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WATER CHEMISTRY IN PRESSURIZED AND BOILING WATER POWER REACTORS

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
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U.S. ATOMIC ENERGY COMMISSION

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NOVEMBER 1967

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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WATER CHEMISTRY IN PRESSURIZED AND BOILING WATER POWER REACTORS

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ABSTRACT

Small nuclear power plants could find many uses if the size, cost and complexity could be reduced. Fraas and coworkers have recently proposed several reactor systems including both pressurized-and boiling-water types aimed at accomplishing these objectives. These reactors, collectively called Terrestrial Low Power Reactors (TLPR), would be small, hermetically sealed units capable of unattended operation for extended periods. The elimination of water purification systems and the development of methods for handling the radiolytic gases generated in boiling-water reactors would greatly simplify such plants and increase the probability of unattended operation. This report consists of a literature survey of the corrosion behavior of materials in aqueous reactor environments as it relates to the need for water purification and a discussion of radiolytic gas generation and recombination in a boiling-water TLPR.

Although conventional aqueous reactors utilizing primarily stainless steel and Inconel as materials of construction have performed well, all such reactors rely on purification systems to prevent the buildup of corrosion products in the water which could cause fuel element fouling. From the standpoint of corrosion and accumulation of corrosion products in the water, titanium appears to be a better choice as a structural material than either stainless steel or Inconel. Although only limited data are available on corrosion and corrosion product release rates for titanium in high temperature water, that which is available appears favorable; corrosion rates of a few hundredths of a mil per year have been reported with most, if not all, of the corrosion products adhering to the base metal. Furthermore, there are no indications that hydrogen-embrittlement will be a problem. However, it should be emphasized that a rather extensive experimental program would be necessary to establish titanium as a structural material for aqueous reactors.

Radiolytic gases pose no problem in pressurized water reactors if the water is sufficiently pure; addition of hydrogen reduces the concentration of oxygen in the water to an insignificant level. In boiling-water reactors, however, the radiolytic gases are swept out of the reactor and collect in the condenser. The proposed method of recombining the hydrogen and oxygen in the boiling system described by Fraas involves returning the radiolytic gases along with excess hydrogen to the high pressure system. This particular reactor concept is well suited to use this method since only about 2% and 0.5% of the fast

neutron and gamma energy, respectively, are absorbed in boiling water; the remainder of the water within the core and reflector does not boil. The designs of the condenser and feed pump are such that large quantities of gas can be entrained in the condensate and pumped back into the nonboiling portion of the reactor where the radiation field recombines the gases before the water enters the boiling region. Analyses showed that this method of recombining radiolytic gas will perform satisfactorily in this type of reactor provided that gases can be circulated as required and that impurities which accumulate in the water do not seriously affect the radiolytic recombination. Experimental work would be required to evaluate these factors.

1. INTRODUCTION

Small water-cooled nuclear electric power plants could find many uses if the size, cost, and complexity could be reduced. Several reactor systems aimed at accomplishing these objectives have been proposed recently.[1] These reactor systems, known as Terrestrial Low Power Reactors, would hopefully be small, hermetically sealed (that is, there would be no requirement for addition or removal of liquids or gases during operation), capable of unattended operation for extended periods, and easily transportable. The elimination of water purification systems and the development of methods for handling the radiolytic gases generated in boiling water reactors would be useful steps in simplifying such reactor plants.

The technology of both pressurized and boiling water reactors is well established and the water chemistry in both types of reactor is reasonably well understood. However, all power-producing, water-cooled reactors presently in operation use water purification systems and all boiling water reactors remove the radiolytic gases from the system. The purpose of this paper is to discuss briefly the water chemistry of both types of reactor, particularly as it relates to the necessity of purification systems, and to consider means whereby small reactors could operate satisfactorily without

water cleanup or special gas handling equipment.

2. PRESSURIZED WATER REACTORS

The primary systems of most pressurized water reactors are constructed so that the coolant is in contact only with austenitic stainless steel, Zircaloy-2 or other zirconium alloys, and Inconel. The latter alloy is used for the heat exchanger tubes because of its resistance to chloride-induced stress-corrosion cracking. The zirconium alloy is used to clad the fuel. The recirculating coolant is water adjusted to a pH of 9 to 11 with lithium hydroxide or ammonia to minimize both total corrosion and the quantity of corrosion products released to the coolant. To suppress the formation of H_2 and O_2 from radiolysis of water, H_2 is added to the extent of about 25 to 50 cm^3/kg of water. In addition, some operating reactors utilize boric acid in the coolant for control purposes; in this discussion, however, the use of boric acid is not considered.

Although both stainless steel and Inconel undergo very little corrosion in the coolant, it is customary to provide a continuous bypass of the reactor water through a cleanup system consisting of ion exchangers and filters. In the purification system both ionic or soluble as well as insoluble impurities (crud) are removed. Removal of the corrosion products reduces the possibility of fuel element fouling, lowers the activity level in the system exterior to the reactor, and favors low concentrations of radiolytic gases. In addition, the ion exchangers can be used to control the pH of the coolant to the desired level.

The corrosion of Zircaloy-2 fuel cladding in pressurized water reactors with excess hydrogen is thought to be the same as that in deaerated water out-of-radiation.[2] Accordingly, the corrosion penetration of the

cladding would be expected to be about 0.03 mils during one year at 550°F. The rate of corrosion decreases with time, and the penetration after a 7-day pretreatment would be about 0.02 mils.[3]

The possibility of operating a pressurized water reactor without a purification system was discussed by Rosenthal et al.[4] The system considered was made of stainless steel with Inconel heat exchanger tubes. Water containing H_2 and adjusted to a pH of 10 to 10.5 was the coolant. It was noted that there were no apparent corrosion reactions which consumed either hydrogen or alkali and therefore they concluded that the environment would not change significantly with time. In fact the H_2 concentration should increase as a consequence of the following reaction:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

Assuming that the primary system is principally stainless steel and that the average corrosion rate is 5 $mg/dm^2 \cdot mo$, they calculated that about 1 ft^3 of H_2 would be produced per 100 ft^2 of surface in one year.

The reactor they considered was to be unattended, and the presence of radioactivity in the coolant and deposition on the interior surfaces of the high pressure system was of no consequence. The only major concern associated with operating the reactor without a purification system was the extent of deposition of corrosion products on the fuel element surfaces and the resultant interference with heat transfer. From a literature survey it was concluded that the release rate of solids from the stainless steel and Inconel surfaces to the coolant would average 2 $mg/dm^2 \cdot mo$ at 500°F. Assuming that all of the solids released deposit on the fuel element surfaces and that the fuel element surface area is one-fifth of the total surface area, the rate of solids deposition on the fuel elements is

10 $mg/dm^2 \cdot mo$. At this rate an average thickness of 0.17 mil would develop in one year. With the modest heat fluxes expected in such a reactor it was concluded that this thickness of corrosion product would have only a minor effect on fuel element temperatures. It was therefore the opinion of the authors that a system such as they defined could operate for at least a year without water purification.

The results obtained during operation of the Shippingport Pressurized Water Reactor without purification generally support the conclusions reached by Rosenthal et al. The reactor was operated for 1478 effective full-power hours during the life of Core 1, Seed 2 without purification.[5] Analysis of the results led to the following conclusions:

1. The trend of long-lived activity buildup on primary system piping did not differ significantly from that observed during operation with purification.
2. Operation without purification resulted in no significant changes in coolant crud concentration; crud bursts of comparable magnitude occurred at all purification flow rates. Steady-state concentrations were essentially the same, that is, 0.5 ppb for full purification operation versus 2 ppb with half or no purification.
3. Corrosion product activity in the primary coolant remained within the scatter observed during operations with purification.
4. Within the accuracy of the instrumentation there was no change in pressure drop across the core regardless of the extent of purification system operation.

Experiments were carried out in the Saxton Reactor to study the effect of crud level in the primary coolant on the hide-out of boron (used for shim control) in the system.[6,7] In these experiments a slurry of ferrous hydroxide was injected into the reactor system to achieve an initial crud level of 2 ppm. At the operating temperature of about 500°F ferrous hydroxide is rapidly converted to magnetite which is the major constituent of corrosion products generated in the reactor system. Although definitive results concerning boron hide-out were not obtained, useful observations about the deposition of solids on the fuel elements were made. The investigators noted that under normal operating conditions (pH of 10 to 10.5, dissolved H_2, and sufficient pressurization on the system to prevent local boiling) crud deposition on the fuel elements was small even when the system contained much greater concentrations of solids than normal. Their results indicated that nucleate boiling was a necessary condition to deposit appreciable quantities of solids on the fuel element surfaces. They also noted that under the same conditions the amount of deposit formed on stainless steel- and Zircaloy-clad fuel elements was comparable.

Numerous other studies concerning corrosion and release rates of materials in pressurized water reactors have been reported; the ones referred to above, however, seem to be the most pertinent for this discussion. From these data it appears that under optimum conditions of water chemistry and with sufficient pressure on the system to prevent nucleate boiling, a pressurized water reactor with stainless steel as the major material of construction should be capable of successful operation for extended periods without a purification system. Furthermore, there are no obvious reasons why a system filled initially with water of optimum quality (high pH and

adequate H_2 concentration) should undergo significant change as a result of corrosion or exposure to a radiation field. Activity levels in the high pressure system would undoubtedly be higher than in a reactor with purification, but the data indicate that they may not be excessive.

In pressurized water reactors, heat is extracted from the fuel elements by water which is used to produce steam in a boiler for a conventional steam cycle. In these secondary, or steam systems, in most cases it is general practice to provide demineralized water for makeup and to filter and demineralize the condensate before returning it to the boiler. Periodic or continuous blowdown is also used to remove accumulations of solids from the steam generator and to prevent buildup of dissolved solids in the water. Treatment of the boiler water with ammonia, morpholine, hydrazine, or octadecylamine is often used to reduce corrosion in the turbine and condensate sections.

Since the nuclear plants under consideration are to be self-contained and unattended, this type of operation cannot be used. Rosenthal et al.[4] discussed the problems involved in conventional steam systems for power generation including simplifications that might be made. They concluded that a sealed secondary system could probably operate successfully for one year or longer without any water treatment at all. The quantity of corrosion products in the steam generator was estimated by assuming an average corrosion rate of 10 $mg/dm^2 \cdot mo$ (without specifying materials) and a surface area of 500 ft^2 exposed to hot water and steam. In one year 750 g of corrosion products would be produced which would correspond to 400 ppm in a steam generator with a capacity of 500 gal. If all of the solids were uniformly deposited on 200 ft^2 of heat-transfer surface, a scale about 6

mils thick would result. Since all corrosion products will not be transported to the steam generator and since they will not all deposit on heat-transfer surfaces, the authors felt that such a concentration of corrosion products as is likely to develop can be tolerated. Accumulation of H_2 produced by corrosion was recognized as likely to be a problem which would require a solution. Also, accumulation of radiolytic O_2 might occur and, thus, provisions for eliminating this O_2 might be required. Whether a secondary system can be operated without water treatment or blowdown depends to a large measure on the materials in the system. With sufficiently resistant alloys such as stainless steel or Inconel, corrosion product accumulation should be minimal and an hermetically sealed steam system appears possible providing that gases can be handled. However, experimental verification of corrosion rates and the extent of fouling of heat-transfer surfaces would have to be obtained before a closed system could be seriously considered.

3. BOILING WATER REACTORS

The water chemistry problems associated with boiling water reactors are similar to those of pressurized systems with two important exceptions. First the bulk boiling of the water strips the radiolytic gases (as well as other gases) from the system, thereby interfering with the radiation-induced recombination reaction; under normal conditions appreciable concentrations of H_2 and O_2 are present in the steam produced. Secondly, heat is removed from the fuel elements by vaporization, a process which increases the probability of deposition of either dissolved or suspended solids on the fuel elements.

The boiling water is usually in contact primarily with stainless steel and with Zircaloy-2 fuel element cladding. The water is highly purified and does not contain either lithium hydroxide or ammonia as is the general practice in pressurized water reactors. This latter fact tends to increase somewhat the corrosion of stainless steel and the concentration of corrosion products in the water over that in a pressurized system, although in both cases the corrosion rate is low. To minimize the impurities, a portion of the water in the high pressure system is recirculated through filters and ion exchange beds to maintain water of suitable purity. In addition, the condensed steam is passed through a full-flow mixed-bed ion exchanger before being returned to the pressure vessel to insure the absence of corrosion products originating in the steam system.

In operating boiling water reactors the gases from the radiolytic decomposition of water (stoichiometric H_2 and O_2) and other non-condensables are separated from the condensed steam and vented to the atmosphere; no attempt is made to effect their recombination. When one considers a reactor operating unattended in a hermetically sealed system, it is clear that some provision for recombining the gases must be made. This problem is dealt with in a later section of this report. In addition, the volume of H_2 produced as a result of corrosion must be considered, particularly from the standpoint of its effect on the efficiency of the condenser. As noted before, this is also true for the secondary system of a pressurized water reactor.

The corrosion rate of Zircaloy-2 fuel cladding in these systems is appreciably greater than that out-of-radiation.[8,9,10] Comparable increases in corrosion under irradiation have been observed in pressurized systems

when the water contains O_2,[9,11,12,13] and it is believed that the increased corrosion is associated with the presence of O_2 in conjunction with fast neutron irradiation.[14] The amount by which the corrosion is increased can be judged from the reported values for the oxide film thickness on fuel element cladding after 900 days operation of a BWR. The reported[9] patch and uniform oxide average film thickness was 30 μ (470 mg/dm^2) compared with predicted weight gains of about 30 mg/dm^2 after 900 days in out-of-pile autoclave tests at 575°F. The 470 mg/dm^2 corresponds to an average corrosion rate of about 0.4 mpy and is very close to the rate (~0.5 mpy) which can be estimated from the reported results for 179 days exposure.[10] Hydrogen uptake amounted to about 7% of that formed by the corrosion reactions; that is, H_2 absorption was not severe.

The possibility of operating a boiling water reactor in an hermetically sealed container was considered by G. O. Haroldsen.[15] He reviewed the pertinent literature on the chemistry of boiling water reactors and considered an experimental program to establish the feasibility of operating the COMPACT reactor for 10,000 hr essentially unattended. The reactor water was to be in contact only with austenitic stainless steel, and the steam system was to be conventional for boiling water reactors. In common with other reactors, continuous purification of the high pressure water was envisaged, and all the condensate would be passed through a mixed bed ion exchanger before return to the high pressure system. Recombination of the radiolytic gas produced by the reactor was to be effected by means of a catalyst bed in the gas phase. One of the aims of the program was to demonstrate that the total solids in the boiling water could be kept to 10 ppb, a level which was estimated to be low enough to insure freedom of sig-

nificant deposits on the fuel elements. The author noted that operation at higher solids concentrations, even as much as a factor of 10, may be possible, but experimental verification is lacking.

Based on values reported in the literature, Haroldsen considered that, after the system had been pretreated prior to power operation, the stainless steel would corrode at a rate of about 5 $mg/dm^2 \cdot mo$ (0.03 mpy) and that most of the corrosion products would not be released to the coolant. To compute the size of the ion exchange beds necessary to handle the corrosion products formed during a 10,000-hr period with adequate safety, the author assumed a corrosion rate of 10 $mg/dm^2 \cdot mo$ (0.06 mpy) and that all of the corrosion products were ionized. Even with this generous safety allowance the bed sizes were not excessive. A test loop was proposed and partially built to determine the adequacy of the proposed purification system and to study the tendency of fouling on hot surfaces as a function of water purity. Unfortunately this program was never completed.[16]

Although boiling water reactors constructed primarily of stainless steel have operated successfully for long periods, none has been operated for extended times without continuous purification of the coolant. When one considers the expected corrosion rate of stainless steel, the products likely to be introduced from the turbine and condenser system, and the fact that the pressure vessel will serve as a collection point for all the impurities, one must conclude, as did Haroldsen, that successful operation of a boiling water reactor for long periods in a stainless steel system without purification is unlikely. As noted previously, boiling at a surface enhances the possibility of fouling when impurities are present in the water, and without purification fuel element fouling to some degree is high-

ly probable. Only an experimental program can determine the extent, and to be completely meaningful in-reactor experimentation would be necessary. The latter statement is based on an extrapolation of results obtained at Bettis which showed that ionizing radiation influences deposition in pressurized water systems.[17]

In addition to the problem of fuel element fouling, another major hazard associated with the use of an austenitic stainless steel in either pressurized or boiling water reactors is stress-corrosion cracking caused by the presence of chloride ions. In water-cooled reactors great care is taken to eliminate chloride contamination, but even with such care several instances of stress corrosion cracking have occurred.[18] This may not be a problem in a sealed stainless steel system; however, as in any system, cracking from contamination on external surfaces can be a problem.

The use of Inconel instead of an austenitic stainless steel appears to eliminate the problem of stress-corrosion cracking. This alloy is highly resistant to chloride induced cracking and has been used successfully in critical areas such as the heat exchanger tubes of pressurized water reactors.

Although the use of Inconel as the structural material solves the problem of stress-corrosion cracking, it is possible that the release of corrosion products to the water may be more severe than with stainless steel. Copson and Berry[19] studied the corrosion and corrosion product release rates of Inconel in flowing alkaline water at 550°F (pH = 8.9 to 9.5 with ammonia and 15 to 50 cm^3 H_2/kg). Their results indicated that under these conditions the release rate of corrosion products was higher for Inconel than for type 347 stainless steel. Both materials had belt-abraded

surfaces. Other experiments[20] with Inconel under comparable conditions except in static systems indicated that surface preparation was important in determining the extent of corrosion and the release rate of corrosion products from the surface; annealed surfaces yielded lower rates than machined or ground surfaces. Thus it appears that it may be possible to produce Inconel surfaces at least as resistant to corrosion as stainless steel.

The above work was conducted with alkaline water for which the corrosion product release rate of both stainless steel and Inconel is low. Thus it appears that, from the standpoint of fuel element fouling in a pressurized water reactor operating without purification, Inconel or stainless steel could be used about equally well as the structural material. In neutral water, as used in boiling water reactors, higher release rates would be anticipated for both stainless steel and Inconel. Although comparable release rate data are unavailable, it is probable that, in a boiling water reactor constructed of Inconel and operating without purification system, the likelihood of fuel element fouling would be about the same as in an all-stainless-steel system.

4. TERRESTRIAL LOW POWER REACTORS

The foregoing discussion has been concerned with the general problems of the water chemistry of pressurized and boiling water reactors. Both the data considered and the tentative conclusions drawn were based on or extrapolated from actual operating experience with more or less conventional reactors, or from development programs in support of these reactors. The following discussion is concerned with a specific type of relatively small

reactor, Terrestrial Low Power Reactors.[1] The general concept could involve either a pressurized or a boiling water reactor. Such a reactor should be able to operate essentially unattended for periods of time up to a year, and the system should be as compact and simple as possible. From the engineering standpoint, one of the most attractive designs is a completely contained boiling water reactor plant in which the steam passes directly from the reactor to the turbine, thus eliminating many components in the system. In addition, the containment shell serves as the condenser. It has already been concluded that such a reactor constructed totally of stainless steel or Inconel and in the absence of a purification system may be troubled with fuel element fouling. In addition, the generation of hydrogen and oxygen in the steam presents the problem of recombining the gases. The remainder of this report discusses (1) the possibility of using titanium as the structural material to minimize corrosion and crud problems, and (2) the production and recombination of radiolytic gases in the proposed boiling water reactors described by Fraas.[1*] Some features of these reactors which are germane to the latter discussion are shown in the sketch in Fig. 1 which is adapted from Ref. 1. Other features are mentioned later.

4.1 Corrosion

The most obvious approach to solving the problem of deposition of stainless steel or Inconel corrosion products on the fuel element surfaces is to use a material more corrosion resistant than stainless steel or Inconel. Outside of the noble metals, titanium is one of the most resistant

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*These will be designated BW-TLPR in the following.

metals to pure water and to many other aqueous environments. In the past the technology of fabricating equipment of titanium was not well developed and the cost was high. For these reasons little consideration has been given to its use in reactors. However, the advantages associated with its high strength-weight ratio have led to a great deal of development work so that in recent years much progress has been made by the titanium industry, the annual production rate has increased steadily, and the cost has materially decreased. Significant further reductions in cost seem assured.[21] Fabricable alloys having excellent strength are presently available, and many of these are readily weldable. Both the Supersonic Transport and the Deep Submergence Programs are based on the extensive use of titanium. It thus appears that titanium or its alloys may well be practical materials for construction of low power reactors and serious consideration should be given to their use. In addition to other desirable properties, titanium has a low density, a fact that will materially reduce the weight of the power plant.

Thermodynamically, titanium is a very active metal, and its corrosion resistance depends on the development of a thin tenacious film which effectively isolates it from the corrosive environment. Its excellent resistance to a number of corrosive environments has been demonstrated at the Oak Ridge National Laboratory as well as at other installations. In one test, titanium specimens were exposed to water containing an overpressure of 200 psi O_2 at 250°C for 1000 hr.[22] In a second test the conditions were the same except the pressurizing gas was 200 psi H_2.[23] Regardless of the pressurizing gas, the specimens developed very thin bluish films corresponding to an oxide thickness of about 2000 Å. Within the

limits of the analytical balance ($\pm$ 0.2 mg) no weight changes were detectable on specimens with an exposed surface area of 5 cm^2. There was no evidence of hydriding on any of the specimens.

At Knolls Atomic Power Laboratory, Cheng et al.[24] exposed three titanium alloys (Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-13V-11Cr-3Al) to a simulated pressurized water environment (NH_3 to a pH of 10, 600°F). All alloys corroded at rates between 0.01 and 0.07 mpy during 1928-hr tests. No change in mechanical properties and no evidence of hydrogen uptake were observed as a result of the exposure. At Babcock and Wilcox Ti-75A was exposed to degassed water (1 to 2 ppm NH_3, pH of 9.5) at 680°F for 2508 hr.[25] The average weight gain was 3.7 mg/dm^2. If the weight gain is attributable to the uniform conversion of titanium to titanium dioxide, all of which remained on the surface, then the weight gain corresponds to a corrosion or penetration rate of 0.007 mpy. In conventional boiler water (pH of 10 to 11, 486°F) titanium corroded at a rate of 0.0003 mpy during a 5600-hr period with no signs of pitting.[26]

Although only limited data have been acquired with titanium in water at high temperatures, much information has been obtained with titanium in considerably more aggressive environments at the Oak Ridge National Laboratory. Three pump loops constructed totally of titanium have been used to circulate uranyl sulfate solutions at temperatures of 150 to 325°C and sodium chloride or synthetic seawater up to 200°C. The former solutions were acid (pH values of 1 to 2.5) whereas the latter solutions were near neutral. After many tens of thousands of hours of circulating uranyl sulfate solutions, the appearance of the exposed titanium surface areas was comparable to that after exposure to water; the film was still thin

enough to show interference colors. Circulation of synthetic seawater at high temperature produced a deposit on the titanium (calcium carbonate, magnesium hydroxide, and calcium sulfate), but removal of the scale indicated that no detectable corrosion of the titanium had occurred. Within conventional means of measurement, the free surfaces of titanium in these loops have shown no attack even in these highly corrosive environments. Similarly, the pump impellers with peripheral velocities in excess of 100 ft/sec have also shown no general attack.

The above cited data indicate that the corrosion rate of titanium in a boiling water reactor might be extremely low and not influenced by the presence of either H_2 or O_2. Hence the quantity of corrosion products available for release and the amount of H_2 formed might be so low as to present no problems with fuel element fouling or with proper functioning of the condenser. Furthermore, titanium is not susceptible to stress-corrosion cracking in aqueous chloride environments. In pressurized water reactors the same considerations apply. Even though it has been concluded that a stainless steel or Inconel system may be adequate, a titanium system would generate much less corrosion product material and greatly enhance the probability of successful performance.

An additional consideration with titanium is the fact that it is resistant to oxidizing acid solutions. This means that a contaminated system could be decontaminated with relatively strong acid solutions which could not be used in stainless steel or Inconel systems. For example, titanium is resistant to mixtures of nitric and hydrochloric acids which might effectively remove radioactive materials deposited on the surfaces. After decontamination, the radioactive solution can easily be concentrated

by evaporation since the acids are volatile. Present methods of decontaminating stainless steel systems involve the use of several different solutions of non-volatile substances, disposal of which is difficult.

4.2 Production and Recombination of Radiolytic Gas in a BW-TLPR

4.2.1. Introduction and General Description

The dominant feature of boiling water reactors from the standpoint of radiolytic effects in the water is the evolution of H_2 and O_2 into the steam in the boiling region. These gases pass through the turbine with the steam and then enter the condenser. Some O_2 also remains in the water. The explanation for the gas evolution is that stripping occurs so fast that radiation-induced recombination is incomplete. The occurrence of O_2 in the water probably is due, in part, to the decomposition of H_2O_2 into O_2 and water which occurs after gas stripping, and, in part, to the occurrence of higher steady-state concentrations of H_2 and oxidants in the absence of excess H_2.

One method which can, in principle, be used to handle the radiolytic gases which enter the condenser is to dissolve them in high temperature water which is exposed to nuclear radiations. The dissolved gases recombine in the radiation field. Also, in principle, excess H_2 can be maintained in those portions of the reactor water which do not boil, and, by this means, the concentration of O_2 in those portions can be maintained at very low levels. The BWR design described by Fraas[1] is very well suited for accomplishing radiolytic gas recombination by this method and for maintaining excess H_2 in the reactor water. The core in this BWR is such that only about 2% and 0.5% of the fast neutron and gamma energy, respect-

tively, are absorbed in boiling water. The remainder of the water within the core and reflector does not boil. The designs of the condenser and feed pumps are such that large quantities of gas can be entrained in the condensate scavanged from the condenser and pumped back into the reactor. The increase in pressure in passing through the pump would be sufficient to put the gas back into solution. It is expected that the amount of gas in the feed stream can be 30 cm^3 (STP) or more per kilogram of water.

The proposed recombination method is then one in which the radiolytic gases are returned from the condenser to the core calandria where radiation effects recombination of the dissolved gases before the coolant reenters the fuel element cooling channels. Excess H_2 is added to the system at the start and maintained during operation to promote rapid recombination of O_2 and H_2 within the calandria and succeeding flow passages, and to insure that low, steady-state concentrations of O_2 and H_2O_2 prevail in the coolant entering the fuel element cooling channels, and in the coolant within the reflector and certain other portions of the high pressure system. Maintenance of the excess H_2 concentration in the reactor water is accomplished by recirculating H_2 from the condenser back into the reactor in the same way that the radiolytic gases are recirculated.

The amount of excess H_2 required for the purposes mentioned above is estimated to be in the range of 8 to 30 cm^3 (STP) per kilogram of feed water depending upon (1) the levels of O_2 and H_2O_2 concentrations which are acceptable in the reactor water, (2) the concentrations of impurities of the kinds which interfere with the radiation-induced recombinations of H_2 and O_2, and (3) the fraction of the H_2 which is stripped from the water during passage through the fuel element cooling channels. In our consider-

ations of the feasibility of this recombination method, we have assumed that 30 cm^3 H_2 (STP) per kilogram of feed water will be needed. This assumption is based on a prior assumption that all of the H_2 will be stripped from the water in the fuel element cooling channels, and on the results of analyses which indicate that the resulting H_2 concentration in the reactor water should produce low levels of O_2 and H_2O_2 concentrations even when the water contains impurities at concentrations which are somewhat above those considered to be likely. It may be noted that the pressures required to hold the H_2 in solution are small relative to reactor operating pressures. A concentration of 30 cm^3/kg corresponds to a dissolved H_2 pressure of about 27 psia at 165°F and to 11 psia at 410°F. It may also be noted that some of the excess H_2 would be formed during the initial corrosion of structural metals. The remainder, if any, could be added as H_2 gas. Any H_2 in excess of the required amount could be removed during operation by injecting a calculated amount of H_2O_2 or O_2 into the system.

Analysis indicates that the excess H_2 will not eliminate O_2 evolution into the steam within the fuel element cooling channels. In our considerations, we assumed that all of the O_2 formed in water in these channels is evolved, and that the rate of O_2 injection into the condenser equals the rate of formation in the water within these channels. In practice, a lesser rate would be expected since some recombination of O_2 and H_2 within the water and within the steam would be expected.

An overall description of the proposed system for the 100 Kwe reactor is given below.

Assuming, as mentioned above, that radiolytic gases are stripped into the steam as fast as they are formed in the fuel channels and that no re-

combination occurs in the steam, the rate of introduction of O_2 into the condenser will be about 0.4 cm^3 (STP)/sec, corresponding to about 2 ppm of O_2 in the entering steam. The concentration of hydrogen in the steam entering the condenser will be about 2.8 ppm when the concentration in the feed water is 30 cm^3/kg. It may be noted that the mixture of H_2 and O_2 in this assumed case is comprised of 95% H_2 and 5% O_2 so that the mixture is non-flammable even if not diluted by steam.

The radiation induced combination of H_2 and O_2 which is utilized in these considerations is that which proceeds when the gases are dissolved in water. It is assumed that the H_2 and O_2 which are in the feed return will dissolve before the feed enters the calandria (the validity of this assumption must be verified experimentally). Then, in the calandria, the dissolved O_2 is rapidly converted to water by reaction with dissolved H_2 under the action of the prevailing radiation fields. A steady-state concentration of radiolytic products will form in which the concentrations of O_2 and H_2O_2 will be the low values expected when excess H_2 is present. If the gases did not dissolve until after passage through the calandria, the O_2 would still be recombined before it could enter the fuel element cooling channels. However, in this case, we would need assurance that the flow passages within the calandria are such that gas pockets would not form there.

Upon leaving the calandria, the coolant mixes with that recirculated from the expansion tank. An appreciable reduction in the concentration of excess H_2 results from this mixing. For example, if all of the H_2 passing through the core is stripped into the steam, the recirculating water will contain no H_2, and the mixing will result in an approximately ten-fold

reduction in concentration of excess H_2. However, the resulting H_2 concentration of about 3 cm^3/kg will suffice to effect low steady-state concentrations of O_2 and H_2O_2 in the water passing into the fuel element cooling channels.

It may be noted here that the recirculating water returning from the expansion tank will probably contain O_2 from radiolytic H_2O_2 which formed in the fuel element cooling channels but did not decompose until after reaching the expansion tank. The maximum amount of O_2 which could recirculate in this way is less than 0.4 cm^3/sec, that is, less than the previously mentioned value for the maximum rate of oxygen formation in the channels. No recombination problem is presented by this recirculating oxygen since the concentration of excess hydrogen is still sufficient to insure rapid recombination of oxygen and hydrogen.

About 25% of the flow from the feed stream passes through the reflector,[1] and, accordingly, O_2 and excess H_2 are introduced into the reflector water. No problem arises from this O_2 since the O_2 will combine with the H_2 under the prevailing radiation fields, and steady-state concentrations of oxidants will be low. In the event that the corrosion of the material of the pressure vessel is sensitive to the presence of O_2 in the water, the flow passages will be arranged so that recombination occurs before the entering water reaches the walls of the pressure vessel.

Methods and information employed in evaluating this proposed recombination system are described in following sections.

4.2.2 Yields of Radiolytic Species at 200-250°C

The yields of radiolytic species in water are usually expressed as G-values, that is, as the number of a species formed in homogeneous distribu-

tion per 100 ev of radiation energy absorbed. The initial products are formed in heterogeneous distribution and are thought to be,

$$e^-_{aq},\ OH,\ H \text{ and } H^+.$$

These products interact as they diffuse, and the species which appear in homogeneous distribution are, for β-γ rays,

$$e^-_{aq},\ H,\ OH,\ H_2,\ H_2O_2 \text{ and } H^+.$$

The product species for fast neutrons include these and, in addition, HO_2. Oxygen is formed in further interactions of these products. The effects of gammas and fast neutrons are believed to be basically the same. They differ with respect to the size of the heterogeneous regions and of the density of radicals therein. The proton recoils from fast neutron collisions form dense tracks of radicals, while β and γ radiations form small spheres or spurs of radicals. A greater number of radical interactions occurs in the proton tracks and, accordingly, the ratio of molecular to radical products in homogeneous distribution is greatest for the proton recoils. The HO_2 is formed in secondary reactions between radicals and molecules.[27]

Since the G-values depend upon the amounts of interactions between radicals while they remain in heterogeneous distribution, and since reaction rates are temperature dependent, it might be thought that G-values would change with temperature. However, it has been shown by Hochanadel[28] that this is not the case for gamma yields. From experimental results at 200 and 250°C, he concluded that the G-values at these temperatures are not substantially different from those at room temperature. We speculate that the explanation for this is that the temperature effects on reaction

rates are substantially counteracted by temperature effects on diffusion into homogeneous distribution. That is, increases in temperature increase the number of reactions occurring in a given time but they also decrease the time available for reactions within the spurs. For neutrons, there is no direct experimental information on effects of temperature on yields. However, we believe it is reasonable to assume that these yields in pure water are also substantially independent of temperature since the processes occurring within the heterogeneous distributions are basically the same for neutrons and gamma rays.

As might be expected, the G-values can be altered by solutes which react with radicals while they are in heterogeneous distribution.[27] Hydrogen peroxide, O_2 and H_2 react with radicals, and they can alter effective yields if they build up to sufficiently high concentrations in solution. In practice, gamma yields at room temperature are not affected appreciably by H_2O_2 or O_2 below concentrations of about 10^{-3} m. Still greater concentrations of H_2 are required to alter yields.[27] As discussed later, the concentrations of H_2O_2 and O_2 expected in the BW-TLPR are less than 10^{-5} m. Accordingly, even with much higher reaction rate constants at 200 to 250°C, the yields will not differ significantly from those in pure water. Neutron yields are more susceptible to alteration by solutes.[27] For example at 10^{-4} m H_2O_2 plus O_2, the effective $G_{e^-_{aq}}$ may be higher than that in pure water while the effective yield of that H_2 which forms from reactions between e^-_{aq} may be somewhat less (analyses described in Ref. 27 indicated that G_{H_2} equals about 1.3 in pure water and 1.1 at H_2O_2 plus O_2 equal 10^{-4} m). In the BW-TLPR, the increases in rate constants will tend to counteract any effects of the lower concentrations of H_2O_2 plus O_2. Ac-

cordingly, we believe that the G-values for neutrons at 200 to 250°C in the BW-TLPR will be approximately the same as those previously evaluated for reactor neutrons at H_2O_2 plus O_2 concentrations of 10^{-4} m at room temperature.[27]

The list of G-values considered applicable to the BW-TLPR is set forth in Table 1. The list was taken from Ref. 27 where the sources of the values were discussed. The G-values for neutrons were evaluated for room temperature solutions containing about 10^{-4} m H_2O_2 plus O_2. Those for γ-rays were for room temperature solutions containing less than 10^{-3} m H_2O_2 plus O_2.

4.2.3 Rates of Formation of Radiolytic Species in the BW-TLPR

Calculated values for the rates of H_2 formation in the fuel channel water for each of the BW-TLPR reactors are listed in Table 2, line 18. The O_2 rates are not listed but are equal to one-half the H_2 rates. Average rates of formation of each of the radiolytic species in the BW-TLPR cores are listed in line 19. Values for other reactor parameters used in these calculations or in some other sections of this report are included in the table. Information on reactor parameters used in this table was obtained from Ref. 1.

4.2.4 Interactions of Radiolytic Species

4.2.4.1 General

Reactions which occur among the radiolytic species at room temperature and the rate constant for each reaction are listed in Table 3. Estimated activation energies at 25 to 100°C are also listed. This table was taken from Ref. 27 where the sources of information and the evaluation

TABLE 1

G-VALUES FOR RADIOLYTIC SPECIES IN GW-TLPR

Specie	G-Value		
	Gamma	Neutron	Average[a]
H_2	.44	1.12	0.78
$H + e_{aq}$	2.86	0.72	1.79
e^-_{aq}	2.31	0.36	1.33
H	0.55	0.36	0.46
H_2O_2	0.70	1.00	0.85
OH	2.34	0.47	1.41
HO_2	0	0.17	0.09

a. Average for system in which the rates of deposition of energy by neutrons and gamma rays are equal.

Table 2

INFORMATION RELEVANT TO ESTIMATING THE EXTENT OF RADIOLYSIS IN BW-TLPR AND RATES OF PRODUCTION OF RADIOLYTIC SPECIES[a]

1	Reactor power (electrical)Kwe	30	100	500	1500
2	Reactor power, thermal (Mw)	0.22	0.56	2.5	7.0
3	Fast neutron power (w)	5.6×10^3	1.4×10^4	6.4×10^4	1.8×10^5
4	γ-ray power (w)	1.5×10^4	3.8×10^4	1.7×10^5	4.8×10^5
5	Water in calandria, (lb) (ℓ, 415°F)	70 (32 kg) 38	70 (32 kg) 38	180 (82 kg) 98	420 (190 kg) 230
6	Water in coolant channels (lb)	0.8 (0.36 kg)	0.8 (.36 kg)	2.5 (1.1 kg)	7.5 (3.4 kg)
7	Fraction of water in channels	0.011	0.011	0.014	0.018
8	Fraction of fast neutron energy in channels	0.017	0.017	0.021	0.027
9	Neutron power in channel water (w)	9.4×10	2.4×10^2	1.3×10^3	4.7×10^3
10	Volume fraction of Metal in core	0.037	0.037	0.041	0.051
11	Weight of Zr-2 in core (kg)	11	11	33	102
12	Volume fraction of UO_2	0.085	0.085	0.095	0.12
13	Weight of UO_2 (kg)	40	40	115	360
14	Total weight in core (kg)	82.6	82.6	230	653
15	γ-ray power density (w/g average in core)	0.18	0.46	0.75	0.73
16	γ-ray power in channel water (w)	66	170	860	2,500
17	Neutron power density in water (w/g average)	0.17	0.44	0.78	0.92
18	Rate of H_2 production in channel water (cc/sec,(STP)) neutrons γ-rays total	 0.25 0.07 0.32	 0.63 0.17 0.80	 3.5 0.88 4.4	 12.0 2.6 14.6
19	Rate of production of radiolytic species in calandria (M/sec/kg)				
	A^b H_2 neutrons		5.1×10^{-5}		10.7×10^{-5}
	γ's		2.1×10^{-5}		3.4×10^{-5}
	total		7.2×10^{-5}		14.1×10^{-5}
	B^b OH neutrons		2.2×10^{-5}		4.5×10^{-5}
	γ's		11.3×10^{-5}		18.0×10^{-5}
	total		13.5×10^{-5}		22.5×10^{-5}
	C^b H_2O_2 neutrons		4.6×10^{-5}		9.6×10^{-5}
	γ's		3.4×10^{-5}		5.3×10^{-5}
	total		8.0×10^{-5}		14.9×10^{-5}
	F^b e^-_{aq} neutrons		2.4×10^{-5}		5.1×10^{-5}
	γ's		10.2×10^{-5}		16.1×10^{-5}
	total		12.6×10^{-6}		21.2×10^{-5}
	M^b H neutrons		0.9×10^{-5}		1.8×10^{-5}
	γ's		3.5×10^{-5}		5.6×10^{-5}
	total		4.4×10^{-5}		7.4×10^{-5}
20	Vapor flow at outlet (kg/sec)	.11	.26	1.2	3.3
21	Liquid flow at outlet (kg/sec)	.95	2.4	10.8	29.7
22	Total liquid flow leaving core (kg/sec)	1.06	2.7	12.0	33.0

a. Reactor parameters taken from Ref. 1

b. Symbol for rate of production of particular species as indicated.

TABLE 3

INTERACTIONS OF RADIOLYTIC PRODUCTS OF WATER, AND RATE CONSTANTS AND ASSUMED ACTIVATION ENERGIES FOR REACTIONS

Reaction Number	Reaction	Rate Constants at or near 25°C (sec^{-1}, M^{-1}, ℓ)	Assumed Activation Energy (kcal/mole)
8	$e^-_{aq} + O_2 \rightarrow O_2^-$	1.9×10^{10}	3
9	$e^-_{aq} + H_2O_2 \rightarrow OH + OH^-$	1.2×10^{10}	3
11	$H + O_2 \rightarrow HO_2$	2×10^{10}	3
12	$H_2 + OH \rightarrow H + H_2O$	4.5×10^{7}	7
14	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	4.5×10^{7}	4.5
15	$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$	3.7	20
16	$2HO_2 \rightarrow H_2O_2 + O_2$	2.7×10^{6}	5
16b	$O_2^- + O_2^- \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^-$	1.7×10^{7}	5
18	$OH + HO_2 \rightarrow H_2O + O_2$	4×10^{9}	3
18b	$OH + HO_2 \rightarrow H_2O_3$	1.1×10^{10}	3
20	$OH + OH \rightarrow H_2O_2$	4×10^{9}	3
21	$H + H_2O_2 \rightarrow H_2O + OH$	4.4×10^{7}	4.5
22	$e^-_{aq} + H^+ \rightarrow H$	2.3×10^{10}	3
23a	$e^-_{aq} + HO_2 \rightarrow H_2O_2$	2×10^{10}	3
23	$H + HO_2 \rightarrow H_2O_2$	2×10^{10}	3
26	$e^-_{aq} + e^-_{aq} \xrightarrow{2H_2O} H_2 + 2OH^-$	5×10^{9}	3
27	$e^-_{aq} + OH \rightarrow OH^-$	3×10^{10}	3
28	$H + H \rightarrow H_2$	1.3×10^{10}	3
29	$H + OH \rightarrow H_2O$	2.5×10^{10}	3
30	$e^-_{aq} + H \xrightarrow{H_2O} H_2 + OH^-$	3×10^{10}	3

methods were discussed. It is reasonable to assume that the same reactions occur at 200 to 250°C. However, it is probable that rate constant values obtained by extrapolation to 200 or 250°C would be seriously in error because of the long extrapolations and because of possible changes in the chemical nature of a species. Along these lines, it may be mentioned that the majority of the HO_2 will probably be undissociated at 200 and 250°C because of an expected low ionization constant for this species at these temperatures.[27] Also, reaction 15 is believed to be important at 200 and 250°C relative to other reactions of HO_2 and H_2O_2.[28] This indicates that the rate constant is greater than the value found by extrapolating the 25°C value using the listed activation energy.

When all of the radiolytic products remain in solution, the interactions lead to the reformation of water and to formation of a steady-state in which the rates of formation and disappearance of a species are equal.[27] As discussed more fully below, the steady-state amounts of decomposition of water into H_2 and H_2O_2 plus O_2 are affected by the presence of excess H_2or O_2 or H_2O_2, and, also when the H_2 and O_2 concentrations both exceed the steady-state amounts, rapid recombination of these species takes place.

4.2.4.2 Effect of Excess H_2 on Radiation Decomposition.

In theory and practice, the presence of excess H_2 in solution reduces the amount of water decomposed at the steady-state.[29] This action can be explained by noting in Table 3 that molecular products are converted to water by reaction with radicals and that chain reactions occur. However, interactions of radicals also occur in which the net result is formation of H_2O without any change in the number of molecular species in solution. Notably, reactions of OH with species other than H_2 lead to removal of

radicals. For example, the net result of reaction 14 followed by reaction 16 is the equivalent of reaction 18,

$$18.\quad HO_2 + OH \rightarrow O_2 + H_2O.$$

This reaction would be followed by reaction 8 or 11 to give, as a net result, the equivalent of reaction 27 or 28,

$$27.\quad e^-_{aq} + OH \xrightarrow{H^+} H_2O,$$

$$28.\quad H + OH \rightarrow H_2O.$$

Reaction 14 followed by reaction 15 does not alter the radical concentration and has the net effect of decomposing H_2O_2 into O_2 and H_2O. When excess H_2 is present in sufficient concentrations, all of the OH react with H_2 according to reaction 12,and the above mentioned reactions in which radicals are lost are eliminated.

Estimates of the concentrations of excess H_2 necessary to minimize decomposition at 200 and 250°C are required for evaluations of the proposed method of recombination in the BW-TLPR. To obtain these estimates for the higher temperatures, we note that, according to the mechanism described above, the maximum effect of excess H_2 occurs when reactions of OH with species other than H_2 are negligible compared to the reaction with H_2. This will be the case at some H_2 concentration above which the steady-state amount of decomposition of water does not change significantly. We also note that the steady-state concentrations of the species other than H_2 which can react with OH are dependent upon radiation intensity, increasing approximately as the square-root of intensity. Now from available information on the concentration of H_2 required to produce negligible concentrations of O_2 in pressurized water reactors we can estimate the concen-

trations required in the BW-TLPR.

It has been reported[30] that O_2 is not detected in pressurized water reactors at 500°F when the H_2 concentration is above 5 cm^3/kg. This statement was made in a report on the Shippingport PWR and presumably applies to that reactor. From reported information on amounts of metal and water in the Shippingport PWR core[31] we have estimated that the average neutron power density in the core water is about 2.5 w/g at full power, 225 Mw, and that the average gamma ray intensity in the seed region is about 2.2 w/g at this power. The ratio of neutron to gamma energy deposition rates in the PWR is then about the same as that in the TLPR (Table 2), while the intensities are higher than those in the TLPR by factors ranging from about fifteen for the 30 Kwe reactor to three for the 1500 Kwe reactor. Accordingly, it is expected that, for any of the TLPR reactors, H_2 concentrations of about 3 cm^3/kg will hold oxidant concentrations to a minimum in those non-boiling portions where the temperature is near 500°F.

The temperatures within that portion of the BW-TLPR where the H_2 concentrations will be about 3 cm^3/kg is actually 485°F (Fig. 1). It is reasonable to assume that the small differences between rate constants at 485 and 500°F will not significantly alter the excess H_2 requirements.

The lower temperature (345 to 415°F) water in the BW-TLPR will contain excess H_2 at a concentration of 30 cm^3/kg. On the bases of available information[32] on excess H_2 effects in the ORR pressurized water loop, we conclude that this concentration is more than sufficient. The experience[32] in that loop showed that H_2 concentrations as low as 6 cm^3/kg maintained O_2 concentrations at 0.01 to 0.02 ppm with water temperatures in the range 300 to 380°F. Details regarding the radiation intensities in the loop were

not available at the time this was written but we believe that the intensities of neutrons and gammas were comparable to those in the BW-TLPR reactors.

4.2.4.3 Effect of Excess O_2 or H_2O_2 on Radiation Decomposition

The effects of excess oxidant on the steady-state amount of water decomposed is the reverse of the H_2 effect, that is, the amounts of decomposition are increased. The explanation for this effect of oxidants is analogous to the explanation for the H_2 effect.

4.2.4.4 Recombination of Excess H_2 and O_2

a. Mechanism and Rates of Recombination.

Hochanadel[28] showed that, at 200 and 250°C, H_2 and O_2 are recombined by gamma radiation at constant rates which are independent of pressure, time of exposure, and temperature when both species are present in excess of steady-state concentrations. He pointed out that the observations could be explained by assuming that reactions 11, 12, 15 and 16 (Table 3) predominate when both H_2 and O_2 are in excess. With these reactions, all OH reacts with H_2 and all $H(+G_{e^-_{aq}})$ reacts with O_2. For his suggested mechanism, the $G\text{-}H_2$ should be equal to $G_H(+G_{e^-_{aq}}) + G_{OH}$. The experimental and predicted values for $G\text{-}H_2$ were in satisfactory agreement.*

Although reactor radiations were not studied, it can be shown that the expected $G\text{-}H_2$ for these is also equal to $G_H + G_{e^-_{aq}} + G_{OH}$ when the small

*The species e^-_{aq} was not differentiated from the hydrogen atom, H, at the time this was reported. However, the basic mechanism and the conclusions remain the same when the differences between e^-_{aq} and H are included in the analysis.

yield of HO_2 for neutrons is neglected. The G-values in this case are averages for the neutron and gamma components of the reactor radiations. It may be noted that net G-H_2 values are given by the above relationships. Production of H_2 and H_2O_2 during the irradiations are taken into account in the derivations.

Now using this information and also using values for the rates of generation of e^-_{aq}, H, and OH, we find for the 100 and 1500 Kwe reactors that the expected constant rates of recombination of O_2 are, respectively 3.4 and 5.7 cm^3/kg/sec. Since the expected maximum concentrations of O_2 in the feed water in these reactors are respectively, 1.5 and 2.3 cm^3/kg, the excess O_2 is combined in less than 1 sec at the constant rates. Exposure times are about 10 sec in the calandria and 30 sec in the header below the boiling channels.[1]

b. Time to Reach Constant Rates.

As described above, reactions 8, 11, 12, 15 and 16 predominate when both H_2 and O_2 are in excess. These are shown below for convenient reference.

8. $e^-_{aq} + O_2 \xrightarrow{H_2O} HO_2 + OH^-$

11. $H + O_2 \rightarrow HO_2$

12. $H_2 + OH \rightarrow H + H_2O$

15. $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$

16. $2HO_2 \rightarrow H_2O_2 + O_2$

Order of magnitude estimates of the time required to achieve constant recombination rates were obtained as follows.

1. For any given rate of OH generation, K_B, and any given H_2 concentration, we can write,

$$\frac{d(OH)}{dt} = K_B - k_{12}(OH)(H_2). \qquad (A)$$

Integrating with (OH) equal zero at zero time,

$$(OH) = \frac{K_B}{k_{12}(H_2)}(1-\exp -k_{12}(H_2)t). \qquad (B)$$

Eq. B shows that (OH) will be within 5% of the steady-state concentration when,

$$t = \frac{3}{k_{12}(H_2)}. \qquad (C)$$

Now at 200-250°C we can expect that the value of k_{12} will exceed 10^8 sec^{-1}, M^{-1},kg. Then for $(H_2) = 10^{-4}$ M,kg^{-1}, ($2cm^3/kg$) the time to reach the approximate steady-state (OH) is 3×10^{-4} sec or less.

2. Similarly, for any given rate of H formation, K_F, and any given (O_2), we find from reaction 11 that the time to reach the approximate steady-state (H) is,

$$t = \frac{3}{k_{11}(O_2)}. \qquad (D)$$

We can expect that the value of k_{11} will exceed 5×10^{10} sec^{-1},M^{-1},kg at 200-250°C. Then for $(O_2) = 5 \times 10^{-7}$ M/kg, (.011 cm^3/kg) the approximate steady-state (H) and (e^-_{aq}) is reached in 10^{-4} sec or less.

3. From the above we can conclude that, effectively, OH reacts with H_2 and that H and e^-_{aq} react with O_2 as fast as the radicals are formed. Then for HO_2 we can write,

$$\frac{d(HO_2)}{dt} = F + M + B - 2k_{16}(HO_2)^2 - k_{15}(HO_2)(H_2O_2) + k_{15}(HO_2)(H_2O_2) \qquad (E)$$

or

$$\frac{d(HO_2)}{dt} = F + M + B - 2k_{16}(HO_2)^2, \qquad (F)$$

where F, M and B are the rates of formation of e^-_{aq}, H and OH determined from the G-values for these species.

Integrating with (HO_2) equal zero at zero time,

$$(HO_2) = \left(\frac{F + B + M}{2k_{16}}\right)^{1/2} \frac{[\exp[8k_{16}(F+B+M)]^{1/2}\ t - 1]}{[\exp[8k_{16}(F+B+M)]^{1/2}\ t + 1]} \qquad (G)$$

Again (HO_2) will be within 95% of the steady-state concentration when,

$$t = \frac{3}{[8k_{16}(F+B+N)]^{1/2}}. \qquad (H)$$

The value of k_{16} will likely be 10^7 or greater at 200-250°C. Using this value together with values of F+B+M for the 100 Kwe reactor from Table 2, we find that the approximate steady-state (HO_2) is reached in 0.02 sec or less.

4. Finally, the rate expression for (H_2O_2) is,

$$\frac{d(H_2O_2)}{dt} = C + k_{16}(HO_2)^2 - k_{15}(HO_2)(H_2O_2), \qquad (I)$$

where C is the rate of formation of H_2O_2 determined from $G_{H_2O_2}$. Assuming that (HO_2) is at a steady-state and substituting from G,

$$\frac{d(H_2O_2)}{dt} = C + \frac{F}{2} + \frac{M}{2} + \frac{B}{2} - \frac{k_{15}}{\sqrt{2k_{16}}}(H_2O_2)\sqrt{F+B+M} \qquad (J)$$

Integrating with (H_2O_2) equal to zero at zero time,

$$(H_2O_2) = \frac{C + \frac{F}{2} + \frac{M}{2} + \frac{B}{2}}{\frac{k_{15}}{\sqrt{2k_{16}}}\sqrt{F+B+M}}\left(1 - \exp - \frac{k_{15}}{\sqrt{2k_{16}}}\ t\sqrt{F+B+M}\right) \qquad (K)$$

As before, the time at the approximate steady-state (H_2O_2) is,

$$t = \frac{3}{\frac{k_{15}}{\sqrt{2k_{16}}}\sqrt{F+B+M}} \qquad (L)$$

The minimum value of $k_{15}/\sqrt{2k_{16}}$ can be evaluated from the reported results of Hochanadel.[28] He found that the (H_2O_2) at the steady-state was $< 10^{-6}$ M/kg. Using this and the values for C, F, M and B for his experimental conditions we find, using Eq. K, that, $k_{15}/\sqrt{2k_{16}} > 2.8 \times 10^3$.

Using this value and values for F, M and B for the 100 Kwe reactor in Eq. L leads to the result that the approximate steady-state (H_2O_2) is reached in 0.06 sec or less.

5. The results of the above considerations indicate that reaction 15 is the limiting step in the approach to steady-state, and that the time to reach the approximate constant rate of combination of H_2 and O_2 will be 0.08 sec or less in the 100 Kwe reactor. This time is negligible in comparison with the available exposure times in BW-TLPR. Accordingly, it can be assumed that combination of H_2 and O_2 in BW-TLPR proceeds at steady-state rates until the excess O_2 is removed.

c. Effects of Solution Impurities on Recombination.

Some impurity ions can interfere with the radiation recombination of radiolytic species by reacting with and thus removing the radicals which bring about the recombination.[29] The H and/or e^-_{aq} may reduce an impurity and the OH may oxidize it back as illustrated in reactions 24, 25 and 26.

24. $M^{+n} + H \rightarrow M^{+(n-1)} + H^+$

25. $M^{+n} + e^-_{aq} \rightarrow M^{+(n-1)}$

26. $M^{+(n-1)} + OH \rightarrow M^{+n} + OH^-$

Because of insufficient information on the kinetics of impurity ion reactions at high temperatures and also insufficient information on the details of thermal and radiation reactions of the radiolytic products of water at high temperatures, we cannot make close estimates of the effects of a given ion on rates of recombination of excess H_2 and O_2 or on steady-state concentrations. However, we have made estimates of the effects on recombination of excess H_2 and O_2 of an impurity which undergoes reactions 24-26 with high rate constants. These estimates used the derived expressions A-13 and A-15.

$$\text{A-13.} \quad X = \frac{P(H_2)}{(H_2) + \frac{2k_{26}}{k_{12}} r},$$

$$\text{A-15.} \quad \frac{T-r}{r} = \frac{k_{26}X((O_2)+T-r)}{k_{12}(H_2)} \left(\frac{F}{k_8/k_{25}} + \frac{M+X}{k_{11}/k_{24}} \right),$$

where

X = rate of reaction of H_2 to form H_2O,

r = concentration of reduced form of impurity, $M^{+(n-1)}$,

T = total concentration of impurity,

$P = \frac{3B+2C+F+M}{2}$

B,C,F,M = rates of generation of OH, H_2O_2, e^-_{aq}, H in radiolysis evaluated from G-values,

k_n = rate constant for reaction n.

The derivations of these expressions are described in the Appendix. Briefly, it was assumed that the following reactions, in addition to 24-26, occur in the presence of excess H_2 and O_2.

8. $e^-_{aq} + O_2 \xrightarrow{H_2O} HO_2 + OH^-$

11. $H + O_2 \rightarrow HO_2$

12. $H_2 + OH \rightarrow H + H_2O$

15. $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$

16. $2HO_2 \rightarrow H_2O_2 + O_2$

The justification for this assumption was discussed in sections 4.2.4.2 and 4.2.4.4a. It was also assumed that the concentrations of H_2 and O_2 remain constant at given assumed values and that concentrations of other species are at steady-state values (which would, of course, vary with assumed T, (H_2) and (O_2)).

Equations A-13 and A-15 show that X is dependent upon several rate-constant ratios. These ratios and the values assumed for our estimates are listed below.

	Assumed values	
	room temperature	200-250°C
k_8/k_{25}	1	1
k_{11}/k_{24}	1	1
k_{26}/k_{12}	200-400	100

At room temperature, k_8 and k_{11} are high values (Table 3) which are near those expected for diffusion controlled reactions. In effect then, we assume that 24 and 25 are also diffusion controlled reactions with rate constants and activation energies equal to those of the diffusion controlled reactions 8 and 11. Assuming that reaction 26 is also diffusion controlled, the expected ratio of k_{26} to k_{12} equals several hundred at room temperature since the value of k_{12} is 4.5×10^7 (Table 3). However, the activation

energy for reaction 12 is probably greater than that of diffusion controlled reactions[27] so that it seems conservative to assume a value of 100 for k_{26}/k_{12} at 200-250°C. Using these assumed values and making appropriate substitution, Eq. A-13 becomes,

$$\text{A-16.} \quad X = \frac{P(H_2)}{(H_2)+200r} ,$$

and Eq. A-15 becomes,

$$\text{A-19.} \quad \frac{T-r}{r} = \frac{100P[(O_2)+T-r]}{(M+F)[(H_2)+200r]+P(H_2)}.$$

Values of X and r were found from these equations for the 100 and 1500 Kwe reactors assuming T equal to 10^{-5} m and assuming several values of (H_2) and (O_2) of interest in our evaluation. Values of B, C, F and M were taken from Table 2. The calculated X values are shown in Figs. 2-4. Also shown are values for the net rate of O_2 reaction which are given by (X-A)/2 (A equals rate of generation of H_2 in radiolysis). Corresponding values of r are shown in Fig. 5.

The calculated X values for the 1500 Kwe reactor indicate that 10^{-5} M/kg of an active impurity in the presence of 1.3×10^{-3} m H_2 (30 cm^3/kg) does not prevent rapid recombination of excess O_2 even when the concentration of O_2 is < 10^{-6} m (< 0.03 ppm). The rate of recombination does decrease with decreasing O_2 but the rate at very low (O_2) is still sufficient to recombine the O_2 returned from the condenser within a few seconds (< 2 sec for the amount of O_2 listed in Table 2). At the lower H_2 concentration of 1.3×10^{-4} m, the assumed impurity does prevent recombination of excess O_2 when the O_2 concentration is reduced to about 6×10^{-6} m (0.2 ppm). However, a rapid recombination occurs at higher O_2 concen-

trations, and, accordingly, a leveling off at about 6×10^{-6} m is indicated. In order to judge the significance of these findings we note that the H_2 concentration in the header below the fuel element cooling channel was assumed (section 4.2.1) to be 1.3×10^{-4} m (3 cm^3/kg). Assuming that the O_2 concentration within this water is 6×10^{-6} m and that the O_2 is stripped from the water within the cooling channels without any recombination, the amount of O_2 entering the condenser would be about double that listed in Table 2. However, this does not present any recombination problems since the fractional increase in gas volume within the condenser would be small and since the additional O_2 would easily be recombined within the calandria where the excess H_2 is 30 cm^3/kg. However, the gas mixture in the condenser would be flammable if undiluted by steam.

The effects of the assumed impurity in the 100 Kwe reactor are comparable to those described for the 1500 Kwe reactor.

In summary, our considerations indicate that appreciable concentrations of impurities will not seriously interfere with either the radiation induced recombination of the O_2 returned to the reactor with the feed stream or with the maintenance of low O_2 in the reflector if the concentration of excess H_2 in the feed stream is about 30 cm^3/kg. It is likely that the amount of O_2 entering the condenser would increase with buildup of impurities. Verification will be required of the effects of the impurities which buildup in a given operating reactor.

4.2.5 Alternative Method of Recombining Radiolytic Gas

In the event that the radiation recombination method does not prove feasible for some reason, the alternative method of recombining the gases over a platinum catalyst remains available. The feasibility of using this

method of recombination of radiolytic gases in a small boiling water reactor was considered by Haroldsen.[33] He concluded that it was feasible and that catalyst beds were moderate in size, for example, a bed 3 in. in diameter and 12 in. long was suggested for handling a water decomposition rate of 5 lb/day. For comparison, if no recombination occurs in the 100 Kwe reactor, the rate of decomposition will be about 7.5 lb/day, and, if complete recombination occurs everywhere but in the channels, the maximum decomposition rate will be about 0.12 lb/day.

4.2.6 Summary of Conclusions

There is very little question that the proposed method of recombination will perform satisfactorily providing:

a. That about 30 cm^3 H_2(STP) per kg feed water can be scavanged from the condenser and entrained in the feed water.

b. That the gas in the feed water dissolves before it enters the calandria. It is possible that it would also perform satisfactorily if the gases were not dissolved until after entering the calandria. However, this possibility was not analyzed in detail.

c. That impurity ions which accumulate in the water do not seriously affect the radiolytic recombination.

Analyses showed that impurities at fairly high concentrations do not seriously affect the recombination. However, experimental work will be needed to determine the impurity concentrations which develop in an operating reactor and to establish the effects of these impurities on radiolysis. It will also be necessary to establish that gas can be circulated

as proposed.

In the event that the radiation recombination method does not prove feasible, the method by which the gases are recombined over a platinum catalyst remains available. Recombination in a small boiling water reactor using this method has been considered by others and is believed to be feasible.

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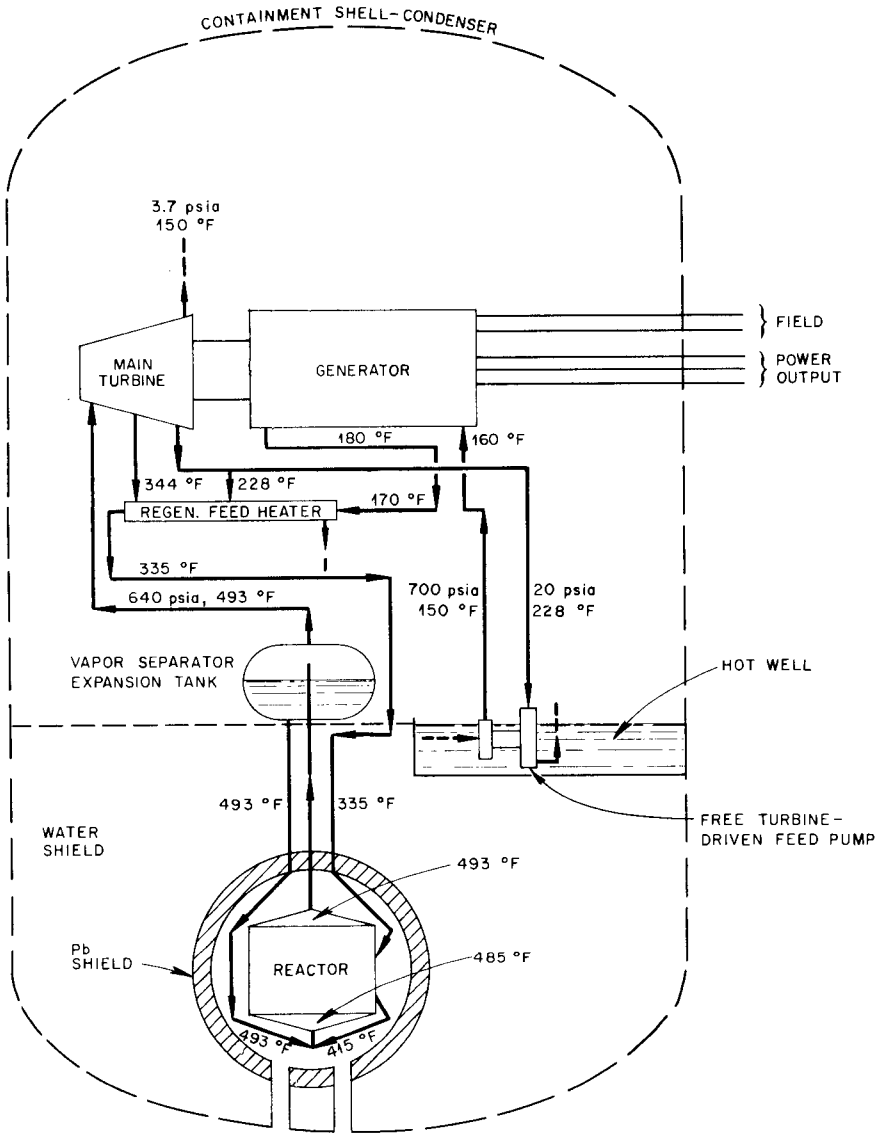

Fig. 1. Boiling Water TLPR.

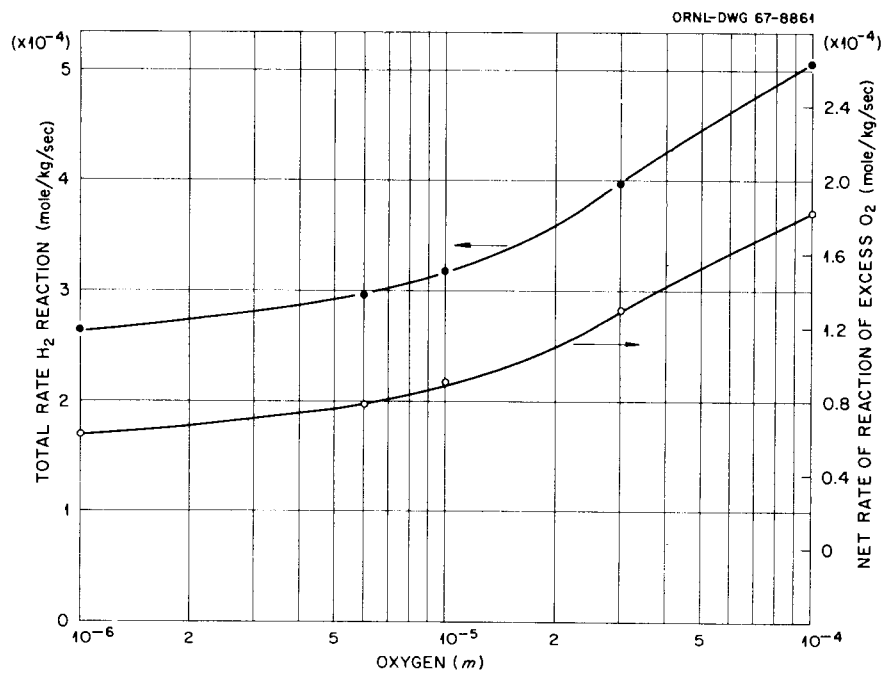

Fig. 2. Total Rate of H_2 Reaction and Net Rate of Reaction of Excess O_2, 1500 Kwe Reactor. Excess H_2 Equal 1.3×10^{-3} m.

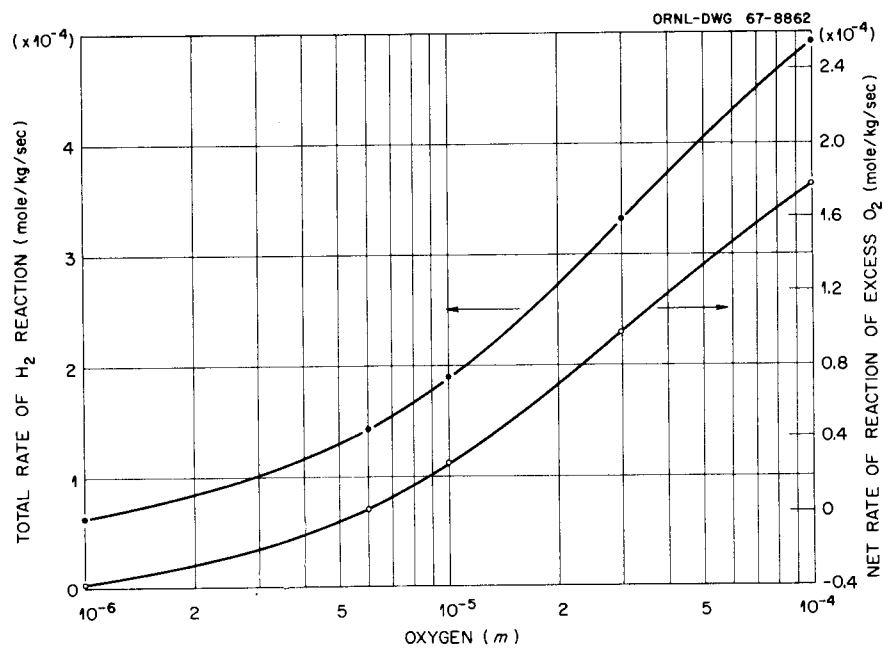

Fig. 3. Total Rate of H_2 Reaction and Net Rate of Reaction of Excess O_2, 1500 Kwe Reactor. Excess H_2 Equal 1.3×10^{-4} m.

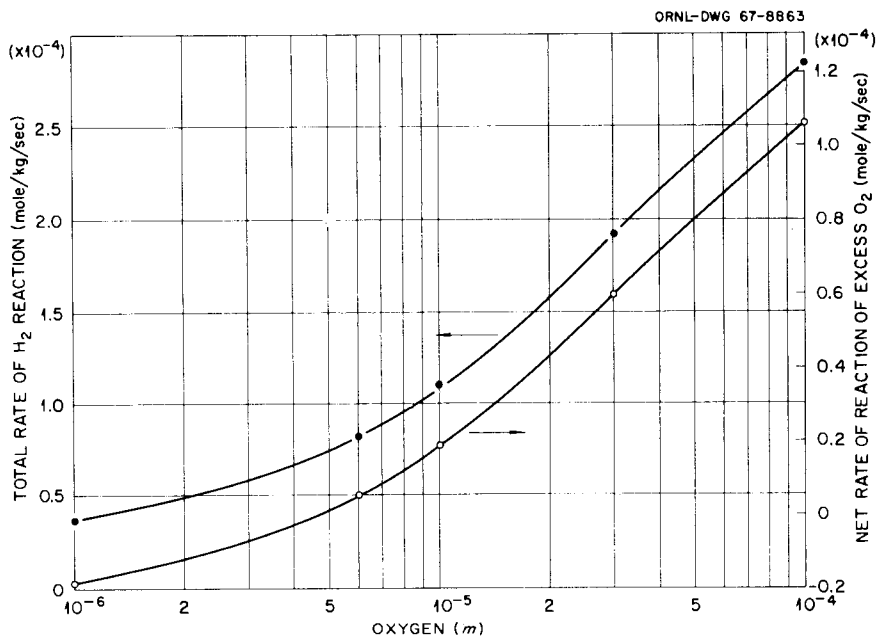

Fig. 4. Total Rate of H_2 Reaction and Net Rate of Reaction of Excess O_2, 100 Kwe Reactor. Excess H_2 Equal 1.3×10^{-4} m.

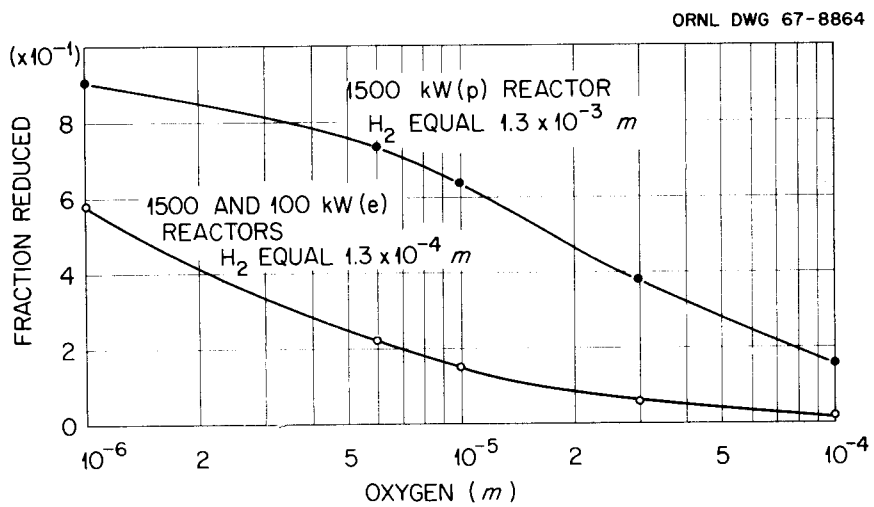

Fig. 5. Fraction of Impurity Reduced.

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APPENDIX

Derivation of Equations A-13 and A-15

Reactions

8. $e^-_{aq} + O_2 \xrightarrow{H_2O} HO_2 + OH^-$

11. $H + O_2 \rightarrow HO_2$

12. $H_2 + OH \rightarrow H + H_2O$

15. $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$

16. $2HO_2 \rightarrow H_2O_2 + O_2$

24. $M^{+n} + H \rightarrow M^{+(n-1)} + H^+$

25. $M^{+n} + e^-_{aq} \rightarrow M^{+(n-1)}$

26. $M^{+(n-1)} + OH \rightarrow M^{+n} + OH^-$

Nomenclature

X = rate of reaction of H_2 to form water

T = total concentration of impurity

a = concentration of oxidized form of impurity, M^{+n}

r = concentration of reduced form of impurity, $M^{+(n-1)}$

$P = \frac{3B+2C+F+M}{2}$

k_n = rate constant for reaction, n

B, C, F, M, and A = rates of generation of OH, H_2O_2, e^-_{aq}, H, H_2 evaluated from G-values for these species

Assumption

(H_2) and (O_2) remain constant at given assumed values, and concentrations of other species, except T, are at steady-state values.

For the steady-state condition, we can write Eqs. A-1 to A-6

A-1. $\frac{dr}{dt} = 0 = k_{24}(H)\ a + k_{25}\ (e^-_{aq})\ a - k_{26}(OH)\ r$

A-2. $\frac{d(HO_2)}{dt} = 0 = k_8(e^-_{aq})(O_2) + k_{11}(H)(O_2) - 2k_{16}(HO_2)^2 - k_{15}(HO_2)(H_2O_2)$

A-3. $\frac{d(H_2O_2)}{dt} = 0 = C + k_{16}(HO_2)^2 - k_{15}(HO_2)(H_2O_2)$

A-4. $\frac{d(OH)}{dt} = 0 = B + k_{15}(HO_2)(H_2O_2) - k_{12}(OH)(H_2) - k_{26}(OH)\ r$

A-5. $\frac{d(H)}{dt} = 0 = M + k_{12}(OH)(H_2) - k_{11}(H)(O_2) - k_{24}(H)\ a$

A-6. $\frac{d(e^-_{aq})}{dt} = 0 = F - k_8(e^-_{aq})(O_2) - k_{25}(e^-_{aq})\ a$

By definition, $X = k_{12}(OH)(H_2)$, so we can write

A-7. $k_{26}(OH)\ r = \frac{k_{26}}{k_{12}}\ X\ \frac{r}{(H_2)}$

Solve A-2 and A-3 to get

A-8. $k_{15}(HO_2)(H_2O_2) = 2/3C + \frac{k_8}{3}(e^-_{aq})(O_2) + \frac{k_{11}}{3}(H)(O_2)$

Rewrite A-4 and substitute from A-7 and A-8

A-9. $0 = 3B + 2C + k_8(e^-_{aq})(O_2) + k_{11}(H)(O_2) - 3X - 3X\frac{k_{26}}{k_{12}}\ \frac{r}{(H_2)}$

From A-9, A-5 and A-6

A-10. $0 = 3B + 2C + F + M - k_{25}(e^-_{aq})a - k_{24}(H)\ a - 2X - 3X\frac{k_{26}}{k_{12}}\ \frac{r}{(H_2)}$

From A-10, A-1 and A-7

A-11. $0 = 3B + 2C + F + M - 2X - 4X\frac{k_{26}}{k_{12}}\ \frac{r}{(H_2)}$

or

A-12. $0 = \frac{3B + 2C + F + M}{2} - X - 2X\frac{k_{26}}{k_{12}}\ \frac{r}{(H_2)}$

or

A-13. $$X = \frac{P}{1 + \frac{2k_{26}}{k_{12}} \frac{r}{(H_2)}}$$

Another relationship between X and r is required for solutions. From A-1

A-14. $$\frac{a}{r} = \frac{k_{26}}{k_{12}} \frac{X}{(H_2)} \left(k_{24}(H) + k_{25}(e^-_{aq}) \right)$$

Substituting from A-5 and A-6 for $k_{24}(H)$ and $k_{25}(e^-_{aq})$

A-15. $$\frac{a}{r} = \frac{k_{26}}{k_{12}} \frac{X}{(H_2)} \left(\frac{F}{\frac{k_8}{k_{25}}(O_2) + T - r} + \frac{M+X}{\frac{k_{11}}{k_{24}}(O_2) + T - r} \right)$$

Equations A-13 and A-15 were employed as described in the text.

It may be noted here that from A-13 the value of X in pure water is P. Then for the net rate of reaction of excess H_2 we have,

$$G\text{-}H_2 = X - A = P - A = \frac{3B}{2} + C + \frac{F}{2} + \frac{M}{2} - A.$$

But by material balance,

$$A = C + B/2 - F/2 - M/2.$$

Therefore,

$$G\text{-}H_2 = B + F + M.$$

This relationship was employed in the text in discussion of H_2 and O_2 recombination in pure water.