

The effect of the pH and dissolved O₂ on a γ -radiolysis of water

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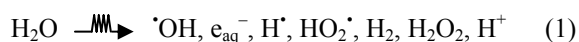
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1. Introduction

Many of the operational and safety issues of nuclear power plants stem from the effects of radiation on the oxidation or corrosion of construction materials. Of particular concern are the effects of chemically reactive species produced by radiolysis of coolant water. Exposed to ionizing radiation, water decomposes to yield a range of chemically reactive species [1]:



Other reactive species such as HO₂, O₂, $\cdot\text{O}_2^-$ and $\cdot\text{O}_3^-$ are also formed through reactions as secondary products. These radiolysis products react rapidly with each other and, if present, with any additional species in solution and on surfaces. If the radiation field is constant, the irradiated system quickly reaches a steady-state chemical equilibrium, in which the concentrations of radiolytical decomposition products of water stabilize at low levels. These low but (pseudo-) steady-state concentrations over long-term irradiation are crucial parameters in determining radiolytic production of hydrogen or radiation-induced chemical effects on corrosion. For example, since the radiolysis products range from oxidizing (e.g., $\cdot\text{OH}$, H₂O₂ and O₂) to reducing (e.g., $\cdot\text{H}$, e_{aq}^- and $\cdot\text{O}_2^-$), these species, even at low concentrations, determine the aqueous redox condition, strongly influencing corrosion kinetics [1~4].

The radiolysis of water in γ -radiation fields has been studied for pure water[4,5] and for water containing low levels of organic species[6,7] and for water containing radical scavengers[1]. Although the qualitative behavior of water radiolysis products has been established as a function of pH, most of the previous experimental studies have been performed at neutral pHs (5~8). Experimental studies on steady-state water radiolysis at higher pHs have been rare, and the results of the reported work at high pHs are contradictory. Pulse radiolysis studies done at pHs(4~10) in oxygenated water have confirmed the importance of transient species such as $\cdot\text{O}_3^-$, which is relatively long lived. The $\cdot\text{OH}$ radical is the precursor for this species, in the form of $\cdot\text{O}^-$ under alkaline condition. At high pHs, species such as $\cdot\text{O}_3^-$ and $\cdot\text{O}_2^-$ may play a significant role in determining the steady-state concentrations of the molecular radiolysis products as well as the time to reach the steady state. The involvement of these transient species in radiolysis reactions at high pHs, however, has not been investigated. In this study, we have performed experiments to determine the effects of

pH as well as dissolved O₂ concentration on the γ -radiolysis reactions of water.

2. Experimental

All solutions were freshly prepared before each experiment with water purified using a NANO pure Diamond UV ultrapure water system from Barnstead International to remove organic and inorganic impurities. Prepared in this manner, the water had a resistivity of 18.2M Ω -cm. The experiments at pH 6 were performed without the addition of any buffer, whereas those at pH 10.6 used a phosphate buffer (10⁻³ mol/dm³). The pH of the solution was measured prior to and at the end of the irradiation period using a pH meter(Symphony). The de-oxygenated water samples were prepared by purging the bulk solution with ultrahigh-purity argon (impurity 0.001%) for more than 1 hr. The final step in the solution preparation was performed inside the glove box by transferring the solutions into vials and sealed inside a glove box. The oxygen concentration in the glove box was maintained below 1000 ppm. In the case of aerated samples, 1 hr purging with high-purity air (medicinal USP grade) was used for saturating the samples and the solution was transferred to the vials and sealed.

Irradiation was carried out in a ⁶⁰Co γ -cell (MDS Nordion), which provided the irradiation chamber with a uniform absorption dose rate of 2.5 Gy/s determined using Fricke dosimetry. The vials were placed in a specially designed sample holder so as to have a reproducible uniform dose during irradiation. Individual vials were taken out of the γ -cell at regular time intervals for H₂ and H₂O₂ analysis. Using a gas-tight syringe one half of the aqueous sample was transferred to another vial for H₂ analysis and the other half of the sample was used for aqueous analysis of H₂O₂.

3. Results and Discussion

In the absence of impurities and without a headspace (i.e., homogeneous phase), the concentrations of gamma radiolysis products, in general, quickly reaches a steady state, since for a given radiolysis product the main production path is generally primary radiolysis whose rate is constant with time, while the decomposition rate increases very rapidly to catch up with the production rate. Under these conditions, the steady-state approximation can be applied to determine the concentrations of the radiolysis products, if the main decomposition reactions can be identified and their rates are known. For the primary products, the production rates are the primary yields, defined using G-values in

units of number of molecules produced per 100 eV absorbed energy. The main decomposition paths vary depending on species: for molecular products such as H_2O_2 and H_2 the main decomposition paths are their reactions with radical products, whereas radicals, such as e_{aq}^- and OH , decompose by reactions with molecular products. The steady-state approximation provides the approximated but simple relationships between the radical and molecular concentrations, which can be used to develop a qualitative understanding on the effects of chemical environments, such as pH and dissolved gases, on water radiolysis.

The effect of the initially dissolved oxygen on the concentrations of molecular products, H_2 and H_2O_2 , is shown in Fig. 1. At pH 6, the steady-state concentration of H_2 in aerated solutions reached $\sim 2.6 \pm 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ while it remained below the detection level in the de-aerated solution (Fig. 1a). The concentration of H_2O_2 in the de-aerated solutions was also below the detection limit ($< 3 \times 10^{-6} \text{ mol dm}^{-3}$), whereas $[\text{H}_2\text{O}_2]$ in aerated solutions quickly reached a steady-state concentration of $0.90 \pm 0.05 \times 10^{-4} \text{ mol dm}^{-3}$ (Fig. 1b).

The H_2O_2 and H_2 concentrations observed as a function of pH are compared with model simulation results in Figure 2 for de-aerated samples. These experiments were performed without headspace. The computer model simulation results are also shown in the figures. Under both de-aerated and aerated conditions, the increase in pH increases the steady-state concentrations of H_2O_2 and H_2 , and the time to reach the steady state. Under de-aerated conditions, $[\text{H}_2\text{O}_2]$ was below detection limit at pH 6 and pH 8.5, while at pH 10.6 it increased from below detection limit to $\sim 3 \times 10^{-5} \text{ mol dm}^{-3}$ in 5 hr irradiation at 2.78 Gys^{-1} . For H_2 , the steady-state concentration increased from $\sim 0.04\%$ at pH 6 to $\sim 0.16\%$ at pH 8.5. At pH 10.6, the H_2 concentration increased continuously with irradiation time to $\sim 0.5\%$ at 5 hr and did not reach a steady state. Under aerated conditions, $[\text{H}_2\text{O}_2]$ and $[\text{H}_2]$ were also increased with an increase in pH, but the increases were less noticeable.

4. Conclusion

Steady-state water radiolysis entails a complex system of both reducing and oxidizing species with competing reactions occurring rapidly. In this work both experiments and a kinetic model analysis were used to identify the effect of the pH and dissolved oxygen that dictate the concentrations of molecular radiolysis products. These concentrations depend on the concentrations of the free radicals that are generated by the radiolysis and by the species that are used to control the solution redox and pH conditions (O_2 and OH^-). We have shown that the following concentrations of the stable molecular products of radiolysis allows one to predict the concentrations of the reactive radicals with confidence, and to be able to predict how to control of the initial solution redox and the pH which can control

the concentrations of the species important in corrosion in irradiation environment.

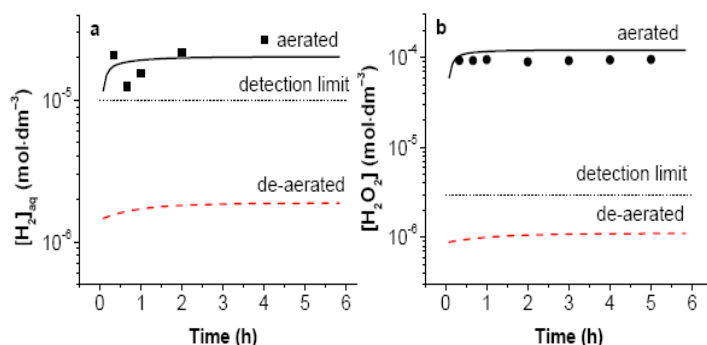


Figure 1. Effect of dissolved O_2 on the steady-state concentrations of molecular products

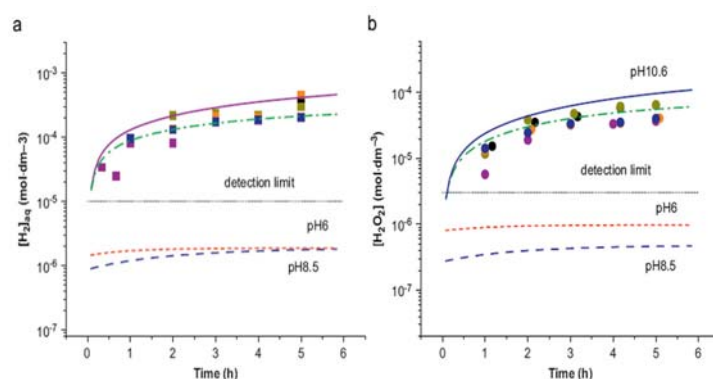


Figure 2. Steady-state concentration of H_2 , H_2O_2 as a function of pH under de-aerated condition.

REFERENCES

- [1] Pastina, *et al.*, "Effect of molecular hydrogen on hydrogen peroxide in water radiolysis" *J. Phys. Chem. A.* 2001, 105, 9316.
- [2] Stefanic, *et al.*, "Temperature dependence of the hydrogen peroxide production in the gamma-radiolysis of water," *J. Phys. Chem. A.* 2002, 106, 447.
- [3] Cowan, R.L. *Water Chemistry of Nuclear Reactor Systems* 7. British Nuclear Energy Society: London, 1996.
- [4] LaVerne, J.A. *et al.*, "Effect of molecular hydrogen on hydrogen peroxide in water radiolysis," *J. Phys. Chem. A.* 2001, 105, 9316.
- [5] Boyd, A.W. *et al.*, "Computed and experimental product concentrations in the radiolysis of water," *Radiat. Phys. Chem.* 1980, 15, 177.
- [6] Wren, J.C., *et al.*, "LIRIC 3.2 an updated model for iodine behaviour in the presence of organic impurities," *Radiat. Phys. Chem.* 2001, 60, 577.
- [7] Glowa, D. P., *et al.*, "Steady state gamma-radiolysis of aqueous methyl ethyl ketone (2-butanone) under postulated nuclear reactor accident conditions," *Radiat. Phys. Chem.* 2000, 57, 37.