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TMI-2 HYDROGEN GENERATION: LICENSING IMPLICATIONS AND DESIGN BASIS ACCIDENTS

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1. Introduction

As a result of the accident at the Three Mile Island - Unit 2 (TMI-2) reactor, the TMI-2 Lessons Learned Task Force has made three "short term" recommendations regarding post-accident hydrogen control systems for PWR and BWR containment (1):

a) Dedicated Penetrations for External Recombiner or Post-Accident External Purge System,

b) Inerting BWR Containments, and

c) Capability to Install Hydrogen Recombiner at each LWR.

Item (c) is a minority view with the majority opinion being that such consideration should be part of the long term reconsideration of the design basis for combustible gas control systems. These recommendations are a result of the production of quantities of hydrogen gas in excess of the amounts required by NRC Regulations to be considered in the design and accident analysis of nuclear power plants. As stated in the report, "The Task Force is continuing to study whether the hydrogen design basis needs to be changed."

It is the intent of this note to discuss the hydrogen design basis, the potential implications of TMI-2 hydrogen generation on design basis accidents in general, and implications for future licensing and safety analysis (in particular, ice condenser plants).

2. Brief History

Following a Loss of Coolant Accident, hydrogen can be generated by

a) metal water reactions, particularly between the zirconium fuel cladding and the reactor coolant (zirconium is oxidized),

b) radiolytic decomposition of post-accident emergency cooling solutions (oxygen is also released in this process),

c) corrosion of metals by solutions used for emergency cooling or containment sprays.

Generation by the metal-water reaction (M-W) is on the time scale of several minutes to a few hours, while radiolytic decomposition time scales are hours to days, and corrosion time scales are even longer.

In the past major consideration has been given to radiolytic decomposition because of the coevolution of oxygen and because the amount of M-W reaction was considered in the design basis is minimal. Consideration has been given to a) containment purging, b) use of recombiners and c) inerting BWR Mark I and II containments, as a means of controlling hydrogen generation.

Discussions dating back to 1969, however, considered the possibility that with total ECCS failure, 25-50% of the clad in the core could react with water to generate hydrogen. In 1971, Safety Guide 7 was issued which required consideration of a 5% metal-water reaction (5% of the clad in the core) in LOCA and containment analysis. In 1974, an attempt was made to have Safety Guide 7 conform to the ECCS Interim Acceptance Criteria which called for a 1% metal water reaction. Regulatory Guide 1.7, which evolved from Safety Guide 7 required either a 1% metal-water reaction or 5 times the calculated value, whichever was higher.

The current design basis for combustible gas control is given in 10 CFR 50.44. Regulatory Guide 1.7 - Revision 2, describes methods acceptable to the NRC Staff for implementing § 50.44. With respect to metal-water reactions, the extent and evolution time of initial core metal-water reaction hydrogen production from the cladding surrounding the fuel is

> "Hydrogen production is 5 times the extent of the maximum calculated under 10 CFR Part 50, § 50.46, or that amount that would be evolved from a core-wide average depth of reaction into the original cladding of 0.00023 in, whichever is greater, in 2 minutes."

Paragraph 50.46 specifies acceptance criteria for ECCS and along with Appendix K specifies an acceptable method of computing the hydrogen generation. The value of 0.00023 inches corresponds to "one percent of the mass" for current designs with thin cladding. Since the reaction is a surface phenomenon, the Staff believes that a strict 1% figure would unnecessarily penalize reactors with thicker cladding. The Staff further believes that a minimum metal water reaction (1% or 5 times that calculated in accordance with §50.46) "provides an appropriate and prudent safety margin against unpredicted events during the course of accidents."

Since conformance with § 50.46 ensures a maximum of 1% for the metal-water reaction (when considering ECCS performance) one of two situations arises when considering combustible gas control:

a) the calculated value is so low (as is 5 times it) that the design basis is 1% or

b) the calculated value is just below 1% so that the design basis approaches 5%.

3. TMI-2 Metal-Water Reactions

Preliminary estimates of the hydrogen generated by the metal-water reaction at TMI-2 vary between:

a) 40% of the cladding wall thickness uniformly oxidized throughout the core (2), or more probably,

b) 40% of the fueled region fully oxidized (2).

c) A maximum of 48.3% and a minimum of 40.6% (3).

It was first estimated (4) that between 25% and 30% of all Zircaloy in the core reacted in the first 3 hours to produce hydrogen with the remaining reaction taking place between 3 and 9 hours, and later work (5) estimated 35%, with bounding estimates of not less that 20% nor more than 60%.

Preliminary analysis (2) also indicates that at most, only 15% of the total hydrogen generated evolved from radiolysis. The figure is probably closer to 0% (3).

4. Hydrogen Generation and Design Basis Accidents

The design basis for ECCS acceptance, limits the metal-water reaction to less than 1%. Similarly the design basis for combustable gas control varies between a minimum of 1% and a maximum of 5 times the calculated metal-water reaction (which cannot be greater than 5%). The TMI-2 metal water reaction involved over 40% of the Zircaloy clad. Clearly, the design basis in each instance was exceeded. The pressure spike at 10 hours (28 psig over ten minutes), attributed to the burning of 225 lb - moles of hydrogen, was however below the design basis of 60 psig for the containment.

Part of the rationale for including the margin in Regulatory Guide 1.7 was to separate the ECCS considerations from containment considerations, and to provide margin for hydrogen control in the event of ECCS degradation. The periods of time in which the ECCS were turned off by the TMI-2 operators essentially represented total degradation (or failure).

In the Reactor Safety Study (WASH-1400), hydrogen combustion as a cause of containment failure was considered for the PWR and BWR studies (5). (The PWR studied was the Surry Reactor, at 788 MWe, with a sub-atmospheric dry containment. The BWR studied was the Peach Bottom Reactor, Unit II, a 1065 MWe plant with a MARK-I containment). It was estimated that in a core meltdown accident (failure of ECCS), 75 ± 25% of the zirconium would react with the water in 45 minutes yielding 600 lb - moles of hydrogen. Although a hydrogen explosion was ruled unlikely, failure of containment due to over-pressure caused by hydrogen burning or in conjunction with a steam explosion was considered. Such events were contributors to Category 2 releases for both the PWR and BWR studied.

These release categories, in terms of fission product release, exceeds the TID-14844 values (100% noble gases, 50% halogens and 1% of the solid fission products), exceed the source terms given to Reg. Guide 1.4 and 1.5 (for PWRs and BWRs), and result in site boundary doses which may exceed 10 CFR Part 100.

Following the methodology of WASH-1400, Chan (6) examined potential failure modes of alternate containments (PWR-Ice Condenser and BWR-Mark III) of the vapor suppression type. He found that the ice condenser containment can be failed in several ways under core melt conditions, including hydrogen burning. Chan estimates a pressure rise of 50 psi in the containment due to hydrogen burning, with breaching of containment. If the amount of metal-water reaction is kept below 25%, failure was estimated to be precluded. For the PWR Mark III case, Chan estimated that a 100% metal-water reaction followed by hydrogen burning yields a peak pressure of 156 psia, well above the 40-50 psia failure pressure range.

Such postulated accidents (e.g core melt followed by containment failure) are considered beyond the design basis, and as such are generally not considered in the licensing process.

The physical phenomena following a hypothesized core-meltdown accident were recently examined and the quantities of fission products that would be expected to be released from containment were determined for the Sequoyah PWR (7). Of particular interest is the potential failure of the containment (Sequoyah is an ice condenser) due to hydrogen burning. The Sequoyah containment is designed to accommodate an internal pressure of 10.8 psig. It is believed that the nominal failure pressure is 27 ± 3 psig (42 ± 3 psia)(7).

The potential for containment rupture due to hydrogen burning depends on composition of the atmosphere, availability of an ignition source and an incremental pressure rise associated with the burning. For the Sequoyah ice condenser PWR, it was found that conditions favorable to hydrogen burning can be met with a well-mixed containment atmosphere (e.g., with the Air Return Fans operating) and if the path from the core to the containment atmosphere is short (e.g. for a hot-leg break where the hydrogen may be above the spontaneous ignition temperature). Analysis indicates that failure "would be a virtual certainty", assuming hydrogen burning, because of the low design pressure.

In addition to these results, fission product release for various containment failures was considered. Using the methodology given in Appendix VII of WASH-1400, LOCA sequences which include hydrogen burning fall into Release Categories 2-5. For the sequence (S_2 HF-$\underline{\gamma}$) falling into Category 2, the following releases were obtained:

Xe-Kr	100%	Ru	4.2%
I-Br	13%	La	0.7%
Cs-Rb	57%	Te	49%
Ba-Sr	6.8%		

(Note: S_2 HF-1) is a small pipe break (1/2 to 2 in) with failure of the ECCS recirculation system and failure of the containment spray recirculation system.)

These fission product releases are also in excess of the design basis source terms.

5. Potential Solutions

The discussion above raises several questions concerning hydrogen generation and control, currently used design basis accidents and future licensing reviews. Of particular concern are ice condenser containments, which because of their low pressure capability, may be vulnerable to hydrogen burning.

In addition to hydrogen recombiners, there are three (or more) potential methods for dealing with the ice condenser containments:

a) inerting the containment,

b) provide auxillary means to suppress hydrogen burning, and

c) employ post-accident filtration (vented containment).

5.1 Inerted Containment

The requirement of inerting BWR-MARK I containments was a means of coping with early versions of 10 CFR 50.44. In principle, the inerting requirement could be placed on ice condenser plants if the design basis for hydrogen generation were changed. There are several negative aspects of inerting ice condenser containments which relate to access.

At the D.C. Cook plant (the only operating PWR with an ice condenser containment), it is required to monitor ice build up on the vent doors (see Figure 1) on a weekly basis. This once a week entry has been made at the suggestion of the resident inspector. In addition, there is more equipment requiring routine maintenance inside a PWR containment than inside an inerted BWR Mark-I containment.

A 160,000 ft^3, BWR-Mark I containment takes 1 day to inert and 1 day to deinert, at a cost of several thousand dollars for the liquid nitrogen. An ice condenser containment, with a free volume of 1,192,000 ft^3 should take a somewhat longer time for inerting and deinerting, and at a larger cost.

5.2 Auxillary Means to Suppress Burning

The provision to suppress hydrogen fires by auxilary means could take several forms. The most conventional approach for combustible gas control is the use of recombiners, now in use commercially and at several power reactors. Because the state-of-the-art is such that long periods of time are required for extensive recombination (several days), recombiners are best suited for control of hydrogen generated by radiolysis. For example, the Sequoyah plant will have two electrical thermal hydrogen recombiners based on a 1.5% zirconium-water reaction and an 8 day period to reach combustable limits. Alternatively, controlled burning of hydrogen as it is produced is also a possibility. While large dry PWR containments may take the pressure rise associated with this option, it is questionable for an ice condenser, especially if the hydrogen is generated very rapidly (on the order of minutes).

The physics of hydrogen flammability can also be used for control. In particular, the presence of a third vapor or gas will influence the flammability limits of hydrogen in air and oxygen atmospheres. Flammability of two vapors can be suppressed by:

a) a suitable increase in the amount of either constituent,

b) the addition of a suitable amount of inert substance or an oxygen scavenger,

c) the addition of a flammable substance in sufficient amounts to exceed the higher flammability limit of the resultant mixture.

Figure 2 shows the effects of steam on the flammability limits of hydrogen/air mixtures. When approximately 60% water vapor is present (80°C), the flammibility limits coincide at 10% hydrogen/30% air. Hence flammability is suppressed for all hydrogen concentrations up to 40% providing there is 60% water vapor present.

Other tertiary mixtures (with hydrogen and air) might include nitrogen, carbon-dioxide, methane and hydrazine. Hydrazine is of interest because it is an oxygen scavenger and has been employed in containment spray systems as an iodine getter (8). (In the Sequoyah containment, the ice will contain sodium tetraborate to enhance iodine adsorption).

In this latter approach, one could make use of the containment spray systems to effectively "inert" the containment. One alternative would be to increase the temperature of the containment slightly and "fog" it with the spray system. The objective is a mixture of steam/air/hydrogen above the flammability limits but at the same time maintaining a pressure below the containment design pressure. A second alternative would be a chemical additive, such as hydrazine in the spray system. As employed now, hydrazine is added to a boric acid/water solution by a metering pump before it enters the containment. The quantity of hydrazine used (100-200 gallons) is large in comparison to Iodine - 131 present because of radiation depletion of hydrazine. For either alternative, the containment spray system would be turned on immediately following an accident.

If such an approach as described above is feasible, there is one item of concern; loss of all AC power. In WASH-1400, a major risk contributor for the PWR studied was a loss of offsite AC power and failure to recover either onsite or offsite AC power within three hours, (followed by failure of the feedwater delivery system). It appears, however, that the emergency AC system design for the Sequoyah plant includes an additional level of redundancy over that of Surry (7). While this redundancy may eliminate the event as a major sequence initiator, its role (loss of all AC power) in other sequences is not clear.

It should also be noted that other methods such as the use of transition elements to form hydrides, molecular diffusion through a diffusive barrier, chemical fixation, regenerative liquefaction and utilization of antideflagration agents (e.g. bromotrifluoromethane) may prove useful for this application. Sufficient information, such as effectiveness in radiation environments, needs to be established.

5.3 Post Accident Filtration

The provision of a post accident filtration system (PAFS) or vented containment as a means of coping with hydrogen generation stems from the general attempt to improve containment effectiveness under core melt conditions. The objective, as described by Gossett et al (9), is to provide an external filter through which the air/steam mixture in the containment could be vented to the atmosphere, thus preventing containment rupture due to overpressurization. It also has the secondary function of removing radioactivity from the containment, even in situations where the containment is leaking. In the original work by Gossett, a PAFS for the BWR-Mark I containment was designed and analyzed. Preliminary results for a PWR dry containment were also presented. A unique feature of these designs is the inclusion of a hydrogen ignition chamber so that unintentional burning or detonation in the filter system is precluded.

When considering a PAFS for an ice condenser containment in conjunction with hydrogen generation, other containment failure modes must be considered. There are several potential failure moles of interest:

a) hydrogen burning

b) steam explosions

c) containment leakage (failure to isolate)

d) core debris fragmentation

e) overpressurization due to noncondensibles, steam or both.

Because of the low design pressure of the ice condenser, failure due to a) and e) are the most probable for a broad spectrum of accidents, even if the containment ESFS operate (7). Hence, the primary function of the PAFS is an ice condenser would be to vent the containment before substantial pressure buildup due to burning and/or the presence of steam and other noncondensible gas.

An important consideration in the design of a PAFS for an ice condenser containment is the interaction between it and the other containment ESF systems (containment spray, air return fan system and the ice itself). In particular, the air return fan system which is actuated on high containment pressure, is delayed for 10 minutes following initiation of the ECCS. The fans, when operating, reduce containment pressure. The 10 minute time delay is intended to provide an increased back pressure during core reflood. Pumps which draw suction from the sump may cavitate if the water were to flash due to a sudden drop in pressure. When the fans are not operating, hydrogen would tend to accumulate in the lower compartment, (368,000 cubic feet). With the fans on, the hydrogen would be distributed throughout the containment. After long periods might accumulate in the upper compartment (should the fans stop working).

Given the compartmentalization of the containment, it is not clear where the entry points for the PAFS should be. Flow rates in the PAFS should be compatible with the air return fan system and the natural driving force of the air/steam mixture through the ice compartment. The operating mode is also dependent on the other ESF functions. For large dry containments, the PAFS would be activated (isolation valves opened) upon high pressures being reached (50-60 psig). For the low pressure ice condenser, the operator has to be prepared to activate the system very soon after initiation, but not so soon that other ESFs are compromised. Inadvertant operation of PAFS may also be a problem.

Last but not least, is the public's attitude toward controlled venting of the noble gasses. The deliberate release of some species, however small their radiobiologic effect might be, might not be acceptable in the public view. Consideration should be given, in terms of cryogenically cooling the charcoal filters, to controlling noble gas release.

6. Recommendations

While it is too premature to recommend any (or all) of the potential options discussed above, the following might be appropriate. For the short term, consideration should be given to inerting ice condenser containments. This would involve lengthening the periods between entry (perhaps on a monthly basis) and/or providing air-pacs to those entering while the containment is inert. Figures 3 and 4 indicate that if the oxygen is reduced to below 4.9% (from 21%), hydrogen ignition is precluded.

For the long term, research should be carried out on the use of chemical additives in conjunction with the containment spray system and in the use of filtered vented containment. The use of containment spray has the advantage that the system is already in place. Vented containment has the advantage that it can potentially cope with other sources of containment failure (e.g. overpressure due to steam explosion and/or non-condensible gases).

Sandia Laboratory has recently initiated a program, under the sponsorship of NRC, to investigate vent-filtered containment conceptual designs for light water reactors. It is recommended that NRC direct Sandia to examine conceptual designs for ice condenser plants at the earliest time so that a decision regarding their possible use can be made on a timely basis.

7. Concluding Remarks

The available information regarding TMI-2 indicates that the design basis for hydrogen generation was greatly exceeded (40% metal/water reaction observed), and the pressure spike of 28 psig at 10 hours in the containment was due to hydrogen burning. In assessing the implications of TMI-2 with respect to hydrogen, particular concern focuses on PWR-Ice Condenser Containments which have a low pressure containment design (10-12 psig).

Preliminary analysis of ice condenser containment failure modes indicates that for a broad spectrum of accidents, beyond the design basis, failure is almost certain from hydrogen burning or overpressurization due to steam and/or noncondensibles. As presented in Sections 5 and 6, there are several potential options for dealing with hydrogen generation beyond the design basis. These include inerting, vent-filtered containment and use of the containment spray system.

These considerations raise several important questions:

1) What should the design basis for hydrogen generation be? Should hydrogen control be predicated on metal-water reactions (short-term) or on radiolysis (longer term).
2) Should accidents which currently lie beyond the design basis be considered in future reviews? Are accidents which terminate with a disrupted core (not necessarily a molten one) be included in the design basis?

3) Considering the extent of metal-water reaction possible (greater than 40%), with failed clad and disrupted fuel (not necessarily molten), are currently acceptable source terms (fission products) still adequate for site evaluation?

4) In view of (3) above, are current or planned methods of hydrogen control adequate? Will such processes as recombination, purging or venting provide larger releases of radioactivity than previously thought possible? What are the possible interactions between fission product release and hydrogen control?

References:

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2. Memo R.O. Meyer to R.J. Mattson, April 13, 1979.
3. Memo W.R. Butler to R.L. Tedesco, April 25, 1979.
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6. WASH-1400 - Appendix VIII, Sections 2.2.7 and 3.2.7. (See also Appendix D to Appendix VIII).
7. Chan, C.K., "On the Failure Modes of Alternate Containment Designs following Postulated Core Meltdown, UCLA-ENG-7661, June 1976.
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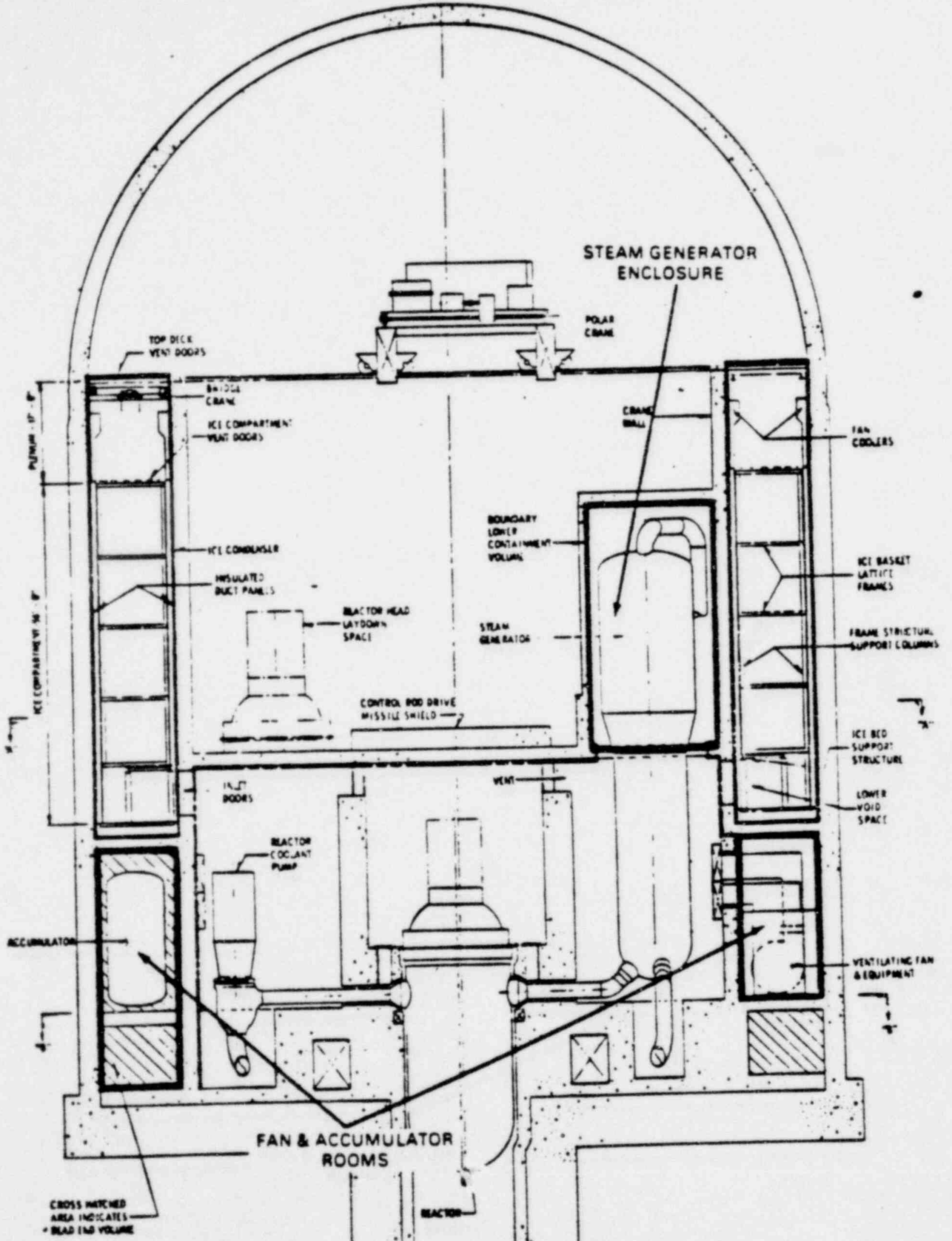

FIGURE 1 --- Sectional Elevation DD -- D. C. COOK
Unit No. 1 Showing Ice Condenser
Containment Volume Boundaries

Hydrogen Flammability
Data and App to PWR - LOCA WAPD-SC
545, Sept 1957

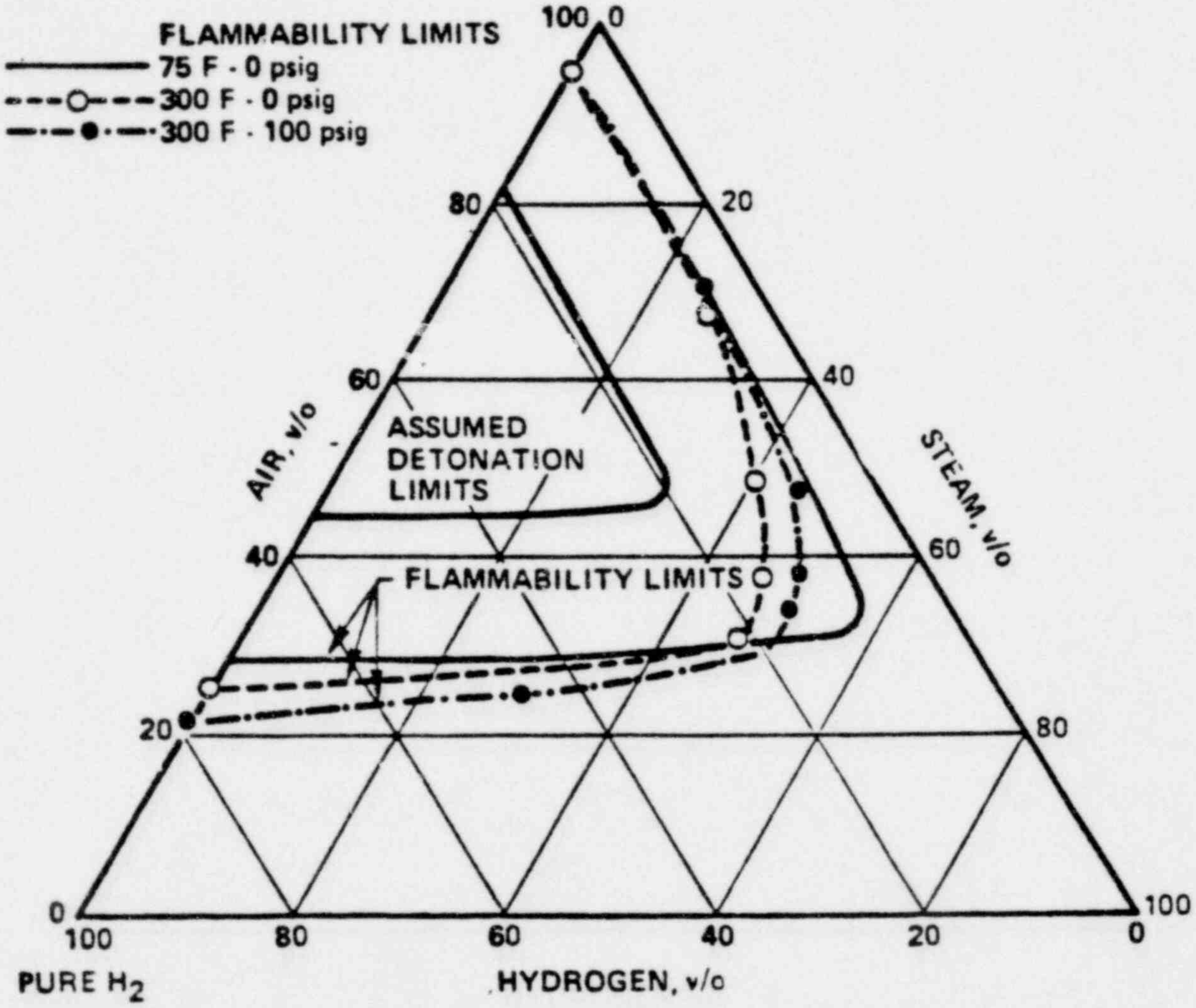

FIGURE 2 -- Flammability Limits of Hydrogen-Air-Steam Mixtures

Influence of Temperature.—In a 35-cc. closed bulb the limits were 9.6 and 90.9 percent at 15° C. and 9.1 and 94 percent at 300° C. (*297*).

HYDROGEN IN OTHER ATMOSPHERES

All Atmospheres of Oxygen and Nitrogen.—The limits of hydrogen in various mixtures of oxygen and nitrogen have been determined at 600 mm. and lower pressures, with downward propagation of flame in a tube 3 cm. in diameter (*88*). (*See also* Ammonia Contact Gas.)

Atmospheres of Composition Between Air and Pure Oxygen.—With downward propagation of flame in a Bunte burette, the lower limit fell gradually from 9.45 percent hydrogen in air to 9.15 percent in nearly pure oxygen. The higher limit rose from 65 percent hydrogen in air to 81 percent in a 40-percent oxygen mixture, 86 percent in a 56-percent oxygen mixture, and 91.6 percent in nearly pure oxygen (*323*).

In a mixture of equal volumes of oxygen and nitrogen, 91.35 percent hydrogen inflamed at 537° C. (*216*).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of hydrogen in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, are shown in figure 7. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*133*). From the ordinates of the "nose" of this curve it may be calculated that no mixture of hydrogen, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 4.9 percent oxygen (*167*).

For some purposes the results are more useful when expressed (*62*) as in figure 8.

This figure shows, for example, that a mixture containing 20 percent H_2, 6 percent O_2, and 74 percent N_2 is flammable; but if 2 percent of the oxygen were replaced by nitrogen the mixture would not be flammable but would become so by admixture with a suitable amount of air. In figure 8, "impossible mixtures" cannot be produced by mixing air, nitrogen, and hydrogen. For more detailed explanations, compare the corresponding section on methane limits in mixtures of air and nitrogen (pp. 44 to 48).

The limits with downward propagation of flame in the same series of mixtures have been determined in a closed tube 5 cm. in diameter and 65 cm. in length. The lower limits are 5 to 6 percent greater and the higher −1 to +10

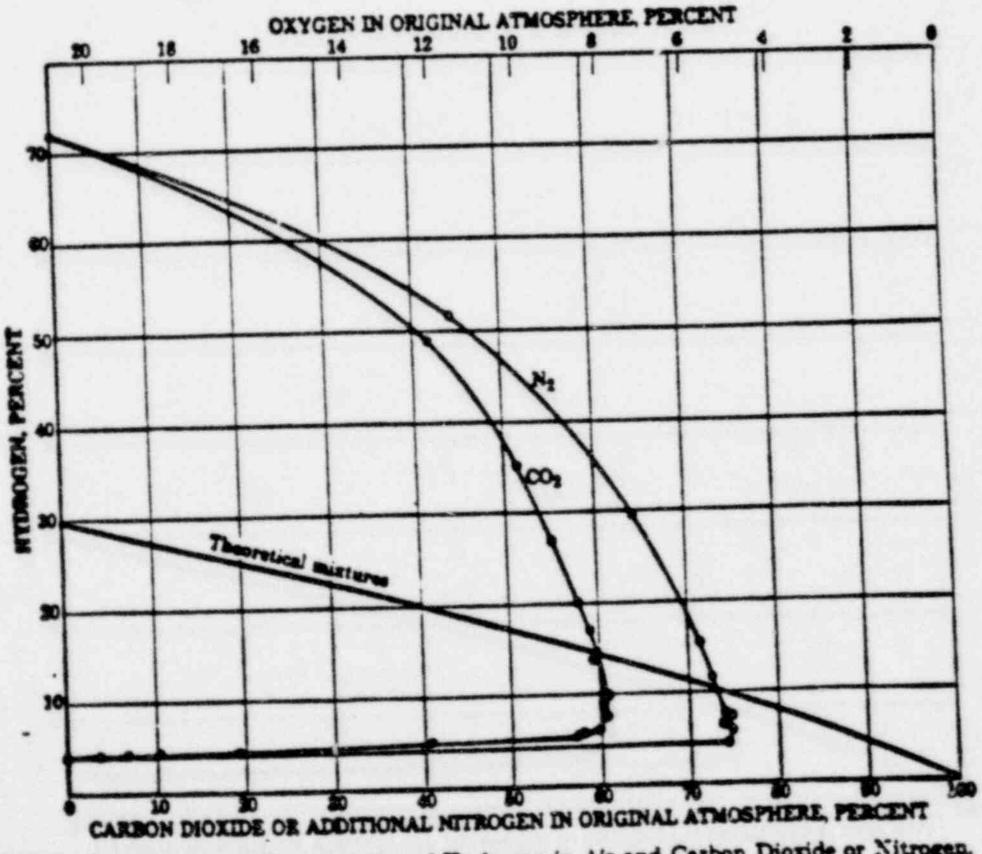

FIGURE 3 -- Limits of Flammability of Hydrogen in Air and Carbon Dioxide or Nitrogen.

Bulletin 503, Bureau of Mines, Coward & Jones (1952)

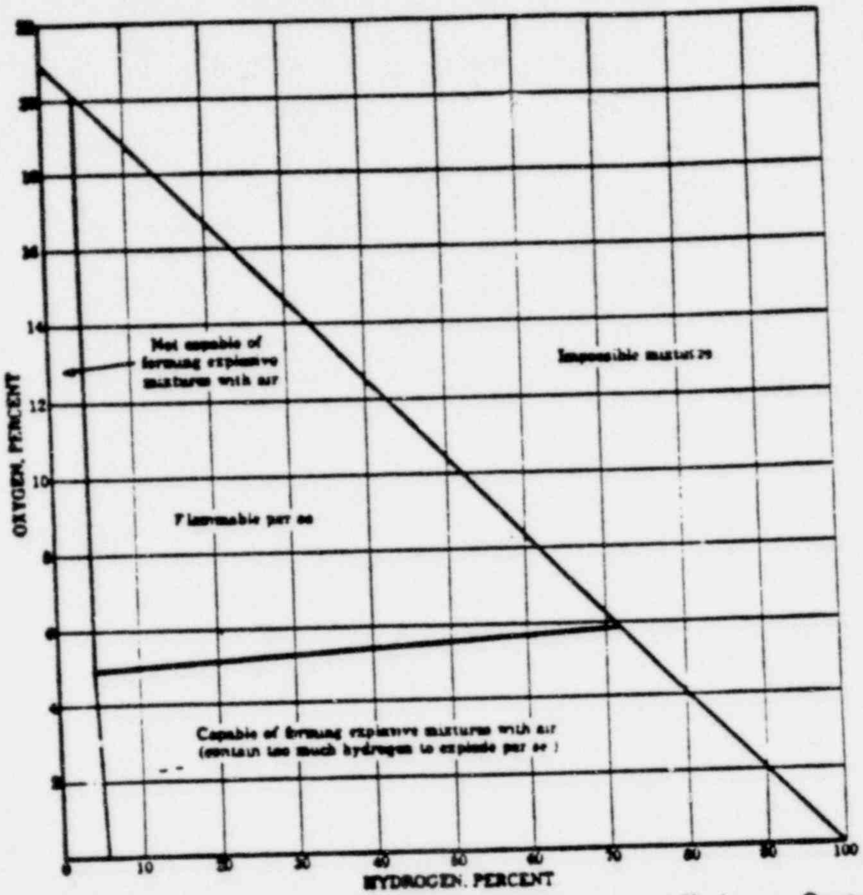

FIGURE 8.—Relation Between Composition and Flammability of Mixtures of Hydrogen, Oxygen, and Nitrogen.

percent greater than those of figure 7. The "nose" of the curve is at the same percentage of additional nitrogen. The addition of 0.5 percent of tin tetramethyl reduces the higher limit and retracts the "nose" of the curve considerably (*318*). The limits for downward propagation in a closed tube 2.2 cm. in diameter have also been determined (*341*).

Atmospheres of Air and Water Vapor.—The limits of hydrogen-air mixtures standing over water in a 350-cc. spherical vessel, and ignited near the water surface, have been determined at various temperatures. As the temperature rises, and consequently the water-vapor content also, the lower limit rises slowly, and the higher limit falls rapidly, as with other diluents. When 60 percent of water vapor is present (86° C.) the limits coincide at about 10 percent hydrogen (*368*).

Earlier experiments, made in a Bunte burette, show similar effects but the range of flammability is smaller (*95*).

Atmospheres of Air and Carbon Dioxide.—The limits of flammability of hydrogen in all mixtures of air and carbon dioxide are shown in figure 7. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*133, 167*).

The limits with downward propagation of flame in the same series of mixtures have been determined in a closed tube 5 cm. in diameter and 65 cm. in length. The lower limits are 5 to 6 percent greater and the higher limits 1 to 4 percent less than those in figure 7. The "nose" of the curve is at 56 percent carbon dioxide in the atmosphere. The addition of 0.5 percent tin tetramethyl reduces the higher limit and retracts the "nose" of the curve considerably (*318*). The limits with downward propagation in closed tubes 2.2 and 1.6 mm. in diameter have also been determined (*217, 341*).

Some earlier observations (*95*) show, as might be expected, a more rapid narrowing of the limits in a Bunte burette. Others (*1*) may be mentioned, but they can hardly be accepted without confirmation because they indicate several improbable conclusions—for example,