

M_{O_2} = the molecular weight of oxygen = 31.998

2 = the number of hydrogen moles produced for each mole of oxygen reacted.

Figure 2-3 shows a plot of hydrogen production versus time for four different temperatures. For these calculations we have assumed that linear kinetics govern the production rate.

In order to calculate the hydrogen production from the steam:steel reaction for a particular reactor we need to estimate the surface area of steel in a reactor that would be exposed to steam and could be expected to reach the necessary temperatures. Such steel surfaces as control-rod cladding, core barrels, control-rod guide tubes, and core support plates should be considered. Additionally, if core slump occurs, then the bottom of the reactor vessel and nearby structures should be considered. Typically, a few thousand square feet of steel may have the potential to participate in the steam:steel reaction.

2.1.4 Radiolysis of Water

Radiolysis of water occurs during both normal operation and accidents. Radiolysis involves the decomposition of water molecules by radiation (α , β , γ , or n). Radiolysis of water (H_2O) can produce OH , H , HO_2 , and H_2O_2 .²⁻⁶ These products can subsequently react with either themselves or other chemicals present in the water to produce a variety of products. An important point to be noted is that H_2 and O_2 can be produced by radiolysis.²⁻⁷ Radiolysis can occur in the core, or elsewhere in the primary system, or in containment (if fission products are transported to those areas).

The rate of hydrogen and oxygen generation is controlled by three factors: (1) the decay energy, (2) the fraction of this energy that is absorbed by the water, and (3) the effective rate of hydrogen and oxygen production per unit of energy absorbed by the water. The yield of a product species due to the radiolysis of water is generally expressed as that product's "G" value (molecules of product formed per 100 eV of energy absorbed). Distinction must be made between the primary or direct radiolytic yield of a species and the net yield of the same species. The direct or primary yield is usually expressed as a subscript to G while the net or actual yield is written as a parenthetical notation. Thus G_{H_2} is the hydrogen formed directly from the water by radiation, while $G(H_2)$ is the net hydrogen formed directly by radiation and indirectly by all subsequent chemical reactions. The $G(x)$ value can be larger or smaller than G_x due to secondary reactions taking place between the various radiolytic species and the solutes. Typical values²⁻⁸ of G_{H_2} in pure water are 0.44 for $\beta + \gamma$ for radiation, 1.12 for fast neutrons,

and 1.70 for the recoil nuclei from the reaction $^{10}\text{B}(n,\alpha)^7\text{Li}$. Since molecular oxygen is not produced directly by radiolysis, $G_{\text{O}_2} = 0$; however, $G(\text{O}_2)$ is not necessarily zero.

A closed water/gas system will eventually attain equilibrium with respect to radiolytic decomposition of the water. The concentration of gaseous products at equilibrium will be a function of the reactor power density, the water pH and temperature, and the impurity (solute) type and concentration. Once equilibrium is attained, $G(\text{H}_2) = G(\text{O}_2) = 0$ (although the concentrations of H_2 and O_2 may not be zero). It is well established that small quantities of hydrogen (less than 10^{-3} moles/liter) dissolved in pure water or boric acid solutions will effectively limit the equilibrium condition to one in which negligible O_2 is present. This technique is employed routinely in PWR nuclear plants.

An open water/gas system will not attain an equilibrium condition because the product species are being continuously removed. A typical BWR power plant operates in such a manner. If the water is boiling vigorously, H_2 and O_2 will be produced in stoichiometric portions and $G(\text{O}_2) = 1/2 G(\text{H}_2) = 1/2 G\text{H}_2$. For pure water exposed to $\beta + \gamma$ radiation, this would result in the production of ~ 22 molecules of O_2 and 44 molecules of H_2 for each 10^4 eV of radiation energy.

The specific accident scenario can have a major effect on the relative importance of radiolytic production of H_2 and O_2 . In order to realistically estimate the effects of radiolysis, it is necessary to know the extent and distribution of fission-product release, the water temperature and pH, the degree of bubbling and turbulence of the water, and the types and quantities of impurities dissolved in the water. Presently we cannot assess the effect of simultaneous variations in several of these parameters. We can state, however, that the rate of production of combustibles from radiolysis is slow compared to the rates from the high-temperature Zr:steam and steel:steam reactions when the latter reactions are occurring.

The rate of radiolytic decomposition of pure water increases linearly with the reactor decay power but the equilibrium concentrations of product species in a closed system increase as the square root of the power. Variations in pH have little effect on α -irradiated water, but not much is known about the effect of pH variations with other forms of radiation. It has been speculated that pH variation may have a significant effect when combined with solutes²⁻⁸. Increasing temperature will tend to decrease equilibrium concentrations of product species in pure water, but it has been suggested that increasing temperature will enhance solute effects due to increased reaction rates between solute molecules and radiolytically produced radicals²⁻⁸.

The effect of vigorous boiling or bubbling of the water can be quite significant. The products of radiolysis are constantly removed from the liquid, and therefore, recombination of the H_2 and O_2 in solution is inhibited. Radiolysis of the vapor phase itself has not been studied extensively, but this may become an important issue in an accident.

The effects of the many possible solutes are not well understood. The impurities can react with the radiolytically produced radicals and upset the chemical balance. Only very small quantities of impurities are necessary to upset this balance (Ref. 2-7).

One of the key questions associated with the accident at TMI-2 concerned radiolytic decomposition of the reactor coolant water and the possibility that a combustible mixture of H₂ and O₂ might exist inside the reactor. Armed with our present understanding of the TMI-2 accident scenario, it can be stated that the probability of such an occurrence was very small²⁻¹ because there was probably an excess of hydrogen and steam and not enough oxygen for the mixture to be combustible. It cannot be stated, however, that the probability was zero (or would be zero for all conceivable accidents).

There are many uncertainties associated with radiolytic decomposition of water in a LOCA. It is most useful to carry out sample calculations as part of a parametric analysis. Consider the two key parameters to be the net yield G value for hydrogen, G(H₂), and the fraction of reactor-shutdown (decay) radiation absorbed by the water, f (Ref. 2-7). In order to proceed we set the product G(H₂)·f equal to 1.0 and then all results can be scaled with the "correct" value of G(H₂)·f. Results of calculations for a 3300 MW(t) reactor are given in Table 2-1. While these calculations probably overestimate the yield and rate by a considerable margin, there are too many unknowns to say that conclusively.

Table 2-1

CONSERVATIVE CALCULATION OF RADIOLYSIS YIELD AND RATE FOR A 3300 MW(t) REACTOR WITH G(H₂)·f = 1.0

Time after Shutdown (s)	Integrated Decay Energy MJ/MW (Ref. 2-7)	Radiolysis Yield and Rate with G(H ₂)·f = 1.0 for a 3300 MW Reactor			
		Total Yield		Average Rate	
		lbm	kg	lbm/s	kg/s
10 ²	6	8.8	4	.0881	.04
10 ³	25	37.4	17	.0322	.0146
10 ⁴	160	242.3	110	.0229	.0104
10 ⁵	800	1207.0	548	.0106	.0048
10 ⁶	3500	5286.3	2400	.0044	.0020

2.1.5 Core:Concrete Interactions

In the unlikely event that a reactor accident progresses to the point of gross fuel melting, the reactor vessel may be penetrated. Collapse of the molten reactor core materials into the reactor cavity could initiate vigorous

The surface area of aluminum has been estimated to be 475 ft² (44 m²) in a typical containment.²⁻¹³ The corresponding mass of aluminum is about 1250 lbm (568 kg). Under LOCA conditions of 300°F (149°C), a maximum of about 139 lbm (63 kg) of hydrogen could be produced over a 7-day period, given the surface area and mass of aluminum identified above and a production rate of 0.88 lbm/hr (0.4 kg/hr). Other estimates of the mass of aluminum in containment have been as high as 4000 lbm (1800 kg).

Organic materials such as cable insulation, epoxy paints, lubricating solutions, and gasket seals may produce combustible gases (primarily hydrogen or methane) due to radiolysis and corrosion. For most nuclear plants, the quantity of combustible gas that could be produced from organic materials inside containment is relatively small.

An example of hydrogen generation from radiolysis of cable insulation (polyethylene) follows. The yield of hydrogen, $G(H_2)$, for polyethylene is 5 molecules for 100 eV of absorbed radiation.²⁻¹⁴ If we take 200 Mrad as a 30-day radiation dose for the cable insulation, then the dose per pound is roughly 6×10^{24} eV (1.3×10^{25} eV/kg). A typical containment might have 10^5 lbm (4.5×10^4 kg) of cable insulation. Therefore, roughly 220 lbm (100 kg) of hydrogen could be generated from radiolysis of cable insulation over a period of 30 days.

2.1.7 Time Sequence of Hydrogen Production

An exact calculation of hydrogen production versus time during a severe accident would require a detailed analysis of the accident scenario as well as modelling of certain physical phenomena that are not well known. However, it is useful to examine the question from a qualitative viewpoint.

Of the sources of hydrogen discussed in this chapter, the most important one is probably the steam:zirconium reaction. This reaction requires temperatures above 1832°F (1000°C) which may occur within the first few hours of a severe accident (after core uncovering).^{*} Large amounts of hydrogen may also be produced from steam:steel reactions. These reactions are initiated after the steam:zirconium reaction due to the higher temperatures required; however, they are still initiated during the first few hours of the accident and can be concurrent with the steam:zirconium reaction.

Core:concrete interactions do not occur unless the core has fallen through the reactor vessel. Once the interactions start, vigorous gas generation results. Corrosion of paint and other surfaces within containment may begin when hot steam is released into containment or the containment sprays are activated. However, these reactions are slow, taking many hours to produce relatively small quantities of hydrogen.

^{*}For the purposes of this discussion, a severe accident is one in which the core becomes uncovered for a period of time and a degraded-core situation occurs.

Radiolysis is always present in a reactor. The rate of radiolysis can increase during the accident as fission products are released from the fuel. However, radiolysis is still a long-term concern relative to the steam:zirconium reactions. Using the information presented earlier in this chapter and making certain assumptions, we can estimate the relative quantities and timing of hydrogen production for the various reactions (see Fig. 2-6). Figure 2-6 should be treated as qualitative in nature, as actual numbers depend upon the specific reactor and accident sequence.

HYPOTHETICAL H₂ PRODUCTION

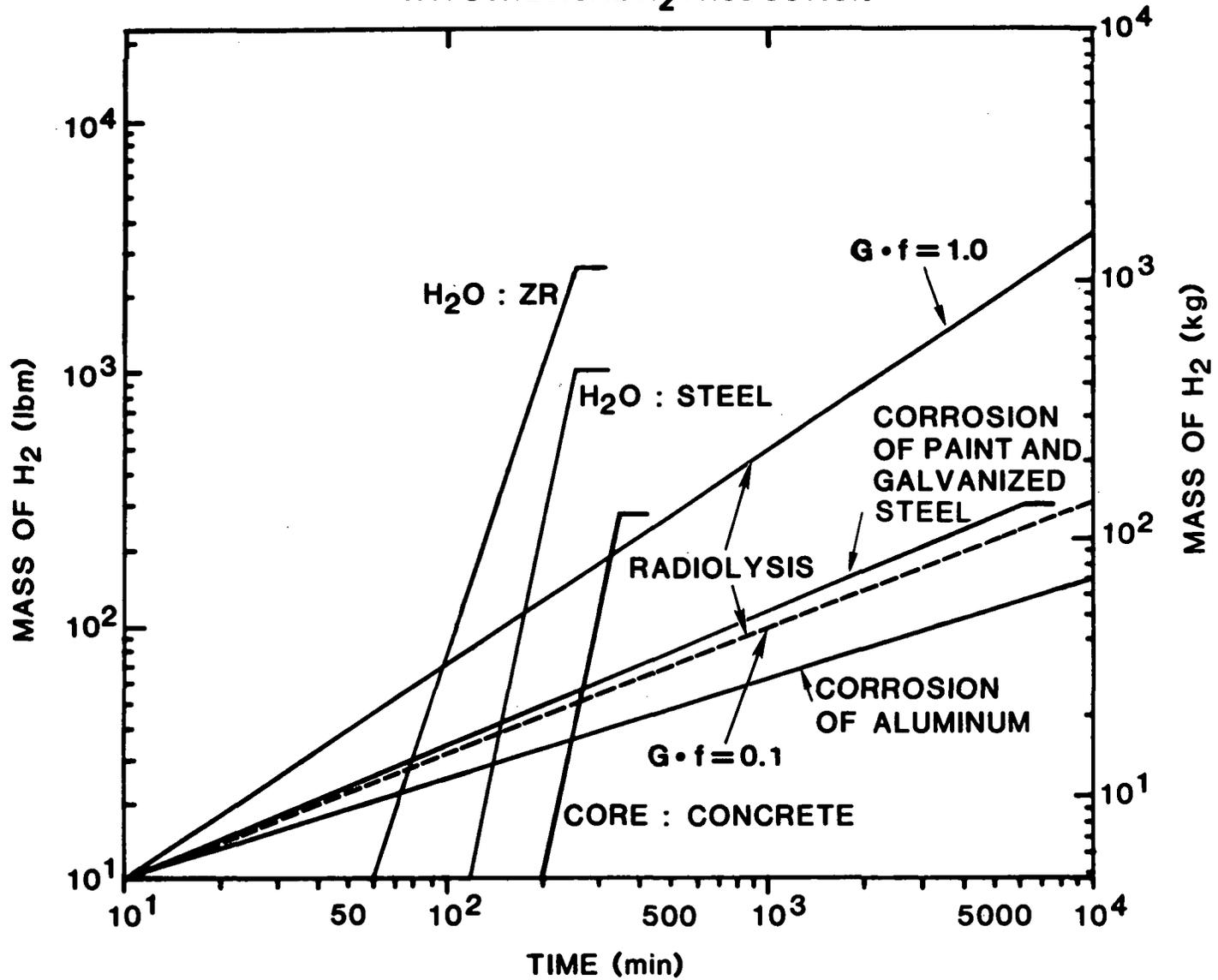


Figure 2-6. Hypothetical H₂ Production for Various Reactions