Monitoring Temperature-dependent Stability of Hydrogen Peroxide as a Radiolysis Product in Various Aqueous Solutions

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***Keywords :** radiolysis, hydrogen peroxide, ferrous oxidation-xylenol orange, spectrophotometry, amperometry

1. Introduction

Radiation-induced dissolution of spent nuclear fuel (SNF) is one of the major processes determining the near-field source term of a repository and initiating radionuclide migration from SNF. The release of radionuclides is primarily dependent on the dissolution rate of the UO_2 matrix in SNF upon contact with water under geological repository conditions. The solubility of UO_2 can increase significantly if the reducing environment near the fuel surface is altered by water radiolysis induced by radiation from SNF, a pathway known as oxidative dissolution. Therefore, the analysis of water radiolysis products such as radicals ($\cdot OH$, $\cdot OH_2$, $e^-_{a}q$, $\cdot H$) and molecules (H_3O^+, H_2, H_2O_2) is essential for kinetic studies investigating the rate of such dissolution processes and their oxidation/dissolution mechanisms.

These radiolytic products are also known to react with metal ions originating from environmental sources, canister corrosion products, and engineered barrier materials in the repository. For monitoring H_2O_2 concentrations in aqueous samples, our previous study demonstrated that both the luminol-based chemiluminescence method and the spectrophotometric ferrous oxidation-xylenol orange (FOX) assay are effective techniques [1]. In this study, we investigated the temperature-dependent stability of H_2O_2 as a radiolysis product in various aqueous solutions, including simulated groundwater and solutions containing transition metal ions such as Fe^{2+}, using the FOX assay and a modified amperometric H_2O_2 sensor.

2. Methods and Results

2.1 FOX Assay for H_2O_2 determination

The FOX assay method was employed to spectrophotometrically determine H_2O_2 concentrations based on the color change (or absorption spectra) of Fe-xylenol orange (XO) complexes. In this method, Fe^{2+}-XO complexes were prepared in working solutions at pH 3, then mixed with H_2O_2-containing samples to allow quantitative oxidation of Fe^{2+} to Fe^{3+}. The absorbance of the Fe^{3+}-XO complex was monitored at its maximum wavelength (λ_{max}) of 560–580 nm using a UV-Vis spectrophotometer (Cary100, Agilent).

The FOX assay exhibited an analytical dynamic range up to approximately 100 µM, with a detection limit of ~1.6 µM. However, it is important to note that significant interference from M^{3+} and M^{4+} metal ions can occur, as these ions form XO complexes that directly contribute to the measured absorbance [1]. To mitigate such interference, all working and sample solutions used in the FOX assay were handled in perfluorinated polymer vessels to prevent contamination from laboratory glassware. Figure 1 presents the absorption spectra obtained during the FOX assay calibration by adding standard H_2O_2 solutions.

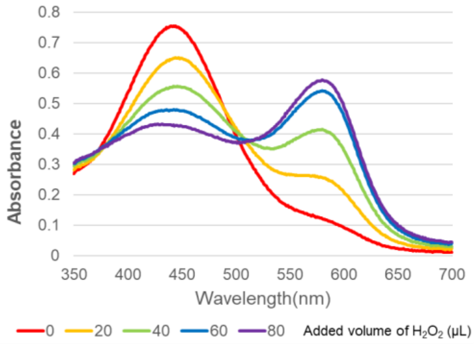

Fig. 1. Typical absorption spectral changes obtained during the FOX assay calibration by adding an aliquot of a standard H_2O_2 solution (2 mM) into each of 4-mL assay working solutions.

2.2 Amperometric detection of H_2O_2l

An amperometric sensor was developed to directly determine H_2O_2 concentrations in aqueous samples. The nitric oxide sensor previously reported in the literature [2] was modified for H_2O_2 detection, featuring a non-coated Teflon gas-permeable membrane, a Pt working electrode at the sensor tip, and a chlorinated Ag wire serving as a combined reference-counter electrode. Current changes upon sample addition were monitored using a potentiostat (SP-200, Biologic) based on pre-calibration data obtained using standard H_2O_2 solutions (Sigma-Aldrich).

2.3 Selected Aqueous Media

Three different aqueous media were selected: ultrapure deionized water (DIW, Milli-Q, Millipore), laboratory tap water (TW) from our facility, and simulated groundwater (sGW) representing typical granitic groundwater composition in Korea. Elemental analysis revealed trace amounts of Cu and Zn ions in TW. The chemical composition of sGW, as reported in our previous study [3], indicated approximately 1 mM carbonate ions and no transition metal ions with redox capability.

2.4 Matrix-dependent H_2O_2 Stability

At room temperature, H_2O_2 exhibited high stability in all tested media (DIW, TW, and sGW), with more than 80% of the initial H_2O_2 remaining active for up to seven weeks. However, in samples kept at 80°C in a heating block, less than 20% of the initial H_2O_2 remained after approximately six weeks. The stability order was DIW > sGW > TW at both temperatures, though the final concentration differences were not significant. This temperature dependency likely results from auto-catalytic H_2O_2 decomposition rather than degradation induced by ionic species in TW and sGW.

2.5 Influence of Fe^{2+} ion on H_2O_2 Stability

The decomposition of H_2O_2 induced by Fe^{2+} ions is postulated as shown in Rxn. (1). Fe^{2+}, in the form of an XO complex, oxidizes to Fe^{3+} while H_2O_2 decomposes into hydroxide ions and hydroxyl radicals. Compared to the kinetics described in Section 2.4, H_2O_2 decomposition in the presence of excess Fe^{2+} was significantly faster, with most H_2O_2 degrading within minutes at room temperature (see Fig. 2). The decomposition rate was highly temperature-dependent, becoming too rapid to monitor via batch spectrophotometry above 70°C, where reactions were completed in less than one minute. Further details on temperature-dependent kinetics will be provided in the presentation.

$$\mathrm{Fe(II)XO} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)XO} + \mathrm{OH^-} + \cdot\mathrm{OH} \qquad (1)$$

3. Conclusions

Quantitative H_2O_2 analysis methods developed in this study successfully monitored H_2O_2 stability in various aqueous media, including DIW, TW, and sGW. In the presence of trace transition metals or groundwater ionic components, H_2O_2 exhibited extended stability up to several weeks. However, Fe^{2+} ions significantly accelerated H_2O_2 decomposition, especially at elevated temperatures. The H_2O_2 reaction monitoring system proved useful for investigating the stability and reaction pathways of radiolytic products under radiation conditions relevant to spent nuclear fuel management systems.

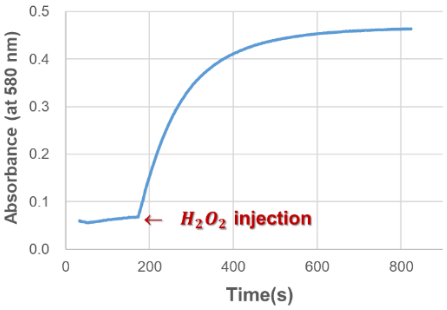

Fig. 2. The reaction kinetic profile of H_2O_2 decomposition in the presence of Fe^{2+} ions (0.2 mM) and XO (0.25 mM) in an aqueous solution at room temperature ([H_2O_2] = 40 µM).

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