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Contents

Executive Summary.....	1
Introduction.....	2
The Formation of Hydrogen from Liquid Water by Radiation.....	4
Radiation-Induced Reactions of Water Adsorbed on Solid Surfaces.....	5
Safety Concerns Associated with Hydrogen Accumulation.....	7
Catalyzed Recombination on Solid Surfaces.....	8
Radiation-Induced Reaction of Hydrogen and Oxygen in the Gas Phase and the Effect of Nitrogen.....	10
Conclusions.....	13
Acknowledgements.....	13
Appendix by Lee Hyder.....	14
References.....	17
Additional Topical References to Hydrogen/Oxygen Reactions.....	20

Figures

Fig. 1. Possible surface reactions in the hydrogen/oxygen system.....	9
Fig. 2. Diagram of the Langmuir-Hinshelwood and the Eley-Rideal reaction mechanisms.....	10

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**Literature Search on Hydrogen/Oxygen Recombination
And Generation in Plutonium Storage Environments**

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Executive Summary

This report briefly summarizes the critical literature available on the gas phase recombination reactions of H₂ and O₂ in the presence and absence of ionizing radiation. The available literature on radiolysis of adsorbed water also is considered. A key conclusion is that substantial H₂/O₂ pressures will not be generated from radiolytic and catalytic decomposition of H₂O adsorbed on PuO₂ and associated impurities during prolonged storage in sealed containers.

Introduction

Radiolytic and catalytic generation of gases in stored plutonium-bearing materials raises the concerns of pressurizing the vessel and of creating gas mixtures that may be flammable or even explosive. The most important flammable gas in this regard is hydrogen, which can be created from radiation-induced decomposition of organic material or water or by spontaneous chemical reaction of water adsorbed on PuO_2 . In the plutonium-bearing materials proposed for long term storage, physisorbed and adsorbed water and organic materials will be minimized by calcination at 950°C . However, up to 0.5 wt% of residual water on plutonium oxide and other surfaces is permissible by both the current and proposed U.S. Department of Energy storage standard. [1, 2]

There are several reactions to consider in predicting hydrogen formation and destruction in stored radioactive materials. These reactions include: (1) radiolytic and catalytic decomposition of adsorbed moisture to produce hydrogen and oxygen, (2) gas-phase oxidation of hydrogen by oxygen in the catalytic and radiolytic environment, (3) catalytic combination of hydrogen and oxygen on solid surfaces including the surface of plutonium oxide and impurities, and (4) oxidation of atmospheric nitrogen in the radiation field, producing nitrogen oxides, solid nitrates and nitric acid.

Recent experiments have provided a basis for the observation that oxygen generally is not produced stoichiometrically with hydrogen from moisture adsorbed on plutonium oxide. [3] [4-10] The literature indicates that oxygen formed from water combines with plutonium dioxide to form the superstoichiometric oxide PuO_{2+x} . Other experiments show that a variety of non-radioactive materials can catalyze the recombination of hydrogen and oxygen. It has been proposed that plutonium oxide is an effective catalyst for H_2/O_2 recombination. [9] Recombination induced by alpha radiation also is a well established

phenomenon. Measurements of headspace gases over plutonium materials stored for up to 20 years generally show a strong depletion in any (initially present) oxygen and an enrichment in hydrogen, but no significant overpressure. [11]

This literature review was undertaken to provide a basis for evaluating H₂/O₂ generation and recombination in plutonium oxide environments. When air is present nitrogen also will enter into radiation-induced reactions. Specifically, this literature search provides a review of: (1) reactions involved in the radiolytic formation of hydrogen from liquid water, (2) radiolytic and catalytic reactions producing hydrogen from water sorbed on a solid substrate, (3) safety concerns associated with hydrogen accumulation (4) catalytic recombination of hydrogen and oxygen on solid surfaces, (5) radiation-induced recombination of hydrogen and oxygen in the gas phase, and (6) the possible involvement of nitrogen in these reactions. The focus of this brief survey is the environment created by prolonged storage of plutonium-bearing materials in sealed containers. The intent is not to provide a comprehensive evaluation of liquid water radiolysis or gas-phase hydrogen/oxygen chemistry. Only selected illustrative references are cited for the latter phenomena.

This literature review was based on several sources. The most useful source was an electronic search of radiation chemistry utilizing a database maintained by the Radiation Effects Laboratory of the University of Notre Dame.

Two additional electronic literature bases were the used: SciFinder and SciSearch SciFinder accesses years 1967-present and SciSearch accesses years 1974-present. Other on-line resources at the Los Alamos National Laboratory library were used as well. The keywords that were searched included; hydrogen-oxygen-reaction, oxidation-hydrogen, and recombination-hydrogen-oxygen. The combination of hydrogen and/or oxygen was also

searched with plutonium oxide, uranium oxide, 304 stainless steel, 316 stainless steel, KCl, CaCl₂, MgCl₂ and radiolysis. A manual search of Chemical Abstract citations since 1976 also was performed but the relatively small number of returns from the search suggested that this approach was not very effective. Many standard texts were also consulted and are listed at the end of this report. These effectively summarize the pertinent literature prior to their publication. An extensive annotated bibliography by N. A. Krohn in 1963, on the effects of radiation on heterogeneously catalyzed reactions and chemisorption, also was consulted in the literature search. [12]. Finally, the search included discussions with Dr. Jay LaVerne of the Notre Dame Radiation Effects Laboratory. In general, alpha radiation studies are heavily represented in the literature prior to the Manhattan Project. Thereafter, gamma radiation studies dominate due to the availability of reactors and convenient sealed sources.

In addition to references specifically cited in this report, additional representative references by subtopic germane to this review are presented at the end of this report.

The Formation of Hydrogen from Liquid Water by Radiation

In most published studies of liquid water radiolysis, gamma radiation was utilized. Particle beams mixed reactor radiation have been used in a few cases. [13] The irradiation of liquid water by charged particles (such as the alpha particles emitted by plutonium) produces microscopic regions along the particle pathway where a dense population of ionized and dissociated water fragments is found. In neutral water, the most important such fragments are the hydroxyl radical and the hydrated electron, H₂O⁻. This latter species has been characterized spectrometrically and is believed to consist of a negative charge that polarizes the water around it to create a hydration shell involving several water molecules. The hydrated electron and is converted to atomic hydrogen in acidic solutions: [13]



The interaction of two hydrated electrons in the dense track region is believed to be responsible for the radiolytic production of hydrogen, H_2 , from liquid water.



The presence of dissolved species that readily react with the solvated electron in the track will suppress hydrogen production. Such species are known to include nitrate, nitrite, oxygen, and other oxidizing solutes. [13] The effect of nitrate in reducing hydrogen generation during alpha radiolysis of water has been quantified by Bibler. [14]

Similar phenomena are observed with the radiolytically generated hydroxyl radical, OH . [15] Two such radicals can form hydrogen peroxide, but hydroxyl radicals also react rapidly with reducing materials such as nitrite or hydrogen gas. Back reactions of radical species with molecular radiation products in liquid water can be quite fast, and correspondingly the steady-state concentrations of hydrogen and hydrogen peroxide are generally quite low. [13] For other details of the radiation chemistry of liquid water, the reader is referred to standard texts, such as that by Spinks and Woods. [15]

Radiation-Induced Reactions of Water Adsorbed on Solid Surfaces

There is substantial literature on the effect of radiation on material adsorbed on solid surfaces, but only a few publications address adsorbed water. Much of the adsorbed water radiolysis literature is due to the work of investigators in the former Soviet Union. Of particular interest is reference, [16] where the authors divide

oxide surfaces into three categories:

1. Surfaces that generate less hydrogen from adsorbed water than would be generated from the radiolysis of liquid water. ($G=0.01$ or less, where G denotes the yield of hydrogen molecules per 100 KeV or less of absorbed energy). These surfaces generally consist of highly oxidizing materials such as MnO_2 or CrO_3 , where a reduction reaction of hydrogen or its precursors with the substrate is possible. However, the non-oxidizing compound ZnO also is placed in this low G category.
2. Surfaces that yield hydrogen with G -values of approximately 1, similar to the hydrogen yield from liquid water. The G -value for hydrogen from gamma radiolysis of liquid water is about 0.45, and from alpha radiolysis is slightly higher than 1. Compounds in category (2) include silica, titania, and oxides of nickel, copper and cadmium.
3. Surfaces where enhanced hydrogen production is observed with G values much greater than 1. These surfaces include oxides of lanthanum, magnesium, zirconium, and also aluminum and (especially) beryllium. [17, 18] Studies at Oak Ridge [19, 20] also placed silica gel in this category. The enhanced decomposition of water is attributed to efficient transfer of radiation energy absorbed by the substrate to the adsorbed water. In such cases the apparent G value for water radiolysis (in terms of energy absorbed directly by the water itself) can exceed 50. The literature suggests that this rate applies only to the strongly adsorbed water and not to weakly physisorbed layers of water. The enhanced production of hydrogen apparently involves the facile transfer of electrons through the crystal phase to the surface adsorbed water. [19, 20] This effect appears to be accentuated by elevated temperatures. Taking into account the total radiation dose adsorbed by the oxide surfaces, the G values for hydrogen production are similar to those values found with liquid water. [17-20]

Safety Concerns Associated with Hydrogen Accumulation

Two obvious concerns when dealing with gaseous hydrogen and oxygen mixtures are deflagration and detonation. For a hydrogen-oxygen mixture in a vessel with a particular geometry and surface composition, spontaneous explosion may occur at certain values of temperature and pressure. [21] Under other conditions, slower reaction outside the detonation regime occurs. The explosion limits are typically indicated by a P-T explosion diagram, where the regions in which autoignition takes place are separated (by an S-shaped curve) from the regions where no auto ignition occurs.

Factors that affect the explosion limit include (1) total pressure, (2) mixture composition, (3) temperature, (4) dimensions of the reaction vessel and the (5) nature of the vessel inner surface. For example, the explosion limit temperature is observed to increase in a vessel coated internally with KCl. [21] This can be attributed to the efficient breaking of chain reaction series leading to explosion. The temperature for self-detonation is increased to greater than 450°C with a heavy surface coating of KCl. In a 7.4 cm diameter glass sphere, internally coated with KCl, the explosion limit of a stoichiometric hydrogen–oxygen mixture is reached only at temperatures above 400°C.

Varying the composition of the salt and the dimensions of the vessel also increase/decrease the self-detonation limit in the hydrogen-oxygen reaction. [21] The smaller the vessel, the higher the pressure and temperature must be before the explosion limit is reached. However, even in rather large (500 mL) vessels, the vessel surface also may have a significant effect. This effect is due to increased reaction chain breaking at the surface of the

container. The explosion limit is also shifted by changes in the salt composition, showing the strong impact of surfaces on radical chain breaking.

From the available thermodynamic, experimental and empirical information, it does not appear to be credible that the combination of temperatures, pressures and other conditions necessary for spontaneous detonation can be attained inside plutonium storage containers.

The lower flammability limit (LFL) of hydrogen in air is about 4% at 25°C at 1 atmosphere for upward propagation of the flame in an experimental tube apparatus. [22] For downward propagation, the LFL is 9.4% at the same temperature and pressure. The LFL decreases slightly with increasing temperature. Based on recently published work, it appears unlikely that LFL concentrations of hydrogen can be generated and/or maintained in containers of plutonium-bearing materials stabilized and packaged according to the existing and proposed standards.[1, 2]

Catalyzed Recombination on Solid Surfaces

It is especially significant for this review that hydrogen/oxygen recombination at gas-solid interfaces are very important. More specifically, the recombination of H₂ and O₂ on the surface of PuO₂ and impure oxides, common salts (KCl, NaCl, MgCl₂, and CaCl₂), and stainless steel are highly relevant to plutonium storage environments. Quigley's recent paper [23] addresses the recombination reaction in a stainless steel environment. Recent papers address H₂/O₂ recombination over PuO₂. [3-5, 9, 10] A few other papers have been published on relevant surface recombination reactions in the presence of common salts. For example, Smith reported that H atoms do not readily recombine to H₂ in the presence KCl but O and H atoms recombine readily to form OH. [24] Other compounds (i.e.,

$K_2CO_3, K_2SiO_3, Na_3PO_4$) strongly induce H atom recombination when dry and less strongly when wet. [24]

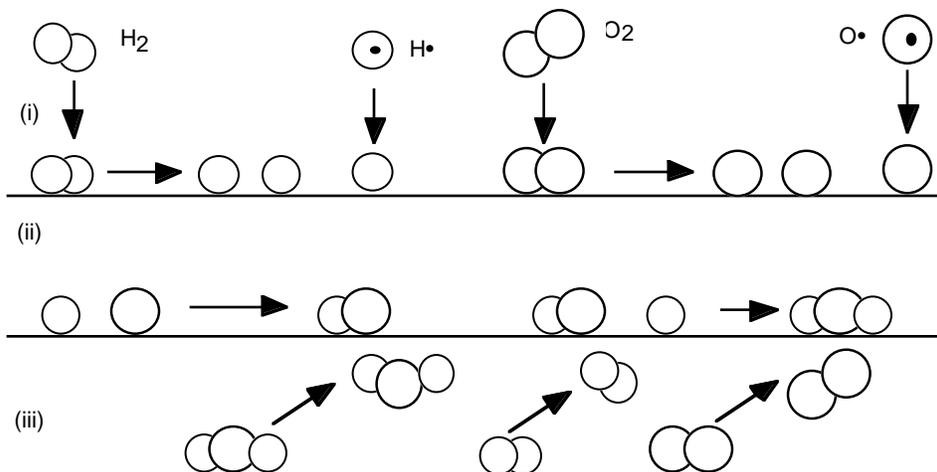


Fig. 1. Possible surface reactions in the hydrogen/oxygen system.

It is well established that surface reactions play a significant role in recombination (chain breaking) reactions of radicals. One possible surface recombination reaction mechanism for the hydrogen/oxygen system is shown in Fig. 1. In Fig. 1(i), hydrogen and oxygen (either as radicals or as molecules) approach the surface, adsorb, and dissociate to produce adsorbed H or O atoms. Adsorbed hydrogen and oxygen atoms then can react with each other to form H_2O or adsorbed products on the surface, as shown in Fig. 1 (ii). In principle, molecular desorption as water, hydrogen or oxygen can occur (Fig. 1 (iii)). Although Fig. 1 depicts a surface chemical processes that can occur in the hydrogen/oxygen system, gas products can form from radiolysis of these or other adsorbed species.

Another consideration is reaction of surface adsorbed species with ions or radicals. Two relevant types of accepted generic surface reactions are depicted in Fig. 2. [25] The Langmuir-Hinshelwood mechanism, in which reaction of molecules or atoms involve surface

adsorbed species, is shown in Figure 2 (i) and was discussed above for the H₂/O₂ system. A second reaction mechanism involves the reaction of gas phase atoms (ions or radicals) with adsorbed atoms. This reaction sequence is called an Eley-Rideal mechanism and is depicted in Figure 2 (ii).

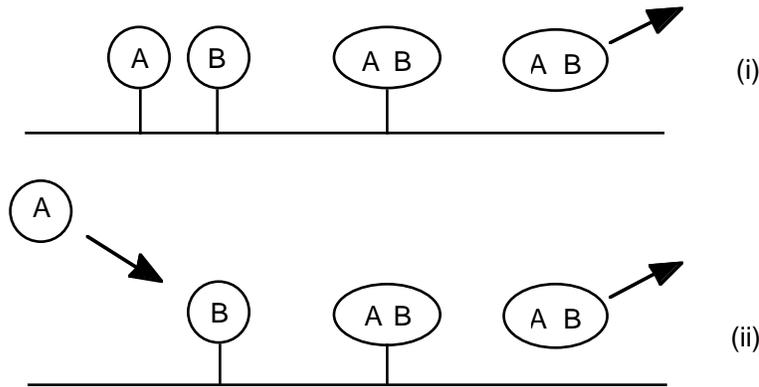
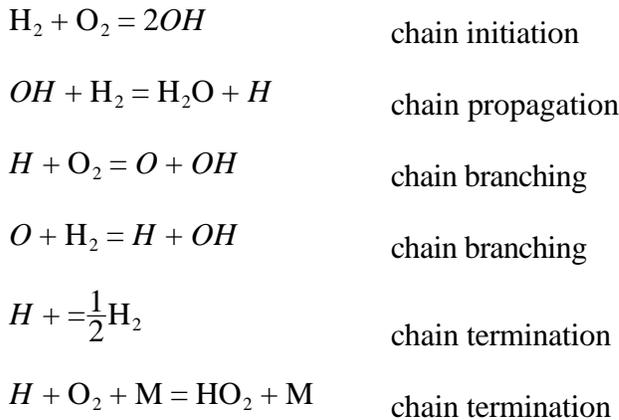


Fig. 2. Diagram of the Langmuir-Hinshelwood and the Eley-Rideal reaction mechanisms.

Radiation-Induced Reaction of Hydrogen and Oxygen in the Gas Phase and the Effect of Nitrogen.

Radical chain reactions form the basis of the H₂/O₂ recombination process in the gas phase.

[26] The most important of these reactions are:



where M is any third body (molecule or surface) that promotes the combination of H and O₂.

Radiation generates ions, excited molecules, and radicals in the gas phase. The energy of such species is far more than sufficient to initiate chain recombination reactions of H₂ and O₂. Accordingly, vary large G values for the recombination of gaseous hydrogen and oxygen have been reported to range from about 10 to several hundred, depending on temperature, pressure, and other conditions. [27-30]

The first reported studies of the radiation-stimulated recombination of hydrogen and oxygen were conducted using radon alpha particles. [27] Although these studies involved “clean” systems of the reacting gases, equilibrium amounts of mercury vapor (from displacement equipment and/or diffusion pumps) may have been present and influenced the results. The reported data allow the calculation of $G(\text{H}_2\text{O}) = G(-\text{H}_2) = \sim 10.2$. Dautzenberg reported similar results [28] [29] and noted that the G-values are dependent upon conditions. Lind also reported measurements as a function of temperature that indicate that G values may increase with higher temperatures. [27]

Haschke, et al. reported that hydrogen/oxygen recombination occurs over pure PuO₂ in a single experiment. [10] Recent work by Morales, with both pure and impure PuO₂ confirmed this result. [9] Both reports concluded that catalytic rather than radiolytic effects dominate under their experimental conditions. However the rates of recombination also can be modeled with radiolytic literature data (see appendix).

Dautzenberg [28, 29] performed an extensive series of studies of the radiation-induced reaction of gaseous hydrogen and oxygen, in a fused quartz container. He reported very high G-values for the recombination reaction, exceeding 100 under certain conditions, indicative of chain reactions. His results showed that the presence of nitrogen gas greatly

increases the rate of reaction and that increasing temperature leads to increasing G-values. Dautzenberg interpreted the complex results in terms of a chain reaction, with chain propagation likely involving the radical HO₂. His results also indicate the significance of surface reactions in determining the reaction chain length.

Kalashnikov et al. [30] also reported that under certain conditions of gas pressure and composition, long chain lengths can be attained with G(H₂O) exceeding 100, confirming very high radiolytic G-values for the hydrogen/oxygen reaction. Therefore, it does not appear credible that significant pressures of hydrogen and oxygen can develop or be maintained in the presence of a strong ionizing source, such as plutonium, because of the efficiency of radiation-induced recombination.

Dautzenberg's work ignored reactions that consume nitrogen and considered it an inert gas. However, in radiolytic systems with an initially high proportion of air, as occurs often in plutonium storage environments, the literature indicates that radiation-induced reactions between oxygen and nitrogen also will occur. These reactions have been shown to produce nitrogen oxides and, if water is present, nitric acid. [31, 32] It also is well known that nitric acid can react with oxide or metal surfaces to form solid nitrates. As mentioned earlier, nitrates dissolved in liquid water retard the radiolytic formation of hydrogen. Therefore, a contributing factor to the generally observed disappearance of oxygen from air-sealed Pu storage containers during storage may be formation of surface-adsorbed nitric acid or nitrate. The G values for nitrogen/oxygen reactions, while significant, are lower than G values for the hydrogen/oxygen reaction.

Radiolysis of a nitrogen-hydrogen-oxygen mixture is reputed to be extremely complex, apparently involving more than two hundred reactions. [27, 31, 33] The production of nitric acid from moist air is reported to proceed with a G (nitric acid) of 2.0.

Conclusions

1. The H₂/O₂ recombination reaction in the absence of ionizing radiation has been studied for more than 70 years. Surface catalytic effects can dominate under some circumstances, apparently including plutonium storage environments.
2. Radiolytically-induced recombination of hydrogen and oxygen can be highly efficient via chain reaction (G>100). The recombination rate is strongly affected by surfaces and the presence of gases, such as nitrogen. Radiolytic reactions of nitrogen/oxygen mixtures can lead to adsorbed nitrates.
3. The literature indicates that G values for radiolytic decomposition of adsorbed water are strongly dependent upon the nature of the sorbent material. G values much greater and much lower than for liquid water are observed, depending upon the surface.
4. Rapid hydrogen/oxygen recombination has been reported in the presence of pure and impure PuO₂, providing a strong technical basis that hydrogen and oxygen cannot be generated or maintained at significant pressures in plutonium storage environments.

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Appendix by Lee Hyder

Radiolysis and its Role in Hydrogen Generation from Water Adsorbed on Plutonium Oxide

Simple calculations show that material sorbed on the surface of plutonium oxide, and the atmosphere in the vicinity of the surface, are subject to an alpha radiation field of several megarad (tens of kiloSieverts) per hour. This can have a strong chemical effect. It is established, for example, that liquid water irradiated by alpha particles decomposes to hydrogen and to oxygenated species (hydrogen peroxide and oxygen) at the rate of about 0.013 molecule per eV of absorbed energy. [13](Radiation chemists refer to this as a G value of 1.3.) This is enough to decompose all sorbed water over a period of a few months. Moist air on irradiation produces nitric acid with a G value of about 2. [31] Hydrogen and oxygen in the gas phase recombine by a chain reaction that corresponds to G values of 12-15 to several hundred, depending upon conditions. [27, 28, 30, 32] It has been established [28] that this chain can be affected by surface conditions, which implies that it proceeds slowly enough for diffusion of some species to the surface to become important.

As indicated in the body of this report, adsorbed materials may or may not behave as liquid water with regard to radiolysis. Hydrogen is produced in the radiolysis of water when two H atoms or hydrated electrons are formed close enough together to unite. (See discussion, [15]) In an alpha track in liquid water this is fairly easy, particularly because hydrogen bonding in liquid water promotes mobility of the “hydrated electron”. In the chemisorbed material, hydrogen bonding between water molecules may be decreased or absent, either because of physical separation of the water molecules, or because of shifts in electron density as a result of interactions with the surface. In this case the hydrogen atoms are probably formed in part from the interaction of electrons in the substrate material with sorbed water or hydroxyl ions. Oxidized material, such as nitrates, sorbed nitrogen oxides, ferric impurities, or higher-valence plutonium oxides, can compete for these electrons. Such

materials are expected to be present as the result of calcination or of subsequent irradiation of air near the surface. The result will be to reduce the hydrogen generation rate below that observed in the liquid. If water is adsorbed to a substantial thickness, it may behave more like liquid water. The literature indicates that the hydrogen release rate will be diminished if nitrogen oxides are also present in the adsorbed water layer.

The anticipated result of these effects is that the rate of hydrogen generation will decrease as radiolysis proceeds. Oxidizing species of one or more kinds will accumulate on the surface and tend to slow the reaction. This is because they are strongly electropositive, and readily interact with diffusing electrons. A steady state with a low concentration of radiation products would be reached, except that the hydrogen can diffuse away from the surface into the gas phase. This loss of hydrogen leaves a net accumulation of oxidized material behind on the surface. The slow rate of hydrogen generation observed in plutonium-bearing materials with low water content (<0.5 wt %) is consistent with these arguments.

Once hydrogen is produced, so long as oxygen is present the radiation-induced recombination of oxygen with hydrogen can occur. This is expected to occur mainly in the interstices of the particle bed, where the overall radiation field is highest. Additionally, the gas phase reaction can be heavily affected by the chemical catalytic nature of the surfaces. (Dautzenberg [28] saw an important surface effect in containers with dimensions of a few cm; inside the particle bed, the dimensions are of the order of micrometers.) This factor complicates the ability to predict the G value for recombination in the gas phase. However, the available data can be examined for their implications. Some of the data of Morales [9] can be fitted by effective G values in the range of 50 to a few hundred, which is in the upper range observed by Dautzenberg. Other experimenters have also reported values in this range. [30] These observations suggest that radiation-induced gas phase

recombination plays a major role in the recombination process, but it is also quite clear from the geometry involved, and from the literature, that heterogeneous reactions must be a part of this process. For example, in addition to chemically initiating the combination reaction, the surface of plutonium oxide may, for example, affect the recombination chain.

Regardless of the mechanism postulated, the experimental data and empirical observations of storage behavior clearly indicate that the recombination reaction is quite efficient in the presence of impure plutonium oxides. Therefore this reaction will strongly limit hydrogen production in the presence of oxygen. (Note that the amount of air in containers may be much smaller than the mass of adsorbed water, and it is possible for the radiation processes to consume all the oxygen.)

Eller has suggested (private communication, 1999) that oxidized impurities such as ferric oxide might become hydrogen getters in the radiation field. This is certainly plausible.

In summary, the principal argument for the premise that radiation is a major contributor to both hydrogen formation and to hydrogen-oxygen comes from the established literature data confirming such reactions in non-radioactive systems. It is also clear from the literature that radiation-induced reactions between nitrogen and oxygen will occur when they are present, with a small but steady production of nitrogen oxides and (in the presence of hydrogen or water) of nitric acid until nitrogen and oxygen are consumed. Whatever model is developed to describe the observed behavior of the system must take these reactions into account. This includes chemically catalyzed recombination of hydrogen and oxygen on the plutonium oxide surface, independent of the radiation field. In any event, the possible mechanisms are ample to support the experimental data on recombination.

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