Evaluation of Silica-Coated Tubing for the Measurement of Hydrogen Peroxide in Hot Water

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Evaluation of Silica-Coated Tubing for the Measurement of Hydrogen Peroxide in Hot Water

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A commercial silica coating for stainless steel tubing was investigated for its ability to inhibit the decomposition of aqueous hydrogen peroxide on the tubing surface. Although the coating proves effective at preventing decomposition up to 200 °C, above this temperature, the coating degrades, as evidenced by enhanced decomposition of the hydrogen peroxide.

I. Introduction

Piping in the primary heat transport system (PHTS) of a nuclear reactor is subjected to extreme conditions of heat, pressure, irradiation, and chemical attack. The materials must be carefully chosen for strength, stability, and corrosion resistance. The water coolant in the heat transport system undergoes radiolytic decomposition induced by gamma, fast-electron, and neutron radiation in the reactor core. Unless mitigating steps are taken, hydrogen peroxide produced by the coolant radiolysis can greatly enhance corrosion of the coolant system materials.[1,2]

To understand and make predictions about the water radiolysis and chemistry in the PHTS, one must be able to model both the radiation deposition and the resulting chemistry. However, the corrosion reactions themselves make laboratory high-temperature and -pressure measurements of peroxide chemistry very difficult. In preparation for measuring the temperature dependence of the hydrogen peroxide radiolysis yield, we measured the temperature stability of aqueous hydrogen peroxide from room temperature to 200 °C in silica-coated stainless steel tubing (Silcosteel tubing, Restek Corp.). The protective silica coating is needed because hydrogen peroxide decomposes on hot metal surfaces.[3] We evaluate the effectiveness of the coating in preventing hydrogen peroxide decomposition in this report.

II. Experimental Section

The experiment was carried out using a standard HPLC system (Spectrasystem, Spectra-Physics), in which the column was replaced with a temperature-controllable heating loop (Figure 1). The heating loop consisted of 3 m of 0.063-in.-o.d./0.020-in.-i.d. Silcosteel tubing wrapped around a stainless steel cylinder. The silica coating provides an inert, glasslike, passivated surface on the stainless steel tubing. Details concerning the coating have been published previously.[4] A 1000-W cartridge heater (Watlow Electric) was inserted into a

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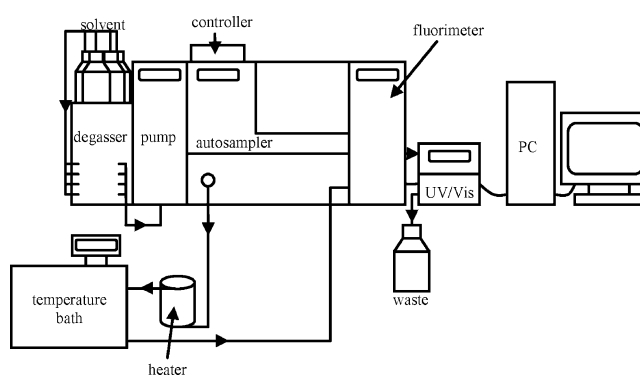
Figure 1. Schematic of the modified HPLC setup with heating loop.

hole drilled in the cylinder. A thermocouple placed inline with the flow monitored the temperature just after the heater. The thermocouple and tube fittings were also given a Silcosteel coating. An additional 1-m length of tubing after the thermocouple was coiled and placed in a circulating water bath set at 25 °C for cooling. The flow rate was 1 mL/min, giving a heating time of ∼35 s and cooling time of ∼12 s. A back pressure of ∼150 bar was maintained by allowing the flow to continue through a 1-m length of 0.004-in.-i.d. stainless steel capillary tubing, also placed in the bath. Immediately after cooldown, the presence of H_2O_2 in the effluent was detected online by integrating the peak intensity of the ultraviolet absorption at 200 nm.

Before measurements were taken, the entire system was first flushed at room temperature for 2 days with spectrophotometric-grade methanol and 2-propanol to remove organic impurities. The system was then flushed with deionized water (18.2 MΩ·cm, Barnstead Nanopure system) for an additional day. Hydrogen peroxide samples were diluted with deionized water from a stock 30% solution (Aldrich) to 0.03% (9 mM). This concentration was chosen as it gave a convenient scaling of the H_2O_2 absorption. Although a few concentrations were examined at first, the results described below did not show a concentration dependence, so only the 9 mM concentration was used for all temperatures. Samples were injected in 5-μL volumes. The time between injection and measurement was 160 s. Percent decom-
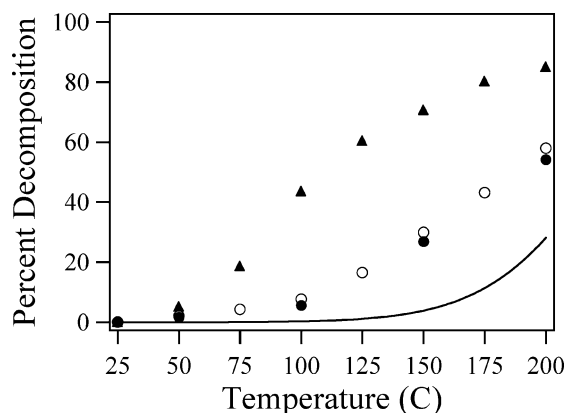
Figure 2. Observed H_2O_2 percent decomposition as a function of temperature. The closed and open circles indicate the first and second data sets, respectively, collected before substantial degradation of the tubing coating. The triangles indicate a second data set acquired after multiple heating cycles. The solid line represents the percent decomposition expected from spontaneous thermal decomposition of H_2O_2.[5,6]

position for each temperature was calculated by taking the ratio of the integrated peak intensity obtained after heating to the integrated peak intensity obtained when no heating was performed. Signals at 200 nm were checked against samples of oxygen-saturated water to confirm no interference from the oxygen absorption.

III. Results and Discussion

Figure 2 shows the percent decomposition as a function of temperature. Two data sets are shown, where the circles represent the first set of data collected and the triangles represent a data set collected 2 days later. In the first data set (closed circles), no substantial H_2O_2 decomposition is apparent at 100 °C or below. Above 100 °C, the percent decomposition significantly increases, and at 200 °C, it has reached a value of 54%. Data were also collected at temperatures above 200 °C, but signals were complicated by a background absorption that continuously grew more intense with time. A spectrum was acquired of the background absorption, which showed increasing intensity toward shorter wavelengths with no peak. Flushing the system with pure water for several hours did not remove the background absorption. Upon cooling to 200 °C and below, the absorption decreased and eventually vanished. Data were again collected as the system cooled and are shown in Figure 2 as the open circles. Upon reaching room temperature, the system was heated to 225 °C, and the background absorption reappeared. Flushing with water, methanol, or 2-propanol did not remove the background absorption. The system was flushed with methanol at room temperature overnight in an attempt to remove any impurities in the system. The system was flushed with water and heated again the following day, and the background absorption grew in again above 200 °C. The system was then flushed with methanol for several hours at 300 °C, allowed to cool back to room temperature, and then flushed with water overnight.

The H_2O_2 decomposition was examined again the next day, and the data obtained are represented by the triangles in Figure 2. The onset of decomposition was observed at much lower temperatures, and yet again, the background absorption grew in above 200 °C.

It is clear that the silica-based coating in the heating loop tubing degrades upon heating at 200 °C and above, possibly producing SiO_2. After the system has been heated and cooled through several cycles, the H_2O_2 decomposition occurs at lower temperatures, possibly because of contact with a greater amount of bare metal tubing exposed after the coating has broken down.

Previous studies demonstrated that the H_2O_2 thermal decomposition reaction has an activation energy of 71 kJ/mol, and the rate constant is given by the Arrhenius expression $6.5 \times 10^5 \exp(-71 \text{ kJ mol}^{-1}/RT)$.[5,6] On the basis of this rate constant and our flow time through the heating coil, we have estimated the percent decomposition as a function of temperature. This is indicated by the solid line in Figure 2. The observed degree of H_2O_2 thermal decomposition in fresh tubing exceeds expectations if we assume that contact with a hot metal surface was completely avoided. Although we attempted to minimize contact with all hot metal surfaces, it is possible that a very small metal surface was exposed at the thermocouple "tee" joint, at the ends of the cut Silcosteel tubing. The limiting behavior might be obtained by coating the tubing after assembly of the system. Such a coating treatment is advertised by the Restek corporation and will be investigated in the future.

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