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Radiolysis of boiling water

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HIGHLIGHTS

- The radiolysis of boiling water was investigated.
- H_2 and O_2 gases were formed with a stoichiometric ratio (2:1) in ultra-pure water.
- The concentration of H_2O_2 was negligible in the liquid phase.
- Addition of NaCl enhanced the gas evolution.
- Deterministic chemical kinetics simulation reproduced the experimental results.

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ABSTRACT

γ-radiolysis of boiling water has been investigated. The *G*-value of H_2 evolution was found to be very sensitive to the purity of water. In high-purity water, both H_2 and O_2 gases were formed in the stoichiometric ratio of 2:1; a negligible amount of H_2O_2 remained in the liquid phase. The *G*-values of H_2 and O_2 gas evolution depend on the dose rate: lower dose rates produce larger yields. To clarify the importance of the interface between liquid and gas phase for gas evolution, the gas evolution under Ar gas bubbling was measured. A large amount of H_2 was detected, similar to the radiolysis of boiling water. The evolution of gas was enhanced in a 0.5 M NaCl aqueous solution. Deterministic chemical kinetics simulation elucidated the mechanism of radiolysis in boiling water.

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1. Introduction

Curie and Debierne observed the continuous gas evolution from aqueous solutions containing $RaBr_2$ in 1901 (Curie and Debierne, 1901), which was the first observation of water decomposition by irradiation. Water radiolysis has been investigated for over a century, during which time a wealth of practical knowledge has been collected (Allen, 1961; Draganic and Draganic, 1971; Buxton, 1987; Buxton et al., 1988). A nuclear accident at the Fukushima Daiichi Nuclear Power Plant was caused by a tsunami on March 11, 2011, following the Great East Japan Earthquake. Due to insufficient amount of cooling water, the reactor cores underwent nuclear melt down. The oxidation reaction of Zr, which is the main component of the cladding material for nuclear fuel, generated a large amount of hydrogen. As a result, reactor buildings were severely damaged by hydrogen explosions. At the time, the reactor unit four (#4) was undergoing an annual inspection and all spent fuels had been removed from the pressure vessel and stored in the spent fuel storage pool (SFP). Despite this, a hydrogen explosion took place in #4 (Kintisch, 2011). At the end of April 2011, the contamination levels in the SFP were measured and found to be low, and the spent fuels did not appear to be severely damaged. At the time, the origin of the hydrogen that had exploded in #4 was unknown. Radiolysis of boiling water in the SFP was discussed as a possible source of hydrogen, but little had been published on the topic. We performed an urgent experiment; the preliminary result confirmed that an explosive amount of H_2 could have been

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formed from boiling water (Yamashita et al., 2011; Katsumura et al., 2011, 2012). Unfortunately, our experiment was qualitative, not quantitative, and we were unable to determine the *G*-values of gas formation.

Gas evolution from the radiolysis of boiling water would depend on many factors such as the degree of boiling, heating rate of the sample, the surface area-to-volume of the sample, the volume of the sample, etc. In this study, we quantified the *G*-values for the evolution of gas and the formation of H_2O_2 in boiling water. We also investigated the effects of interface between liquid and gas, and NaCl addition. In addition, we performed the deterministic chemical kinetics simulations with FACSIMILE software that reproduced the experimental results and elucidated the mechanism of radiolysis in boiling water.

2. Experimental

2.1. Sample preparation

Water treated with commercial purification equipment retained trace amounts of organic contaminants; it was not pure enough to obtain reproducible experimental results. A protocol was developed to further purify the water for dosimetric experiments: the feed water was passed through filters and ion-exchange columns, distilled twice, and then introduced to the Millipore Reagent Water System®. Water prepared by this procedure was pure enough for the experiment described herein; it provided reproducible results when used with aqueous dosimeters, e.g., Fricke and Cerium types (Katsumura et al., 1992).

2.2. Irradiation equipment

A still pot fitted with a reflux condenser for irradiation setup is shown in Fig. 1. The equipment comprised a 1 L reaction vessel, placed in a heating mantle, and a cooler, in which isothermal water (30 °C) was circulating. The lower and upper sampling ports in the radiolysis reactor, sealed with silicone rubber septa, were used for injecting and sampling the gases, respectively. In general, the space of the inner tube of the condenser would be open to outside during operation; however, in the present experiment, the space was closed to the outside environment. The glass branch on the cooler was extended with silicone rubber tubing, which was immersed into a water reservoir in a closed measuring cylinder, as shown in Fig. 1(a). This setup contained the gas that evolved during the experiment. During boiling experiments, the heater power and the temperature of the cooling water were set to 450 W and 30 °C, respectively, to ensure reproducible experimental conditions. We verified that the silicone rubber did not produce a detectable amount of H_2.

In order to evaluate the effect of interface between liquid and gas, the water radiolysis during Ar gas bubbling was also done with another equipment composed of a sample vessel and a diaphragm pump, as shown in Fig. 1(b). The vessel and pump are connected with stainless tubes having a sampling port at the outlet tube of the pump. The volumes of gas phase in the equipment and water sample in the vessel were 1007 and 500 mL, respectively. The gas was injected into the water sample through a glass ball filter to make fine bubbles and circulated with a flow rate of 1090 mL/min.

2.3. Irradiation and gas analysis

Irradiation was carried out at the Co-60 γ-irradiation facility in the Takasaki Advanced Radiation Research Institute, which is part of the Japan Atomic Energy Agency (JAEA). Prior to irradiation, the equipment and water sample were flushed completely with Ar gas through the lower sampling port; then the sample was heated.

Dosimetry was performed with Fricke and Cerium aqueous dosimeters (Matthews, 1982) and an alanine dosimeter (Kojima et al., 1993). Dose rates of 67 and 15 Gy/min were determined for the higher and lower dose rate positions, which are hereafter called positions A and B, respectively. Cycles of 15 min of irradiation followed by 15 min of measurement were repeated to obtain

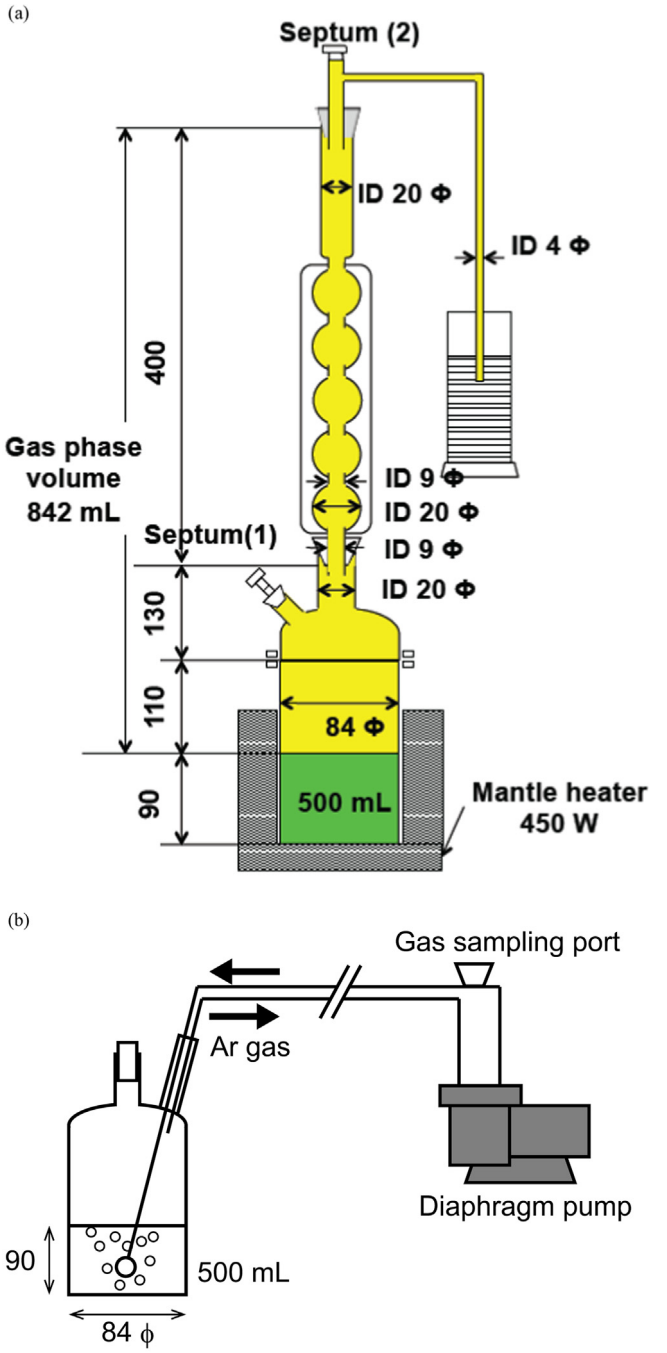

Fig. 1. (a) The irradiation setup with two sampling ports: Septum (1) and (2) for the experiment. The branch of the cooler is extended with silicone rubber tube and its end is immersed into the water in a measuring cylinder in order to keep the evolved gas inside the equipment separated from outer environment. (b) The irradiation setup composed of a sample vessel and a diaphragm pump for water radiolysis during Ar gas bubbling. The volumes of gas phase in the equipment and water sample in the vessel were 1007 and 500 mL, respectively. The gas was injected into the water sample through a glass ball filter to make fine bubbles and circulated with a flow rate of 1090 mL/min. The size is in mm unit.

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