FORMATION OF Tc(IV) OXIDE COLLOIDS BY BREMSSTRAHLUNG IRRADIATION OF PERTECHNETATE

T. Sekine[1], H. Narushima[1], H. Kudo[1], M. Lin[2], Y. Katsumura[2]

[1] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[2] Nuclear Engineering Research Laboratory, School of Engineering, The University of Tokyo, Ibaraki 319-1106, Japan

The formation mechanisms of technetium(IV) oxide colloids formed by bremsstrahlung irradiation of aqueous solutions of pertechnetate (TcO_4^-) are discussed.

Pertechnetate solutions (5.5×10^{-5} - 2.9×10^{-4} M) were irradiated with bremsstrahlung from an electron linear accelerator at 40 and 17 ± 3°C. The color of the irradiated solutions gradually changed to brownish black, suggesting the formation of Tc(IV) oxide colloids ($TcO_2 \cdot nH_2O$). A transmission electron microscopy (TEM) analysis showed that the diameter of colloids distributed from 30 to 130 nm. The characteristic X rays from technetium and oxygen were detected from colloid particles through the TEM measurements. Round-shaped colloids were produced by the irradiation at 40 °C, whereas irregular-shaped colloid particles composed of tiny particles (2 nm in diameter) were produced at 17 °C. Electron diffraction of the colloid particles showed no clear patterns, indicating an amorphous structure.

Gradual coagulation of the colloids was occasionally observed in a few days after irradiation, resulting in precipitation of $TcO_2 \cdot nH_2O$. The colloid formed in Ar-saturated solution was quite stable, and electrophoretic analysis of this turbid solution revealed a negative charge on the colloid particle in the pH range from 7 to 3. The charge turned into positive at pH 1.5, indicating that a point of zero charge of $TcO_2 \cdot nH_2O$ colloids should lie in pH between 1.5 and 3.

The TcO_4^- concentration of the target solutions gradually decreased with an increase of the absorbed dose, reflecting the colloid formation. The TcO_4^- fraction sharply decreased in the solution containing 0.2 M *t*-butyl alcohol deaerated by Ar bubbling before irradiation, but the decrease was strongly suppressed in the solution saturated with oxygen (O_2) or nitrous oxide (N_2O) gas. The fact suggests that hydrated electrons produced by radiolysis of water play an important role in the course of reduction of TcO_4^- to Tc(VI). The successive disproportionation reactions of Tc(VI) and Tc(V) afford Tc(IV) oxide colloids.