

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

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- MEMORANDUM FOR: Charles N. Kelber, Assistant Director for Advanced Reactor Safety Research
- THRU: JM 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 Syst. s (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

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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- b. Evaluate radiolysis and recombination release and sink rates of the following in reactor coolant system, containment building and auxilliary building:
  - (1)  $H_2^0 \rightleftharpoons H_2, H_2^0_2, H^+, OH^-, HO_2^+$   $OH^- + H_2 \twoheadrightarrow H^+ + H_2^0$   $OH^- + H_2^0_2 \dashrightarrow HO_2^+ + H_2^0$   $H^+ + H_2^0_2 \dashrightarrow OH^- + H_2^0$   $H^+ + O_2 \twoheadrightarrow HO_2^{+1}$  $OH^- + H_2^0 \nrightarrow HO_2^{+1}$

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<sub>2</sub> 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  $H_2 + O_2$  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:

2H20 2H2 + 02

However, if the aqueous solution is boiling, the H<sub>2</sub> on the right side of the above equation will be stripped out of solution into the gaseous phase resulting in a depletion of H<sub>2</sub> concentration on the right side of the above equation. If the H<sub>2</sub> 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<sub>2</sub> STP/Kg

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

 $H_{2}0 \Rightarrow H_{2} + 0_{2}$ 

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 H<sub>2</sub> STP/Kg water. If necessary, small quantities (2-15 cc H<sub>2</sub> STP/Kg water) of H<sub>2</sub> should be added to the reactor coolant via the charging system to levels exceeding 2 cc H<sub>2</sub> STP/Kg water to suppress decomposition.

(3)  $H_2O_2$  Addition

Radiolysis of dilute solutions of H<sub>2</sub>O<sub>2</sub> injected into primary coolant containing dissolved H<sub>2</sub> results in a rapid, completely reproducible rate in equimolar quantities, the overall reaction being

 $H_2 + H_2 O_2 \rightleftharpoons H_2 O$ 

"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<sup>-</sup> to Cl<sup>-</sup>, we think of the well known Nernst chain reaction between H<sub>2</sub> and Cl<sub>2</sub> and propose that our chain is carried on by the<sup>2</sup> steps:

$$OH^{-} + H_2 \implies H_2O + H^{+}$$
  
 $H^{+} + H_2O_2 \implies H_2O + OH^{-}$ 

Hydrogen peroxide also shows a chain-stopping reaction that is evidently not possible with Cl<sub>2</sub>, since in the case of Cl<sub>2</sub> the reaction chains are much longer and the rate does not noticeably decrease with increasing Cl<sub>2</sub> concentration. The reaction

 $CH' + H_2O_2 \neq H_2O + HO_2^+$ 

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  $H_{202}^{00}$ . The only difficulty now is to dispose of the H02, which evidently did not react with  $H_{202}^{00}$  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 Point Beach 1 & 2 Fort Calhoun H. B. Robinson Kewaunee Prairie Island 1 & 2 Maine Yankee

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(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 discolved nitrogen introduced into the primary coolant may come from two sources:

(a) <u>accumulators</u> - 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. (b) Boric acid tank - The presence of dissolved nitrogen in injected makeup water could lead to the formation of NH<sub>4</sub>OH by radiolysis with dissolved H<sub>2</sub> in the primary coolant by the following reactions:

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$$3H_{2} + N_{2} + 2H_{2}0 \rightleftharpoons 2NH_{4}OH$$

#### 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 Wayne Lanning (Research coordinator of ccolant technology testing at Harrisburg). Lanning just relieved Bixby (DOE-Idaho) of this responsibility.
- b. Obtain complete primary coolant, containment building and auxilliary building H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, T<sub>2</sub>, 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.

# Charles Kelber

- Consult with Dr. Jay Young, Manufacturing Chemists Association, d. Washington, DC, who is an expert in practical radiation water and physical chemistry problems. At his present position at Manufacturing Chemists Association we is also very knowledgable 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, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, etc., and NH<sub>3</sub> from start of accident. Preliminary analysis<sup>2</sup> of Samples indicate an increase in pH which may be accounted for by radiolysis of dissolved N, and H, to form NH,,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

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.
  - Immediately establish direct NRC contact with KAPL, and Los ΰ. Alamos to perform needed Zirconium-water reaction and radiolysis material balances in reactor coolant system, containment building and auxiliary building (Systems approach very important).
  - Review Safety Analysis Reports and Safety Evaluations Reports C. 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.

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