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UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

June 13, 1979

MEMORANDUM FOR: Roger Mattson, Director
Division of Systems Safety

FROM: Thomas E. Murley, Director
Division of Reactor Safety Research

SUBJECT: HYDROGEN/OXYGEN GENERATION DURING THE TMI ACCIDENT

As you requested, this is an interim report on the status of the analyses that the RES staff and our contractors have done concerning the generation and behavior of Hydrogen and Oxygen during the TMI accident. I have separated the discussion along the following lines:

- What do we know now?
- What did we believe at the time of the accident?

As you probably know, we do not have definite answers to many of the questions. We have started some research work and plan a more comprehensive program to answer as many questions as we can concerning the hydrogen generation and behavior in the TMI accident.

A. What do we know now?

1. How much hydrogen was generated in the accident?

We believe that nearly all of the hydrogen present was generated in zircaloy-water reactions and not from radiolysis. Preliminary calculations show that 30-40% of the zircaloy in the core was oxidized. Further calculations will be made as part of the NRC investigation of the TMI accident.

2. How much hydrogen escaped out the relief valve to containment and how much remained in the primary system?

We have no answer to this question yet; a study is still under way.

3. How much of the "hydrogen bubble" in the reactor vessel was actually hydrogen (or other noncondensable gases) and how much was steam?

774237

We have no answer to this question yet. Preliminary calculations show that some if not most of the compressible volume in TMI could have been steam.

4. If the compressible volume was a hydrogen gas bubble, how was it removed from the primary system?

We have no analyses currently under way on this question. However, rough calculations during the period of April 1-4 indicated that it was unlikely that the rate of removal of hydrogen in solution via the letdown system and pressurizer spray system could account for the reported rate of decrease in hydrogen bubble volume.

5. How much oxygen was formed by radiolysis?

The consensus now is that there was essentially no net production of oxygen gas during the event because the coolant was rich in hydrogen.

6. What were the probable concentrations of hydrogen gas and oxygen gas in the primary system?

We believe that there was essentially no oxygen gas concentration in the primary system. There was clearly some hydrogen in solution, and there may have been some hydrogen gas in a bubble or in bubbles. We do not have a good estimate yet of the hydrogen gas concentration in the primary system. Further calculations will be made as part of the NRC investigation of the TMI accident.

B. What did we believe at the time of the accident?

1. What was the hydrogen concentration in the primary system?

At the beginning of our involvement in the TMI events on Friday, March 30, we were told that measurements at the site indicated there was a noncondensable hydrogen gas bubble with a volume of 1000-1500 cu ft. at 1000 psi and 280°F. To my knowledge this assertion was not seriously questioned during the period March 30 - April 4. Subsequently, (about April 5) RES staff questioned whether the compressible volume could in fact have included a significant amount of steam.

Roger Mattson

- 3 -

JUN 13 1979

2. What was the oxygen gas concentration and rate of increase of oxygen concentration in the primary system?

Information from RES contractors and consultants on March 30 and April 1 indicated that the assumed 1000 cu. ft. hydrogen bubble could have included oxygen generated from radiolysis. There were various estimates of the oxygen gas concentration in the hydrogen bubble, ranging from essentially none to a conservative estimate of oxygen gas concentration in the hydrogen bubble that was increasing at the rate of 1% per day after reactor scram. There was some difficulty in calculating the oxygen concentration because the rate of recombination of oxygen with hydrogen in solution was not known. Later in the day on April 1, the consensus of advice to RES was that there was probably no free oxygen in the primary system.

I am enclosing a number of memos and references as background information.



Thomas E. Murley, Director
Division of Reactor Safety Research

Enclosures: As stated

cc: S. Levine
L. S. Tong
C. N. Kelber
L. C. Shao

774239

H₂ IN TMI REACTOR VESSEL

- Q - Can a H₂/O₂ mixture at elevated temperature and pressure detonate?
- A - Yes it can. SAND-74-0382 Chapter 10 presents a variety of experiments indicating detonation at temperatures up to 500°C (930°F). However, detonation will not occur if water vapor is present in quantities \approx 60%
- Q - Can H₂/O₂ mixture ignite spontaneously?
- A - Yes at a temperature of approximately 550°C (1020°F) or higher (see SAND p. 10-28). However flammability limits are affected by water vapor content above 25% concentration. At 60% water vapor the mixture will not burn (ref. KAPL report).
- Q - What is the effect of increasing temperature on the limit of detonation?
- A - The lower limit of H₂ concentration is reduced and the upper limit is increased. The range is broadened over which ignition can occur. For H₂-Air @ 17°C range is 9.4 - 71.5% (SAND p. 10-9)
 @ 400°C range is 6.3 - 81.5% (and Figure 10.4).
 Not a major effect over this range - but ignition can occur over a broader range.
- The above is for H₂-Air mixtures (i.e. H₂-O₂-N₂) if the N₂ is considered a diluent. Mixture behavior with water vapor would be different if N₂ diluent is replaced by steam diluent, as discussed above.
- Q - What is the effect of increased pressure on detonability?
- A - The lower limit does not seem to change much but the upper limit (for H₂/Air) increases from 68 to 74% as the pressure is increased to 140 atm (2060 psi) (See SAND Figure 10.5, p. 10-11). Data are not available for the affect of water vapor concentration with increased pressure.
- Q - How much steam must be present in an H₂/O₂ mixture to avoid detonation?
- A - There is no effect of water vapor below 7%; however, as the amount of water vapor increases above this value, the probability of an explosion decreases. Flammability limits will not be affected until you have concentrations above 25% water vapor. At 60% water vapor, the probability of burning H₂ and O₂ is zero. The effect of pressure has yet to be determined (ref. KAPL report on TMI-2 Incident).
- Q - How do diluents (N₂ or steam) in H₂O₂ mixture affect peak pressures?
- A - Addition of diluent narrows the range of flammability or detonability (see ternary diagram, p. 10-20), reduces flame velocities (see Figure 10.8, p. 10-14) and reduces peak pressure (see Table 10.11 part 2, p. 10-17). The effect of steam is discussed in the previous Q/A.



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APR 25 1979

MEMORANDUM FOR: Thomas E. Murley, Director
Division of Reactor Safety Research

Charles N. Kelber, Assistant Director
for Advanced Reactor Safety Research

FROM: Louis N. Rib, Special Assistant
Advanced Reactor Safety Research

SUBJECT: SUMMARY OF PARTICIPATION IN TMI-2 INCIDENT--EVALUATION
OF HYDROGEN GAS IN PRIMARY COOLANT SYSTEM AND
CONTAINMENT BUILDING ATMOSPHERE

Following the TMI-2 incident on 3/28/79, Lenny Rib and John Larkins of ARSR with the support of Roy Person (NMSS) and Frank Witt (OSD) provided support to RES in: (1) the evaluation of the quantities of H_2 that could be dissolved in the primary coolant water following a $Zr-H_2O$ reaction in the core, (2) means by which the H_2 in the primary coolant system might be reduced and (3) estimates of the hydrogen reduction in the containment atmosphere. Support in the evaluation of items (2) and (3) was obtained from engineers and scientists at KAPL and ARSR contractors at LASL and Sandia.

The evaluations are summarized in the following attachments:

1. Summary of Hydrogen Evolution (from saturated solutions) Calculations for TMI-2. Attachment 1
2. Report on Hydrogen Solubility Data Base and Estimated Hydrogen Releases at TMI-2. Attachment 2
3. Upper Limit Estimates of Hydrogen Formation. Attachment 3
4. Radiation and Physical Chemistry of LWR Primary Coolant. Attachment 4
5. Hydrogen Reduction Methods - Summary. Attachment 5

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Thomas E. Murley, Charles Kelber -2-

APR 25 1979

6. KAPL Summary of Efforts on TMI-2. Report in progress, (will be supplied at a later date.)

L. N. Rib

Louis N. Rib, Special Assistant
Advanced Reactor Safety Research

cc: S. Levine, RES
R. Budnitz, RES
R. Benaro, SD
G. Arlotto, SD
L. Person, NMSS
F. Witt, SD
J. Larkins, RSR
K. Steyer, SD
R. Minogue, SD
V. Stello, DOR
R. Mattson, DSS
R. Scroggins, RES

774242



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MEMORANDUM FOR: Thomas E. Murley, Director
Division of Reactor Safety Research

FROM: Louis N. Rib, Special Assistant
Advanced Reactor Safety Research

SUBJECT: SUMMARY OF HYDROGEN EVOLUTION CALCULATION FOR TMI

The attached table summarized the calculations of hydrogen gas at several pressure and temperature conditions corresponding to a system cooldown, controlled pressure reduction and also for a rapid depressurization.

L.N.R.
Louis N. Rib, Special Assistant
Advanced Reactor Safety Research

cc: S. Levine
R. Budnitz
C. Kelber

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H₂ Evolution from System Temperature & Pressure Changes*

| <u>Case</u> | P ₁ psig | T ₁ °F | P ₂ psig | T ₂ °F | H ₂ (ft ³) evolved at P ₂ T ₂ , ft ³ | Comment |
|-------------|------------------------|----------------------|------------------------|----------------------|---|---------------------------|
| 1 | 1000 | 280 | 0 | 212 | 27,000 | depressurization accident |
| 2 | 1000 | 280 | 1000 | 212 | 98 | stepwise cooldown |
| 3 | 1000 | 280 | 1000 | 140 | 106 | continued cooldown |
| 4 | 1000 | 140 | 350 | 140 | 400 | pressure reduction |
| 5 | 1000 | 280 | 350 | 280 | 760 | pressure reduction |

* calculations based on H₂ saturation concentrations checked against recent experiment in Provo, Utah, and obtained from J. Chem. Eng. Data, 5 10 (1960), D. M. Himmelblau, Dept. of Chem. Eng., Univ. of Texas (Austin).



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April 11, 1979

MEMORANDUM FOR: Charles N. Kelber, Assistant Director
for Advanced Reactor Safety Research
Division of Reactor Safety Research

THRU: *JK* Louis N. Rib, Special Assistant
Advanced Reactor Safety Research
Division of Reactor Safety Research

FROM: LeRoy S. Person
Fuel Reprocessing and Recycle Branch
Division of Fuel Cycle and Material Safety

SUBJECT: REPORT ON HYDROGEN SOLUBILITY DATA BASE AND ESTIMATED
HYDROGEN RELEASES AT THREE MILE ISLAND

In order to bound the limits of hydrogen solubility and release, a parametric appraisal was performed to help determine possible conditions of the reactor coolant at Three Mile Island-II.

Three references were examined for solubility data for hydrogen; I. S. Andersen's "Correlation of Solubility Data for Hydrogen and Nitrogen in Water," WAPD/TM-633, D. M. Himmelblau's, "Solubility of Inert Gases in Water 0° C to Near the Critical Point of Water," and the Reactor Handbook, 1, pp. 852, 1960. Comparison was also done of experimental data from Roger Billings at Provo-Utah.

Data from the "Correlation of Solubility Data for Hydrogen and Nitrogen in Water" was very similar to that obtained from the Solubility of Inert gases in water i.e., the difference in the Henry's law constant for each in the temperature range of interest (140° F to 280° F) was less than one percent. Information obtained from Volume 1 of the Reactor Handbook showed a discrepancy between what was reported there and the two above mentioned references (approximately 10 percent difference).

These calculations were compared with experimental values obtained from Provo-Utah and the differences were approximately 20 percent for Himmelblau and Andersen's Data. There was not enough information from the Reactor Handbook to compare with the experimental information.

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Charles N. Kelber

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April 11, 1979

It is believed that the measurements from Provo-Utah were not taken at equilibrium conditions (the approximate situation at Three Mile Island-II) and this is the reason for the discrepancy of 5 percent in the calculations. Therefore, the information developed by Himmelblau and Andersen was subsequently used in the calculations. A table is attached showing values obtained for the various conditions analyzed.

LeRoy S. Person

LeRoy S. Person
Fuel Reprocessing and Recycle Branch
Division of Material Safety and Safeguards

Enclosure: As stated

cc: R. E. Cunningham
J. B. Martin
L. C. Rouse
R. A. Scrano

774246

MAXIMUM HYDROGEN SOLUBILITY AND RELEASE DATA

| | CASE I | CASE II | CASE III | CASE IV |
|---|--|---|--|---|
| Moles in Solution per 100 Coolant | (1000 psi, 280°F) to (18 psi, 212°F) to $7.48 \times 10^{-2} \rightarrow 8.33 \times 10^{-4}$ | (1000 psi, 280°F) to (1000 psi, 140°F) $7.48 \times 10^{-2} \rightarrow 4.84 \times 10^{-2}$ | (1000 psi, 280°F) to (350 psi, 280°F) $7.48 \times 10^{-2} \rightarrow 2.76 \times 10^{-2}$ | (1000 psi, 212°F) to (1000 psi, 140°F) $5.73 \times 10^{-2} \rightarrow 4.84 \times 10^{-2}$ |
| Moles of hydrogen Released | 2.52×10^4 | 8.849×10^3 | 1.58×10^4 | 2.98×10^3 |
| Hydrogen Evolution Volume (cubic feet) | 27,000 | 124 | 760 | 42 |
| Diameter of Gas Phase If spherical (ft) | 37 | 6.19 | 1132 | 4.31 |

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MAXIMUM HYDROGEN SOLUBILITY AND RELEASE DATA

| CASE V | CASE VI | CASE VII |
|--|---------------------------------------|---------------------------------------|
| (1000 psi, 280°F) to (1000 psi, 212°F) | (1000 psi, 140°F) to (350 psi, 140°F) | (1000 psi, 212°F) to (350 psi, 212°F) |

7.48 x 10⁻² → 5.73 x 10⁻² 4.84 x 10⁻² → 1.76 x 10⁻² 5.73 x 10⁻² → 2.006 x 10⁻²

Moles in Solution per Kg Coolant

Moles of Hydrogen Released

Hydrogen Evolution Volume (cubic feet)

Diameter of Gas Phase if spherical (ft)

| | | |
|------------------------|------------------------|------------------------|
| 6.15 x 10 ³ | 1.03 x 10 ⁴ | 1.22 x 10 ⁴ |
| 97.7 | 400 | 527 |
| 6.71 | 9 | 10 |

774248



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APR 11 1979

MEMORANDUM FOR: C. N. Kelber, Assistant Director
for Advanced Reactor Safety Research
Division of Reactor Safety Research

THRU: *JK* L. N. Rib, Special Assistant
for Advanced Reactor Safety Research
Division of Reactor Safety Research

FROM: J. T. Larkins
Experimental Gas-Cooled Reactor
Safety Research Branch

SUBJECT: UPPER LIMIT ESTIMATES OF HYDROGEN FORMATION

Using available information and data (I & E reports, plant status reports, etc.) an upper limit estimate has been made of the amount of hydrogen generated via the zirconium-water reaction and from radiolysis. Also, using available data and expert comments an estimate is included on the amount of hydrogen that could be absorbed by the zirconium cladding.

A hydrogen explosion was reported to have occurred as the primary system was being depressurized to allow operation of the Residual Heat Removal (RHR) system. An estimate of 70,000 scf of hydrogen was assumed to have been burned. This would have represented a hydrogen concentration of 3.33% in containment (2.1 million cubic feet) therefore, the burning or explosion must have been localized or the estimate of the amount of gas involved is too low.

On March 31, 1979 it was estimated that the containment building contained 1.7% hydrogen and that there was a hydrogen bubble in the reactor vessel of approximately 1,000 ft.³ at 1,000 psi. Based on available solubility information these three sources would provide a total hydrogen inventory of approximately 113,000 scf of hydrogen. This total inventory in containment would have given a hydrogen concentration of approximately 5.3% (exceeds flammability limit of 4%). Assuming that all of the hydrogen generated (including that which was burnt) was generated from the zirconium-water reaction this would calculate to 42-44% of the available zirconium being oxidized.

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APR 11 1979

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On April 4, 1979 it was reported that the containment had a hydrogen concentration of 2.3% (48,000 scf) and there existed a bubble of approximately 200 ft.³ in the reactor vessel (~10,000 scf) and with a saturated coolant (27,000 scf) and waste gas tank (1938 ft.³ volume and 100 psf) of approximately 56% hydrogen (~5,400 scf) there was a hydrogen inventory of approximately 90,600 scf. This total inventory in containment (4.3%) would still have exceeded the set flammability limit.

The amount of hydrogen being formed from radiolytic decomposition is probably very small, however, using a normal decay curve (B&W report) LASL using the COGAP code calculated and an upper limit of 7 lbs. of hydrogen (1,256 scf) per day being formed in the core and based on 1% of available fission products in the coolant another 2.5 lbs. (449 scf) per day in the coolant. The contribution from the coolant (100,000 gallons) in the containment is approximately 50 scf per day. The total inventory of hydrogen from radiolysis would be 1,755 scf (.08% volume percent in containment) per day. These calculations were based on a G value of 0.45 (molecules of hydrogen evolved 100 ev of radiation absorbed) and do not take into account the amount of hydrogen recombination occurring. The amount of hydrogen recombining to form water could be significant and reduce the amount of hydrogen generated by a factor of 10.

Two hydrogen recombiners were made operational on April 1, 1979 and one unit reportedly started processing gas on April 3, 1979. Using the efficiency given that for a 4% hydrogen concentration entering the recombiner that the exiting gas was .1% hydrogen and a process flow rate of 60 cubic feet per minute, I calculated it would take approximately one week to drop the concentration by 25% and 17 days to drop the concentration by 50%.

From an assemblage of various references and conversations, I have concluded that the amount of hydrogen that could have been absorbed by the zirconium cladding was small. Assuming 100 ppm of hydrogen were absorbed in the zirconium cladding, one would calculate only ~815 scf of hydrogen absorbed, which is less than 1% of the amount of hydrogen generated.

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C. M. Kelber

-3-

APR 11 1979

Lastly, on the use of chemicals for gettering dissolved and gaseous hydrogen, Sandia has used unsaturated hydrocarbons (dimerized parapropylphenyl ether) in the weapons program for controlling hydrogen build-up in a closed system. The effects of radiation and thermal stability have been investigated somewhat, however, some further work would be needed. Sandia has proposed its use in LWR safety for gettering hydrogen from a core-melt accident and it appears to have a good potential for use in preventing hydrogen build-up in a LOCA. I anticipate receiving more information on this subject.

John T. Larkins

John T. Larkins
Experimental Gas-Cooled Reactor
Safety Research Branch

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APR 25 1979

MEMORANDUM FOR: Charles N. Kelber, Assistant Director
for Advanced Reactor Safety Research

THRU: *LM* Louis N. Rib, Special Assistant
Advanced Reactor Safety Research

FROM: Frank J. Witt, Nuclear Engineer
Fuel Process Systems Standards Branch
Office of Standards Development

SUBJECT: RADIATION AND PHYSICAL CHEMISTRY OF LWR PRIMARY
COOLANT

1. Introduction

A thorough review of the radiation and physical chemistry of LWR primary coolant is urgently needed since an understanding of this field may effect the design or primary coolant chemistry treatment of LWRs. The present safety philosophy used in the preparation of Safety Analysis Reports does not consider the uncovering of the core via steam and gas bubble formation since the redundant Emergency Core Cooling Systems (ECCS) are designed to prevent this happening in the event of a loss of coolant accident (LOCA). However, operator errors can lead to bubble formation in the reactor vessel.

Since the Three Mile Island accident scenario could happen again, it is prudent to thoroughly evaluate the radiation and physical chemistry of LWR primary coolant so that safeguards can be established to prevent or minimize the hydrogen problem in potential accidents. It is extremely important that this thorough evaluation consider the complete reactor system, containment and auxilliary buildings to understand what is going on).

2. Scope

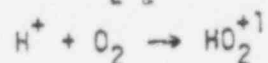
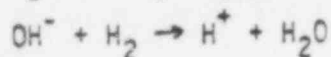
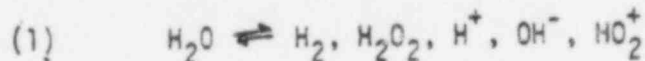
- a. Perform complete systems evaluation on reactor coolant system, containment building and auxilliary building including material balances on: (a) hydrogen, (b) oxygen, (c) nitrogen, (d) tritium, (e) fission gases, (f) particulate fission products, (g) particulate activated corrosion products, and (h) dissolved activated corrosion products.

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APR 25 1979

- b. Evaluate radiolysis and recombination release and sink rates of the following in reactor coolant system, containment building and auxilliary building:



The radiolysis product in neutral water is the solvated electron (the H atom in water might conceivably take on a proton to assume the acid form H_2 or might lose a proton, leaving behind a solvated electron, which would be the basic form of H.

(2) Recombination

C. I. Hochinadil, Oak Ridge National Laboratory, has a U. S. patent (about 1960) covering the recombination of $\text{H}_2 + \text{O}_2$ to form water provided that there is an excess of dissolved H_2 in an aqueous solution. In effect the following equilibrium equation will proceed to the left:

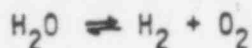


However, if the aqueous solution is boiling, the H_2 on the right side of the above equation will be stripped out of solution into the gaseous phase resulting in a depletion of H_2 concentration on the right side of the above equation. If the H_2 concentration is depleted below a minimum concentration, recombination (equilibrium reaction to the left) will not occur and decomposition (equilibrium reaction reverses to go to the right) will result.

This is extremely important at the present time at Three Mile Island. Because of the combination of feed and bleed and degassification, the dissolved hydrogen may be reduced below the minimum required (about 2 cc H_2 STP/Kg

774253

coolant) to suppress radiolytic decomposition and the very undesirable reversal of the equilibrium reaction,



will occur leading to the possible formation of another Hydrogen gas bubble in the reactor vessel. Therefore, the dissolved hydrogen concentration must not be permitted to decrease below 2 cc H₂ STP/Kg water. If necessary, small quantities (2-15 cc H₂ STP/Kg water) of H₂ should be added to the reactor coolant via the charging system to levels exceeding 2 cc H₂ STP/Kg water to suppress decomposition.

(3) H₂O₂ Addition

Radiolysis of dilute solutions of H₂O₂ injected into primary coolant containing dissolved H₂ results in a rapid, completely reproducible rate in equimolar quantities, the overall reaction being



"The high rate of this reaction indicates that it is probably a chain process. Such a result is rather unusual in chemical kinetics. It suggests the idea that peroxide undergoes two reactions with radicals, of which one stops the chain and the other carries it on. The reactions which carry on this chain are not difficult to propound. Because of the similarity of OH⁻ to Cl⁻, we think of the well known Nernst chain reaction between H₂ and Cl₂ and propose that our chain is carried on by the steps:



Hydrogen peroxide also shows a chain-stopping reaction that is evidently not possible with Cl₂, since in the case of Cl₂ the reaction chains are much longer and the rate does not noticeably decrease with increasing Cl₂ concentration. The reaction



has all the properties demanded by our chain stopper and in addition had been proposed many years before (Haber, F. and Weiss, Joseph, Proc. Roy. Soc A147, 332 (1934) in connection with other reactions with H_2O_2 . The only difficulty now is to dispose of the HO_2^{\cdot} , which evidently did not react with H_2O_2 to carry on the chain, otherwise its formation would not stop the chain." (Quotation from "The Radiation Chemistry of Water and Aqueous Solutions," Augustine O. Allen, Senior Chemist, Brookhaven National Laboratory, P. Van Nostrand Company, Inc., 1961, page 77.)

The above radiolysis theory was proven in practice by additions to numerous operational commercial nuclear reactor power plants as reported in EPRI report No. NP-692 "Effects of Hydrogen Peroxide Additions on Shutdown Chemistry Transients at Pressurized Water Reactors," Nuclear Water and Waste Technology, S. T. Sawaochka, et. al., April 1978. Hydrogen Peroxide was added successfully to commercial nuclear power plants to study the effect on activated core crud deposits and the resultant effect on shutdown primary coolant component radiation levels. The following plants were involved in this R & D program:

| | | |
|-------------------|----------------|----------------------|
| Turkey Point 3 | Indian Point 2 | Prairie Island 1 & 2 |
| Point Beach 1 & 2 | Fort Calhoun | Maine Yankee |
| H. B. Robinson | Kewaunee | |

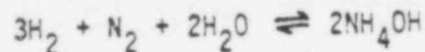
(4) Nitrogen Radiolysis

This radiolysis reaction should be evaluated in detail since it is conceivable that it may have been the most effective mechanism for the collapse of the hydrogen bubble at Three Mile Island. The dissolved nitrogen introduced into the primary coolant may come from two sources:

- (a) accumulators - The accumulators on pressure vessels filled with borated water and pressurized with nitrogen gas. During normal operation each accumulator is isolated from the Reactor Coolant System by two check valves in series. Should the reactor coolant pressure fall below the accumulator pressure, the check valves open and borated water is forced into the reactor coolant system.

APR 25 1979

- (b) Boric acid tank - The presence of dissolved nitrogen in injected makeup water could lead to the formation of NH_4OH by radiolysis with dissolved H_2 in the primary coolant by the following reactions:



3. Proposed Program

- a. Determine first hand at Three Mile Island what experimental tests are being conducted to support reactor coolant technology. Experimental work is being performed at Idaho by EG&G as well at Provo, Utah, by Billings Energy Research Corporation. It is vital that first hand information is obtained from Wlyne Lanning (Research coordinator of coolant technology testing at Harrisburg). Lanning just relieved Bixby (DOE-Idaho) of this responsibility.
- b. Obtain complete primary coolant, containment building and auxilliary building H_2 , N_2 , O_2 , NH_3 , T_2 , fission product gas, and fission product particulate analysis to perform essential material balances. Must be done first hand, can't use second and third information. It is possible that this information is not presently available and additional analysis would be required from laboratories that have performed radiochemical analysis (Bettis, Battelle Columbus, Oak Ridge, Idaho National Labs, Savannah River, B & W, etc.).
- c. Work directly with KAPL personnel who have developed applicable computer programs. KAPL has provided theoretical complex computer analysis of primary coolant radiolysis and recombination for several urgent Three Mile Island problems. KAPL and Los Alamos Scientific Laboratory have computer codes that are directly applicable to the complex radiolysis and recombination reactions that are taking place at Three Mile Island. One computer code evaluates the solution of fifteen simultaneous differential equations which has been verified by experimental data. First hand NRC contact with KAPL personnel is essential to define the problem precisely and to provide latest data from Three Mile Island. This will provide an orderly flow of information with the minimization of side-tracking or snafo.

774256

APR 25 1979

- d. Consult with Dr. Jay Young, Manufacturing Chemists Association, Washington, DC, who is an expert in practical radiation water and physical chemistry problems. At his present position at Manufacturing Chemists Association he is also very knowledgeable in the explosive and flammability ranges, and catalysts and conditions that initiate hydrogen-oxygen explosions and deflagration.
- e. Evaluate TMI trends in primary coolant pH, Li, Tritium, dissolved gas, H₂, O₂, N₂, etc., and NH₃ from start of accident. Preliminary analysis of samples indicate an increase in pH which may be accounted for by radiolysis of dissolved N₂ and H₂ to form NH₃.



Must get addition primary coolant samples for proper physical chemical analysis.

4. Conclusions

- a. Task force should be set up to evaluate radiation and physical chemistry of LWR primary coolant. This task force may recommend upon conclusion of evaluation that LWR radiation and physical chemistry should be factored in the safety models of LOCA Computer programs and should be developed to account for Zirconium-Water reactions and radiolysis.
- b. Immediately establish direct NRC contact with KAPL, and Los Alamos to perform needed Zirconium-water reaction and radiolysis material balances in reactor coolant system, containment building and auxiliary building (Systems approach very important).
- c. Review Safety Analysis Reports and Safety Evaluations Reports to recommend where additional information and discussion of reactor coolant radiation and physical chemistry of LWR's is necessary.
- d. One individual should coordinate all activities relating to primary coolant physical chemical and radiation analyses as well as any laboratory testing relating to the above.

F. J. Witt
Frank J. Witt, Nuclear Engineer
Fuel Process Systems Standards Branch
Office of Standards Development

774257



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WASHINGTON, D. C. 20555

APR 25 1979

NOTE TO: Saul Levine
Robert Budnitz
Thomas Murley

FROM: Louis N. Rib

SUBJECT: HYDROGEN REDUCTION METHODS - SUMMARY

The following information was developed and informally transmitted on 4/8/79 for the purpose of making it available on a timely basis. For the record, it is summarized below.

1. H₂ radiolysis/recombination

A group of engineers and scientists at KAPL have been providing assistance to us on the TMI-2 incident with the aid of Frank Witt (NRC/SD) who worked at KAPL for a number of years. Frank and I have posed several questions on which we requested KAPL analyses. The following preliminary information has been received:

- (1) Assuming an opening in the Primary Coolant System, leaving the reactor vessel full of water up to the pipe elevation in the Reactor vessel, no dissolved H₂ in the water and decay power at 10 MW(th); what radiolysis may occur?

Response: 15 scf/day H₂ + O₂ generated.

Note: With a minimum concentration of H₂ in the water, hydrolysis is unlikely. Hochinadl (ORNL) has a long standing patent in this area.

- (2) Consider primary coolant water spilled in containment (10⁵ gal) at 100°F, 10⁴ microcuries/cc; How much radiolysis may occur?

Response: Negligible amount, especially with H₂ in containment atmosphere. (Other variations of quantity of water and temperature are being considered.)

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APR 25 1979

- (3) Containment atmosphere made up of air, water vapor (condensed steam) at 100°F and a high radiation field (30,000 R/hr); what will occur?

Response: Recombination in gas phase of H_2 and O_2 to produce water at an estimated rate of 2600 scf/day.

- (4) Same containment condition with a 60 cfm recombiner operating.

Response: 1680 scf/day H_2 removal.

2. H_2 recombination

An initial suggestion was made (4/1/79) that the presence or addition of N_2 to the water might promote the formation of ammonia (NH_3 , NH_4OH) which is soluble, as a mechanism for removing H_2 . The gradual release of H_2 from solution, by cautiously reducing pressure, then bleeding the gas out of the system was suggested (4/4/79) as possibly the best of the available approaches and the addition of concentrated hydrogen peroxide solution as the next best approach. The background on the use of hydrogen peroxide was mainly obtained from an EPRI report (EPRI-NP-692, Effects of Peroxide Additions on Shutdown Chemistry Transients at PWRs, April 1978).

(1) Provo, Utah experiments

I contacted Tom Murley at his home about 11 a.m. on 4/8/79. We discussed the Provo, Utah, H_2 solubility tests including the unsuccessful H_2O_2 addition test. Tom was going to discuss a test at relatively high temperature (280°F) with H_2O_2 addition in the presence of a Platinum catalyst. The idea being that the radiation field in the primary coolant system would be approximated by the platinum catalyst in the Provo test.

(2) Hydrogen Peroxide Addition ($H_2 + H_2O_2$ produces water)

I contacted Milt Levenson at the TMI site on 4/8/79. I informed him of this EPRI report. He was generally familiar with the technique but not this specific report which summarized actual reactor plant experience with this technique. He noted the report number. Milt indicated that this approach was limited in use now because they were short coolant storage space and whatever fluid volume was added, a like amount would have to be removed and stored. In the meanwhile, they were trying to

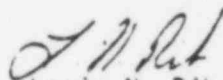
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APR 25 1979

determine the quantity of H_2 dissolved in the primary system coolant by lowering the system pressure by 25 psi increments and looking for a pressure increase resulting from H_2 coming out of solution.

(3) Removal of H_2 by organic absorbers

Another hydrogen removal suggestion was offered by Harry Gray (Cal. Tech.). C. N. Kelber first spoke to Dr. Gray on 4/6/79. Dr. Gray called back on 4/9/79 with the suggestion that the addition of a high boiling point oilfin with a catalyst (such as cobalt cyanide) would absorb the hydrogen at a good rate. If we wished to pursue this suggestion further, he recommended Jack Halprin at the University of Chicago as an expert on the kinetics of this reaction. Sandia also suggested an unsaturated hydrocarbon as a hydrogen getter. Future efforts in hydrogen removal approaches should review the feasibility of this option.



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