Radiolytic Water Splitting: Demonstration at the PM-3A Reactor

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The current interest in nontraditional methods for the generation of hydrogen has prompted a revisitation of radiolytic splitting of water, where the interaction of ionizing radiations (α, β, and γ) with water can produce molecular hydrogen. This reevaluation was further prompted by the current availability of large amounts of radiation sources contained in the fuel discharged from nuclear reactors. The spent fuel is usually stored in water pools, awaiting permanent disposal or reprocessing.

The observed yield of hydrogen resulting from the irradiation of water with β and γ radiation is low (G-values = <1 molecule per 100 electron-volt of absorbed energy) but this is largely due to the rapid reassociation of the species arising during the initial radiolysis. If impurities are present or if physical conditions are created that prevent the establishment of a chemical equilibrium, the net production of hydrogen can be greatly enhanced.

In the operation of nuclear reactors, where intensive radiation fluxes are created by fission and radioactive decay processes, the generation of hydrogen could be hazardous. The radiolytic production of reactive oxygen-containing species may lead to excessive corrosion of materials of construction. Considerable effort has been expended to suppress the radiolysis of water in nuclear reactors and in spent fuel storage pools.

This author was involved in 1962-63 with the PM3-A, a small nuclear power reactor (Pressurized Water Reactor) at the McMurdo Station in Antarctica. During the first year of operation, considerable quantities of hydrogen was continuously generated in the closed containment tank in which the reactor pressure vessel, surrounded by shielding water, was located. This unexpected development was caused by the improper design of the shield water recirculation loop: water was withdrawn at a point located in the high radiation zone near the reactor pressure vessel were radiolytic hydrogen was generated. After passing through a cooler and ion-exchange purifier, the water was returned through a sprinkler ring located above the shielding water level. This provided for an efficient degassing and subsequent buildup of hydrogen in the closed containment tank. Temporary remedial methods, such as continuous purging of the containment atmosphere with air or the use of a catalytic recombiner, were adequate to permit the continuation of reactor operation. Eventually, the recirculation loop was modified so that the recirculated water was removed just below the water/air interface and then returned at a point close to the pressure vessel. This avoided the withdrawal of water with high dissolved hydrogen content and eliminated the efficient stripping of hydrogen previously provided by the sprinkler ring. This modification completely suppressed the generation of hydrogen in the containment tank. An analysis of this occurrence and a review of the remedial actions are very useful in the evolution of conceptual designs of radiolytic hydrogen generating systems.

Several investigations have shown that the production of radiolytic hydrogen can be significantly enhanced by the use of catalysts, the presence of materials with large specific contact surfaces (e.g. small particles and porous substances), elevated temperature, the presence of chemically reactive impurities that scavenge the primary or intermediate species that are necessary for the reforming of water, and the continuous removal of molecular hydrogen to prevent the establishment of a chemical equilibrium in the radiation zone.

The application of γ. radiation may also be useful in combination. with other techniques for hydrogen production.