Introduction: Importance of radiolysis effects on the corrosion of metals in supercritical water

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1. Introduction

In the past decade, there has been an increasing interests in the field of supercritical water (>373°C, >221 atm) as a good solvent for chemical separation, reaction in chemistry, destruction of hazardous compounds, and so on [1]. Compared to normal water, supercritical water is a relatively non-polar solvent because of reduced hydrogen bonding and dielectric constant. Non-polar compounds which are normally insoluble in water are nearly completely soluble in supercritical water. In the meantime, supercritical water is still a relatively good solvent though its solubility significantly decreases.

It is possible to study the reactions of radicals with various substances in supercritical water and pulse radiolysis technique is a useful and powerful tool for the investigation of fast radical reactions. Because a huge amount of data is available for radiation induced reactions in normal water at room temperature, it will be important to know the processes in supercritical water and to compare with those at room temperature for a thorough understanding of water radiolysis. In addition, the study of water radiolysis at supercritical conditions is important on the evaluation of radiation-induced corrosion in the supercritical water nuclear reactor [2] and for understanding radical processes taking place in supercritical water [3].

In the present work, the basic properties of supercritical water and the recent research on the radiolysis of water were investigated in order to understand the radiolysis impact on the corrosion of structural materials.

2. Radiolysis of Supercritical Water

2.1 Basic properties of Supercritical Water

Unlike organic compounds, water molecules at room temperature are specially stabilized by forming hydrogen bonds among the water molecules. At high temperature and high pressure conditions, water molecules can be stable with lack of hydrogen bonding. It is called supercritical region of the water. As the degree of hydrogen bond determines the properties of water, the physico-chemical properties of water depend on the temperature and pressure under the exposed system. Among the important properties of water, the dielectric constant decreases gradually with increase of temperature. The ionic product of high temperature water and steam is illustrated in Fig. 1. Supercritical water behaves like non-polar solvents with low solvency for ionic compounds, whereas most non-polar gases and organic compounds easily dissolve in this medium. Diffusion constant and thermal conductivity are also the function of temperature and pressure.

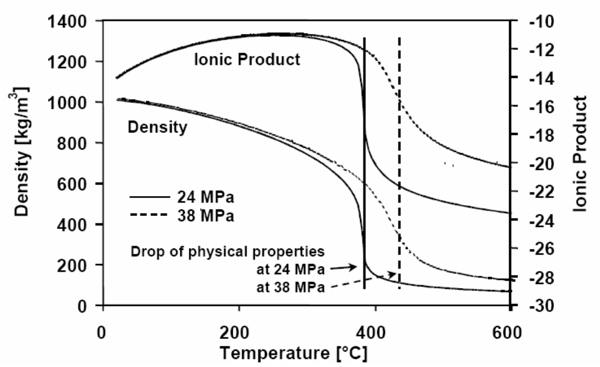

Fig. 1. Drop of physical properties of high temperature water at different pressures. The drop shifts towards higher temperatures at higher pressures [4].

2.2 Radiation Sources for Radiolysis of Water

In general, three kinds of radiation sources are introduced in the field of water radiolysis. The first is a gamma ray using ^{60}Co as a radiation source material. Many commercial cells are developed for gamma ray irradiation. The second is a pulse electron beam using a linear accelerator. This technique has been used for the radiolysis of water at supercritical conditions. The last is neutrons from the fissile materials in reactors. Recently, a radiolysis experiment with neutron irradiation using a research reactor is designed as a part of the development of supercritical water cooled reactors.

2.3 Characteristics of radiolysis of Supercritical Water

The radiolysis characteristics of water are suddenly changed at supercritical conditions, as the cluster of water has different configuration at the conditions. Pulse radiolysis technique by a linear accelerator as mainly used for the study of radiolysis of water at supercritical conditions. At subcritical conditions, the values of G of water radiolysis linearly increase as the temperature increases. On the other hand, the values of G of water are higher at supercritical conditions. The trend of G value (for hydrated electrons), however, decreases as the temperature and density of water increase at supercritical conditions.

3. Summary

The radiolytic products of water, such as various radicals and oxidizing species, produced at supercritical conditions have longer life time compared to those at subcritical conditions. And the radiolytic products may play an undesirable role in keeping the design life of structural materials in high temperature water. Therefore, the study of water radiolysis at supercritical conditions is indispensable for the evaluation of radiation-induced corrosion in the future generation of supercritical water nuclear reactor.

REFERENCES

[1] Savage, P.E., Organic chemical reactions in supercritical water. Chem. Rev. 99, 603–.621, 1999.
[2] Koshizuka, S., Oka, Y., Supercritical-pressure, lightwater-cooled reactors for economical nuclear power plants. Progress in Nuclear Energy. 32 (3/4), 547–.554, 1998.
[3] Ferry, J.L., Fox, M.A., Temperature effects on the kinetics of carbonate radicals reactions in near-critical and supercritical water. J. Phys. Chem. A. 103, 3439–.3441, 1999.
[4] P. Kritzer, N. Boukis, E. Dinjus, Review of the corrosion of nickel base alloys and stainless steels in strongly oxidizing presssuried high-temperature solutions at sub-and supercritical temperatures, Corrosion. 56, 2000.