Research Program on Water Chemistry of Supercritical Pressure Water under Radiation Field

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In a supercritical water-cooled reactor, property of water changes significantly around the critical point. It is expected that irradiation and change of water property will affect the chemistry and material corrosion. Deep understanding of interactions between supercritical water and materials under irradiation is important. However, comprehensive data on radiolysis, kinetics, corrosion and thermodynamics have not been obtained due to the severe experimental condition. To get such data by experiments and computer simulations, a national program has been started since December 2002. In this program, three sub-themes were settled and five Japanese institutes shared the R&D items. In each R&D item, temperature and pressure were selected as key parameters.

1. Introduction

In terms of design of an advanced nuclear power plant, various characteristics such as core design, reactor physics, thermal hydraulics and structural materials are key issues to be studied. Also in water-cooled nuclear power plants, water chemistry has played important roles in material integrity, dose rate reduction and radioactive waste problems.

The supercritical-water cooled reactor (SCWR) is an innovative candidate to meet the needs from world's energy market. The major advantages over the current generation light water reactors (LWRs) include [1]: 1) The estimated thermal efficiency is exceeding 40 % due to high-pressure, high-temperature steam at the turbine inlet. 2) Thermal components, such as heat exchangers and turbines, are compact. 3) The systems for steam separation, re-circulation of core flow and steam generators are eliminated because of the high enthalpy content of the supercritical-pressure (SCP) water and because of no phase change in supercritical regime. 4) The R&D costs and duration would be minimized because this technology is based on the existing LWR plant technologies as well as existing SCP fossil power plant technologies. 5) High cooling efficiency of the SCP water facilitates designing the moderator volume to achieve either thermal or fast neutron spectrum.

To make these advantages viable, a Japanese joint team consisting of University of Tokyo, Kyushu University, Hokkaido University, Hitachi Ltd, and Toshiba Co. started a development project of SCWR with a national fund in the fiscal year 2000.

In LWRs, water chemistry is established as a science based on industrial phenomena. Primary parameters in water chemistry are high-temperature and irradiation. Along the change of these two parameters, three categories of fundamental phenomenon has been studied for a long time: i) Change of water quality by radiolysis and temperature. ii) Corrosion of material faced to high-temperature water. iii) Stability and transportation behaviors of corrosion products (CP)

Studies conducted in these three categories have been contributed to establishing countermeasures for material integrity, dose rate build-up, and radioactive waste problems. However, it is difficult to establish an almighty water chemistry to attain these goals simultaneously.

For example, Hydrogen Water Chemistry (HWC) has been applied to many Boiling Water Reactors (BWRs) to mitigate the susceptibility of Stress Corrosion Cracking (SCC) [2]. This technology is based on the decrease of oxidizing species concentration due to the radiolysis in the core. This water chemistry control leads to the decrease of Electrochemical Corrosion Potential (ECP) and following decrease of SCC susceptibility. However, due to the change of water chemistry, chemical species of impurities such as radioactive nitrogen (i.e. N-16) and transition metal oxides containing Co-60 will shift to more reduced forms and cause adverse effects of radiation fields in BWRs.

In SCWR, water changes its characteristics drastically around the critical point, namely in the core. It is expected that irradiation and change of water characteristics will affect the water chemistry and material corrosion. Deep understanding of interactions between supercritical water and materials under irradiation is important. However, comprehensive data on radiolysis, kinetics, corrosion and thermodynamics have not been obtained due to the severe experimental condition of SCWR.

To get such data by experiments and computer simulations, a national program "Fundamental R&D program on water chemistry of supercritical pressure water under radiation field" funded by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been started since December 2002. This paper describes the outline and some of the obtained data in this program.

2. Outline of the program

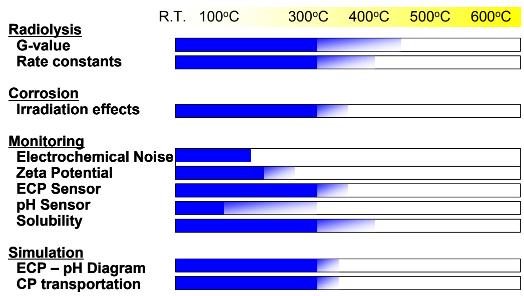
2.1. Contents of R&D items In this fundamental program, water chemistry will be investigated from three viewpoints as follows: 1) Radiolysis and kinetics of supercritical-pressure water (SCW). 2) Influence of radiolysis and radiation damage on corrosion. 3) Behavior of CP on the interface between water and materials

Data of these categories in high temperature water up to 300 °C has been obtained and water chemistry in existing nuclear power plants are discussed based on present knowledge. Table 1 summarizes the current status of each database and technology for water chemistry. A few data were obtained under supercritical condition.

In way of expanding the database beyond the critical point, drastic change of water characteristics will arise for each fundamental phenomenon. In this program, temperature and pressure are selected as key parameters for each experiment and computer simulation. Below the critical point, pressure can be defined when temperature is given and dependency on temperature corresponds to that on pressure. However, in supercritical condition, pressure can be changed even when temperature is fixed and some parameters such as water density varies with temperature. Therefore, it is required to measure the data changing not only with temperature but also with pressure.

The database obtained in this program will be useful not only for the design of SCWR but also the other industrial technology such as supercritical water oxidation and advanced nuclear power plants using high temperature water. Fig. 1 illustrates these extending effects in various industrial fields.

Table 1. Current status of proven technologies



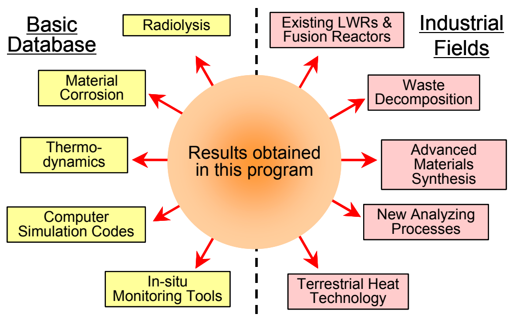


Fig.1. Extending effects of this program on various fields

2.2. Organization To accomplish this program, five Japanese institutes gathered and share the experimental and simulation items of three sub-themes.

1) Radiolysis and kinetics of SCW
- Radiolysis Experiments
  University of Tokyo
- Modeling and simulations
  Hitachi Limited and Toshiba Corporation

2) Influence of irradiation on corrosion

- Irradiation damage experiments and simulations
  Japan Atomic Energy Research Institute
- Gamma-ray irradiation experiments
  Hitachi Limited

3) Behaviors of CP on the interface

(a) CP characterization

- In-situ CP identification by Laser Raman spectroscopy
  Central Research Institute of Electric Power Industry
- ECP-pH diagram calculation
  Toshiba Corporation

(b) CP behavior in SCW

- Zeta potential measurements
  Central Research Institute of Electric Power Industry
- Solubility measurements
  Toshiba Corporation
- Modeling and simulations of CP in reactors
  Toshiba Corporation

(c) Monitoring of corrosion environment

- Electro-chemical noise measurements
  Hitachi Limited
- Development of monitoring sensors
  Hitachi Limited and Toshiba Corporation

Each experiment and simulation will be conducted at various temperatures. Temperature range is divided into four regions.

- RT - 300 °C: Existing LWR condition
- 300 °C - 400 °C: Around critical point
- 400 °C - 500 °C: Supercritical condition I
- 500 °C - 600 °C: Supercritical condition II

Due to the difficulty of experiments caused by reagents stability and equipment materials, supercritical condition is divided into two regions. Temperature of experiments and simulations will be increased step by step from existing LWR condition to supercritical condition I. For some experiments and simulations, supercritical condition II will be considered.

Data of these three categories in high temperature water can be used as a common database. For example, concentrations of oxygen and hydrogen in irradiated supercritical water can be evaluated from the results of radiolysis experiments and simulations. These evaluated concentrations will clarify the preferable conditions of experiments conducted in other categories.

Table 2 shows current schedule of this program. Experimental equipments of supercritical condition have been prepared in the first two years. Coding of model calculations will be conducted following the experiments to use the data evaluated from the results of experiments as inputs.

3. Scope and progress of each sub-theme

3.1. Radiolysis and kinetics of SCW

(1) Radiolysis experiments Due to radiolysis of water, radicals such as hydrated electron (e_{aq}^-), H, and OH are formed. Concentrations of these radicals are dominant factors of corrosive environment. To understand the water chemistry in core of LWRs, radiolysis experiments of high-temperature water has been investigated extensively for over-20 years.

To evaluate the concentrations of the radicals in irradiated water, primary yield of each radical (G-Value) and rate constants of chemical reactions between the species are necessary. These parameters can be evaluated by pulse radiolysis experiments at elevated temperatures.

In radiolysis experiments, some kind of chemical reagents are used as scavengers of radicals. Scavenger reacts with specific radicals and forms another kind of radicals to be detected by an absorbance measurement. At elevated temperature, chemical stability of reagent should be considered.

Methyl-viologen is one of the promising scavengers to determine G-value of hydrated electron (G (e_{aq}^-)) and G-value of water decomposition (G (e_{aq}^- + OH + H)) at elevated temperature below 400 °C. Fig. 2 shows G (e_{aq}^-) and G (e_{aq}^- + OH + H) dependencies on water density around critical point. Beyond the critical point, large dependencies of G-values on water density were obtained. This suggests the importance of water density change due to pressure.

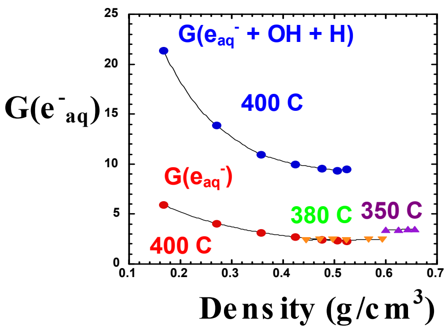


Fig. 2. G (e_{aq}^-) and G (e_{aq}^- + OH + H) dependencies on water density around critical point

(2) Modeling and simulations Model calculation of concentrations of oxygen and hydrogen in LWRs [3] is a common way to evaluate corrosive condition for structural material. G-values and rate constants in supercritical condition are necessary to construct a model for SCWR.

There are a few reported data of G-values in supercritical condition. However, some rate constants of radicals in supercritical condition are reported [4] for supercritical water oxidation (SCWO) processes. In this program, reported data will be compiled and evaluated to use as a database for SCWR.

3.2 Influence of irradiation on corrosion

(1) Radiation damage experiments and simulations

For irradiated materials, radiation induced damage of materials may affect the corrosion behavior. From this viewpoint, change of material characteristics will be simulated and corrosion tests of simulated material will be conducted in this sub-theme.

In this program, we will select typical structural materials such as stainless steel and Ni base alloy. Up to now, corrosion test equipments at elevated temperature in Japan Atomic Energy Research Institute have been improved for a use in supercritical condition.

(2) Gamma-ray irradiation experiments In Hitachi Limited, facility of corrosion test with gamma ray irradiation at elevated temperatures had been used to evaluate the effects of irradiation. Using this facility, corrosion tests of typical structural materials such as stainless steel and Ni base alloy were conducted in pure water of 400 ^{o}C. Ceramics for monitoring sensors have been tested also. In this year, this facility will be up-graded to use at higher temperature to conduct corrosion tests for the condition of SCWR.

3.3 Behaviors of CP on the interface

(1) CP characterization In existing LWRs, corrosion products released from structural materials are assumed to be deposited and activated on fuel cladding. The activated corrosion products (ACP) are main source of workers' exposure during annual outages.

In terms of deposition on fuel cladding, evaluation of stable chemical forms of CP is important. For example, nickel ferrite is known to be one of stable oxide forms of CP under BWR condition. Due to the similar chemical properties of Ni and Co, Co tends to be incorporated into nickel ferrite and activated to Co-60, which has relatively long half-life and becomes dominant nuclide of dose rate build-up.

To understand the stability of CP compounds under SCWR condition, two approaches will be chosen in this program. As an experimental approach, laser Raman spectroscopy of typical CP compounds will be conducted in SCW. Another approach is calculation of ECP-pH diagrams of typical CP compounds. In this calculation, "modified HKF model" will be applied. Fig.3 shows the result of ECP-pH diagram calculation in 400 and 450 ^{o}C water at 50 MPa for Fe compounds. Increasing the temperature at the same pressure will decrease the stability of soluble species of Fe.

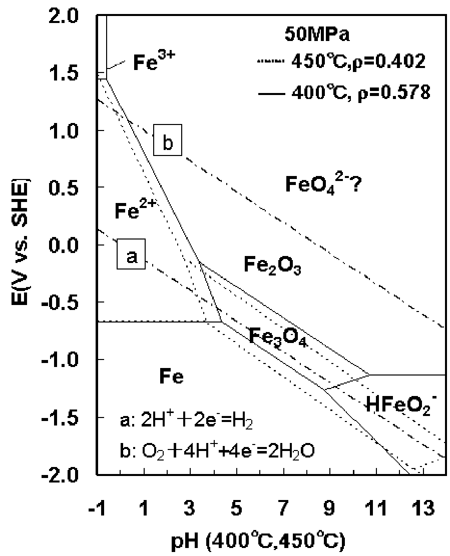


Fig. 3. ECP-pH diagram of Fe compounds in 400 and 450 ^{o}C water at 50 MPa

(2) CP behavior in SCW In LWRs, CP and ACP exist as soluble form and insoluble form. The soluble CP precipitates when the concentration of constituent transition metal ion exceeds the solubility in water. Once an insoluble compound formed, each precipitate behaves as a particle to be attached to surfaces of structural material and fuel cladding. This behavior will be affected by zeta potential of the particle.

In this program, zeta potential and solubility of typical CP will be measured in supercritical condition. Solubility data experimentally obtained will be compared with the results of thermodynamics calculation. In fiscal year of 2003, measurement systems for zeta potential and solubility in SCW will be constructed and measurements will be started.

In addition to the laboratory experiments, a model of CP transportation in SCWR will be constructed based on existing models for BWR plants. Measured and calculated data of CP will be used as input parameters of this model.

(3) Monitoring of corrosion environment Parameters obtained in experiments and / or calculations depend on water environment. For example, stability of a CP compound can be expressed as a function of ECP and pH in water. However, sensors to measure ECP or pH in supercritical water have not been established yet.

In this program, ECP sensor and pH sensor for SCW will be manufactured to get the data in experiments conducted in this program. Also, electro-chemical noise analysis will be tried to get the data in supercritical water condition.

4. Whole scope of the program

As described above, many kinds of experiments will be conducted to clarify the fundamental phenomena in this program. Fig. 4 illustrates the whole scope of the phenomena to be clarified. Due to the severe experimental conditions, calculations and simulations will be used as supplemental verification approaches efficiently.

Each phenomenon is independent R&D item, however, it is important to share the specifications of experimental conditions to be considered. One of the target conditions should be that of in-core of SCWR. Considering the upper limit of conditions for equipments and chemical reagents used in experiments, we chose 25 MPa of pressure and 500 ^{o}C of temperature as common conditions for all experiments.

5. Conclusions

In SCWR, property of water changes significantly around the critical point. It is expected that irradiation and change of water property will affect the chemistry and material corrosion. However, due to the severe conditions of high temperature and irradiation, comprehensive data of water chemistry and corrosion have not been obtained. To get such kind of data, a national program funded by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been started since December 2002.

In this program, water chemistry will be investigated from three viewpoints as follows.

1) Radiolysis and kinetics of SCW

2) Influence of radiolysis and irradiation damage on corrosion

3) Behavior of CP on the interface between water and material

To accomplish above sub-themes, a Japanese joint team consisting of five institutes gathered and shared the R&D items. Temperature and pressure are selected as key parameters for these experiments and calculations.

Major R&D items in this program have been just started. In each item, condition of supercritical water is slightly different due to the experimental limit. However, common conditions of temperature and pressure were chosen in consideration of SCWR in-core condition.

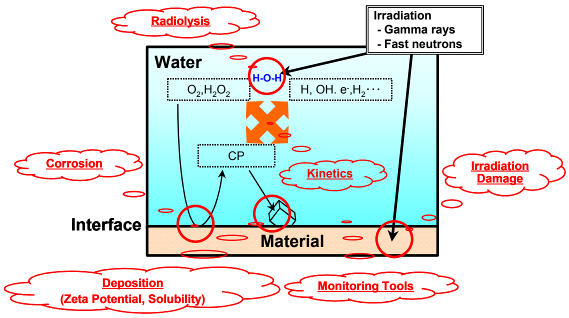


Fig. 4. R&D items of SCW chemistry under radiation field

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References and Notes

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