An experimental study for measurement of critical point of multicomponent geofluids by using spectroscopic measurement

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Geofluids are multicomponent fluids due to reaction with various crustal materials, and they exist in the supercritical state under high temperature and high pressure conditions inside the Earth. In order to investigate reaction mechanisms under high temperatures and high pressures, it is extremely important to know phase state and the critical point of the geofluid, and advanced critical point (CP) measurement technique is required. In the previous studies, there are two major conventional CP measurement methods as follows:

(1) Observing appearance and disappearance of gas-liquid boundary (meniscus).

(2) Estimating by calculation of equation of state based on experimental data.

In the method (1), it was difficult to accurately determine the CP because the appearance and disappearance of the boundary occurs gradually. In the method (2), the more complex the components of the fluids, less accurate the calculation of CP. Sekiguchi *et al.* (2014) determined the CP by analyzing the transmitted light of the fluid. At the CP, it is possible to observe a specific scattering phenomenon called critical opalescence, the transmitted light of the fluid decreases and the scattered light increased significantly. In method of Sekiguchi *et al.* (2014), although the CP was determined by spectroscopic measurement of the change of the transmitted light, there was a problem that the change of the transmitted light at the CP was not clear. Therefore, we propose CP measurement method using spectral characteristics of scattering light in fluid and are aiming to establishing accurate and easy method to estimate the CP. In this study, we conducted an experimental study to improve reproducibility of the measurement system and procedure.

In this experiment, H_2O is used as the test fluid. The H_2O is injected into vacuumed autoclave with transparent sapphire window for observation at a filling ratio 45% and temperature and pressure inside the apparatus was increased to 400 °C, 30 MPa. Halogen bulb were used as light source. Incident light of which spectral are between 400 and 800 nm was applied to the pressure vessel from one side, and scattered light was observed through transparent sapphire window which attached orthogonal oriented to the incident beam line. In addition, H_2O during the experiment was observed by a digital camera. The temperature inside autoclave was measured by thermos couple, and pressure was also measured by pressure sensor. Integrated value of the spectral distribution in the measurement wavelength range (Total Scattering Intensity : TSI) was calculated, and we tried to determine the critical point by analyzing the behavior of TSI with temperature. We performed heating and cooling processes of geofluids, in other words the fluid heated up above the CP, and then the supercritical fluid cooled down to subcritical state through the CP. Critical opalescence can be observed clearly during the cooling process.

Firstly, we focused on experimental results of the heating process. In the heating process, TSI decreased as the temperature approached the critical temperature, TSI became minimum value at the CP. Above the critical temperature, TSI did not appear to change significantly. This is considered to be due to the fact that homogeneous of the temperature distribution inside the apparatus in the heating process is lower

than cooling process. On the other hand, in the cooling process, although TSI decreased as the temperature approached the critical temperature, TSI increased significantly near the CP and TSI became maximum value at the CP. The temperature at which TSI became maximum value almost agree with the literature value of critical temperature. Therefore, in this method, the CP can be determined by spectroscopic measurement in the cooling process. In addition, the change of the scattered light at the critical point is more clear than the transmitted light, and the proposal method is considered to be effective as the CP measurement method. In the lecture of the day, the results of the critical point measurement of NaCl aqueous solution and sea water using the proposed method are also discussed.

Keywords: Supercritical fluid, Critical point, Spectroscopic measurement