooling to avoid impacting the containment heat removal capability. Using a representative fuel such as methane as follows,



estimates were made of some of the combustion parameters. In order to reduce the containment oxygen concentration from the original 20 percent to the required level of 5 percent (conservatively neglecting the addition of CO_2), two tons of methane

would be required and 82 million BTU would be generated. To inert the containment within 30 minutes, an average airflow of 54,000 scfm would be required.

The installation and operation of a gas turbine oxygen removal system would have a significant impact on existing plant systems and features. Several major auxiliary systems would be required to support operation of the turbine. First, a forced-air circulation system with extensive ductwork would be necessary to allow high volume throughput.

Maintaining a steady, dry combustible air/fuel mixture even with such a circulation system would be difficult under postaccident containment conditions. As the overall oxygen concentration became leaner, airflows much higher than the 54,000 scfm would be required to prevent flameout and restart. A number of other auxiliary systems would be needed to support turbine operation such as cooling of the lubricating oil and the combustion chamber walls. Finding adequate space in the lower compartment of the containment for the gas turbines and these supporting systems would be difficult.

The 82 million BTU heat load would be comparable to the heat load from combustion of the amount of hydrogen generated by a 75-percent metal-water

reaction (1500 lbs H_2). However, unless several distributed gas turbines were used, the local heating effects from rapid inerting could be severe if supplemental cooling were not provided. In addition, the gas turbine would pose other hazards to the containment or equipment, including the presence of a flammable fuel and the potential for internal missile generation. The reduction in the volume of noncondensibles in the containment due to depletion of the oxygen concentration could necessitate opening the vacuum relief valves to avoid exceeding the negative pressure capability. Opening these valves would introduce air which could deinert the containment after hydrogen had been released. Also, it would not be desirable to have to defeat any containment isolation feature. Preventing the formation of a flammable mixture during long-term accident recovery and hydrogen disposal could be a difficult problem. Since purging the containment with air would have to be avoided, provisions for nitrogen (or some other inertant) purge would be required.

For the gas turbine system to inert the containment by the time hydrogen could be released, it must be initiated in time to perform its function. The previous estimate of 30 minutes to deplete the oxygen is probably a reasonable minimum time. It would be

difficult, for all scenarios, for the operator to determine that the event was serious enough to warrant initiating the gas turbine that far in advance of hydrogen release into the containment. In addition, the operator would naturally be reluctant to activate a system that would impose such a heat load, cause ice melting, and force a plant shutdown for several months until he was absolutely sure it was necessary.

In summary, our evaluation of the oxygen removal concept using gas turbines has identified major impacts on existing plant features, potentially severe local heat loads, fire and missile hazards, and perhaps most important, undependable actuation of the system when needed. These drawbacks prevent the further consideration of gas turbines for hydrogen mitigation.

5.2.2 Postaccident Inerting Using Carbon Dioxide

As stated in section 3.2.2, carbon dioxide (CO_2) could be injected into the postaccident containment atmosphere in sufficient quantities to inert against the eventual release and combustion of hydrogen. Such a system would be very similar to the Halon postinerting system described in section 5.1.2. The evaluation in that section would be applicable to a CO_2 system except that more CO_2 would be required to

inert the containment and that no corrosion problems would result from the use of CO₂. The excessive pressure resulting from the additional amount of gas required is the major drawback associated with the CO₂ postinerting concept. A comparative analysis of the physical properties of Halon, carbon dioxide, and nitrogen and the containment pressures following their injection was submitted in Appendix C of TVA's first quarterly progress report December 15, 1980. This analysis showed that the overall pressure following CO₂ injection after a degraded core accident would be well above the containment design pressure. The deliberate overpressurization of the containment above its design pressure was rejected by TVA for use at Sequoyah, especially since other hydrogen mitigation methods such as controlled combustion using thermal igniters would be able to prevent excessive postaccident pressures.

6.0 Concept Accepted for PHMS

Controlled combustion using thermal igniters has been selected by TVA as the only suitable candidate for the PHMS. As stated in section 3.1.1, this concept is the same one employed by TVA in the Interim Distributed Ignition System (IDIS) that has been installed in Sequoyah units 1 and 2. The operating principle is straightforward: to reliably ignite hydrogen throughout the containment at concentrations near the lower flammability limit to achieve periodic or continuous lean burning in order that the energy addition rate to the containment may be distributed as evenly as possible throughout the duration of the hydrogen combustion part of the accident. Since the containment pressure response is rate-dependent, this moderated energy addition rate would allow the active and passive containment heat sinks to absorb the heat of combustion more effectively and reduce the overall containment pressurization.

The design of the thermal igniter system as evaluated for PHMS selection is described in some detail in section 7.0. The basic design as presently contemplated includes a total of 60 igniters in two trains distributed throughout the containment with at least one pair of redundant igniters located in each region. Manual control capability is provided in the main control room.

TVA believes that, in principle and in practice, a controlled combustion system using thermal igniters would satisfy the operating license condition of being an "adequate hydrogen control system . . . that provides adequate safety margins." It

has been demonstrated to meet the requirements of the interim rule. In addition, analyses have shown that a margin of safety is maintained below the containment design pressure for a small break LOCA (S_2D). The thermal igniter system should have good flexibility to mitigate other hydrogen transients that might be stipulated in the rulemaking and still maintain a margin of safety below the containment ultimate capability. Enhancements such as spray fogging are potential additions if necessary and feasible.

The thermal igniter concept is feasible for immediate implementation at Sequoyah. Based on testing and extensive analyses performed for the IDIS over the past year by TVA and others, the major issues have been identified and resolved and the system design parameters have been well established. TVA believes that any remaining issues could be resolved and NRC confirmation obtained consistent with the January 31, 1982, license condition. However, as noted in section 1.0, due to the protection capability of the currently installed IDIS and to avoid a forced shutdown for modifications inside containment, TVA plans to request approval to replace the IDIS with the PHMS at the first refueling outage on each unit.

The implementation of an upgraded thermal igniter system would not have a major impact on present plant features or systems. Nominal amounts of normal and emergency electrical power would be required, along with containment penetrations for the power supplies. One switch per train of igniters would be required in

the main control room. Existing containment instrumentation would be adequate to monitor system performance. No additional cooling capacity is required since the thermal igniter system is designed to depend on the ice condenser and containment sprays for cooling. Likewise, no added forced circulation is required since the air return fans do an acceptable job of mixing and distribution.

Licensing issues to be addressed to support the addition of the upgraded thermal igniter system should not be extensive since TVA has already made a number of submittals during the past year that satisfactorily supported TVA's position that the IDIS provided, with reasonable assurance, protection against breach of containment. For example, resolution of the equipment survivability and local detonation issues were addressed in TVA's report submitted to the NRC in May 1981.

The impact on operations of a thermal igniter system would not be severe. The system poses no threat to personnel since it is not required during normal operation and would normally be deenergized. Inadvertent actuation of the system during any phase of plant operation presents no threat to personnel or equipment. This would prevent reluctance by the operator to activate the system and would enable him to activate it at a point in the accident before hydrogen could be released to the containment. The relatively short warmup time for the thermal igniters following activation would contribute to the high likelihood of their availability.

Preoperational testing of the thermal igniter system would involve verifying that individual igniter temperatures were adequate. At that time, the current in each circuit would be recorded as a baseline for future use in surveillance tests. The complete igniter system will be periodically tested. This test, consisting of measuring the current in each circuit and comparing it with the original baseline, can be performed at the electrical distribution panel outside containment and can detect the failure of one or more igniters. Maintenance on the thermal igniter system is expected to be minimal since the system consists of electrical components such as thermal igniters (heaters), transformers, circuit breakers, control switches, indicating lights, and electrical cables that do not require adjustment or periodic replacement. The reliability of a thermal igniter system should be extremely good since there are no moving parts (other than switches) or no variable controls (just ON/OFF).

The cost of design and hardware should be moderate for a thermal igniter system since the technology is proven and does not need extensive development. Installation costs should not be excessive if the work is performed during the first refueling outage instead of during a special forced outage.

In conclusion, after examining a number of hydrogen mitigation concepts and evaluating controlled combustion using thermal igniters enhanced by spray fogging, postaccident inerting using

Halon 1301, and controlled combustion using catalytic combustors in particular, TVA has selected controlled combustion using thermal igniters for the Permanent Hydrogen Mitigation System at Sequoyah. Although a considerable amount of experience has been accumulated with the thermal igniter concept through work on the IDIS, as described earlier, TVA is pursuing additional confirmatory studies which are outlined in section 8.0.

7.0 Preliminary Details of the PHMS

As described in the previous section, controlled combustion using thermal igniters has been selected for the PHMS at Sequoyah. Design of the system is currently underway. Preliminary information about the system implementation is provided in this section including a design requirements document, a description and justification of igniter locations, and basic operating procedures.

7.1 System Design Requirements

The design requirements document used internally by TVA is provided as Attachment C.

7.2 Description and Justification of Igniter Locations

The principle of the controlled combustion concept selected for the PHMS is to ignite hydrogen at any containment location as soon as the concentration exceeds the lower flammability limit. To assure this, a total of 60 igniters will be distributed throughout the major regions in which hydrogen could be released or to which it could flow in significant quantities. There will be at least two igniters, powered from separate trained sources, generally located near the top of each of these regions. See figures 2 through 8 in Attachment C for igniter locations.

Following a degraded core accident, any hydrogen which is produced would be released from a break or the pressurizer relief tank into the containment in the lower compartment inside the crane wall. To cover this source region, there will be 18 igniters (equally divided between trains) located

high in the lower compartment inside the crane wall. Four of the igniters will be equally distributed around the interior of the crane wall between ice condenser inlet doors at elevation 730'. Two igniters will be located at the lower edge of each of the five steam generator and pressurizer enclosures at elevation 731'. A pair of igniters will be located in the top of the pressurizer enclosure at elevation 772'. Another pair of igniters will be placed above the reactor vessel in the upper reactor cavity at elevation 730'. Since there are no potential hydrogen sources in the steam generator enclosures and significant flows into these enclosures are not expected from the rest of the lower compartment, igniters will not be located in the top of these enclosures. The pair of igniters located at the entrance to each steam generator enclosure would ignite any flammable mixtures that may pass by them.

Any hydrogen not burned in the lower compartment would be carried up through the ice condenser and into the upper compartment. To cover these regions, there will be 22 igniters (equally divided between trains) located in the ice condenser and the upper compartment. Since steam would be removed from the mixture as it passed through the ice bed, thus concentrating the hydrogen, a nonflammable mixture in the lower compartment could become a flammable mixture in the ice condenser upper plenum. To provide controlled combustion in this region, four igniters will be equally

distributed around the upper plenum at elevation 792'. Six more igniters will be equally spaced on the crane collector rails above the ice condenser top deck blanket at elevation 809'. Four igniters will be located around the upper compartment dome at elevation 846'. Four more igniters will be spaced around the inside of the crane wall below the upper plenum exit at elevation 787'. An "A" train igniter will be located above the "A" train air return fan at elevation 755' and a "B" train igniter will be located above the "B" train fan at elevation 746'. One igniter is also located on the outer face of each of the two steam generator chambers at elevation 742'.

The two air return fans provide recirculation flow from the upper compartment through the accumulator rooms, pipe chase, and HVAC rooms (the sum of which are referred to as the "dead-ended" volume) and back into the main area of the lower compartment. To cover these regions, there will be 20 igniters (equally divided between trains) distributed throughout the rooms through which the recirculation flow passes. Four igniters will be equally spaced around the pipe chase at elevation 689'. A pair of igniters will be located in each of the four accumulator rooms, the two HVAC rooms, the instrument room, and the heat exchanger room between elevations 700' and 716'.

7.3 Operating Procedures

Since the principle of controlled combustion using thermal igniters is to ignite mixtures as they become flammable at any

containment location is fairly straightforward, no sophisticated operating procedures are necessary. TVA has not identified any reasonable rationale for individual or group control of igniters to try to achieve local or partial combustion. Therefore, manual initiation of all igniters by the operator before any potential release of hydrogen into the containment is the only major objective. Basically, the PHMS will be initiated manually from the main control room following any event that requires the use of Emergency Operating Instruction 1 (EOI-1), "Loss of Reactor Coolant." The igniters will be divided into two redundant groups (trains A and B), with a control switch and status (ON/OFF) indication for each group located in the main control room. More detailed information about the system design of the PHMS and its interaction with other key systems will be provided by the end of October 1981.

8.0 Ongoing Work

As mentioned in several sections of this report, TVA is continuing to pursue information to confirm the effectiveness and characteristics of controlled combustion for hydrogen mitigation. The major portion of this effort is being coordinated by the Electric Power Research Institute (EPRI). A number of areas are being investigated at several research facilities. Hydrogen combustion properties such as flame speeds, burn completeness, lower flammability limits, propagation between mixtures of different concentration, and effects of obstacles and turbulence are being examined at the Whiteshell Nuclear Research Establishment along with the effectiveness of various types of igniters. At Acurex Corporation and Factory Mutual Research Corporation, the effects of sprays and fogs are being studied. A large-scale model of an ice condenser containment is being used at Hanford Engineering Development Laboratory to investigate hydrogen mixing and distribution. A detailed explanation, test matrix, and schedule for the EPRI program was submitted by TVA to the NRC in our third quarterly report on June 16, 1981.

TVA is presently exploring details of an igniter endurance testing program to be conducted at our Singleton Laboratory. Items being investigated include methods to continuously inject controlled amounts of hydrogen and air into the combustion chamber, methods for detecting the presence of a hydrogen flame, and the extent of the test matrix. This program is currently scheduled to be complete by the end of October 1981.

TVA is making arrangements to establish an environmental qualification testing program for the thermal igniters at Wyle Laboratories in Huntsville, Alabama. The igniters will be subjected to the design basis environmental conditions listed in section 3.11.2 of the Sequoyah FSAR. No hydrogen ignition tests will be performed by Wyle since they are being conducted at Singleton. Test schedules, when available, will be provided.

TVA has committed verbally to analyze the effects of extending the design basis hydrogen transient into the core reflood and accident recovery phase. In addition, sensitivity studies of further hydrogen-producing scenarios will be performed. The results of these additional analyses are scheduled for submittal in October 1981.

E71163.04

ATTACHMENT A



FINAL TECHNICAL REPORT

SYSTEM FEASIBILITY ANALYSIS OF USING HALOW 1301
IN AN ICE CONDENSER CONTAINMENT

Submitted to:

Tennessee Valley Authority
400 Commerce Avenue
Knoxville, TN 37902

American Electric Power
2 Broadway
New York, NY 10004

Duke Power Co.
Design Engineering Department
Post Office Box 33189
Charlotte, NC 28240

Contract TV-55205A

Submitted by:

Edward T. McHale

Atlantic Research Corporation
5390 Cherokee Avenue
Alexandria, Virginia 22314

ARC No. 42-6522

February 1981

ATLANTIC RESEARCH CORPORATION
ALEXANDRIA, VIRGINIA • 22314

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FOREWORD

This study was jointly funded by Tennessee Valley Authority, Duke Power and American Electric Power under Contract No. TV-55205A. The following persons made major technical contributions to the program: A. J. Biedermann of C. P. Dillon and Associates (Section 6.0); N. P. Rossmeyssl of Atlantic Research Corporation (Section 2.0); Dr. S. A. Turner of Southern Service Applications, Inc. (Section 4.0); and Dr. G. von Elbe of Atlantic Research Corporation (Section 5.0).

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1.0 INTRODUCTION AND SUMMARY

A development program had been conducted during the mid-seventies under sponsorship of the Maritime Administration, which established that Halon 1301 could provide protection against any combustion hazard that hydrogen gas might present following a loss-of-coolant accident in relatively small LWR containments of nuclear-powered ships. That program comprised analytical study, laboratory experiments and large-scale testing to define the requirements for a Halon 1301 system and to examine certain operational problems that were hypothesized. Full details are contained in reference (1), available through NTIS.

The present study reported here examined the question of whether a Halon system would be suitable for an ice condenser containment. There are two aspects to the suitability question -- one concerns safety and is related to licensing. The conclusion of the study is that a Halon system would provide full safety. The other aspect of the question concerns potential corrosion of metals in the primary and secondary cooling systems, which might arise from a small amount of decomposition of Halon. This is not a safety question but rather an economic matter related to system recovery after a LOCA. The conclusion of the study is that any corrosion problem can probably be eliminated by adjusting the water chemistry, and might even be self-eliminating.

Halon 1301, which has the chemical formula CF_3Br , is a well-known fire extinguishing and explosion suppressing agent. An inerting system for nuclear-related application would consist of a predetermined quantity of Halon stored as a liquified gas in several storage vessels near the containment. In the event of a LOCA, the system could be immediately activated, or alternatively if hydrogen concentration reached a certain point, 1301 could be discharged either automatically or manually into the containment through a piping and valve system. Many operational advantages are associated with the simplicity of a 1301 system. For example, there are few moving parts, minimal power requirements, complete reliability, relative economy, storage convenience, ease of periodic testing, and once activated the system requires little further attention.

The quantity of Halon varies with the particular application, being dependent mainly on containment volume and amount of hydrogen that could develop.

For an ice condenser containment of the Sequoyah type, the exact requirement as determined in this study is 236,300 lb mass. This amount of agent would be stored in four 12-foot diameter vessels, each containing 59,075 lb. In principle, it is possible to use gases other than Halon 1301 for inerting, such as nitrogen or carbon dioxide. In practice, however, the storage requirements and the pressures that these gases would produce in the containment would be excessive. Halons other than 1301 also have been considered. Halon 2402 does not have sufficient vapor pressure for such application. Halon 1211 may be comparable to 1301.

Halon 1301 is well suited for containment vessels because of its physical and chemical properties and because of its favorable toxicological characteristics (2,3). Some physical properties are listed in Table 1 and Figure 1. The chemical properties of Halon 1301 of interest concern its compatibility with materials of construction, its reactivity and thermal stability. Relevant toxicity and chemical behavior are discussed later in the report.

It is of interest to consider the pressures and temperatures that would be expected in the event that a noninerted hydrogen-air mixture were ignited. The theoretically calculated values for such mixtures are presented in Figure 2. These were computed using JANNAF data and the Atlantic Research thermochemical code. The explosion curves of Figure 2 refer to the case of ordinary slow (subsonic) combustion in a closed vessel. The detonation curves give the pressures and temperatures associated with the supersonic combustion. The detonation limits are ordinarily given as 18 to 59% hydrogen in air. The explosion or flammability limits for hydrogen are usually cited as about 4 to 95%. Concerning the lower flammability limit, it is true that small flamelets can be made to propagate at this concentration; however, no significant overpressures develop until a mixture strength of about 7% is reached. This can be seen in the data of Figure 3, which is taken from reference (4). (In the figure, overpressures are not produced below about 8%, but the authors reported that with repeated sparking the limit was lowered to about 7%.) The tests of Figure 3 were performed in a 12-ft. sphere with central spark ignition. Above about 12% hydrogen, the experimental measurements coincide closely with calculated pressures.

Table 1. Physical Properties of Halon 1301

Chemical Formula	CF_3Br
Molecular Weight	149
Boiling Point:	-72°F
Freezing Point	-270°F
Critical Temperature	152.6°F
Critical Pressure	575 psia
Critical Density	46.5 lbs/cu ft
Heat of Vaporization	35.5 BTU/lb @ 70°F
Surface Tension of Liquid	9.7 dynes/cm @ 0°F 4.5 dynes/cm @ 70°F
Density: Liquid	82.2 lbs/cu ft @ 120°F 98.0 lbs/cu ft @ 70°F
Saturated Vapor	16.2 lbs/cu ft @ 120°F 7.4 lbs/cu ft @ 70°F
Heat Capacity	0.257 BTU/lb °F @ 120°F 0.205 BTU/lb °F @ 70°F 0.176 BTU/lb °F @ 0°F
Vapor Pressure	400.4 psia @ 120°F 213.7 psia @ 70°F 71.2 psia @ 0°F
Thermal Conductivity	0.025 BTU ft/hr °F ft ² @ 70°F
Solubility in H ₂ O	100 ppm at 15 psia and 120°F 300 ppm at 15 psia and 70°F

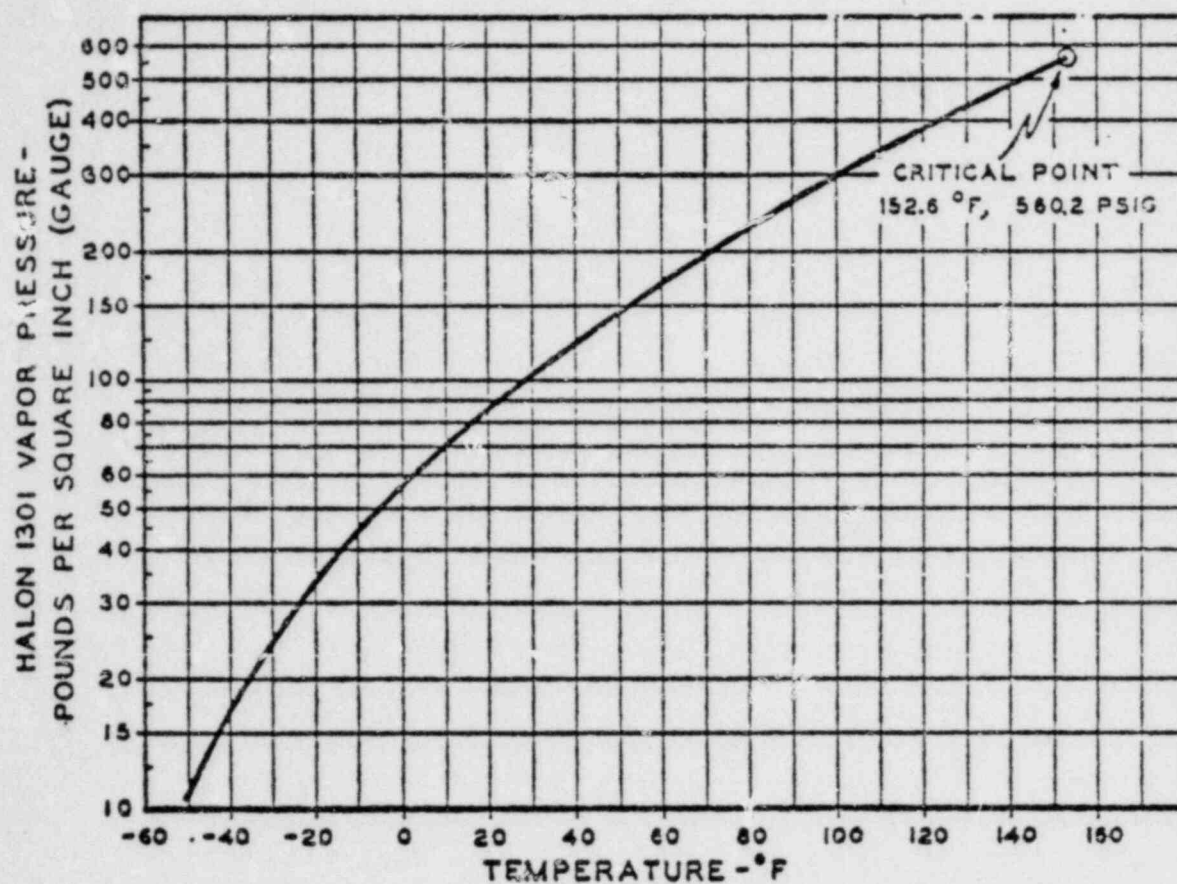


Figure 1. Vapor Pressure of Halon 1301 Vs. Temperature.

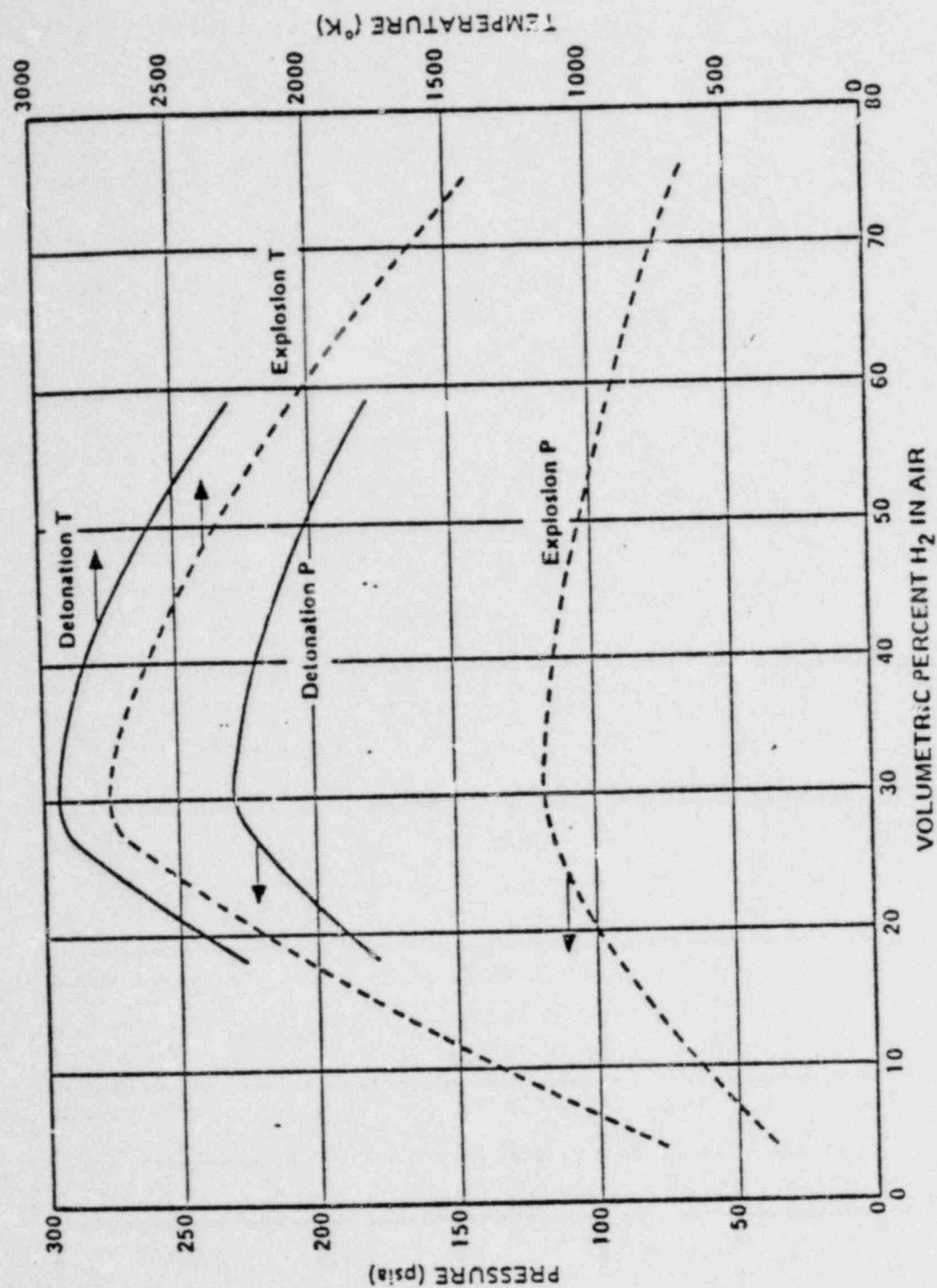


Figure 2. Calculated Adiabatic Constant Volume Explosion and Chapman - Jouget Detonation Pressures and Temperatures for H₂-Air. Initial P = 14.7 psia, T = 298°K.

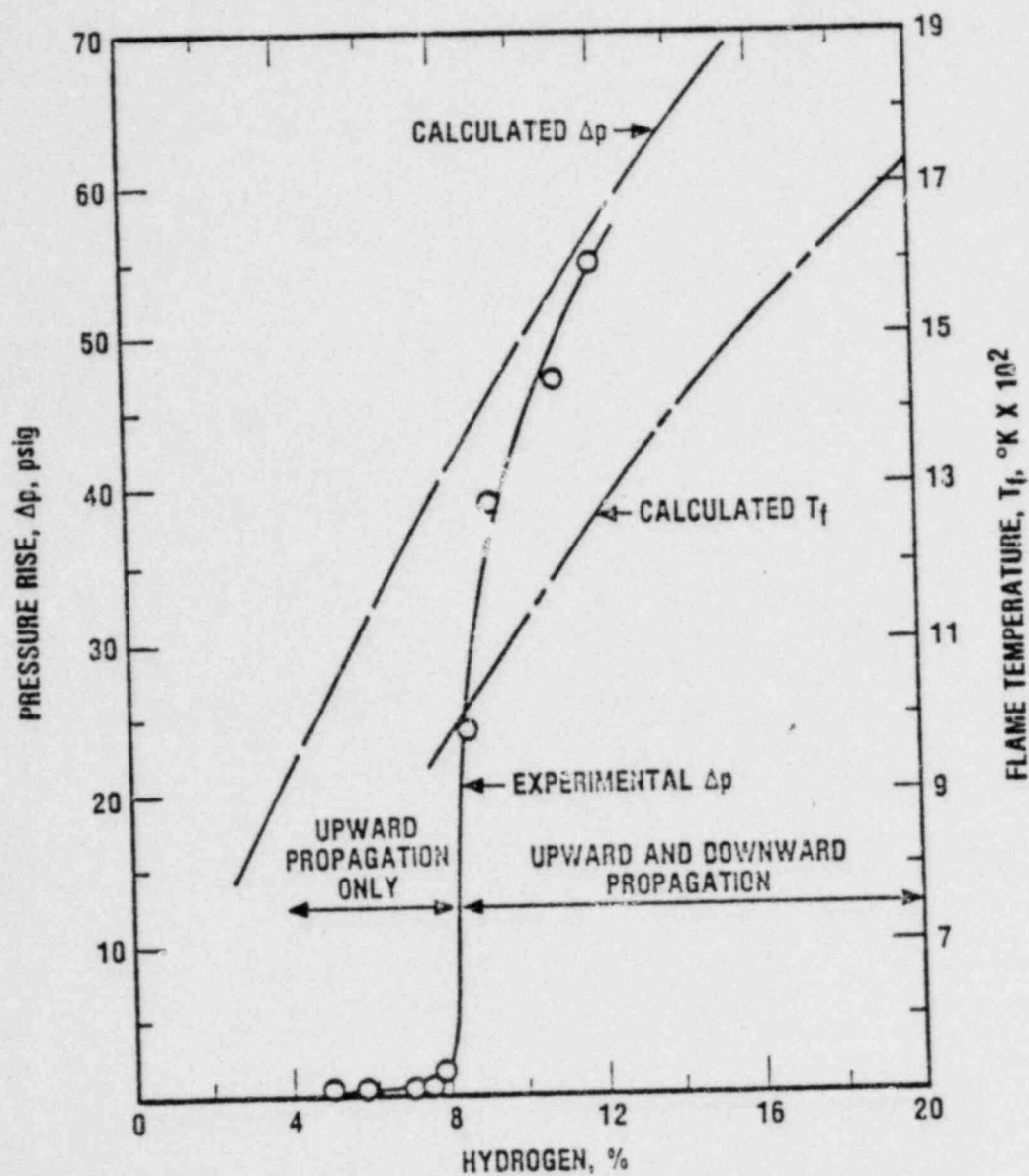


Figure 3. Measured Explosion Pressures for Lean Hydrogen-Air Mixtures Ignited with Central Spark in 12 ft³ Spherical Vessel (Reference 4).

2.0 SYSTEM DESIGN

Prior to discussing any potential problems associated with the use of Halon 1301, which items are dealt with in following sections of the report, we will first determine the Halon requirements and present a conceptual scheme for a system design. The requirements include the amount of agent needed for inerting, storage, injection system, and H_2 post-LOCA monitoring.

In order to compute the amount of Halon required for inerting, the following information is needed:

- Containment Free Volume - Sequoyah taken as $1,191,500 \text{ ft}^3$, including upper and lower compartments and ice condenser when empty of ice.
- Containment Initial Temperature and Pressure - Taken to be 70°F and 1 atm, respectively.
- Hydrogen Release - 1450 lb mass of H_2 or $277,800 \text{ ft}^3$ at 70°F , equivalent to 75% zirconium cladding reaction. (Additionally, it is assumed that all Halon must be injected within 1000 seconds.)
- Oxidant - Assumed to be ordinary air with no oxygen enrichment.
- Total Maximum Water Inventory - Assumed to be $5.9 \times 10^6 \text{ lbs}$.
- Containment Leak Rate - Assumed to be zero.

Tests were performed in the work of reference (1) from which can be determined the amount of Halon required for any given oxygen content of the atmosphere. No credit is taken for steam inerting. The flammability diagram shown in Figure 4, taken from (1), can be used to specify Halon, since the oxidant is air. The peak percentage is selected, conservatively, as 25 volumetric percent Halon. The peak percentage represents the quantity of Halon required to inert against hydrogen-air mixtures of any composition. The amount of Halon required is then calculated to be $489,800 \text{ ft}^3$ at 70°F , or 191,500 lb mass.

Knowledge of the total water inventory allows the estimate of Halon loss by radiolytic decomposition in solution (4540 lb mass; see a later section of the report), and loss by dissolution (885 lb mass assuming

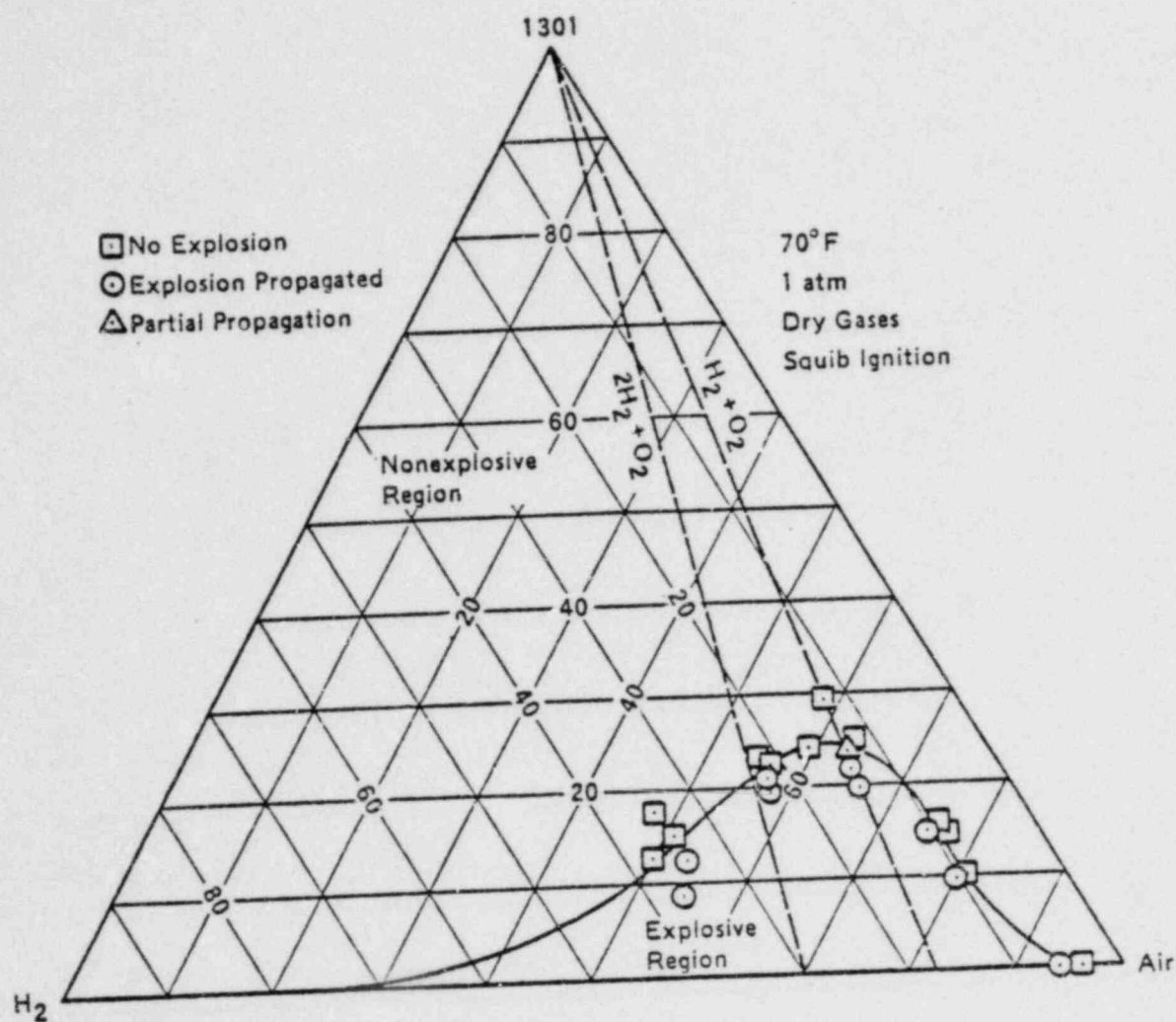


Figure 4. Explosion Limits, H₂-Air-1301.

Halon solubility of 150 ppm; see reference (1)). The Halon requirement therefore will be 196,900 lb mass. Per standard good safety practice, a nominal excess is specified (for example, 10%), bringing the total to 236,300 lb mass of Halon. The partial pressures corresponding to the containment gases will be:

Air	1.000 atm	=	14.70 psia	
H ₂	0.233 atm	=	3.43 psia	
Halon	<u>0.507 atm</u>	=	<u>7.46 psia</u>	
	1.740 atm		25.59 psia	= 10.89 psig

Due to the presence of steam and elevated temperature (possibly 160°F) the sum of the partial pressures in the containment early in the LOCA might be as high as 30 psia.

The assumption of 75% zirconium reaction should be examined. As will be seen in a later section of this report, if insufficient Halon is present for inerting, substantial overpressures might develop upon ignition, possibly approaching those pressures that would be reached if no Halon were present at all. Therefore, it is prudent to ask what would happen for the case of greater than 75% zirconium reaction. Consider the worst case, that of 100% reaction. This case represents 1933 lb H₂, or 959 lb moles. The mass of air in the containment is about 90,000 lb, or 3,100 lb moles. Accordingly, the 25% Halon peak percentage requires 1353 lb moles or 201,600 lb mass of agent to inert against 100% zirconium reaction. Adding the losses of 4540 and 885 lb mass gives an amount of 207,025 lb. Thus the 236,300 lb design quantity for 75% zirconium reaction still represents a 14% excess for the 100% reaction case.

The Halon system would consist of storage vessels to contain the 236,300 lb of agent stored as a liquified gas, which vessels would be connected to a manifold, to which spray nozzles would be attached for Halon injection if required. The present design calls for the 236,300 lb of Halon to be stored in four vessels with a fifth vessel containing 59,075 lb serving as a reserve in the event of failure of one of the required four. The storage tanks are sized to contain the Halon at temperatures above 130°F where the liquid density (77.6 lb/ft³) is less than at 70°F. Each tank would be of 316 stainless steel, with an equivalent spherical diameter of 12 feet and a wall thickness calculated to be three inches. This provides a working pressure of 600 psig for the system, conforming to Section VIII of the ASME Unified Pressure Vessel Code. A diagram illustrating the system design is shown in Figure 5.

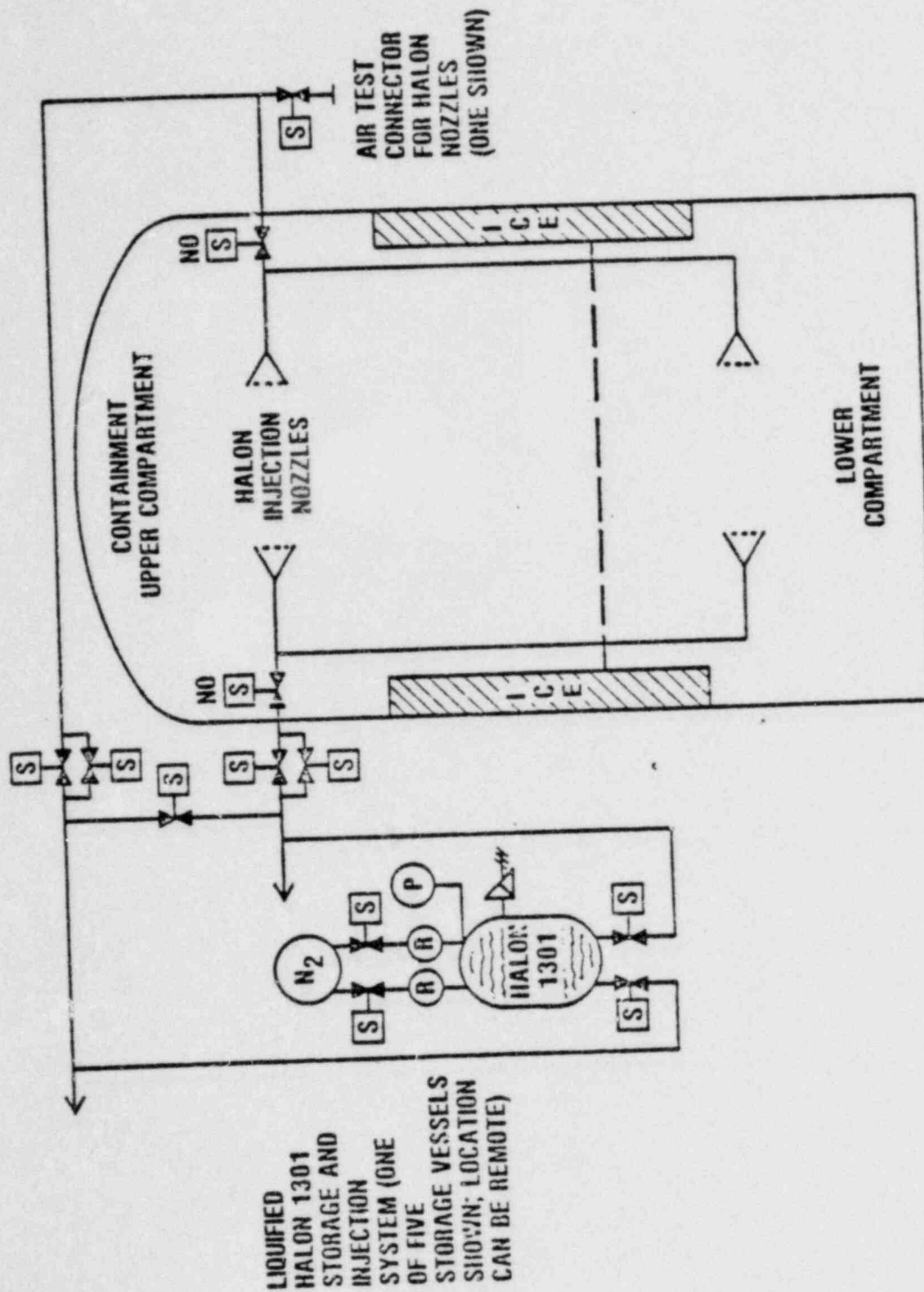


Figure 5. Conceptual Diagram of Halon 1301 Post-LoCa Hydrogen Suppression System for Ice Condenser Containment.

Each storage vessel would have an associated tank of nitrogen gas (approximately 7.5 ft diameter tanks containing N_2 (or air) at nominal 3000 psi) connected to it which would maintain a delivery pressure of 600 psig if the Halon had to be discharged (per NFPA standards; see reference (3)). The five Halon tanks are valved independently to two manifolds of 4-1/2" SS Schedule 40 pipe. The manifold piping diameter may have to be larger if a total run of much more than about 500 feet is required. The requirement to be met is that the Halon pressure at the discharge nozzle should exceed the vapor pressure at the ambient temperature (e.g., 434 psig at 130°F) to insure that agent is injected as a liquid. Therefore, a pressure drop of more than about 160 psi is not allowed. A 4-1/2" SS pipe will permit a 500 ft. run with a pressure drop of about 0.3 psi/ft. Two penetrations of the containment will be required for the pipes. The piping will conform to ANST B-31.10 classification. Inside the containment, the piping branches to the upper and lower compartments.

An array of spray nozzles comes off each manifold pipe inside the containment. The requirement is to deliver 236,300 lb. Halon in 1000 seconds, or 1366 gpm at 130°F. One arrangement to accomplish this is to use 20 full cone nozzles of 15/32" orifice on each manifold, one of which is sufficient. This feature of the system design is being left open at present. The exact nozzle system configuration would have to be determined by actual inspection of the containment and computation of the requirement in each area. The nozzles would simply be sized based on a constant area equivalent to that of the total twenty 15/32" orifices. The flow into the upper and lower compartments would be proportioned according to the volume of each. Other sections such as the pressurizer and steam generator enclosures, accumulator rooms, and instrument room, may be provided with a separate proportionately-sized nozzle, although the sizing is not critical since the air return fans will provide adequate circulation and mixing. Once the gases are mixed, demixing will not occur.

The storage vessel, piping and valving configuration is based on the guiding principle that the system must function properly even if three independent malfunctions occur. The configuration is shown in Figure 6 for all five Halon tanks, wherein standard symbolism is used in the drawing. Referring to Figures 5 and 6, it can be seen that any three valves in the system can fail to open and the required Halon injection could still be made. (The symbol NO of the figure indicates a normally open valve.)

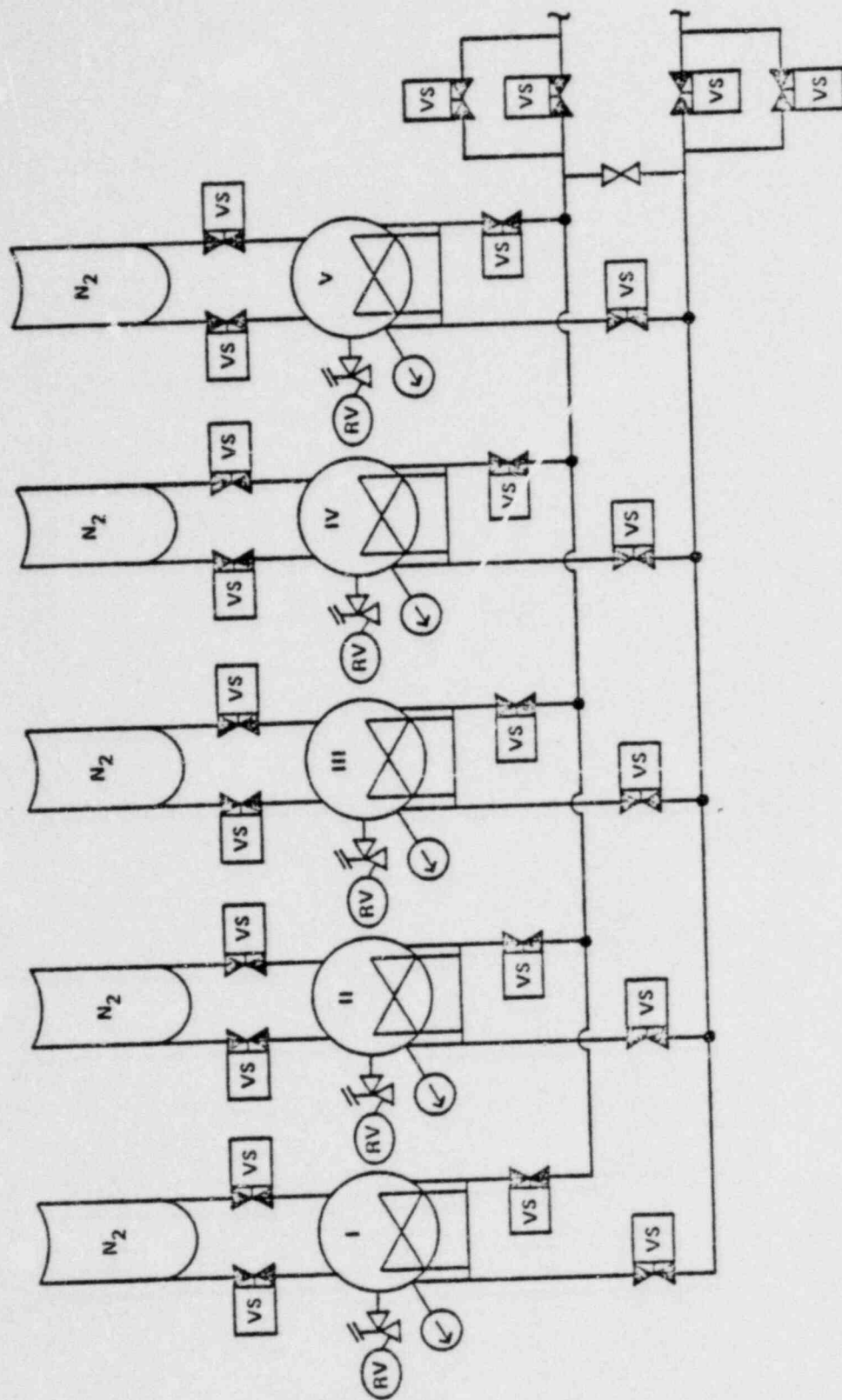


Figure 6. Diagram of Valving and Piping for Five Halon Storage Vessels.

Inasmuch as there are no other moving parts or parts requiring power, it is hard to see how any other malfunction could occur except with the nitrogen gas regulators. The nitrogen tank valves would be controlled by the pressure sensors, so that if a regulator failed to produce the correct pressure level, that side of the nitrogen flow would be stopped and the other side opened.

In the event of a LOCA the Halon system could be activated either manually or automatically. The present study required that Halon injection be designed for a rate of delivery of the total required amount in 1000 seconds, corresponding to a design basis accident. Following injection, the Halon and hydrogen concentrations of the containment would be monitored continuously during the post-LOCA period. The method of choice for monitoring is gas chromatography. Any method that functions on the principle of thermal conductivity, heat of combustion on a catalytic wire, or any other measurement that depends for its calibration on a two-component mixture being present will not be suitable, since a three-component mixture is present in the post-LOCA containment -- H_2 , air and 1301 (steam can be condensed, and air is considered a single component since its composition is constant).

In reference (1) an evaluation of gas chromatography was performed and the method found to be suitable for the present application. The principle of operation of the method is as follows. A mixture of gases to be analyzed is passed into a tube that is packed with some type of absorbent (charcoal, silica gel, molecular sieves, etc.). A carrier gas, typically helium, sweeps the gases through the column. The absorbent material exhibits different affinity for each component of the gas mixture and thereby retains each gas for a different length of time. Accordingly, each component elutes separately from the column at its own characteristic retention time. As it elutes, it passes through some type of detector which responds and provides a quantitative measure of the amount of that component.

To separate all components, two column packings are required. One is a material known as Porapak Q, an organic polymeric absorbent, which will separate Halon from air and hydrogen. It will also separate the Halon from other impurities or decomposition products such as CF_2Br_2 , C_2F_6 , CO_2 , CF_4 . In series with Porapak Q, a molecular sieve column is placed which separates H_2 , O_2 and N_2 .

The total instrumental method would consist of a commercially available process chromatograph, with the column console, programmer and readout located on an instrument panel in the control room. Sampling would be provided at several locations within the containment via an automatic stream selector. We have obtained product literature from vendors for virtually off-the-shelf packages. No additional penetrations of the containment would be required over those normally present.

No cost analysis for a Halon system is being performed in the present study; however, it can be noted that duPont is quoting a price (January 1981) of \$2.70 per lb for 1301 in tank car quantities (120,000 lb per car).

3.0 INADVERTENT ACTUATION CONSIDERATIONS

When Halon is injected as a liquid into a gaseous atmosphere it will vaporize, drawing its enthalpy of vaporization from sensible heat of the atmosphere, thereby lowering the temperature of the atmosphere. A corresponding decrease in pressure might occur. Since the ice condenser containment is not designed for much more than one psi underpressure, the question arises as to what pressure drop might result if Halon were inadvertently injected. The problem is limited to the discharge of a single vessel out of the five storage tanks, since no common mode failure exists that would allow more than one tank to inadvertently inject.

The problem could be set up in a formal way since the pressure decrease is offset by a pressure increase due to Halon gas being added to the containment. However, a straightforward example will answer the question:

Halon Discharged	=	59,075 lb.
Heat of Vaporization	=	35.5 BTU/lb. (70°F; less at higher temperature)
Heat Absorbed	=	2.1×10^6 BTU
Containment Air	=	1.2×10^6 ft ³ = 90,000 lb.
Specific Heat Air	=	0.25 BTU/lb °F
Temperature Drop from Heat Absorbed	=	93°F
Corresponding Drop in Air Pressure	=	0.17 atm = 2.50 psia (Ideal Gas Law)
Pressure Increase from Halon Addition	=	7.46/4 psia = 1.87 psia (See Section 2.0)
Net Pressure Drop from Inadvertent Halon Injection	=	0.63 psia

Thus it can be seen that the inadvertent discharge of one Halon tank would not be cause for concern. Furthermore, the above estimates are conservative in that heat from the containment vessel would be absorbed and would lead to less pressure drop. Fairly soon the pressure would be restored to ambient.

A corollary question can be asked which concerns whether there is sufficient heat to vaporize the Halon if all 236,300 lb. had to be discharged. This question was tested in reference (1) wherein the situation was similar in that there was not enough sensible heat in the air to provide the heat of vaporization. In tests using a "minicontainment" it was found that no vaporization problems were encountered, the Halon receiving heat from the containment vessel itself. It is noted that the total heat of vaporization requirement is about 8.4×10^6 BTU which is about 2.5 percent of the total blowdown energy of 3.35×10^8 BTU.

Short term cooling of certain (small) components in the containment could conceivably occur if Halon were inadvertently injected directly onto them. No problem is envisioned from this effect.

If one tank of Halon were to be discharged into the containment, the concentration would exceed ten percent. This amount is not considered safe for human exposure for any extended period of time and therefore, personnel, if any were present, would have to immediately evacuate the area and the containment would have to be purged. Reference (5) details the extensive studies that duPont and others performed on Halon toxicity. The key piece of information seems to be the classification of Underwriters' Laboratories, which it is emphasized is based on animal studies and not human exposures. Underwriters' places Halon 1301 in its least toxic Group 6, "Gases or vapors which in concentrations up to at least 20% by volume for durations of exposure of the order of 2 hours do not appear to produce injury." Carbon dioxide is considered more toxic and placed in Group 5A.

It is to be noted that in order for an inadvertent injection of a tank of Halon to occur, two independent solenoid valves which are normally closed must be activated and the malfunction left unremedied for some time.

The containment can be purged of Halon fairly easily following inadvertent discharge. The containment atmosphere would be vented through charcoal filters. It has been established that there is no deleterious effect on such filters and that they adsorb iodine compounds just as effectively with Halon present in the atmosphere. Even at a low purge rate of, say, 2000 cfm, a complete change of air in a containment would occur in 10 hours. Several complete changes would be required to render the atmosphere habitable.

4.0 HALON DECOMPOSITION AND WATER CHEMISTRY

There had been concern that Halon might dissolve in emergency cooling water and radiolytically decompose as it passed near the reactor core and encountered radiation from decay products. Even though Halon is only slightly soluble in H_2O , if decomposition occurred and the agent was continuously replenished, one can calculate a high level of loss. This question was experimentally investigated in reference (1) wherein the main conclusion is illustrated in Figures 7 and 8. These show that Halon in water when irradiated does decompose to some small extent, but that the process is self-arresting when the Br^- concentration builds to about 5.2×10^{-3} moles/liter. Figure 8 shows the measured pH change associated with the process. (The water contained small amounts of $K_2C_2O_4/H_3PO_4/KOH$ and the pH was set to 11.0 at start of irradiation (see reference (1), Phase III, Section 4.1).)

Based on these experimental data the rate of decomposition of Halon in the Sequoyah reactor was calculated. It is necessary to know fission product release to the water, from which decay energies are determined and the accumulated radiation dose calculated for a given water inventory. These computations were performed by Dr. Stanley E. Turner of Southern Science Applications, Inc., and the following material is principally that which was reported by Dr. Turner. The assumptions were the following:

- TID-14833 fission product releases (100% of noble gases, 50% of the iodines and 1% of solids).
- SRP 6.2.5 relationships for energy deposition in the water.
- Halon radiolysis rate relationship in reference (1).
- Instantaneous injection of all Halon (to 7.46 psia partial pressure) at time zero. (Actual Halon injection rate would perturb the early decomposition rates but not very significantly.)
- Uniform mixing of water and re-pumping through the core for emergency cooling.
- Equilibrium solubility of Halon at all times (i.e., that consumed is instantly replenished.)

Halon Decomposition

Since the net decomposition of Halon ceases at equilibrium Br^- concentration of 5.2×10^{-3} moles/l, the total quantity of Halon decomposed

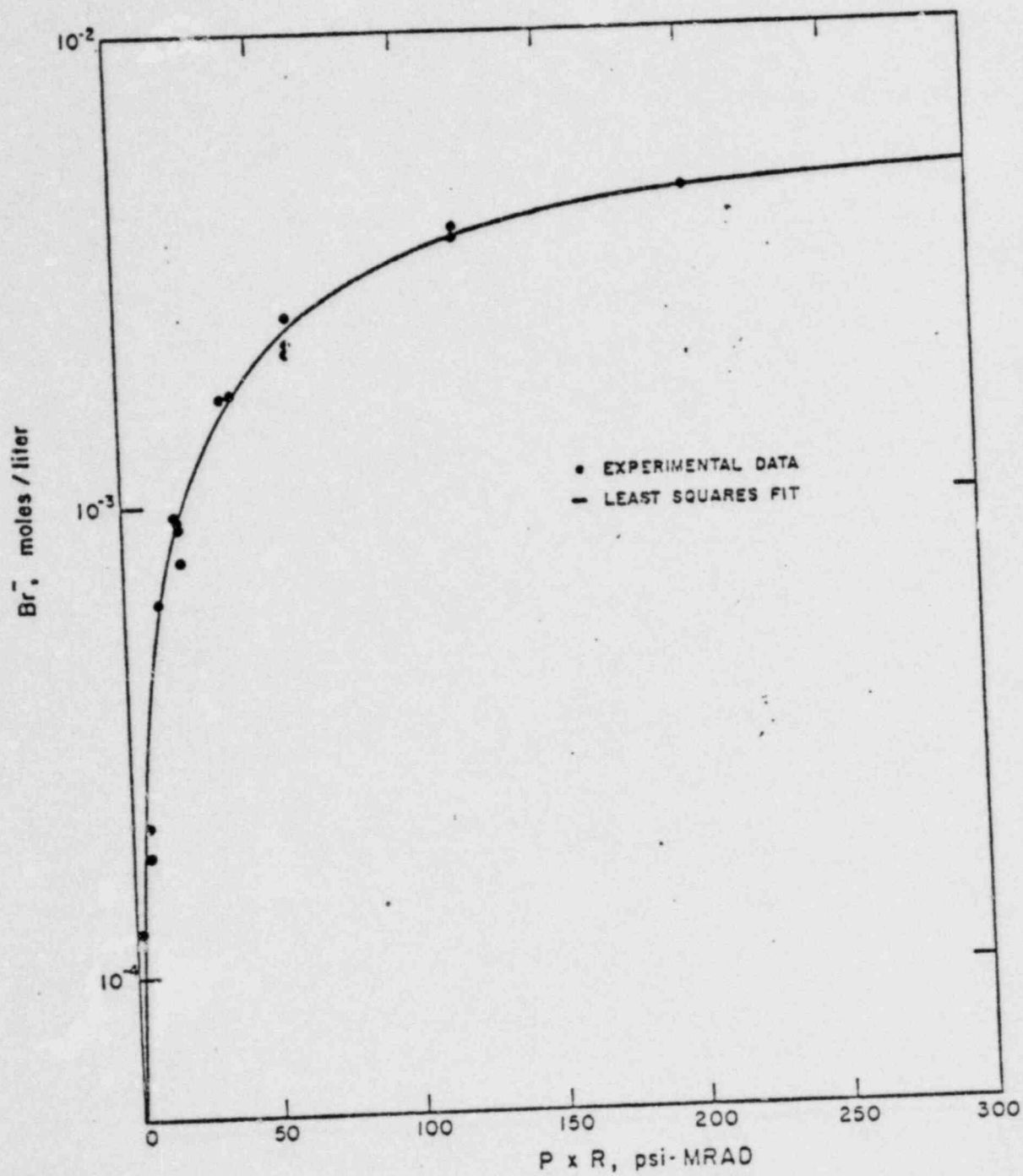


Figure 7. Bromide Ion Concentration as a Function of the Halon pressure (P) and Radiation Dose (R)

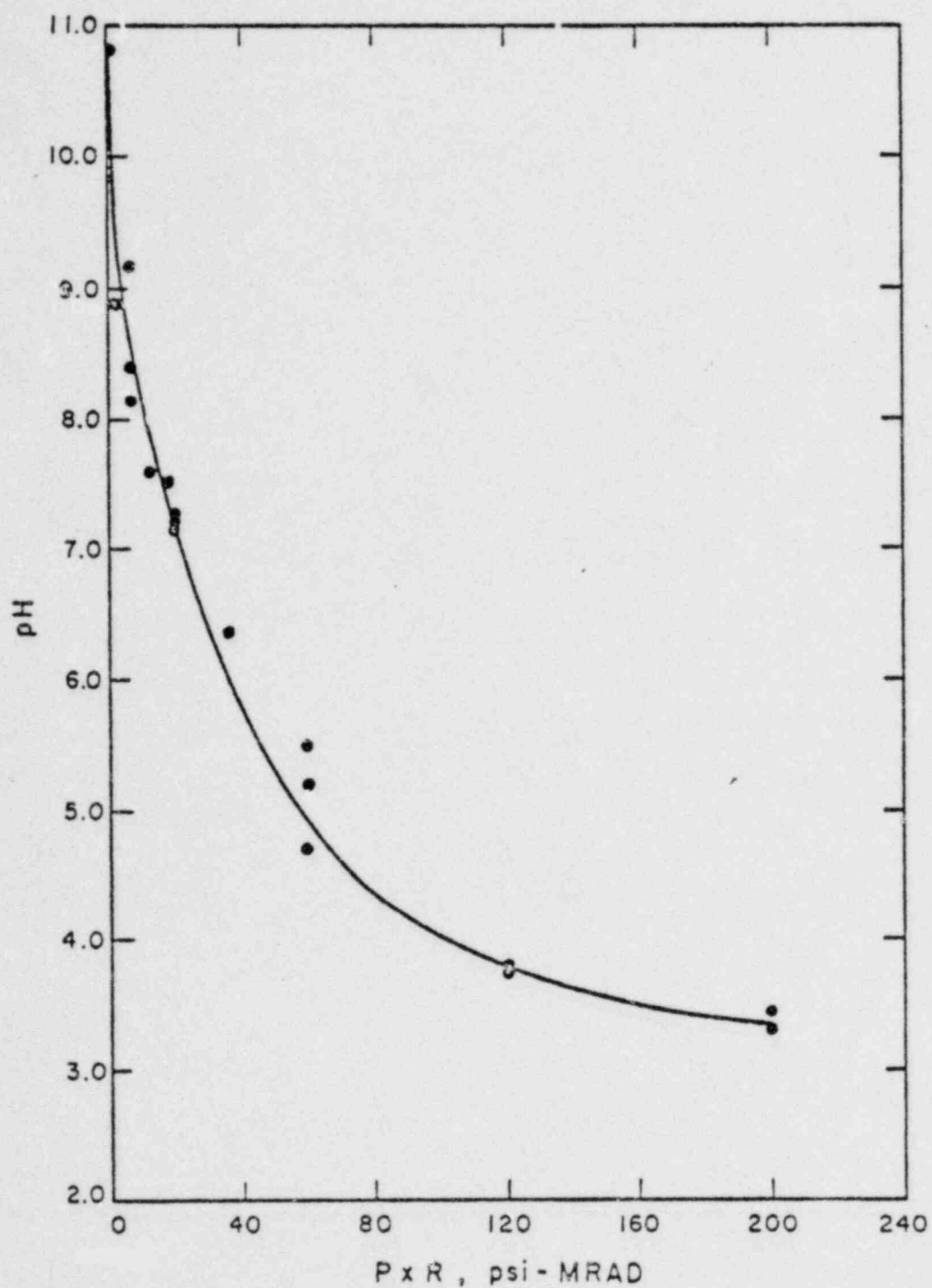


Figure 8. Variation in pH as a function of the Halon pressure (P) and Radiation Dose (R).

depends (at equilibrium) upon the total quantity of water in the containment (6.46×10^{-3} lbs Halon decomposed per gallon of water). For the maximum amount (702,950 gallons, re: TVA letter of Oct. 31, 1980), the quantity of Halon decomposed is 4540 lb, independent of the fission product release to the water. An additional 885 lb will remain dissolved in the 702,950 gallons of water.

The rate of Halon decomposition also depends upon the quantity of water in the containment. Figure 9 shows the time-dependent quantity of Halon decomposed for several potential values of the containment water inventory. Figure 10 shows the time-dependent concentration of Br^- for the same assumed values of water (time zero on these figures refers to the beginning of the assumed accident sequence and assumes Halon injection starts at this point). The final saturation concentration of Br^- is 5.2×10^{-3} moles/l in all cases.

Water Chemistry and pH

Br^- is presumably formed as HBr, and decomposition of Halon also produces HF at concentrations 3 times that of HBr. HF ionization, however, is suppressed by the H^+ from HBr ionization, and at equilibrium most of the HF is undissociated. Thus, Figure 10 may also be interpreted as the HBr concentration with the HF concentration being 3 times that indicated for Br^- .

The pH changes depend upon the initial chemical composition and pH of the water in the containment system. Although the system water will likely be slightly alkaline ($\text{pH} > 7$) and perhaps buffered (presence of sodium borate, for example, to prevent criticality), calculations of the pH changes have been made conservatively assuming pure water (pH of 7.0) in the containment system initially. Assuming complete ionization of HBr and an ionization constant of 3.53×10^{-4} for HF, the resulting pH is shown in Figure 11. At equilibrium, the pH would be ~ 2.2 , determined principally by the HBr, with HF ionization largely suppressed. Further discussion of the adjustment of pH and of Br^- concentration is given later in connection with materials corrosion. The F^- concentration was not measured but is calculated to be 8.3×10^{-4} moles/l, and the calculated HF concentration 14.8×10^{-3} moles/l.

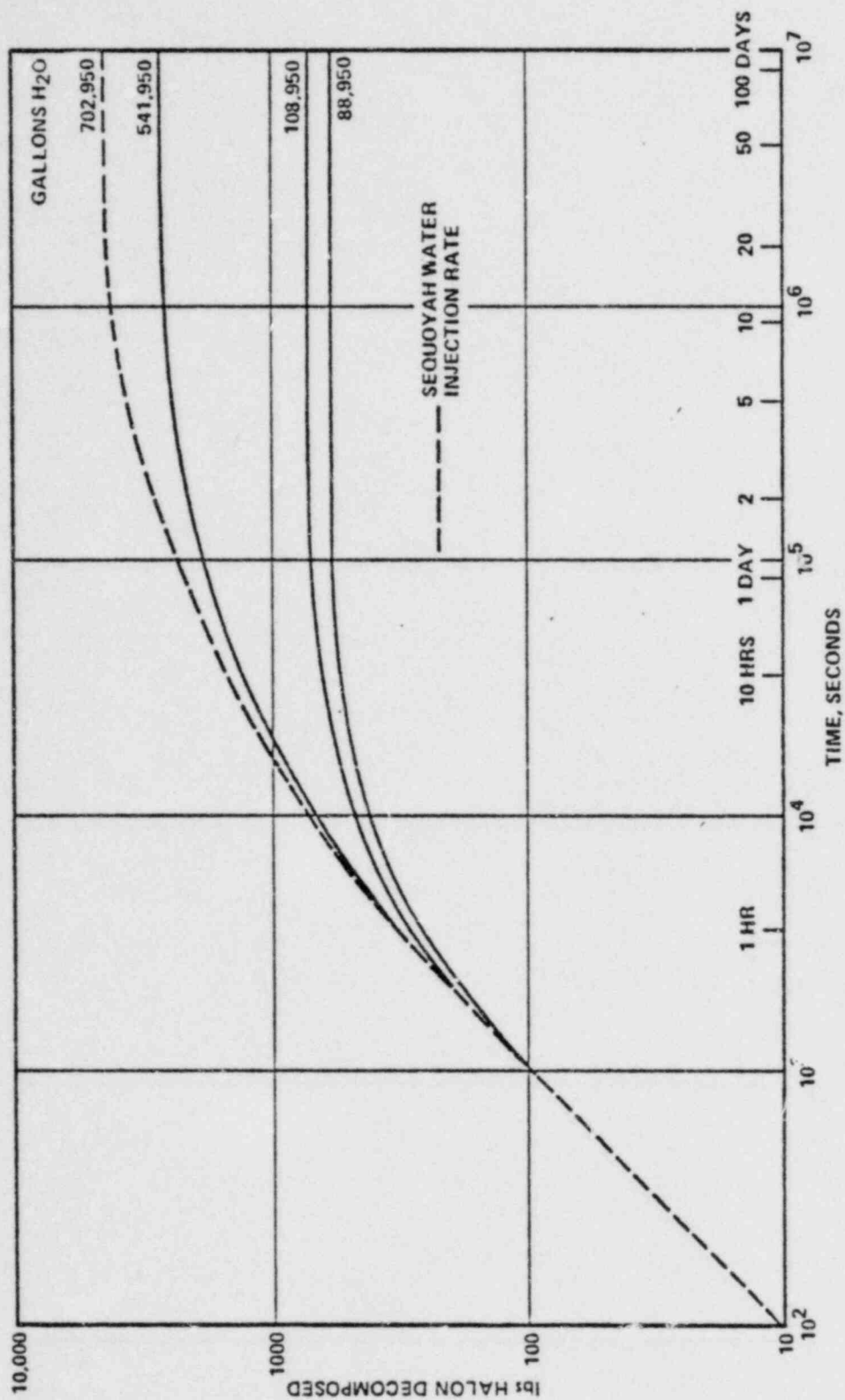


Figure 9. Halon Radiolytic Decomposition Rate in Water.

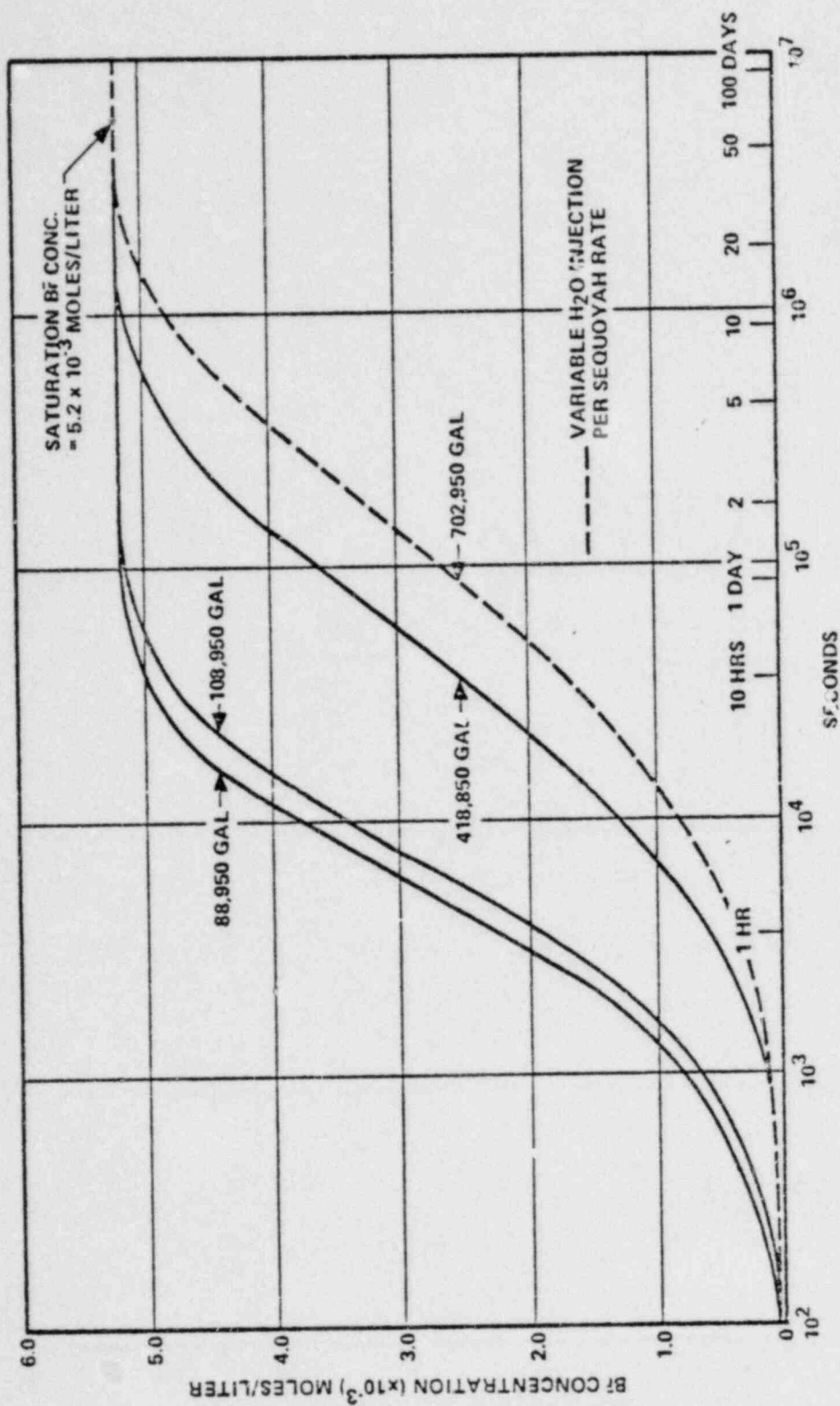


Figure 10. Time-Dependent Br^- Concentration.

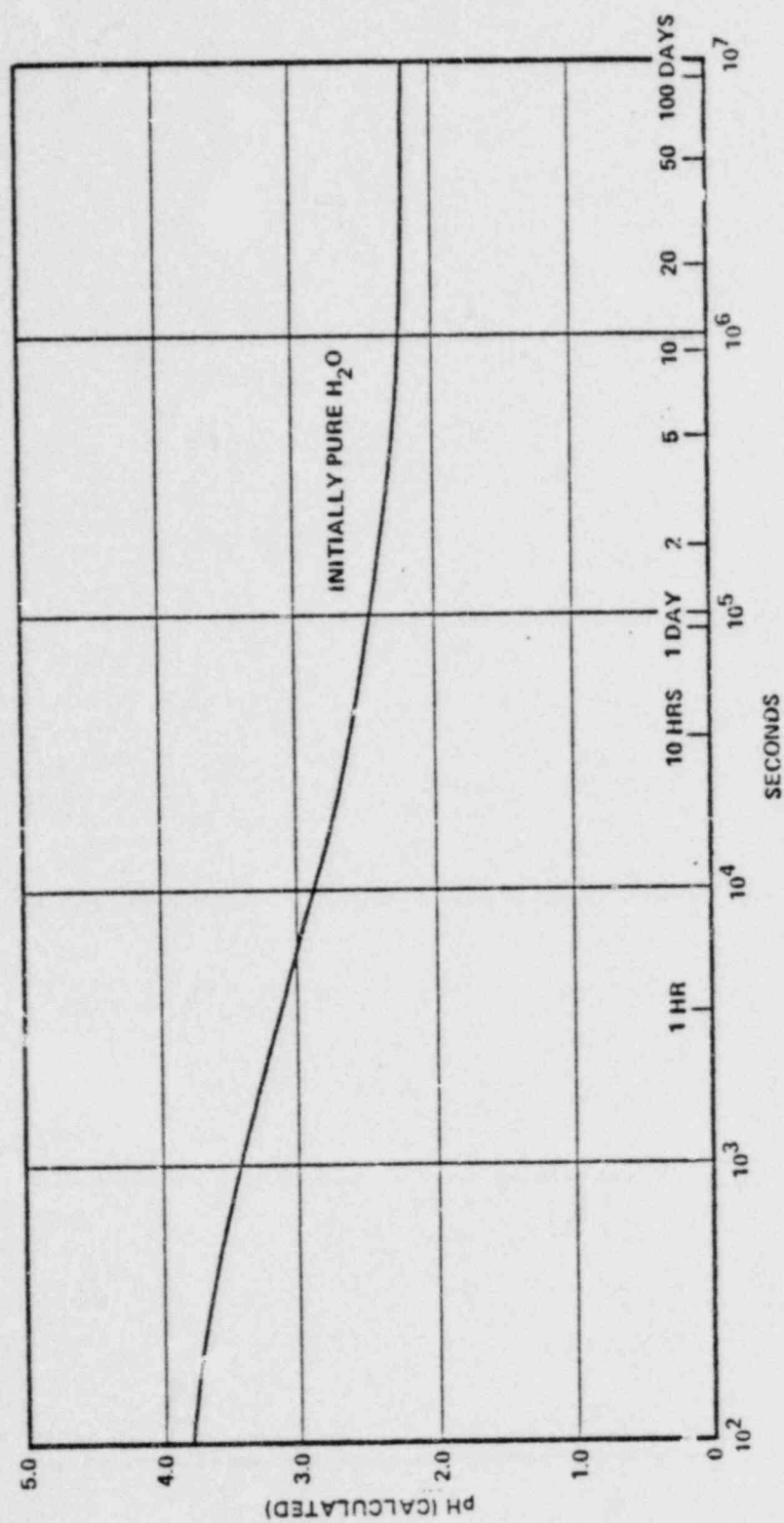


Figure 11. pH Changes in Containment Water.

Halon decomposition will only occur by water radiolysis. It has been shown (1) that gas phase radiolytic decomposition is negligible. Neither should Halon decompose by contact with hot surfaces. It should not come into direct contact with the core, and other surfaces will not be hot enough. Reference (2) reports that only 1.6% decomposition occurred in 25 hours when Halon was exposed to 316 stainless steel at 600°F (surface area of steel and quantity of Halon not given). Tests at 250°F with ten different metals for 44 months showed negligible effects. In general, temperatures of about 1000°F must be reached before rapid decomposition occurs. A literature search on Halon decomposition failed to turn up any data beyond these cited (see for example, reference (6)).

5.0 IGNITION OF HYDROGEN-AIR-HALON MIXTURES

The question has been considered whether hydrogen-air mixtures that are inerted with Halon 1301 against ignition by sparks and squibs could be ignited by another ignition source, such as a shock wave that might emanate from the detonation of a pure uninerted hydrogen-air mixture. In a containment application, it is hypothesized that a pocket of uninerted mixture might develop. In the absence of experimental data, the question was answered by a fundamental analysis of the processes of ignition and flame propagation, performed by Dr. Guenther von Elbe and presented in the following subsections of this report. For further details the reader is referred to reference (7).

The conclusion of the analysis is that if a mixture is inerted against spark or squib, it cannot be ignited by a shock wave. The reason is that mixtures that are inerted are outside of the flammability limits (for the present Halon design they are far outside the limits). Any ignition source that is applied will, in the very process of trying to produce ignition, perturb the mixture in the vicinity of itself. Such limit mixtures are very sensitive to perturbation and self-quench themselves by the small turbulence of their own gas produced by the ignition attempt. Therefore, a "stronger" ignition source than a spark or squib would be represented by a more quiescent one. In this sense a shock is a weaker source because it produces perturbation of the gas. However, even a calm ignition, if one could be imagined and if it produced an incipient flame, would not lead to sustained propagation, since the inerted mixture is so sensitive to perturbation that the flame would soon self-quench by the gas disturbance its very propagation produced. These matters are discussed further below.

Literature search was conducted but did not produce any reports of experimental work bearing exactly on this question of shock ignition. Several other relevant points can be mentioned. In reference (8), various uninerted hydrogen-air mixtures were ignited by flame and also by detonation, and no lowering of the limit was produced. Also at the "Workshop on The Impact of Hydrogen on Water Reactor Safety" held January 26 - 28, 1981, in Albuquerque, New Mexico, it was reported⁽⁹⁾ by an attendee that hydrogen-air mixtures inerted with Halon could not be ignited by a detonation wave. No written report of the work is available.

The improbability of obtaining a hydrogen-air pocket has not been considered, but the fact is that the Halon spray configuration is designed to prevent such pocketing. Moreover, there is a misconception that if uninerted hydrogen-air mixtures reach a concentration of 18% hydrogen, a detonation will occur upon ignition. While 18% is considered the lower detonation limit, the value refers to tests performed in shock tubes with shock or blast wave initiation, i.e., the strongest and most ideal conditions. In configurations other than tubes, such as spherical geometries, to our knowledge, detonations have never been produced with anywhere near limit concentrations. In reference (10), for example, spherical detonations could only be produced with stoichiometric H_2 /air mixtures, and then only if one gram of high explosive was used as initiator. The authors predicted that limit mixtures might be made to detonate if one quarter pound of high explosive were used to initiate the process. These data are cited to provide some idea of the difficulty, if not the impossibility, of detonating anything much below stoichiometric mixtures, and the strength the initiator required.

There is one required precaution that must be taken when specifying the Halon requirement for inerting. If insufficient agent is present, mixtures may combust with substantial overpressure. The perception that the combustion intensity would be reduced even if agent concentration were deficient is not true. This may be seen in Figure 12, taken from reference (11), where the data refer to methane rather than hydrogen (Atlantic Research experiments with deficiently-inerted hydrogen mixtures showed a similar but not quite so sharp a limit behavior). The CH_4 -air mixture used in reference (11) was rendered inert with 3.6 percent Halon but produced high overpressure with 3.4 percent. The present containment design calls for 20 percent excess Halon beyond the maximum required to inert for 75% zirconium-water reaction.

5.1 Flame Propagation and Flammability Limits

One may ask whether flammability limits determined in small-scale laboratory apparatus are in fact applicable to systems of very large dimensions such as the containment vessel. In practice this has already been affirmed by experience with coal mine atmospheres and numerous other hazard situations. (For example, in a case that occurred in Pittsburgh in the 1920's, a very large gas reservoir that contained an explosive mixture of coal gas, (hydrogen and

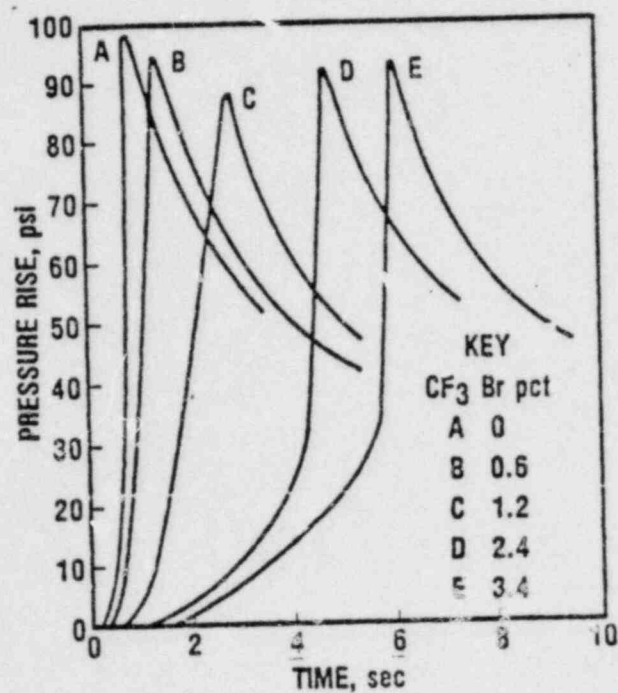


Figure 12. Explosion Pressure Growth for Stoichiometric CH_4 -Air Mixtures with Added CF_3Br in 12-ft Diameter Sphere (3.6% of CF_3Br renders this mixture inert). From Reference 11.

carbon monoxide) and accidentally admitted air had to be made safe for work with welding torches. This was accomplished by admitting engine exhaust gas until the laboratory-determined flammability limit was reached.) With Halon the safety of a Halon-inerted atmosphere of hydrogen and air has been demonstrated by a test in a vessel with linear dimensions of the order of ten feet. An understanding of the subject requires a discussion of combustion waves and the quenching of combustion waves by convection currents.

A local ignition source in a volume of flammable gas generates a combustion wave by igniting a layer of the ambient unburned gas, which in turn ignites the next layer, and so on. The wave thus comprises a zone of chemical reaction and heat release across which the gas temperature rises from the ignition temperature of the unburned gas to the flame temperature of the burned gas; and a preceding zone of unburned gas which receives heat from the reaction zone by thermal diffusion, and across which the temperature rises from the ambient to the ignition temperature. If there is no external heat loss, the heat flux from the reaction zone to the preheat zone is balanced by the convection of heat back into the reaction zone as the preheated unburned gas ignites and the reaction zone advances, so that the overall process is adiabatic. In this case the temperature increases continuously across the wave from the ambient to the adiabatic flame temperature, which is calculable from thermodynamic data.

The wave propagates into the unburned gas at a velocity corresponding to the diffusion flux across the isothermal plane of the ignition temperature. The magnitude of this "burning velocity" is thus dependent on the rate of chemical heat release in the reaction zone and on the diffusion parameters. At high reaction rate the temperature gradient across the wave is steep, the burning velocity is large, the width of the wave is small, and vice versa. At approximately stoichiometric composition of the flammable gas mixture, the flame temperature is at its maximum, hence the strongly temperature-dependent reaction rate is at its maximum, the slope of the temperature gradient is at its maximum, the burning velocity is at its maximum, and the wave width is at its minimum. On dilution of the mixture either by an excess of fuel or oxygen, or by an inert gas such as nitrogen, or by an agent such as Halon which acts both as an inert gas and a chemical inhibitor, the flame temperature decreases, the reaction rate decreases, the slope of the temperature gradient decreases,

the burning velocity decreases, and the wave width increases. Burning velocity and wave width are inversely related by the ratio thermal diffusivity/burning velocity, which has the dimension of length and represents a characteristic length of the wave width.

The strongest mixtures have burning velocities of the order of 100 cm/sec or more with corresponding wave widths in the 10 to 100 micron range. The theory of adiabatic combustion waves places no limit on the stability of the wave down to an asymptotic approach of the burning velocity to zero and corresponding approach of the wave width to infinity. In practice, the burning velocity can be decreased only to the order of 10 cm/sec with corresponding wave widths in the millimeter range. Experience shows that flammable mixtures in this range cannot be diluted beyond some limit at which a combustion wave becomes extinct as it draws away from an ignition source. In this way, one obtains a "lean" limit of flammability if the diluent is excess oxygen or air; a "rich" limit if the diluent is excess fuel; or a limit defined by the required inert-gas addition to a given fuel/oxygen or fuel/air mixture, or for the present purpose a limit defined by the required Halon addition to a post-LOCA hydrogen/air mixture.

The existence of flammability limits implies that in the indicated range of low burning velocities the chemical reaction in the wave is quenched by heat loss. This is attributable to a convection process which is not shown in the idealized model of a plane combustion wave but occurs in real waves. The mechanism of this process is illustrated by the sketch in Figure 13a, which shows the profile of a combustion wave propagating toward the closed end of a tube, the other end being open. It is seen that the thermal expansion of the gas in the wave generates a flow of burned gas, and that the resulting thrust against the unburned gas generates a current along the wave front which transports heat laterally away from the center. This flow pattern follows from theoretical consideration but has also been verified experimentally. The illustrated wave and flow configuration is stable in the flammable region of mixture compositions if the flow of burned gas is in the laminar range, but in a limit mixture the wave is gradually quenched by the lateral heat convection. Figure 13b illustrates the same mechanism of quenching for the case of flame propagation in a large volume. The flow field becomes turbulent and the consequent random distortion of the wave generates lateral heat convection. It has been observed

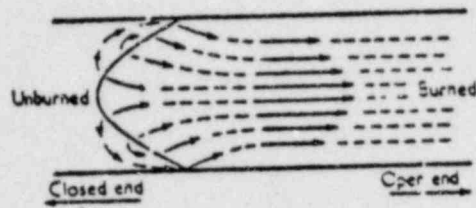


Figure 13a. Flame Propagation in a Tube.

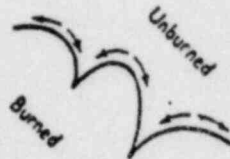


Figure 13b. Unconfined Flame.

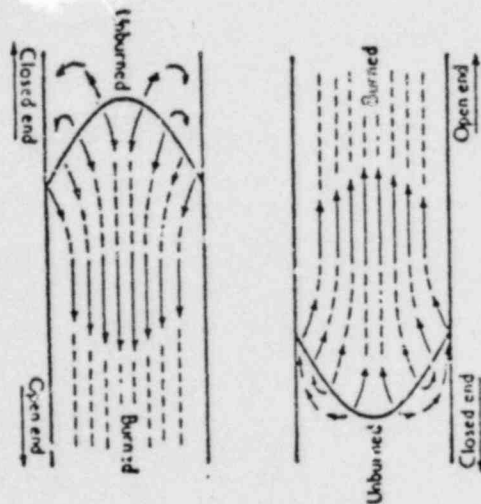


Figure 13c. Upward and Downward Propagation of Flames in Vertical Tubes.

experimentally that extinction occurs in random areas of a turbulent combustion wave even if the mixture is well inside the region of flammability. The effect depends on mixture composition and turbulence level, and the holes that are thus formed in the wave sheet close up again. At the flammability limit, this does not occur and extinction progresses over the whole wave area. It follows that flammability limits depend on the combustion wave parameters, viz., the burning velocity and wave width, and on the thermal stress which is exerted on the wave by the heat-dissipating convection currents. The wave parameters are determined by the mixture composition, whereas the thermal stress depends on the turbulence level and other environmental conditions. A conservative value of the flammability limit is obtained if the thermal stress is reduced to the minimum that may occur in practice. It is well known that limits for upward flame propagation require a larger mixture dilution than limits for downward propagation, and accordingly, limits are always determined for upward propagation. The difference between limits for upward and downward propagation is due to the effect of gravity on the thermal stress. This may be visualized with the aid of Figure 13c. In upward propagation the thrust of the buoyant flame gas against the unburned gas is added to the thrust of the thermal gas expansion, with the result that the lateral convection is shifted to a region that is not as close to the wave as in downward propagation, and the thermal stress is correspondingly reduced.

In special laboratory apparatus known as flat-flame burners, the thermal stress is minimized by passing the unburned gas through a grid of orifices in proximity of the combustion wave. In this way, the lateral heat convection can be so much restricted that mixture compositions corresponding to burning velocities of less than 5 cm/sec and as low as 2 cm/sec become flammable. But for practical purposes, the flammability limit for upward propagation, as determined in standard apparatus at low turbulence levels, furnishes a proven standard of safety.

5.2 Halon Percentage Required for Preventing Ignition of Post-LCCA Hydrogen/Air Mixtures by Detonating Hydrogen/Air Pockets

It has been found (1) that the Halon percentage required to prevent ignition by strong condenser sparks is somewhat smaller than the percentage required to prevent ignition by squibs, i.e., by electrically ignited match heads.

Inasmuch as squibs release more energy than the condenser sparks that had been used in the work, it may be thought that the Halon requirement depends on the source energy, and hence, that the limit percentage determined with squib igniters is too low in a post-LOCA situation where the ignition source might be a detonating pocket of hydrogen and air. This reasoning is based on a misconception of the cause of the observed difference between ignition by sparks and squibs. The energy that is generated by these sources already vastly exceeds the minimum energy required for initiating a combustion wave (of the order of a millijoule); hence, the source energy is not a factor in determining the critical Halon percentage. The difference between sparks and squibs arises from the fact that a condenser spark releases its energy explosively and thus generates locally a zone of high turbulence which tends to quench the incipient combustion wave. Accordingly, even though the critical Halon percentage that prevents ignition by sparks may not be sufficiently large to make the mixture non-flammable, or in other words, to prevent the propagation of a combustion wave through the mixture volume, the wave that forms in the high-temperature field of a spark is quenched by the spark-generated turbulence and does not reach the calm region beyond the zone of turbulence where it can propagate; thus, no ignition occurs. In contrast, the relatively slow energy release that occurs in firing a squib generates a much less disturbed temperature field that allows the wave to develop and propagate through a weak but flammable mixture of this kind, so that ignition occurs. But if the Halon percentage is increased, the wave that propagates from a squib flame eventually becomes so slow and wide that it is quenched by the convection currents which are induced by the thermal expansion of the burning gas, as discussed previously. In this inerted state the mixture cannot be ignited by any local energy source, including a source that is as large, hot and powerful as a detonating hydrogen/air pocket in a post-LOCA situation. Such detonation would produce a large volume of hot flame gas and an additional volume of mixture that is heated by shock compression, and a combustion wave would develop within the temperature field that is thus formed; but the wave would decay as it draws away from the vicinity of the pocket and the pressure increase in the huge containment vessel would be negligible. There would, in fact, be very little combustion outside the volume of detonation products

because the flame-quenching convection currents would be strongly augmented by the high turbulence at the site of the detonation. Accordingly, a Halon percentage that prevents ignition by such an optimal ignition source as a squib is certainly sufficient to prevent ignition of a post-LOCA atmosphere by any source including a detonating hydrogen/air pocket.

It may be mentioned that (ironically) a low-voltage electric arc is an ignition source similar to a squib flame and thus should be regarded as relatively more hazardous than a hydrogen/air pocket. But the recommended dose of Halon in a post-LOCA atmosphere eliminates any such consideration.

6.0 EFFECTS OF HALON 1301 AND DECOMPOSITION PRODUCTS UNDER POST-LOCA CONDITIONS ON MATERIALS OF CONSTRUCTION

In Section 4.0 of this report and also in reference (1), it is shown that Halon 1301 can decompose in water solution. The decomposition proceeds until the bromide ion concentration reaches 5.2×10^{-3} moles/liter, equivalent to 415 ppm by weight. Without control measures, the pH would fall to about 3. This process could give rise to corrosion if it occurred in the reactor cooling water and was left uncontrolled for extended periods. The following study of the situation has been conducted by A.J. Biedermann of the corrosion consulting firm of C.P. Dillon and Associates.

6.1 Corrosion Mechanisms

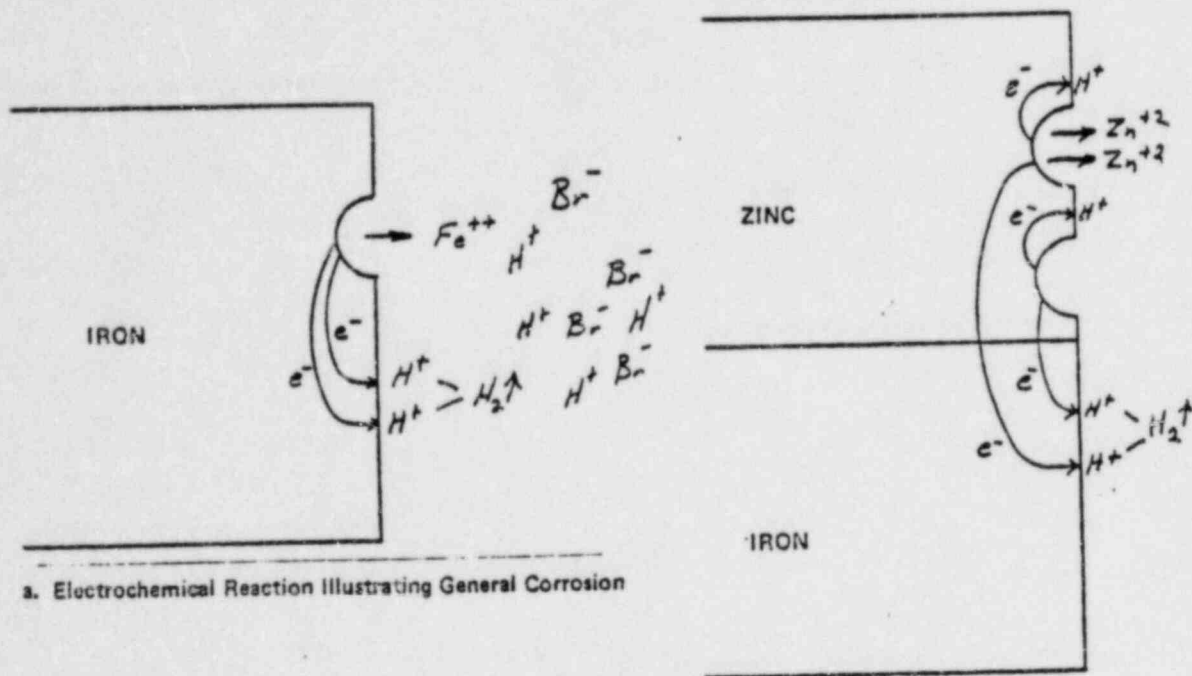
It is worth presenting descriptions of the potential types of corrosion that could result in the containment post-LOCA case. These descriptions will familiarize the reader with terms used in following sections. It is emphasized that the corrosion assumes no mitigation procedures or inhibitor addition.

General Corrosion (Uniform Thinning) - General corrosion occurs by chemical or electrochemical reaction over the entire exposed metallic surfaces resulting in general thinning. For example, a piece of zinc or steel immersed in dilute acid will dissolve at a uniform rate over its entire surface. The reaction equation is:



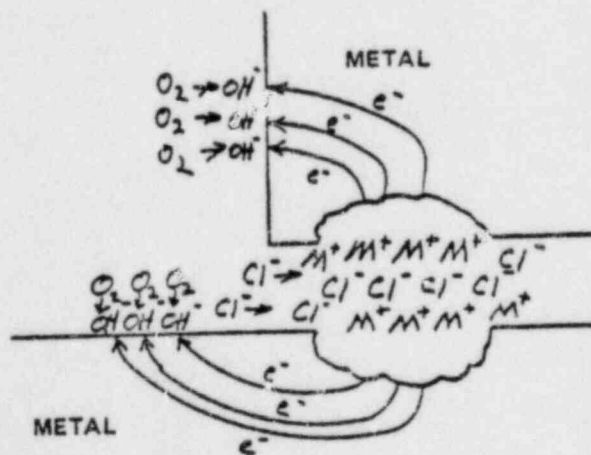
Since bromide ion is not involved in the reaction, the iron reacts with hydrogen ions to form ferrous ions and hydrogen gas. The reaction is depicted in Figure 14a.

Galvanic Corrosion (Cathodic Protection) - When dissimilar, contacting metals are immersed in a corrosive or electrically conductive solution, a potential difference develops that produces electron flow between the metals. Corrosion of the less corrosion-resistant metal is usually increased and that of the more resistant metal is decreased. This effect is depicted in Figure 14b. In this case the zinc (anode) is corroded at an increased rate while the iron (cathode) is not corroded, i.e., cathodic protection is produced. In the following list of metals an upper metal will be protected while the lower material will undergo accelerated corrosion.



a. Electrochemical Reaction Illustrating General Corrosion

b. Electrochemistry of Galvanic Corrosion - Cathode Protection



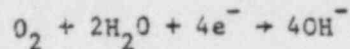
c. Electrochemistry of Crevice Corrosion

Figure 14. Diagrams Illustrating Various Types of Metallic Corrosion Mechanisms.

Galvanic Series of Commercial Metals

Titanium
Silver
Stainless Steel (passive)
Copper
Tin
Lead
Stainless Steel (active)
Cast Iron
Steel
Aluminum (2024)
Zinc
Magnesium

Crevice Corrosion - Intense localized corrosion can occur in crevices, i.e., holes, lap joints, under bolt heads, in incomplete welds and under gaskets when exposed to corrosives. The initial reaction around and inside a crevice is the same as for general corrosion; however, due to the stagnant condition inside, oxygen is consumed by the following reaction:



As metal continues to dissolve, the crevice is filled with excess of positively charged metal ions which is balanced by migration of halogen ions into the crevice resulting in high concentration of metal halide. The phenomenon is illustrated in Figure 14c, and requires some initiation time (usually months) to form; however, the time is significantly affected by temperature and pH, high temperature and low pH being the worst case.

Pitting Corrosion - Intense localized corrosion can occur at random locations by the mechanism of crevice corrosion; however, no pre-existing crevice or void is required. Since halides stimulate metal dissolution by breaking down the protective surface film, solutions containing halides can cause pits primarily in acid environments; however, neutral and alkaline systems can still pit. Again, as in crevice corrosion, high temperature and low pH are the worst case.

Stress Corrosion Cracking - Stress corrosion cracking occurs by the simultaneous application of tensile stress (applied or residual) and a

specific corrosive medium. Since the mechanism involved is not well understood, the most reliable and useful information can only be determined by testing. As in pitting and crevice corrosion, for example, halides break the passive film or enriched surface layer on stainless steel allowing more rapid corrosion at various points, thereby initiating cracks. Breaking of films ahead of the advancing crack prevents healing and propagation continues. The requirement of corrosion in stress cracking was demonstrated when advancing cracking was stopped by application of cathodic protection (12).

6.2 Literature Search

Extensive literature searching was conducted to determine exactly what could be expected in the aftermath of a LOCA and use of Halon 1301 for combustible gas control. Unfortunately, very little published corrosion information is available on Halon 1301, and practically nothing is published on hydrogen bromide and bromide ion corrosion in the low concentrations expected in the post-LOCA system.

Since, according to Hise (13), "... bromide solutions are quite comparable to the other halogen solution in the sense that pitting of stainless steel is somewhat common," available corrosive data were collected and reported here for chloride systems as well as for bromide systems. The following are summaries from specific references that were found:

- Testing has induced stress corrosion cracking in 304 stainless steel at temperature as low as 60°C where NaCl was deposited from solution, i.e., chlorides collected and concentrated in a humid environment (14).
- Stress corrosion cracking occurred at 80°C in neutral solution at chloride concentration of 100,000 ppm (15).
- Stress corrosion cracking has been produced in tests at 260°C to 343°C in oxygenated water ($O_2 > 2$ ppm) containing from 0 to 200 ppm chlorides where there is evidence that at reduced oxygen levels higher chloride levels are required (16).
- Cracking of 304 stainless steel occurred at a pH of 2 (8000 ppm NaCl and 141°C) and (40,000 ppm NaCl and 82°C) (17).

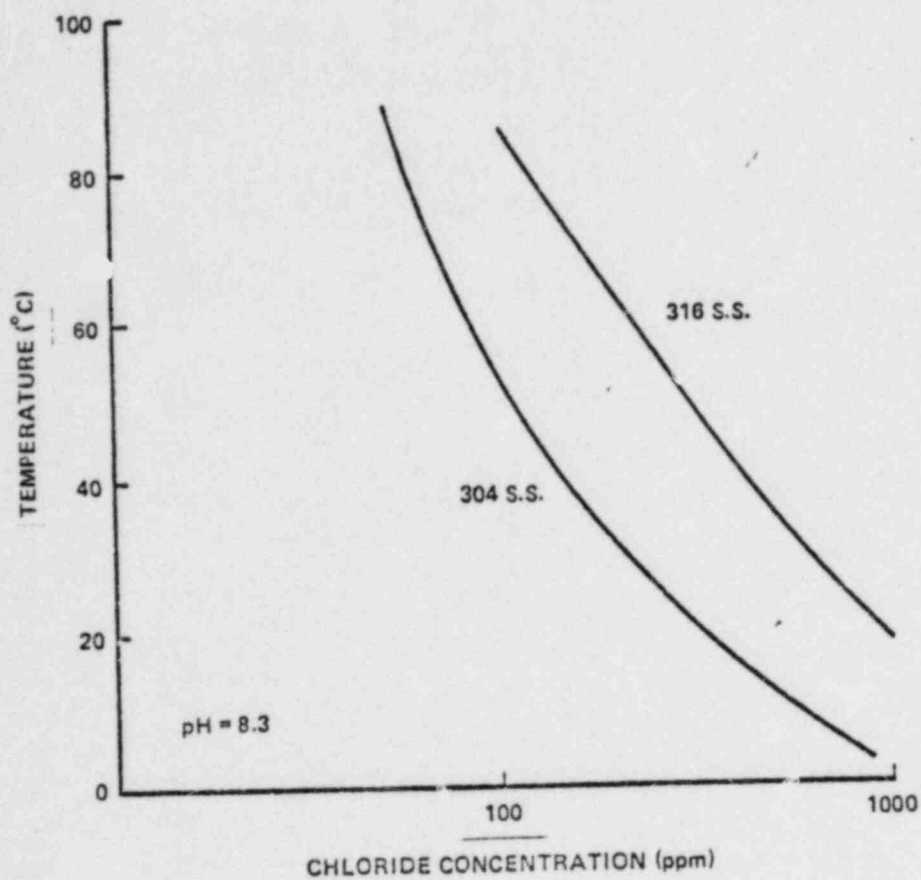


Figure 15. Localized Corrosion for 304 and 316 S.S. in River Water at Various Chloride Levels.

- The curves of Figure 15 predict the onset of crevice corrosion for stainless steels at various chloride concentrations (18).
- It is known that at temperatures above 150°F chloride stress corrosion cracking is a problem during refinery shut-down where moisture would reach chloride deposits in stainless steel equipment (19).
- Nitrate and carbonate solutions are used to avoid stress cracking of stainless steel (20).
- The presence of chloride ion, water, oxygen, or some oxidizing agent upon the surface of an austenitic stainless steel held in tension (stressed) above room temperature is necessary to induce cracking. The time to failure is temperature dependent, decreasing rapidly above 65°C (21).
- Bromides have caused cracking of 316 stainless steel (22).
- Bromide ion pitting of titanium will occur in aerated 1 M HBr at 23°C (23).
- Bromide ion environments are markedly less dangerous than chloride environments (24).

The following is a summary of some relevant effects of plain Halon 1301 on construction materials per reference (2):

- Negligible corrosion occurred on various metals including aluminum, stainless steel, steel, and brass at 250°F, 130°F, and room temperature and at moisture levels of 2 ppm (commercial material) and 72 ppm (75% saturation). (Galvanized steel was not tested.)
- Pure Halon 1301 at 600°F exhibits the following metallic corrosion rates:

<u>Metal</u>	<u>Mils per Year</u>
Inconel	3.0
316 Stainless Steel	7.5
Steel	14.4

- Pure Halon 1301 at room temperature significantly damaged ethyl cellulose, cellulose acetate/butyrate, and Silicone rubber. Polyethylene resin, cellose acetate, acrylic resin, "Teflon", as well as butyl, "Adiprene," and "Viton" were slightly damaged.

6.3 Discussion of Corrosive Effects Expected in Containment Cooling Water

Metals (Without Treatment) - If a Halon system were used during a LOCA with no effort at corrosion control, and clean-up did not occur within a few months, potential exists for the following detrimental effects:

- Probable stress corrosion cracking of stainless steel of heated surfaces.
- Possible stress corrosion cracking of stainless steel in water held above 150°F for an extended period.
- Extensive crevice corrosion, pitting and galvanic corrosion initiated during the period of low pH and high temperature perpetuated by increased conductivity of the water and presence of bromide ion.
- General corrosion by hydrogen ion would be limited to that produced by the ionization of HBr.
- The following informative estimates can be made concerning the amount of metals that would react with the total bromide ion inventory. Referring to equation (1) on page 35, it can be calculated that the 2465 total pounds of bromide from Halon decomposition would consume approximately 860 lbs. of iron in steel. In so doing, the solution would deplete itself of hydrogen ion and self-neutralize. This amount of iron is somewhat less than two cubic feet in volume.

As an illustration, if this volume of metal came from, say, the inside surface of the reactor pressure vessel, the loss on the surface would be about 8 - 10 mils. Similar estimates yield consumptions of 277 lbs of Al, or of about 1,000 lbs of zinc. As predicted by the galvanic series, the zinc on the galvanized steel would be rapidly attached followed by aluminum, then steel.

Metals (With Treatment) - If the Halon system were used during a LOCA, corrosion control should be possible in one or more of the following ways, testing being required to determine which method is suitable:

- Halon decomposition may be avoidable by addition of bromide ion (NaBr, KBr, LiBr); likewise, the pH depression may also be avoided. Another approach would be to let decomposition of Halon occur and control pH (8 - 10) with caustic addition (NaOH, KOH, or LiOH). Either of these should mitigate the general corrosion and reduce the potential for stress corrosion cracking.
- Inhibitors can be added which may prevent localized corrosion. For example, chromates, nitrates, borates, silicates, and zinc have been effective in similar systems.
- The use of sacrificial zinc or magnesium anodes could potentially eliminate both the pH depression and the localized corrosion problems as well.

Non-Metals (With or Without Treatment) - It is doubtful that the various non-metals will be significantly affected due to the very low concentrations of corrosives involved.

6.4 Conclusions From Materials Corrosion Study

The use of Halon 1301 to suppress post-LOCA hydrogen burning may result in significant corrosion problems if allowed in place for years without adequate control procedures. The exact effects with or without corrosion control are unknown since little corrosion study is reported for HBr or bromide salts in the concentrations expected.

Projections based on available bromide data along with HCl and chloride salt data indicate that lack of corrosion control would result in minor general corrosion; however, localized corrosion (pitting, galvanic, crevice, and stress corrosion cracking) could be serious.

Corrosion mitigation would employ pH adjustment, addition of inhibitors (chromates, nitrites/borates, silicates, and zinc), possibly cathodic protection and sacrificial metal. Corrosion testing is indicated to determine the effects on the system with and without treatment.

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ATTACHMENT B

Memorandum

TENNESSEE VALLEY AUTHORITY

TO : W. P. Joest, Supervisor, Codes, Standards and Materials Section,
W10D184 C-K

FROM : R. O. Lane, Supervisor, Singleton Materials Engineering Laboratory,
SME-K

DATE : April 2, 1981

SUBJECT: SEQUOYAH NUCLEAR PLANT - EFFECTS OF 1200 PPM HF ON 304 STAINLESS STEEL
AT 200°F (TR 2-18-81)

An evaluation of the corrosive action of a 1200 ppm HF solution on 304 stainless steel at 200°F was conducted as follows:

1. Two solution-annealed U-bend samples from as-received stock in solution-annealed condition were prepared by bending 1/4-in. wide strips of 16 ga 304 stainless steel around a 3/4-in. mandrel. Bending was stopped approximately 15 degrees prior to the point where the legs of the U-bend became parallel. A 304 stainless steel bolt inserted in holes in the legs of the U-bend was used to draw the legs approximately 15 degrees beyond parallel. Edges of the U-bend were prepared prior to bending by water-cooled grinding on a 240-grit belt to produce a flat, which would easily reveal any cracks or fissures upon subsequent evaluation.
2. Two additional U-bends of the same material were prepared in a similar fashion as above, except they were given a sensitization heat treatment at 1200°F for 3 h in argon.
3. A HF solution was prepared by adding 1/2 ml of a 49 percent solution of HF to 200 ml of deionized water. The ph of this solution was 3.0, and the fluoride ion concentration was measured to be 1170 ppm by specific ion techniques.
4. This solution was placed in a nalgene bottle, heated to 200°F, the four U-bends added, sealed, and placed in a convection oven to maintain 200°F.

After 24 h the samples were removed and examined under a stereomicroscope at magnifications of 20 to 70X. Rapid corrosive attack at the grain boundaries of the sensitized samples was evident, particularly at the square edges of the specimen. No cracks were found. The unsensitized samples did not reveal any appreciable effects after 24 h. All samples were beginning to develop a black adherent film on their exposed surfaces.



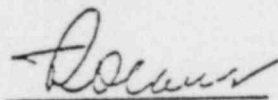
W. P. Joest
April 2, 1981

SEQUOYAH NUCLEAR PLANT - EFFECTS OF 1200 PPM HF ON 304 STAINLESS STEEL
AT 200°F (TR 2-18-81)

After an additional 96 h (120 h total) the four U-bend samples were reexamined and found to be covered with a black film obscuring visual or microscopic evaluation. Ultrasonic cleaning in inhibited HCl at room temperature eliminated the black film. Stereomicroscopy revealed advanced intergranular corrosive attack of the sensitized U-bends--actual grains and clusters of grains had fallen out of the prepared surfaces. Intergranular corrosion had virtually eliminated the square edges of these U-bends.

The unsensitized samples, on the other hand did not show intergranular corrosion. Rather, some pitting corrosion had taken place on the U-bend surfaces (edges) which had been prepared by grinding. Pitting was not observed, however, on the outer surface of the U-bend representing the rolling plane of the as-received material.

Detailed metallography will follow in a supplementary report.



R. O. Lane

ROL:PVG:PGK

cc: Frank Van Meter, 500 SPT-K
MEDS, 14B37 C-K

Memorandum

TENNESSEE VALLEY AUTHORITY

TO : C. E. Roberts, Supervisor, Codes, Standards, and Materials Section,
W10D186 C-K

FROM : R. O. Lane, Supervisor, Singleton Materials Engineering Laboratory,
SME-K

DATE : June 6, 1981

SUBJECT: SEQUOYAH NUCLEAR PLANT - EFFECTS OF HF AND HBr SOLUTIONS ON 304 STAINLESS
STEEL U-BENDS

Initial tests evaluating the effects of a 1200 ppm HF solution on both sensitized and solution annealed 304 stainless steel U-bends at 200°F were reported in SME 810403001. This memorandum covers additional tests involving similarly prepared U-bends in a solution containing 1200 ppm HF and 400 ppm HBr at a pH of 2.9 and a portion of the same solution buffered to a pH of 7.0 with NaOH, both at 200°F. Two solution annealed U-bends and two sensitized U-bends prepared identical to that described in the previous memorandum were placed in each solution contained in an enclosed Nalgene bottle and maintained at 200°F. Results are as follows:

After 24 h all samples were examined under a stereomicroscope at magnifications of 20 to 70X. An extremely rapid attack of the sensitized samples was present in both buffered and unbuffered HF plus HBr. Figures 1 and 2 show stereomicrographs of the samples after ultrasonic cleaning with an inhibited HCl solution.

The sensitized samples in the unbuffered 1200 ppm HF plus 400 ppm HBr show uniform grain boundary attack on both the tensile and compressive surfaces with the neutral axis of the sample showing light attack. Near the tensile surface the grain boundary attack tends to create fissures normal to the specimen axis. See figure 1a. Also, the sharp edges of the tensile surface are completely eliminated through removal of grains by the grain boundary corrosion.

The sensitized samples exposed to the buffered 1200 ppm HF plus 400 ppm HBr showed very severe but localized grain boundary attack after 24 h. See figure 2a. The attack shown in this photograph at the tensile surface consists basically of deep pits. Fissures of the type seen at the right side of the photograph were also observed. Pitting was observed predominantly on the tensile surface but also was seen on the compressive surface. Conventional intergranular cracking was not observed.



C. E. Roberts
June 6, 1981

SEQUOYAH NUCLEAR PLANT - EFFECTS OF HF AND HBr SOLUTIONS ON 304 STAINLESS
STEEL U-BENDS

The unsensitized samples (solution annealed) were returned to their respective solutions and allowed to remain for a total of 120 h at 200°F. Macrographs are given in figures 1b and 2b. In the unbuffered HF plus HBr solution, uniform etching of the specimen surface took place with minor pitting of the type seen in figure 1b in the center of the photograph. Macrosegregation was also delineated as seen by the dark line extending through the midposition of the sample. Otherwise the samples remained in good condition with no observed cracking.

The unsensitized samples exposed to the buffered HF plus HBr for 120 h at 200°F revealed much the same as for the unbuffered solution samples except to a lesser degree. See figure 1b.

Figures 3a, 3b, and 3c show comparative macrographs of the previously reported samples exposed to a 1200 ppm HF solution for 120 h. After 120 h in 1200 ppm HF (pH 3.0) at 200°F, the sensitized samples exhibited less severe attack than in the unbuffered bromide solution for only 24 h. Compare 3a with 1a. Similarly exposed unsensitized (solution annealed) U-bends compare with those exposed to the bromide solutions. See figure 3b. Figure 3c shows an enlarged view of the nature of the grain boundary attack in the unbuffered 1200 ppm HF solution. No cracking was observed in either the solution annealed or sensitized samples in the HF solution.

W. H. Childress
For R. O. Lane

PVG:ASH
cc: MEDS, E4B37 C-K

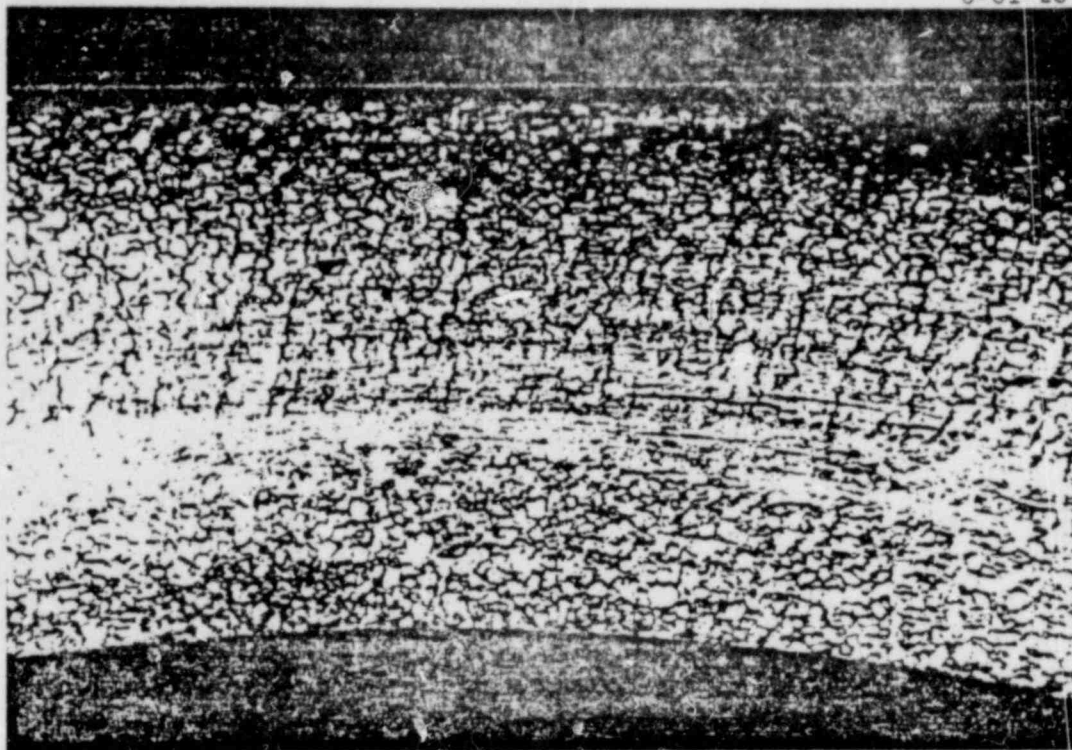


Figure 1a. Sensitized 304 stainless steel U-bend sample immersed in a solution of 1200 ppm HF plus 400 ppm HBr at 200°F for 24 h. 46X

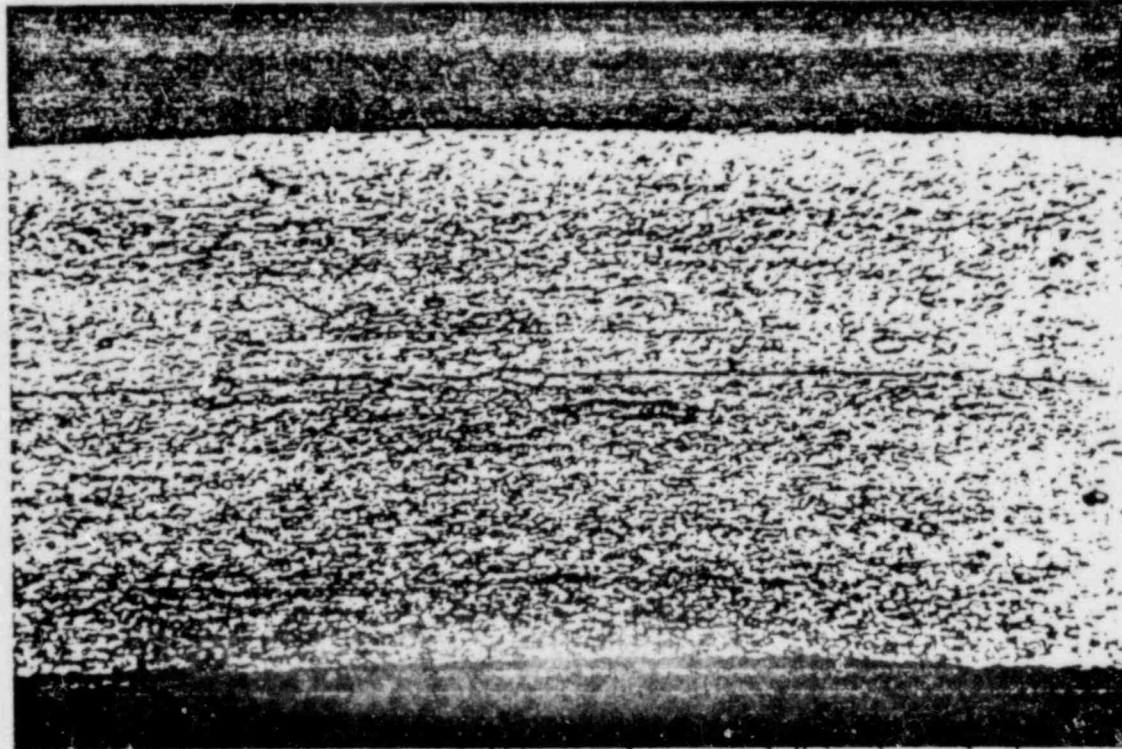


Figure 1b. Solution annealed 304 stainless steel U-bend sample immersed in a solution of 1200 ppm HF plus 400 ppm HBr at 200°F for 120 h. 46X

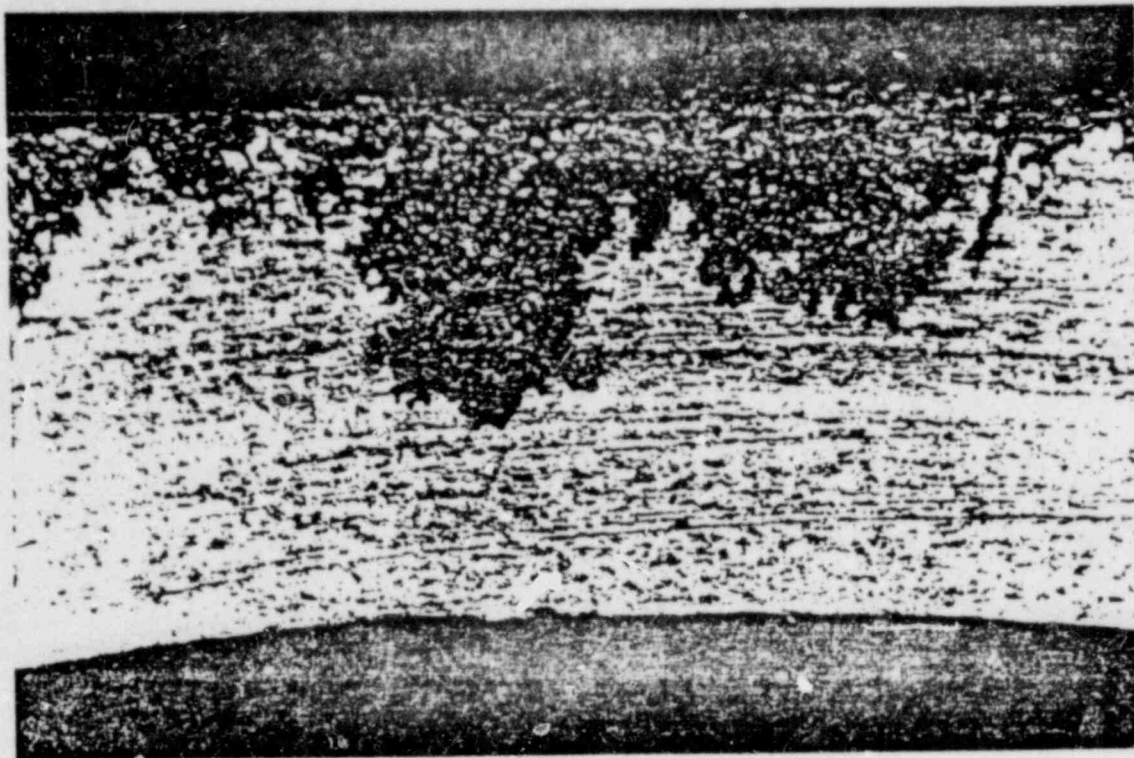


Figure 2a. Sensitized 304 stainless steel U-bend sample immersed in a solution of 1200 ppm HF plus 400 ppm HBr buffered to a pH of 7.0 with NaOH for 24 h at 200 F. 46X

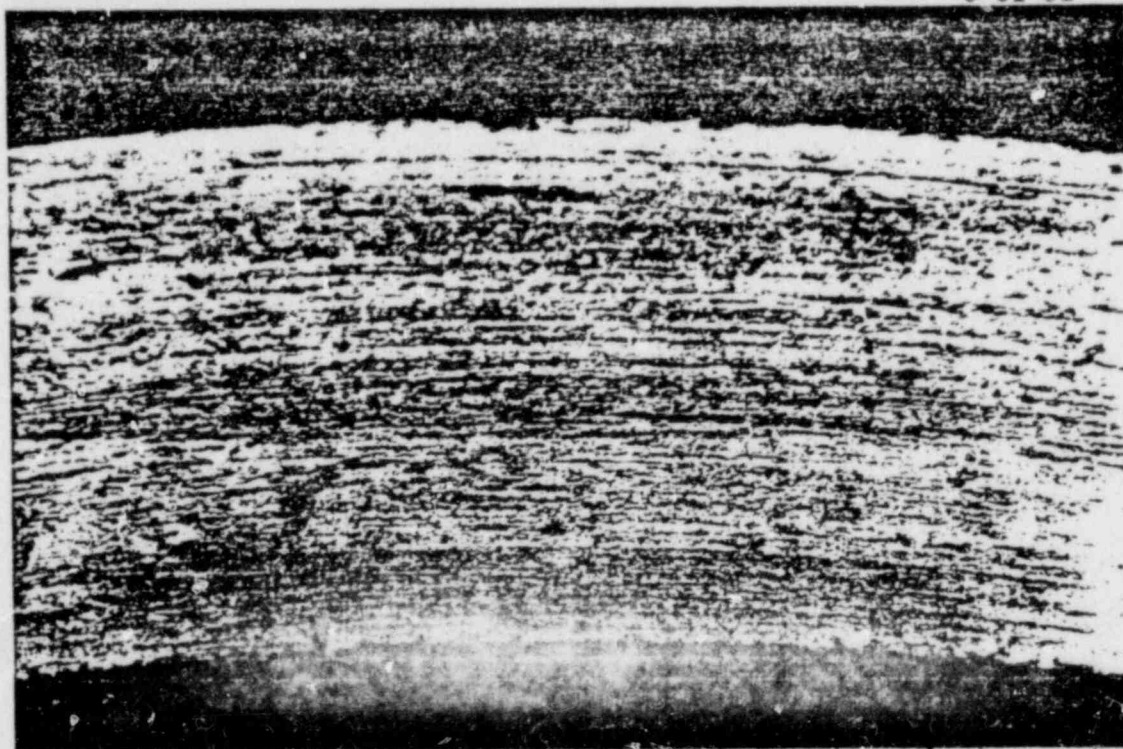


Figure 2b. Solution annealed 304 stainless steel U-bend sample immersed in the same solution of figure 2a for 120 h at 200 F. 46X

4-81-19

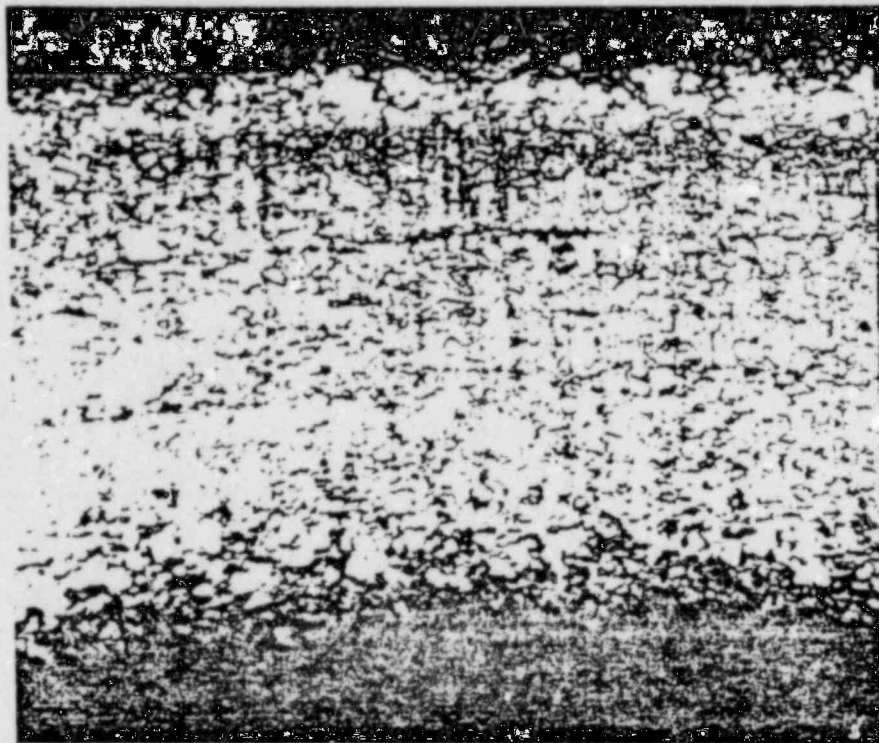


Figure 3a. Sensitized 304 stainless steel U-bend sample immersed in a solution of 1200 ppm HF at 200°F for 120 h. 46X

6-81-32

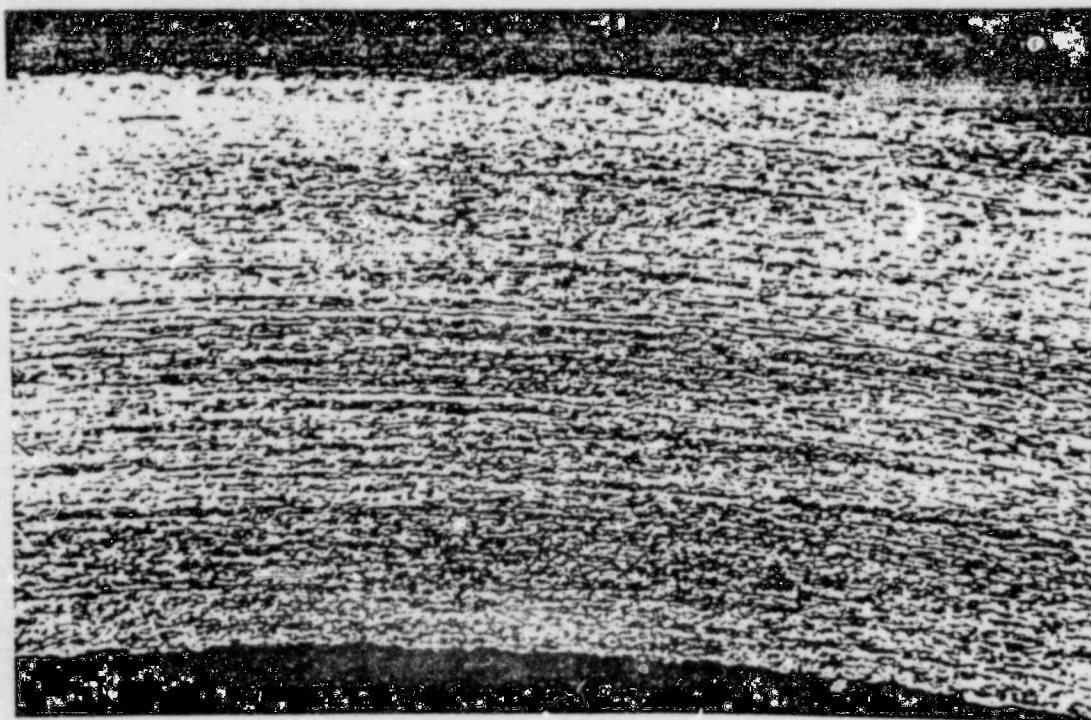


Figure 3b. Solution annealed 304 stainless steel U-bend sample immersed in same solution as figure 3a for 120 h. 50X



Figure 3c. Enlarged view showing grain boundary attack of figure 3a. Note loss of grains and clusters of grains from surface. Right side of photograph is specimen edge. 200X

ATTACHMENT C

DESIGN REQUIREMENTS
FOR A PERMANENT HYDROGEN MITIGATION SYSTEM

June 12, 1981

SEQUOYAH NUCLEAR PLANT

UNITS 1 AND 2

REVISION 1

1.0 SCOPE

- 1.1 This document provides the functional requirements, the environmental requirements, the system features, and control and power source requirements for a permanent hydrogen mitigation system (PHMS).

2.0 GENERAL DESCRIPTION

- 2.1 This PHMS shall consist of the igniters and the control and power circuits.

3.0 FUNCTIONAL REQUIREMENTS

- 3.1 The igniters shall be a reliable ignition source, capable of igniting hydrogen at low concentration levels (5 to 12 volume percent) in a post-LOCA environment.
- 3.2 The igniters shall be controlled manually from the main control room. Control of the igniters shall be divided into redundant groups with the status of each group displayed in the main control room.
- 3.3 The PHMS is not required during any phase of normal plant operation.

4.0 SPECIFIC SYSTEM DESIGN CONDITIONS AND REQUIREMENTS

4.1 Environmental Requirements

The PHMS components inside containment shall be qualified to maintain their functional capability under the full range of main steam line break and post-LOCA temperatures, pressures, humidity, radiation, and chemical sprays present in the containment. These components of the system must survive the effects of multiple hydrogen burns and shall be protected from containment spray impingement and flooding. All components of the system outside containment shall be qualified to operate in the environment in which they are located.

4.2 System Features

The PHMS shall have the following features:

1. Meet the requirements of seismic Category I.
2. Operate in the environment specified in paragraph 4.1.
3. Redundancy
4. Maintain electrical separation per paragraph 4.3.2.

4.3 Control and Power Requirements

4.3.1 Igniter Control

The total number of igniters shall be divided into two groups, A and B, with the status of the groups indicated in the main control room. Group A shall consist of one-half of the total number of igniters. Group B shall consist of the remaining half. The igniters will be normally deenergized. Activation of the igniters shall be manually from the main control room.

4.3.2 Power Requirements

The ignition system shall receive its power from the class 1E ac auxiliary power system. Provisions shall be made for manually loading the ignition system onto the diesels from the main control room upon loss of offsite power. One-half of the igniters (Group A) shall receive power from the train A diesel and the remaining igniters (Group B) from the train B diesel (see figure 1). The controls and power cables for the ignition system shall maintain the required separations and be identified as specified in SQN-DC-12.2. The igniters of each group shall be provided with a minimum of five power feeds per panel from the 120-volt ac distribution panels.

4.3.3 Number and Location of Igniters

There shall be a total of 60 igniters distributed throughout the containment. A minimum of two igniters, one from Group A and one from Group B, shall be located in each enclosed volume and at the entrance to the pressurizer and steam generator chambers (see figures 2 through 7).

4.3.4 Igniter Requirements

4.3.5.1 The igniters shall operate from a regulated 120V ac \pm 10 percent power source. The maximum power requirements of each igniter shall not exceed watts.

4.3.5.2 Thermal igniters shall reach a minimum surface temperature of 1500° F within 90 seconds under the environmental conditions stated in paragraph 4.1.

4.3.5 Penetration Requirements

Containment electrical cable penetrations shall be provided with redundant overcurrent protection and be designed in accordance with paragraph 4.2.

4.3.6 Failure Criteria

4.3.6.1 The Class IE power system shall be protected from failures in the PHMS.

4.3.6.2 A failure in one of the 120V ac circuits of a group shall not prevent the remaining 120V ac circuits in that group from performing their function when required.

5.0 TESTABILITY

5.1 Both groups of igniters (A and B) shall be capable of being tested periodically to ensure operability of all the igniter in that group. To confirm the operability of the system, the current in each 120-volt circuit shall be monitored and compared to the current recorded in that circuit during preoperational testing.

HYDROGEN IGNITION POWER SYSTEM
UNIT-1 SHOWN
(UNIT-2 TYPICAL)

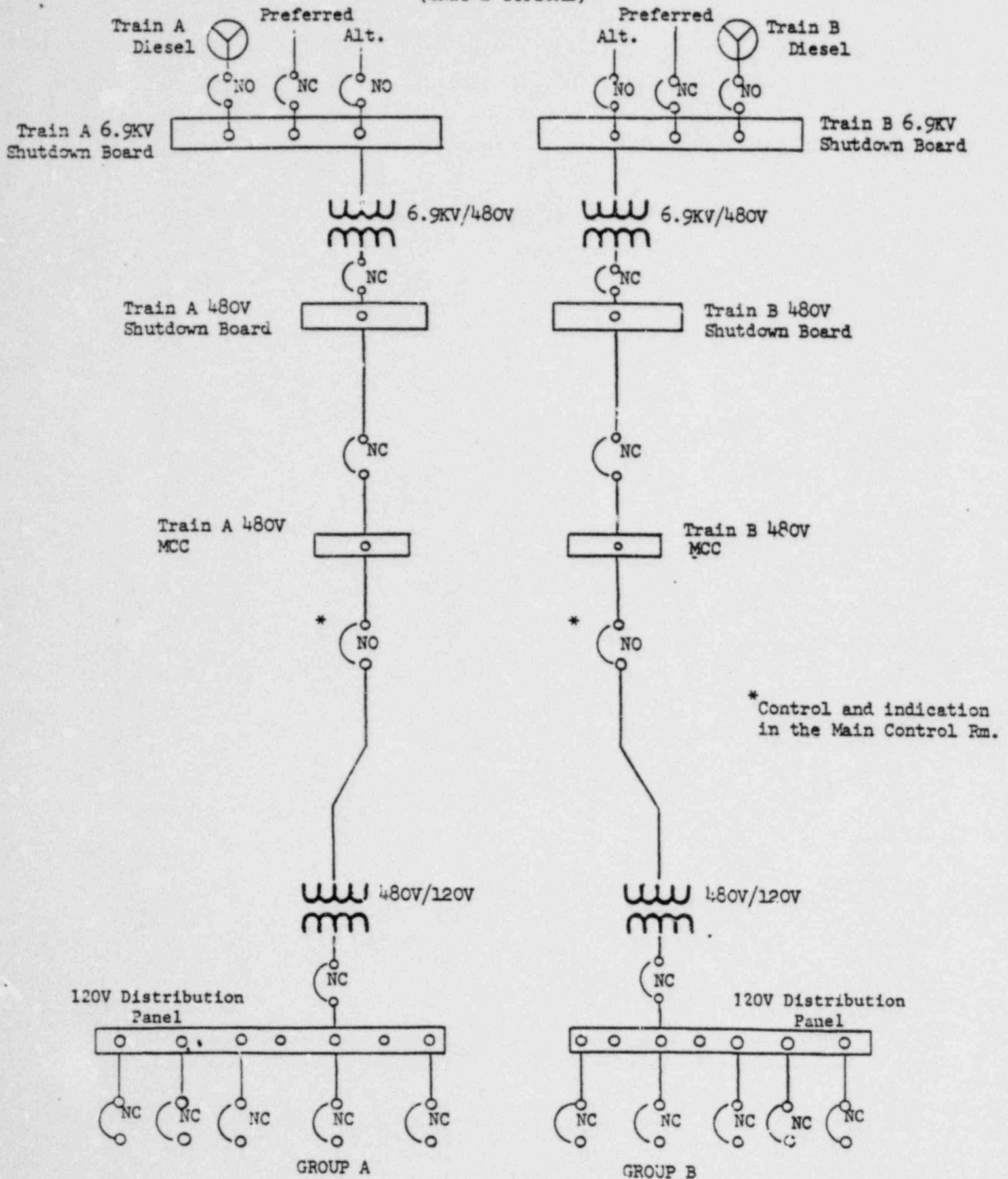


FIGURE-1

KEY TO FIGURES 2 THROUGH 7

⊗ - Denotes Hydrogen Igniter Location

Igniter Identification

Format: "X"

X is power train designation.

E71090.04

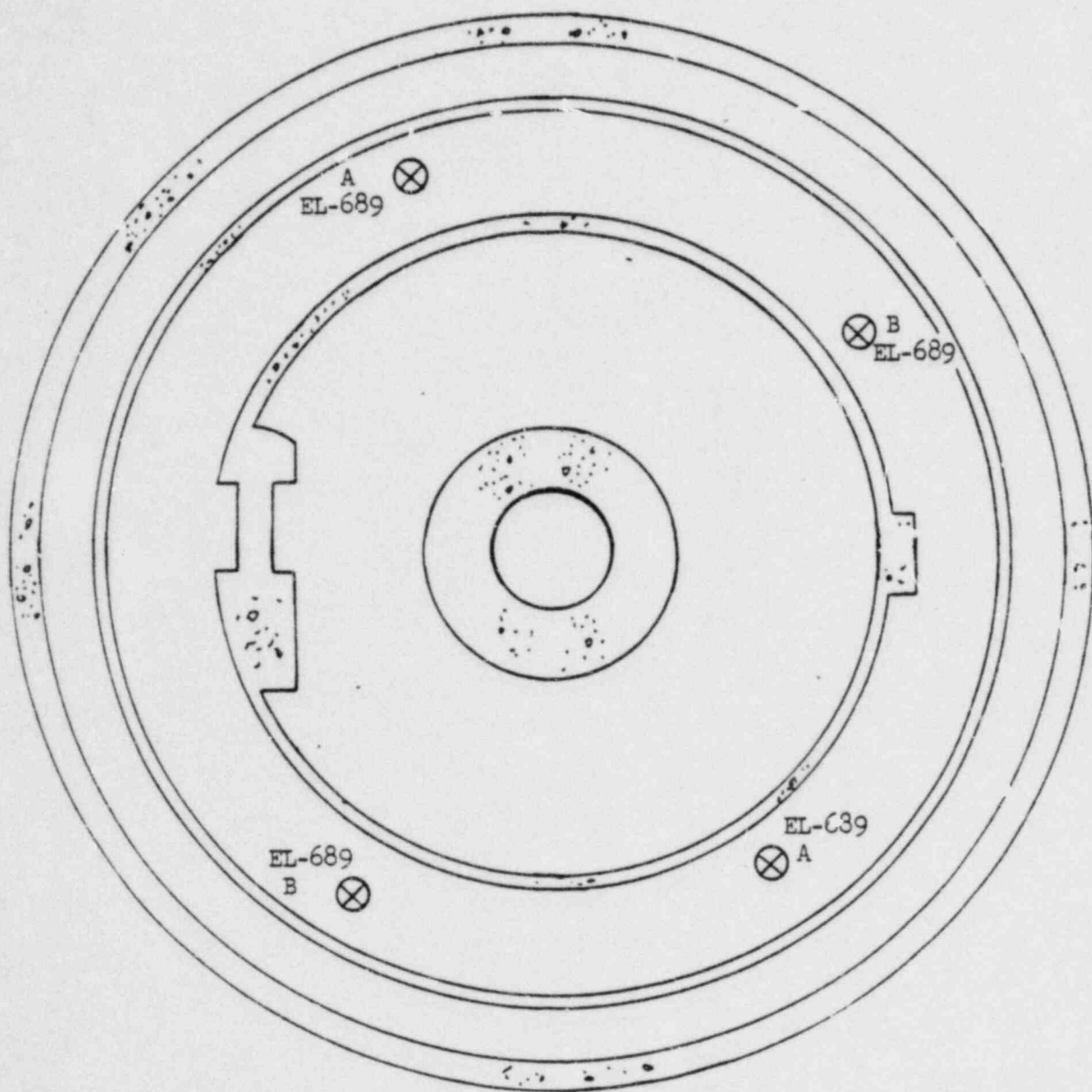


FIGURE -2

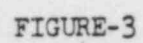


FIGURE-3

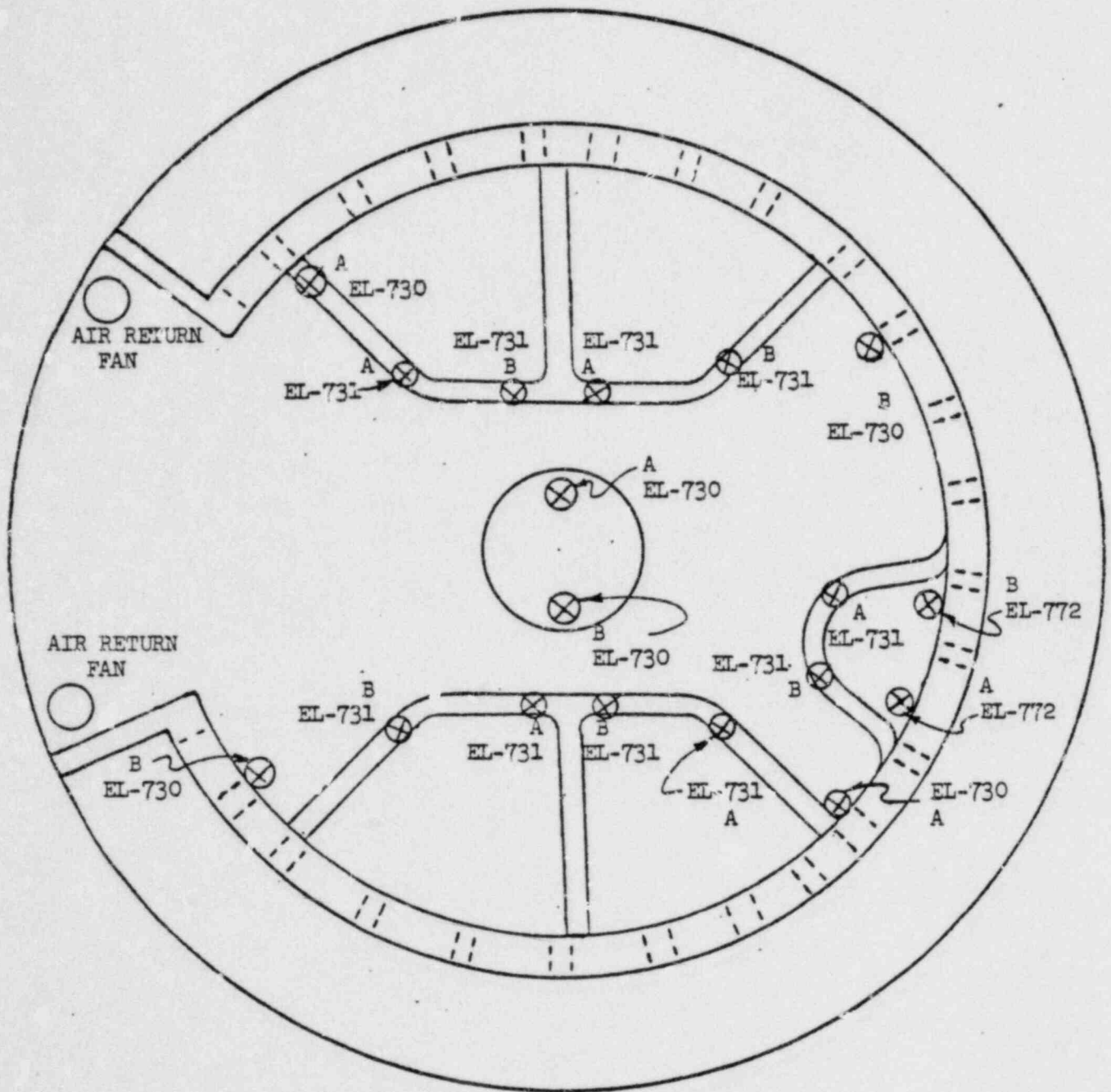


FIGURE-4

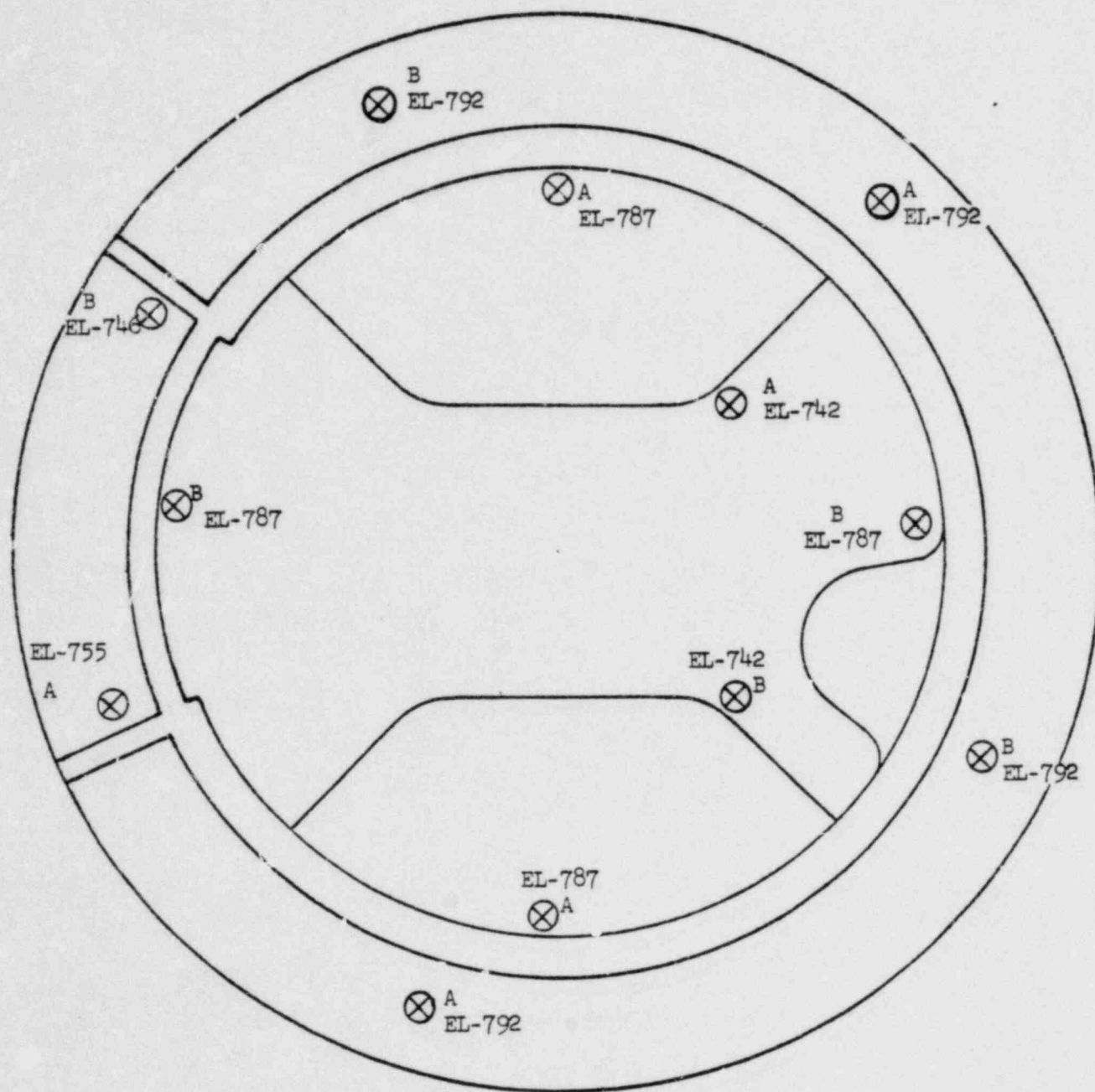


FIGURE-5

Igniters in: 1. Upper plenum of ice condenser
2. Upper Compartment

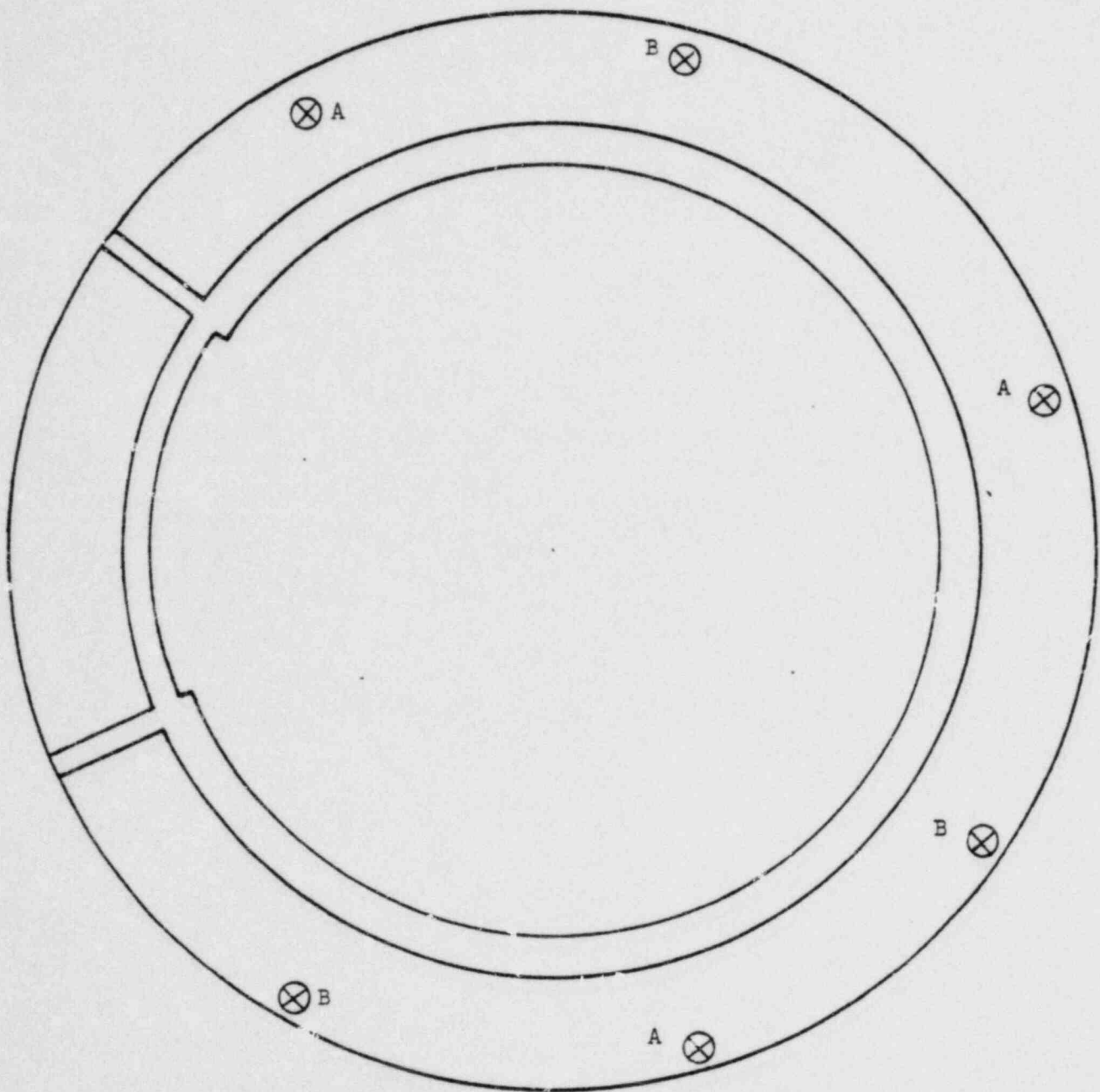


FIGURE-6

Igniters on Crane Collector Rails EL-809.0'

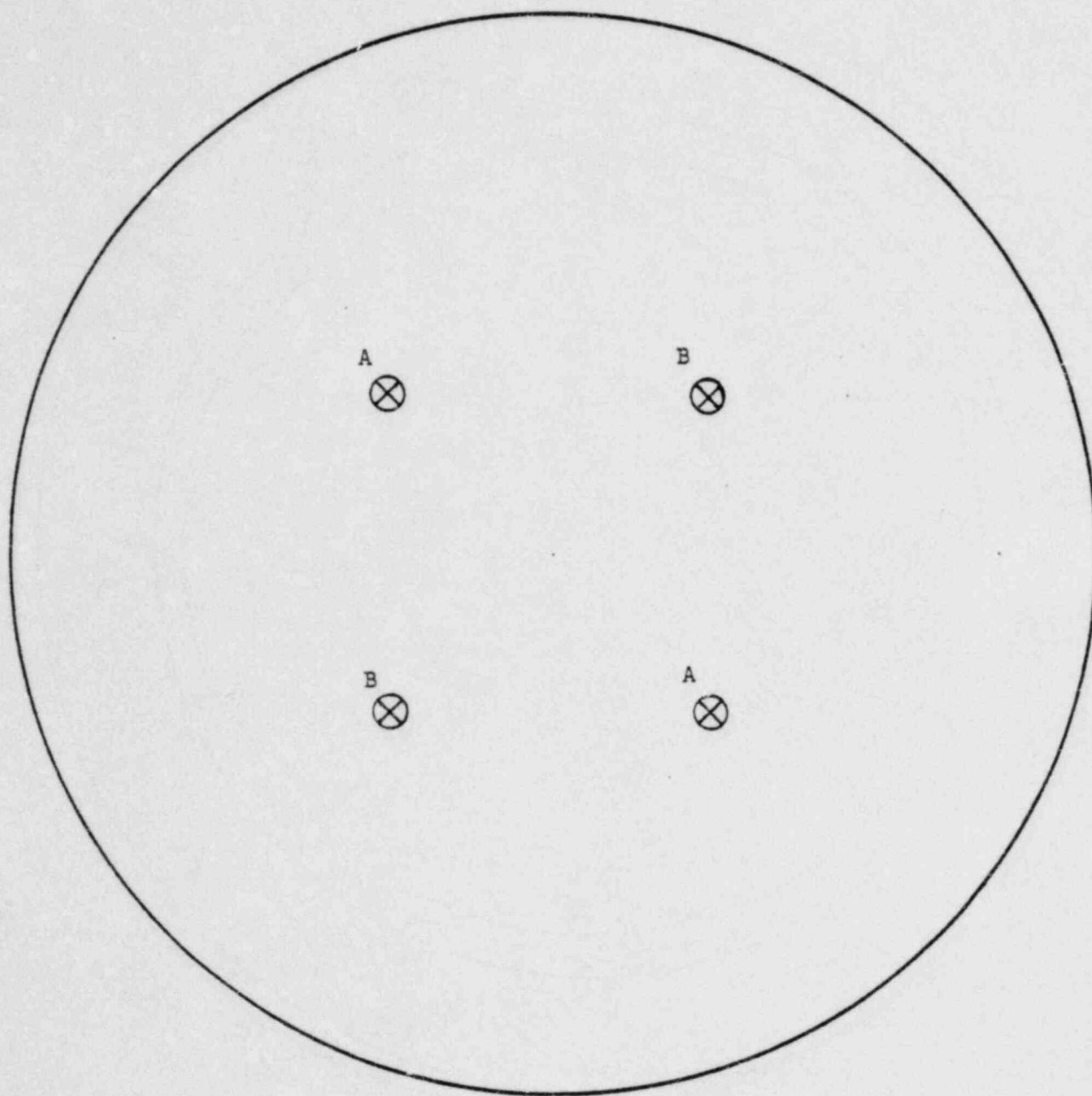


FIGURE-7

Igniters on Lighting Brackets at EL-846'- $5\frac{3}{16}$ "

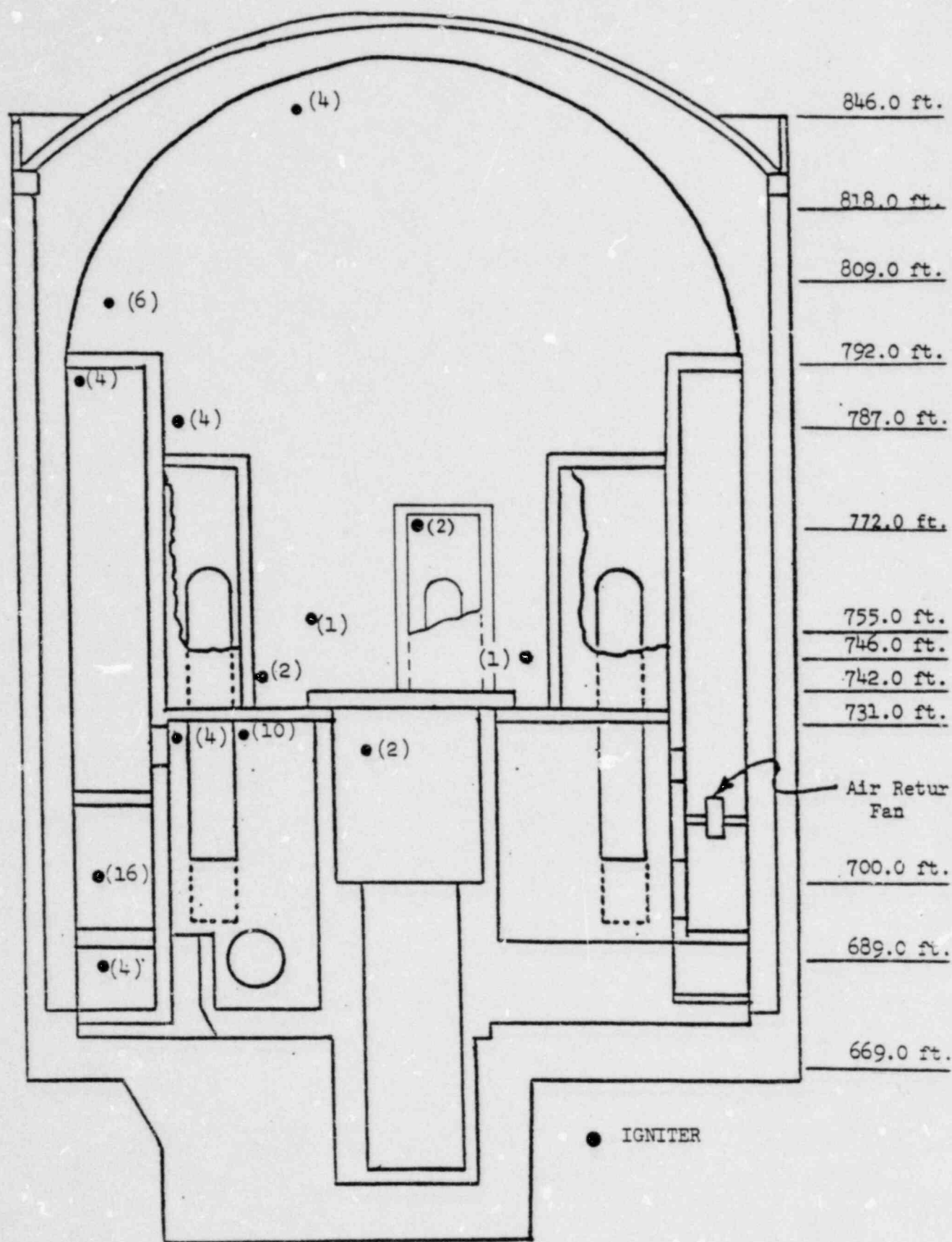


FIGURE-8