CHEMISTRY REC. 23

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THREE MILE ISLAND--2
ACCIDENT OF MARCH 28, 1979

OXYGEN GENERATION AND GAS COMPOSITION OF BUBBLE

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(4)

1. Sources of Oxygen--Upper Bound Estimate

Oxygen entered the Three Mile Island-2 System from two sources. These are, (a) oxygen introduced with the injection water, and (b) oxygen created by radiolysis of the water in the system by the decay radiation energy of the core.

.1 Oxygen in Injection Water

It is assumed conservatively that the injection water was air saturated at ambient temperatures, and thus would have an oxygen content of approximately 8 ppm. It is further assumed that during the incident 250,000 gallons of water were injected into the system. This calculates to a total volume from this source of 180 ft^3(S.T.P.).

$$1 \text{ ppm} = \frac{22{,}400 \text{ cc/g mole}}{32{,}000 \text{ mg/g mole}}$$

$$= 0.7 \text{ cc } O_2/\text{kg } O_2$$

$$250{,}000 \text{ gal} \times 8 \frac{\text{lb}}{\text{gal}} \times \frac{0.454 \text{ kg}}{\text{lb}}$$

$$= 908{,}000 \text{ kg } H_2O$$

$$\text{Total ft}^3 = 8.0 \text{ ppm} \times 0.7 \frac{\text{cc } O_2}{\text{ppm - kg } O_2}$$

$$\times 1 \frac{\text{ft}^3}{28{,}317 \text{ cc}}$$

$$= 180 \text{ ft}^3 \; \underline{O_2}$$

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In view of the extent of radiolysis as a source, it is not worthwhile to attempt to refine this estimate.

1.2 Radiolysis of Reactor Coolant

The mechanism of radiolysis of water by reactor radiation (gamma, beta, and neutrons) under non-boiling and boiling conditions is discussed in detail in Chapter 5 of Ref. 1. In summary, under non-boiling conditions, radiolysis of pure water is not continuous with energy input, but rather achieves an equilibrium degree of radiolysis which is proportional to the square root of the energy deposition rate. The equilibrium value is increased if the water contains an initial excess of oxidizing species (oxygen, hydrogen peroxide) and is decreased if the water contains an initial excess of reducing species (hydrogen). The latter condition is the preferred method of operation of pressurized water reactors, in which, by maintaining an excess of H_2 in the water (nominally 25 ccH_2/kg of water) radiolysis is effectively suppressed in the reactor operating at full power.

Under vigorously boiling (or bubbling) conditions radiolysis is a continuous function of energy input. The amount of gas formed is 0.45 molecules of H_2 and 0.225 molecules of O_2 per 100 ev of energy absorbed under these conditions. From the decay energy curve for the reactor it is therefore possible to calculate the "maximum" amount of oxygen which could have been generated from the energy available if all the other requirements had been met. The "maximum" or upper bound yield per MW-hr of decay energy available from the core is calculated as follows. The decay energy is approximately equally divided between gamma photons with an average energy of 0.7 Mev and beta particles with an average energy of 0.4 Mev.[Ref. 2] The beta particles have a limited range and for low enrichment fuels (UO_2) are not significant.[Ref. 1] The gamma photons have a relatively long range and are absorbed by all the materials in the core, in proportion to the masses exposed. The fraction of the gamma energy absorbed in the water is therefore conservatively estimated as follows, assuming further that all of the gamma energy released from the fuel is absorbed in the core region.

Mass fraction of water in core region, equal to fraction of gamma energy absorbed in water in core is calculated from the fuel assembly volume fractions,[Ref. 3] and the material densities at temperature as shown below.

Fuel	0.303 x 10.00	= 3.030
Water	0.580 x 0.7	= 0.406
Zircoloy	0.102 x 6.4	= 0.653
	Sum	= 4.089

Mass fraction of water = 0.406/4,089

= 0.10

The total radiolytic energy (R.E.) available for radiolysis in water per MW of decay energy is therefore

R.E. = (0.1) x gamma + 0.0 x beta

= 0.1 x 0.5

= 0.05 MWRE/MW Decay

The yield of gases from radiolysis, per MW hr of decay energy _s now calculated as follows.

$$1 \text{ MW} \times 0.05 \frac{\text{MWRE}}{\text{MW}} \times 10^6 \frac{\text{watts}}{\text{MW}}$$

$$\times \frac{3600 \text{ secs}}{\text{hr}} = 1.8 \times 10^8 \frac{\text{watt seconds Radiant Energy}}{\text{MW hr}}$$

$$\div 1.593 \times 10^{-19} \frac{\text{watt seconds}}{\text{electron volt}}$$

$$\div \frac{100 \text{ ev}}{(100 \text{ ev})} \quad \times \frac{0.45 \text{ mol } (H_2)}{(100 \text{ ev})}$$

$$5.08 \times 10^{24} \text{ molecules } H_2/\text{MW hr}$$

$$\div 6.02 \times 10^{23} \frac{\text{molecules}}{\text{g mole}}$$

$$\times 22.400 \text{ cc/g mole}$$

$$= 1.892 \times 10^5 \frac{\text{cc}}{\text{MW hr}}$$

$$\div 28.317 \text{ cc/ft}^{-3}$$

$$= 6.68 \text{ ft}^3 \; H_2/\text{MW hr}$$

or $3.34 \text{ ft}^3 \; O_2/\text{MW hr}$.

Table 1, shows the decay energy for TMI-2 as a function of time after shut-down, and the corresponding values of "maximum" oxygen generation. The decay en~rgy values are taken from Ref 4.

TABLE 1

Time Period, After Shut-down, hrs.	Average Decay Energy MW	Max O_2 in time Interval, ft^3
2- 3	26.06	87.0
3- 4	23.00	76.8
4- 6	21.07	140.7
6- 8	19.13	127.8
8-10	17.74	118.5
10-12	16.63	110.1
12-14	15.25	101.9
	Total/14 hrs =	762.8

2. Hydrogen Generation--Composition of Gases

The state of cooling of the core, during the course of the accident cannot be specified in sufficient detail to calculate the actual radiolysis. That part of the core immersed in water remains cool, and the water covering the core, which for the most part will be boiling, will undergo radiolysis. The amount of gas generated will be approximately that fraction of the values of Table 1 corresponding to the fraction of the core covered by water. The uncovered part of the core heats up rapidly to temperatures where the reaction of zircoloy cladding with the steam generated from the boiling section is quite rapid.[Ref. 5,6] The hydrogen released, and the decreased absorption in the low density steam result in low radiolysis in that portion of the core.

Essentially, the oxygen content of the gas released from the core was a maximum during the period when the system was boiling down in the early part of the accident. This is presumed to have occurred when the last operating pump was shut down at 100 minutes after the turbine trip.[Ref. 7] The state of the system, prior to uncovering of the core seems well described by the analysis of attachment 11, [Ref. 5] which illustrates the formation of steam voids in the system. Actually, core damage may have started earlier, as indicated by a high reading on In-Core Thermocouple 10-R at 32.5 minutes.[Ref 7]

Most of the gas generated in the early part of the incident, largely hydrogen from the zircoloy-water reaction, is presumed to have been vented to the containment. This is inferred from the evidence for a hydrogen explosion in containment at 9 hrs 50 minutes. It has been estimated that 226 lb mol of hydrogen burned at that time.[Ref 7; Ref 4, p. A12, A34, Attachment B] Additionally it was estimated that 80 lb mol of hydrogen remained in containment, and that 76 lb mol of hydrogen was present in the final bubble. The latter figure apparently was estimated from the bubble volume, and the assumption, here believed to be erroneous, that the bubble gas was a stoichiometric mixture of two volumes of hydrogen and one volume of oxygen. This is supported by the following calculation.

Assume bubble volume was 1000 ft^3 at 250°F and 1000 psi Ref 8,9 The partial pressure of gas is 1000 - 30 = 970 psi (30 psia partial pressure of water at 250°F). The standard condition volume of gas is given by

$$V_{B(STP)} = 1000 \times \frac{970}{14.7} \times \frac{492}{460+250}$$

$$= 45,720$$

$$V_{H_2}(\text{Ref. 4}) = 76 \times 359 = 27,284$$

$$V_{H_2+O_2} = 1.5 \times 27,284 = 40,926$$

The values are close enough to indicate that the writer of Ref. 4 Attachment 11, did indeed assume that the bubble was composed of radiolytic gas, or had some high oxygen content.

The bubble could only have arisen from compression of gas in the system above the reactor vessel after recovery and isolation of the system. This probably included the following volumes (Ref. 3).

2 x 1/2 Steam Generator	2017 ft^3
2 Hot Legs	738 ft^3
Upper Head of Vessel	508 ft^3
2/3 of Upper Plenum	550 ft^3
1/2 of 2 Cold Legs	238 ft^3
	4061 ft^3

During the entire period of preceding recovery, the void was superheated, to at least 700°F. Ref 8, Fig. 22. The cold leg temperature varied, between a low of about 150°F and about 200°F just prior to recovery. The pressure, Ref. 8, Fig. 5 was about 400 psi. We can calculate the standard volume of gas in the voids as

$$4060 \times \frac{400}{14.7} \times \frac{492}{700+460} = 46.857 \text{ ft}^3$$

This is almost identical to the amount of gas in the final bubble.

The close agreement may be fortuitous but the argument is believed to be sound. Thus the oxygen content in the bubble will not be greater than the average oxygen content for the major incident period plus some additional supply from radiolysis as the core was finally covered. We estimate that as follows:

Average composition of gas before final covering:

O_2 = 3/4 of max radiolysis for 10 hrs (Table 1)

3/4 x 550.8	413 ft^3
10/14 of 180 ft^3 (injection) =	129 ft^3
	542 ft^3

H_2 = Total volume of H_2

= (226 + 80 x 114) lb mol (x 359 ft^3/lb mol) =	150,780 ft^3
O_2/H_2 =	0.0036

O_2, Oxygen addition on final covering,

3/4 of max radiolysis 10-14 hrs, Table 1 (212 x 0.75) =	159 ft^3
O_2 in injection water 180 ft^3 x $\frac{4}{14}$	51 ft^3
	210 ft^3
H_2 = Volume of bubble =	45,000 ft^3
$\frac{O_2}{H_2}$ =	0.0047

Total $\frac{O_2}{H_2}$ = 0.0083 = 0.83%.

This is believed to be a conservative estimate with respect to identified sources of oxygen and processes within the reactor system during the incident. The true value is probably lower.

3.0 Summary and Conclusions

It is evident that hydrogen resulting from the zirconium water reaction was the major source of gas in the TMI-2 reactor system. A minor quantity of oxygen may have been introduced via the injection water. Radiolysis of water was a minor source of additional hydrogen, and the probable source of most of the oxygen. The total amount of oxygen available in the system was quite small relative to the hydrogen. The oxygen to hydrogen ratio in the gas was high only at the beginning of the accident, during the first formation of a steam void in the system, before the core was uncovered, when the only significant source of gas was radiolysis. At this time however, the steam pressure was high, and the relative quantity of gas was low, rendering the mixture non-explosive.

Toward the end of the incident, as the core was recovered, the relative oxygen content increased, into a high hydrogen content void, but only to a final value which is estimated to be less than one (1%) percent of the hydrogen, and thus non-explosive at the existing conditions of approximately 1000 psi and 250°F.

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3. Three Mile Island-2 Data Package, Met. Ed.

4. NUREG-0557-Evaluation of Long-Term Post-Accident Cooling of Three-Mile Island Unit 2, May 1979, Fig. 6.2, pp. 6-16.

5. G. P. Marino, Preliminary Assessment of Core Damage for Three Mile Island Incident. Memo for Files Fuel Behavior Research Branch Division of Reactor Safety Research, NRC April 25, 1979.

6. M. L. Pickleseimer, "Bounding Estimates of the Damage to Zircoloy Fuel Rod Cladding in the TMI-2 Core at Three Hours After the Start of the Accident," Fuel Behavior Research Branch NRC, April 26, 1979.

7. TMI-2 Interim Operational Sequence of Events as of May 8, 1979 EPRI.

8. Preliminary Annotated Sequence of Events, TMI-2 Accident of March 28, 1979, G.P.U.

9. PNO-79-67D.