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In-situ neutron tomography on mixing behavior of supercritical water and room temperature water in a tubular flow reactor

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Abstract

We have synthesized metal oxide nanoparticles through hydrothermal reaction at around 400°C and 25 MPa by mixing the stream of metal ion solution at room temperature with another stream of supercritical water in a continuous flow-type reactor. In order to visualize the mixing behavior of the two streams, we performed neutron tomography measurements. By performing tomography measurements while rotating the mixing piece with supplying supercritical water and room temperature water, we succeeded in obtaining the three dimensional distribution of neutron attenuation. The results clearly showed how the two streams mix, which serves as a reference for numerical simulation.

Keywords: tomography; flow-type reactor; supercritical water; mixing; hydrothermal reaction

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1. Introduction

Water is the most common liquid on the earth and is involved with almost all phenomena. So far, various studies have been performed in aqueous phases at different temperature and pressure conditions. Among them, supercritical water, whose temperature and pressure are higher than the values at the critical point (374°C and 22.1 MPa) plays important roles in chemistry, mechanical engineering, and geology. Their properties including *p*-*V*-*T* diagram (Wagner et al. (2002)), heat capacity, the solubility of ions, and dielectric constant have been extensively studied because they are important factors in hydrothermal processing, material synthesis, heat exchange, petrography, and geochemistry.

In these chemical processes, the mixing of supercritical water with other stream is crucial for better operation. For example, the size and shape of the products in hydrothermal synthesis depend largely on the mixing behavior of supercritical water and the reactants (Adschiri et al. (2004), Byrappa et al. (2008), Toft et al. (2009)). The rapid mixing results in the narrower distribution of reaction time and therefore the uniformity of products. Because such processes are performed at high temperature and pressure, the containers are made from metallic alloys, which made the observation of mixing behavior difficult. So far, model experiments that mimic the real process have been performed (Blood et al. (2004), Aizawa et al. (2007)). Numerical simulation that considers flow dynamics in the reactor has been also studied (Sierra-Pallares et al. (2009)). However, these approaches were difficult to observe the mixing behavior in the junction used for existing reactors.

In order to overcome these problems and to visualize the mixing behavior of supercritical water, we proposed neutron radiography. Neutron is largely scattered by hydrogen atoms and can transmit in most metals. Therefore neutron radiography can visualize the density of water in a container made from metal alloys. Because the density of water is a function of temperature at a constant pressure, we could obtain the temperature distributions of the water. We have verified our idea by applying neutron radiography to the experiments (Takami et al. (2012), Sugioka et al. (2014)). However, the obtained images were two dimensional images and showed the averaged density of water along the neutron beam path. In this study, we performed neutron tomography at the junction where supercritical water and room temperature water were mixed.

2. Experimental

Experiments were performed at the B4 port of the Research Reactor Institute of Kyoto University. The experimental setup was similar to our previous studies except for using a rotational stage for tomography measurement (Fig. 1). A stream of water was fed by a high-pressure pump (P_{top}) and heated by a heater. Another stream of water was also fed by a high-pressure pump (P_{side}). The flow rate of the streams was summarized in Table 1.

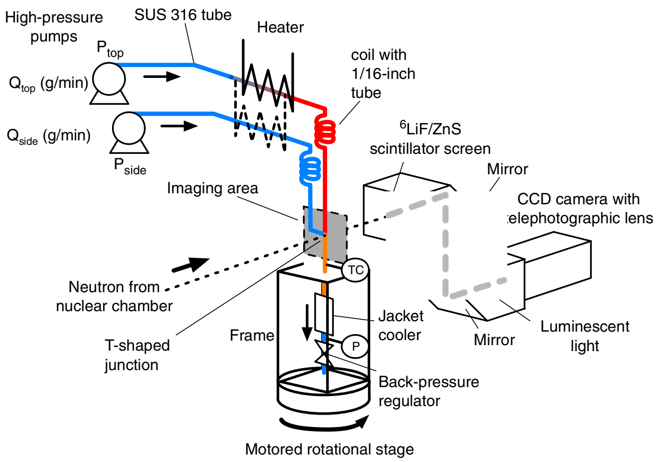

Fig. 1. Schematic diagram of experimental apparatus for neutron tomography.

Table 1. Experimental conditions

Q_{top} (g/min)	T_{top} (°C)	Q_{side} (g/min)	T_{side} (°C)	T_{mix} (°C)	Re_{mix}
12.0	~385	6.0	30	335	2.0×10^3
6.0	30	12.0	~391	355	2.3×10^3

The two streams were mixed at a T-shaped junction. A 1/8-inch Swagelok union T-component was used as the junction with the inner diameter of 2.3 mm. In this study, supercritical water was supplied from either top or side of the junction. When supercritical water was supplied from side, the water stream from the high-pressure pump P_{side} was heated by a heater. The tubes and Swagelok components were covered by heaters or thermal insulators. The temperature of the mixed stream was monitored by a thermocouple just below the junction and shown in Table 1. We could not measure the temperature of supercritical water because the insertion of thermocouple might interfere the rotational movement of the mixing piece. Therefore we estimated the temperature of the supercritical water before mixing by considering the heat balance between before and after the mixing. The estimated values are also shown in Table 1. The mixed stream was then cooled by a jacket cooler and released from a back-pressure regulator that maintained the pressure of the system at 25 MPa. In order to obtain neutron radiography images, neutron beam from the nuclear reactor was irradiated to the junction. The transmitted neutron beam was converted to fluorescence light by a ^{6}LiF/ZnS converter (Chichibufuji Co.) and the fluorescence light was monitored by a CCD camera (PIXIS-1024B, Princeton Instruments Co.) with the resolution and bit depths of 1024×1024 pixels and 16 bits. The size of the imaging area was 6.53×6.53 cm^2. In our experiments, the Kyoto University research reactor was operated at 5 MW and the flux of neutron beam at the B4 port was 5×10^7 n/ cm^2 s. The junction, jacket cooler and back pressure regulator were tightly fixed on a frame that was rotated using a motored stage (KST-160YAW, Sigma Koki Co.) to perform tomography measurements. In order to compensate the rotational motion of the junction and the lower reaches, the junction was connected with the two high-pressure pumps through coiled 1/16-inch SUS tubes, which were covered with ribbon heaters. During the tomography measurements, the junction was exposed to neutron beam for 60 s to obtain one radiograph, then the stage was rotated for 0.90 degree to obtain next images. This sequence was repeated for 200 times while feeding and mixing supercritical water and room temperature water. Special care was taken to stabilize the whole system including the temperature of mixed flow before starting the tomography measurements.

The radiography images were processed as follows. The image brightness, $I(x, y, n)$ ($1 \leqq x, y \leqq 1024$, $1 \leqq n \leqq 200$), was subtracted with the dark current image, $I_d(x, y)$, which was obtained while neutron beam was not irradiated. Similarly, the background image, that is, the two-dimensional distribution of irradiated neutron, $I_0(x, y)$, was obtained and subtracted with the dark current image. Transmitted neutron beam, $T(x, y, n)$, was calculated by Eq. (1).

$$T(x,y,n) = \frac{I(x,y,n)-I_d(x,y)}{I_0(x,y)-I_d(x,y)} \quad (1)$$

In order to perform computed tomography reconstruction, we used the Octopus software (ver 8.6, Dierick et al. (2004)). A set of radiography images ($I(x, y, n)$), the dark current image ($I_d(x, y)$), and the background image ($I_0(x, y)$) were used as the input images. The representative parameters for CT reconstruction were as follows: Spot filter: 10, Ring filter: 5, Noise filter: 0 %.

3. Results and discussion

Figure 2 shows representative transmitted images of neutron beam ($T(x, y, n)$). In these images, we can confirm the dark regions corresponding to the Swagelok components and tubes, suggesting the existence of water with higher density (low transmission of neutron, that is, lower temperature) and we can recognize the flow pattern at the junction. When supercritical water was fed from top (Fig. 2(a)), the room temperature water with darker

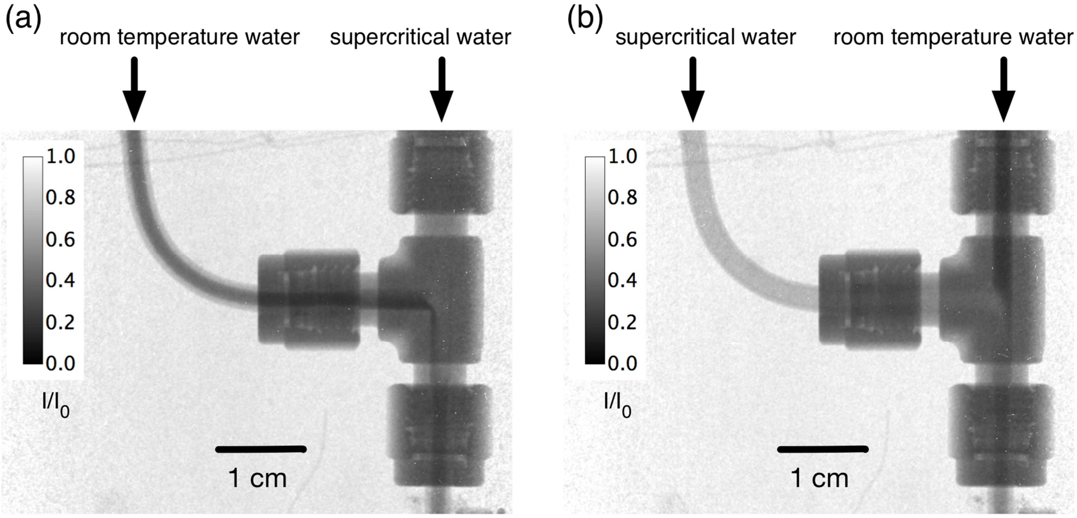

Fig. 2. Neutron radiography images when supercritical water was supplied from (a) top; (b) side.

brightness was mixed from side and flowed along the left side of the vertical tube after the junction. On the other hand, when supercritical water was fed from side (Fig. 2b), the room temperature water was fed from top and flowed at the right side of the vertical tube after the junction and gradually mixed with supercritical water. These tendencies are the almost same as the previous experiments (Sugioka et al. (2014)). However, the detailed mixing behavior cannot be distinguished, because the images were superimposed with mixing pieces and the images were the average along the direction of neutron beam.

Using 200 neutron radiography images that were obtained while rotating the junction, we reconstructed three dimensional distribution of neutron attenuation. Figure 3(a) shows a vertical cross sectional image at the center of the mixing piece with supplying supercritical water from top. The area with lighter color corresponds to the region where neutron beam was less attenuated. Fig. 3(a) clearly showed the change in the density of water streams in the mixing components and tubes. Supercritical water that was fed from top was mixed with the room temperature water from side at the mixing point. After mixing, the room temperature water with high density flowed along the side wall of the vertical tube. Fig. 3(b) showed the cross sectional images of the tubes around the junction. In the side tube, the stratified flow behavior can be observed, where the supercritical water with smaller density penetrated into the side tube. Even though some noises exist, we can confirm that the image brightness at the upper part in the side tube was lighter than that at the lower part, indicating that supercritical water penetrated into the side tube and mixed with room temperature water there. The lower part of room temperature water still had large water density and therefore, they flowed down after mixing. The room temperature water flowed down along the side wall of vertical tube (darker areas) while the rest of region were filled with supercritical water. The interface between two flows gradually mixed after the junction.

Figure 4(a) shows a vertical cross sectional image while supplying supercritical water from side. In this case, the room temperature water from top flowed at the right side of the tube in the mixing piece, because the supercritical water flowed in from left (12.0 g/min). After mixing, supercritical water flowed at the center of the tube and mixed with the room temperature water. Figure 4(b) shows the cross sectional images of the tubes. The brightness of water stream in the side tube was almost the same, suggesting no penetration of the room temperature water into the side tube. Similarly, the brightness of the room temperature water before mixing was almost the same. This might be because the flow rate of 6.0 g/min was large enough to prevent the penetration of supercritical water into the vertical tube due to the buoyancy force before mixing. As the result, the two streams were mixed at the mixing junction and then flowed downward in the tube.

These results clearly show that the neutron tomography provides detailed information about the mixing of supercritical water and room temperature water in the continuous flow-type reactor. Such cross sectional images of the tube around the junction cannot be obtained by conventional neutron radiography. These three-dimensional distribution images of neutron attenuation can be used to understand the mixing behavior of supercritical water and to verify the validity of flow-dynamics simulation of subcritical and supercritical water.

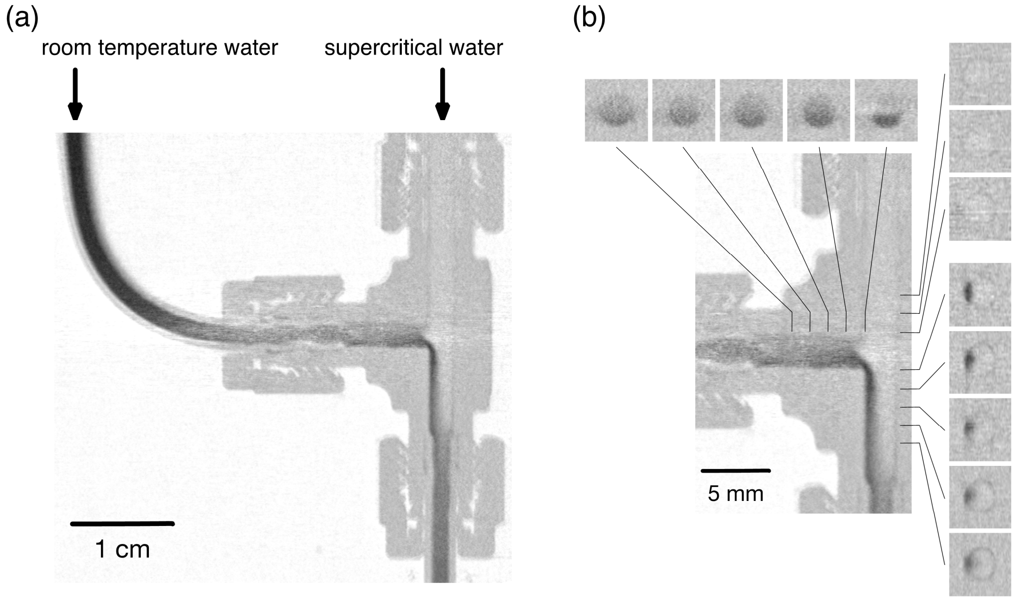

Fig. 3. (a) Reconstructed vertical cross sectional image of neutron attenuation at the center of mixing piece when supercritical water was supplied from top; (b) Horizontal cross sectional images around the mixing piece.

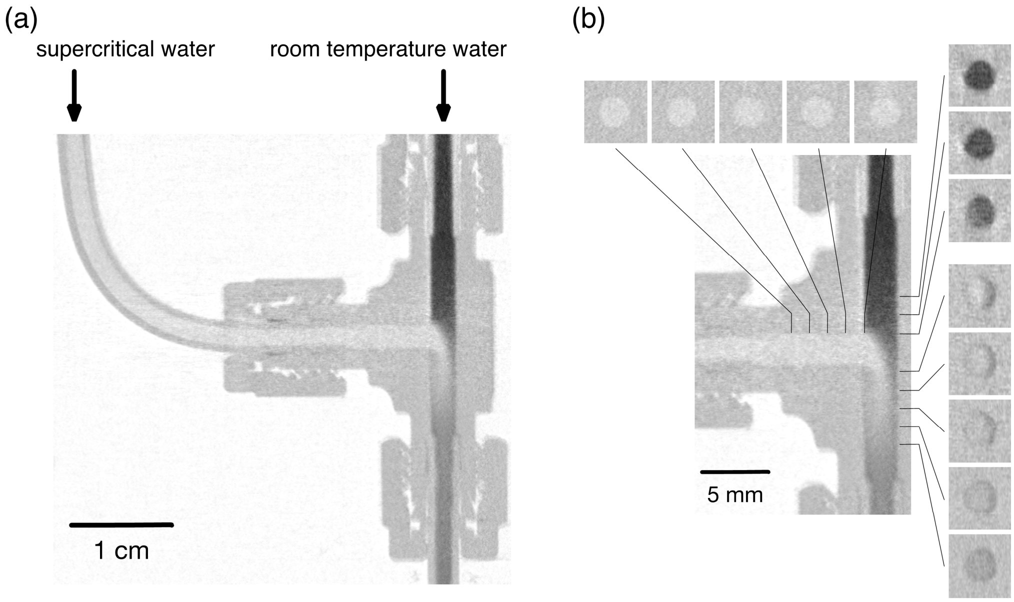

Fig. 4. (a) Reconstructed vertical cross sectional image of neutron attenuation at the center of mixing piece when supercritical water was supplied from side; (b) Horizontal cross sectional images around the mixing piece.

4. Conclusion

We have performed neutron tomography measurements on a tubular flow reactor for supercritical hydrothermal synthesis. The obtained images showed three dimensional distribution of the density of water in stainless steel tubes and the T-junction. This result demonstrated that neutron tomography clearly showed the mixing behavior of supercritical water and room temperature water. We believe that these results can be used to verify the validity of fluid dynamics simulation.

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