

Technetium(IV) Oxide Colloids and the Precursor Produced by Bremsstrahlung Irradiation of Aqueous Pertechnetate Solution

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Mechanisms of the radiolytic formation of $^{99}\text{Tc}^{\text{IV}}\text{O}_2 \cdot n\text{H}_2\text{O}$ colloids were studied by bremsstrahlung irradiation of an aqueous pertechnetate ($\text{Tc}^{\text{VII}}\text{O}_4^-$) solution under different conditions; pH of the target solution, concentration of TcO_4^- and presence or absence of radical scavengers and of seed particles of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Colloid particles (30 – 130 nm) of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ — a coagulate of nanoparticles with the size of 2 nm — were radiolytically produced at pH higher than 3, whereas a soluble Tc(IV) species but colloid was formed at lower pH. The soluble Tc(IV) species transformed to the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid when the pH of the solution was raised to 3 or higher after the irradiation. This fact suggests that the soluble Tc(IV) species is a precursor of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid. The presence of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ seed particles in the target solution of TcO_4^- did not enlarge of the particle size, revealing that the solidification would take place rather in the solution than on the surface of nanoparticles. The reduction of TcO_4^- in acidic solutions proceeded mainly through processes involving a bimolecular reaction of TcO_4^- with hydrogen radicals, followed by the successive disproportionation reactions of Tc(VI) and Tc(V).

1. Introduction

In terms of high-level radioactive waste disposal in deep underground, the formation of colloids in groundwater is one of the most important factors that promote migration of long-lived radionuclides in the environment.¹ A number of studies have shown that mobile colloids, abundant in the subsurface of earth, would facilitate the transport rate of radioactive contaminants higher than predicted by aqueous-phase transport models.^{2,3} Much remains to be investigated to elucidate specific conditions necessary for stability and movement of colloids.⁴

Technetium (^{99}Tc) is a long-lived ($t_{1/2} = 2.11 \times 10^5$ y) nuclear fission product that has entered the earth's surface and groundwaters as a result of atmospheric nuclear testing as well as disposal of medical and nuclear waste. It also exists as an important subsurface contaminant at numerous nuclear facilities.⁵ At the Hanford Site (USA), four large ^{99}Tc groundwater plumes exist and new ones are forming as ^{99}Tc released to cribs and leaked from single-shell high-level waste tanks. The ^{99}Tc migrates through the vadose zone. Over 1.48 TBq of $^{99}\text{Tc}(\text{VII})\text{O}_4^-$ is envisaged to be discharged to the Columbia River in future years, making it one of the site's major risk-driving contaminants.⁶

The environmental geochemistry of Tc is dominated by the IV ($\text{TcO}(\text{OH})_2$) and VII (TcO_4^-) oxidation states. The VI, V and III oxidation states are known, but the VI and V states are generally unstable and disproportionate.⁷ The III state requires extremely low redox potentials.⁸ The highly soluble pertechnetate ion (TcO_4^-) would not form significant aqueous complexes or discrete concentration-limiting solid phases under environmental conditions. This species migrates rapidly concurrent with vadose zone water and groundwater, weakly sorbed under most geochemical conditions.⁹ In contrast, Tc(IV) readily precipitates as an insoluble hydrous oxides unless complexed.^{10,11} Conversion of $\text{Tc}(\text{VII})\text{O}_4^-$ to $\text{Tc}(\text{IV})\text{O}(\text{OH})_2$, which would not migrate due to its strong adsorption on rocks and minerals,¹² offers a potential capability for immobilization of Tc in the

environment. At present, however, knowledge on the formation and stability of Tc(IV) colloids is limited.

In addition to general routes of colloid formation, a radiolytic effect on the formation of colloids should be taken into account in this case, because an extremely high radiation dose from the spent nuclear fuel will be continuously given to the surroundings for a long period of time.

The radiolytic colloid formation has been extensively investigated,^{13,14} because it is one of the unique means to prepare nanoparticles of noble metals and bimetallics in terms of technological applications of nanoparticles. In radiolyses of aqueous solution, hydrated electrons (e_{aq}^-) and hydrogen radicals (H), which are radiolytic products of water, are effective reductants for metal cations to produce nanoparticles. As for technetium, Said et al.¹⁵ reported that a brown turbid solution was obtained by γ -irradiation (^{60}Co source) of an aqueous solution of pertechnetate ($\text{Tc}(\text{VII})\text{O}_4^-$). This was the first evidence for the formation of colloidal $\text{Tc}(\text{IV})\text{O}_2 \cdot n\text{H}_2\text{O}$ by radiolysis. In contrast, Lefort reported the redissolution of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ by irradiation of ^{60}Co γ -rays.¹⁶ Recently, we have found the formation of technetium(IV) oxide ($\text{Tc}(\text{IV})\text{O}_2 \cdot n\text{H}_2\text{O}$) colloids by bremsstrahlung irradiation of aqueous pertechnetate solution. The color of irradiated solutions gradually changed to brownish black, suggesting the formation of the colloids.¹⁷ Here, we report characteristic features of the radiolytically produced colloid and its formation processes.

2. Experimental

Ammonium pertechnetate ($\text{NH}_4^{99}\text{TcO}_4$) crystals were thermally decomposed under oxygen gas flow (flow rate = $100 \text{ cm}^3 \text{ min}^{-1}$) in a glass tube heated with an electric furnace to 300°C . Technetium heptaoxide (Tc_2O_7) that was vaporized and deposited on the inner surface of the glass tube was dissolved in triply distilled water. This solution was kept as a stock solution of pertechnetic acid (HTcO_4). The TcO_4^- concentration of the solution was adjusted to the range of $2.56 \times 10^{-6} - 1.12 \times 10^{-4}$ M. The target solutions were bubbled with Ar, O_2 , N_2 , or H_2 gas, and sealed in polypropylene vials (5 mL in volume). The

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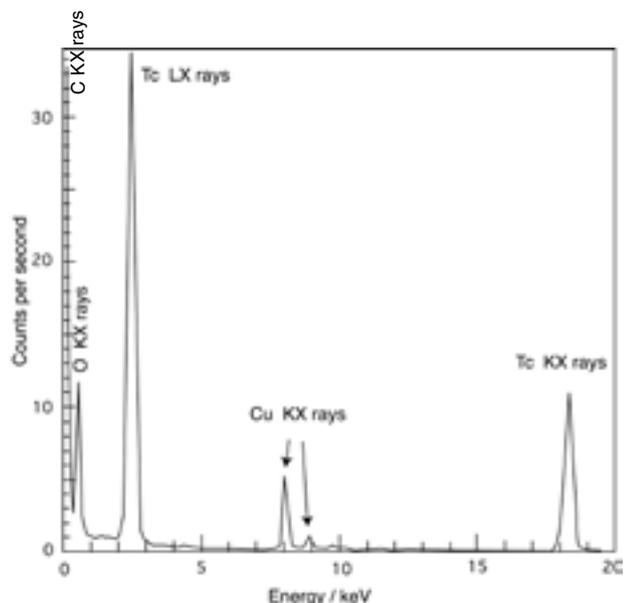


Figure 1. Energy dispersive X-ray spectrometry (EDXS) of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids on copper grid.

target solutions of pH 1.8 and 2.7 were prepared by acidifying with sulfuric acid.

The target solutions were irradiated with bremsstrahlung from an electron linear accelerator of the Laboratory of Nuclear Science, Tohoku University. The irradiation setup was described elsewhere in detail.¹⁷ The irradiation time was ranged from 5 min to 2 h. The pulse duration was 3 μs and the repetition rate of electron pulses per second (pps) was varied from 6–300 pps. Target temperature was also varied from 8–40 °C.¹⁷ The irradiated solutions were kept in an ice reservoir until chemical analysis.

The amount of Tc(IV) colloids was determined by ultrafiltration. One milliliter of the irradiated solution was passed through an ultrafilter (Millipore, nominal molecular weight limit = 3,000 or 10,000) by centrifugation (4000 rpm, 2 h). The concentration of ⁹⁹Tc was measured with a liquid scintillation counter (Aloka LSC 5100). UV–vis spectra were recorded on a Shimadzu MultiSpec-1500 in the range of 190–800 nm before and after ultrafiltration. Separation of soluble Tc species was performed by paper chromatography (Chromatography papers No. 51B, Advantec Toyo Co.). The chromatogram was developed for 20 cm length with an aqueous eluent having the same acidity of the target solution. Technetium species on the paper were visualized by using an imaging plate (Fuji Photo Film, BAS-IP SR-2005) and analyzed by a Bio Imaging Analyzer (Fuji Photo Film, BAS-5000).

A transmission electron microscope (TEM, JEOL JEM-2000 EXII) was used for evaluation of a mean size of colloids. Chemical composition of the colloids was confirmed by the energy dispersive X-ray spectroscopy (EDXS; Oxford Instruments Link-ISIS).

3. Results

Characterization by energy dispersive X-ray spectrometry (EDXS) of one colloid particle revealed that the colloid consisted of technetium and oxygen (Figure 1). The observed X-rays peaks were assigned to technetium, oxygen, copper and carbon; $K\alpha_1$ (Tc) 18.41 keV, $L\alpha_1$ (Tc) 2.424 keV, $K\alpha_1$ (O) 0.523 keV, $K\alpha_1$ (Cu) 8.047 keV, $K\alpha_1$ (Cu) 8.904 keV and $K\alpha$ (C) 0.282 keV. The X-rays of copper and carbon arose from a copper grid coated with graphite used as a sample holder in the EDXS measurement.

As reported in the previous paper,¹⁷ the size of colloid particles distributes around 30–130 nm in diameter. The shape of

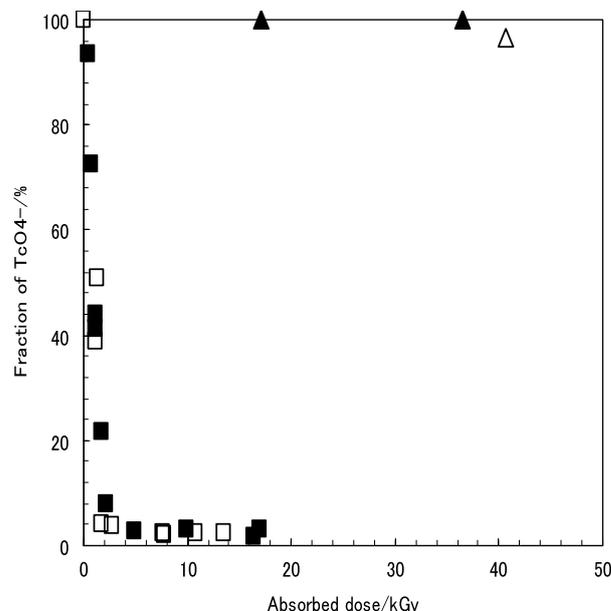


Figure 2. Fraction of TcO_4^- in the irradiated solution against absorbed dose. The initial concentration of TcO_4^- was 1×10^{-4} M and pH = 6/7 (neutral). The target solution was saturated with: \square , H_2 ; \blacksquare , Ar; \triangle , N_2O ; \blacktriangle , O_2 .

colloid produced depends on the temperature of target solutions during irradiation. Spherical particles were formed by the irradiation at 40 °C (3–7 h), while irregular-shaped colloid particles composed of tiny particles (2 nm in diameter) were formed at 17 °C. The irregular surface feature was independent of the kind of dissolved gases and the absorbed dose. This is true for almost all particles produced by irradiation at 17 ± 3 °C. Assuming that the tiny spherical particles has the same density as the TcO_2 crystal (3.02 g cm^{-3}),¹⁸ we can describe that about 30000 of tiny particles (2 nm in diameter) coagulate to form colloids in a larger size. The colloids afforded by bremsstrahlung irradiation were amorphous.

The fraction of TcO_4^- in the irradiated solution are plotted against the absorbed dose up to 50 kGy in Figure 2 for samples with an initial concentration of 0.1 mM. The fraction of TcO_4^- sharply decreased in the H_2 - and Ar-saturated solutions even in the low dose range. In the O_2 - and N_2O -saturated target solutions, the colloid formation was not found up to 200 kGy.

The formation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid was only observed in the solutions irradiated at pH 6–7 (neutral) and pH 4.6 (Figure 3(a)). The polymeric Tc(IV) species, the presence of which was suggested by Vichot et al.¹⁹ was formed only in the solution at pH 1.8, acidified with sulfuric acid. Both Tc(IV) colloids and the soluble Tc(IV) species were formed at pH 2.7. Here, the polymeric Tc(IV) species was formed first in the low dose region followed by generation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids (Figures 3(a) and 3(b)). The effect of the presence of sulfate ions was examined by adding Na_2SO_4 (0.01 M) to the target solution (pH 4.6). Only the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids but polymeric Tc(IV) species were formed in the solution.

The presence of own seed particles which might enhance the formation rate of colloids by γ -radiolysis was also examined in this experiment. The fraction of TcO_4^- was determined for the irradiated TcO_4^- solution in the presence and absence of seed $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids. The results are shown in Figure 4 for the lower dose range up to 8 kGy. There is no significant difference in the TcO_4^- fraction, irrespective of the irradiation with or without $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ seed particles.

In the neutral target solutions (pH 6–7), the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid yield or the decrease in TcO_4^- fraction in the solution depends on the initial concentration of TcO_4^- as summarized in Table 1. The $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid was not formed at 2.56×10^{-6} M of the initial concentration, the TcO_4^- fraction remaining

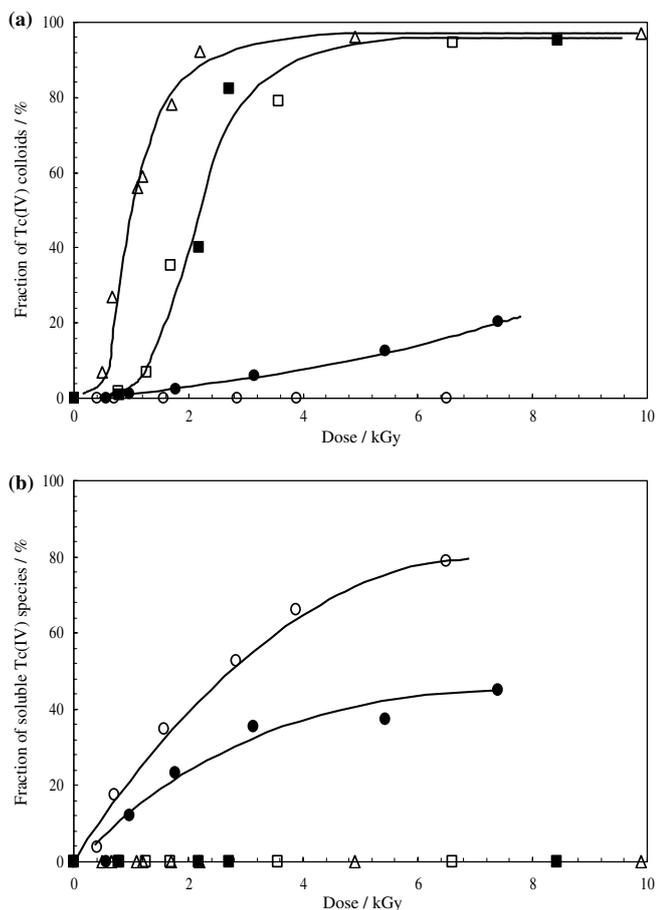


Figure 3. Fraction of Tc(IV) colloids (a) and soluble Tc(IV) species (b) in the irradiated TcO_4^- solutions as a function of dose. pH of the target solutions was: \triangle , neutral (6/7); \blacksquare , pH 4.6; \square , pH 4.6 + 0.01 M Na_2SO_4 ; \bullet , pH 2.7; \circ , pH 1.8. Solid lines are a guide for eyes.

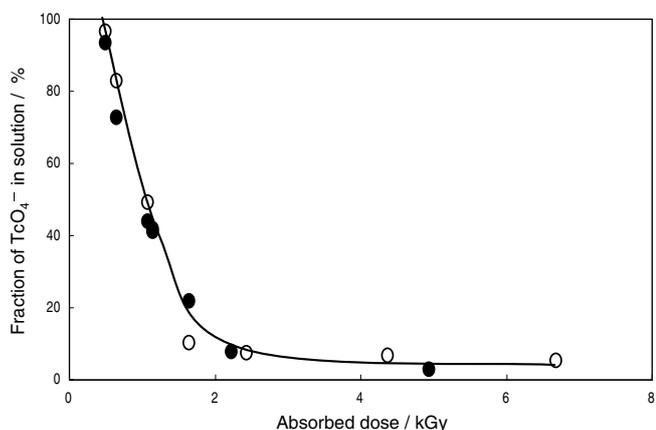


Figure 4. TcO_4^- fraction in the solution against absorbed dose. The solution was Ar-saturated and the initial concentration of TcO_4^- was 1×10^{-4} mol dm^{-3} , in the presence (\circ) and absence (\bullet) of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid. The temperature was 8 ± 2 °C during irradiation.

100%. The yield of colloid was fluctuated between 6 to 10% at the absorbed dose above 0.8 kGy. The final concentration of TcO_4^- reached 7.44×10^{-6} M for $[\text{TcO}_4^-]_{\text{initial}} = 1.12 \times 10^{-4}$ M and 7.51×10^{-6} M for $[\text{TcO}_4^-]_{\text{initial}} = 7.86 \times 10^{-5}$ M.

4. Discussion

Pertechnetate ($^{99}\text{TcO}_4^-$) ions were radiolytically reduced to tetravalent technetium before the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid formation. In general, the reduction reaction in radiolysis is brought about by reducing agents arising from radiolysis of water:



The reducing agents are hydrated electrons (e_{aq}^- , G -value =

TABLE 1: Pertechnetate Fraction (%) in the Irradiated Samples for Different Initial Concentrations and Absorbed Doses. The Target Solutions were Neutral (pH 6–7)

$[\text{TcO}_4^-]_{\text{initial}}/\text{M}$	Dose/kGy	TcO_4^- fraction/%
1.12×10^{-4}	0.18	62.9
	0.24	10.2
	0.5	8.2
	0.69	6.5
	1.6	6.5
	2.9	6.7
	6.8	7.1
	13.7	6.6
	23.8	6.9
	30.7	6.2
7.86×10^{-5}	0.15	50.9
	0.28	14
	0.44	14.7
	0.68	13
	1.8	11.4
	2.6	12
	9.7	9.8
	20.5	10.2
	28.4	8.7
2.56×10^{-6}	1.7	100
	6.3	100
	5.8	100

2.7) and H radicals (G -value = 0.6)²⁰ in neutral solution. The hydrated electron (e_{aq}^-) is a reducing agent stronger than the H radical. In the O_2 -saturated solution, e_{aq}^- and H are effectively scavenged by O_2 to give O_2^- . In the N_2O -saturated solution, N_2O rapidly reacts with e_{aq}^- giving rise to an OH radical that is a strong oxidizing agent. In H_2 - or Ar-saturated solution, scavenging of e_{aq}^- and H radicals would be minimized because of the low O_2 concentration (< 0.2 ppm). Moreover, the presence of H radicals in the H_2 -saturated solution will scavenge the existing O_2 molecules. Since the e_{aq}^- (stronger reducing agents) is effectively scavenged by dissolved O_2 and N_2O , the formation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids does not take place (Figure 2). These facts suggest that e_{aq}^- plays a fatal role at an initial stage in the reduction of TcO_4^- . Details of the role of e_{aq}^- in the radiolytic reduction of TcO_4^- were discussed in the previous paper.¹⁷ Other possible reduction reactions of TcO_4^- ions could be initiated by H radicals. In addition, hydrated electrons are converted to H radicals in acidic water,²¹ and the contribution of H radicals in the radiolytic reduction of TcO_4^- should be effective in acidic solutions of the target.

Pertechnetate (TcO_4^-) solution was electrochemically reduced at pH 1.5 as reported by Vichot et al.^{22, 23} They suggested the occurrence of soluble polymeric Tc(IV) species ($\text{Tc}_n\text{O}_p^{(4n-2p)+}$ with $n > 2$) in acidic solution. The species was proposed to be $\text{Tc}_3\text{O}_4^{4+}$ (Ref. 23) from the similarity of properties to $\text{Mo(IV)}_3\text{O}_4^{4+}$ clusters²⁴ observed in acidic media. They also reported that the polymeric Tc(IV) species was soluble in an acidic solution and would aggregate each other at higher pH, resulting in $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.

When the acidic solution (pH 1.8) was irradiated in the present experiment, the colloids were not formed (Figure 3(a)), although a soluble Tc(IV) species were formed (Figure 3(b)). This result suggests that H radicals effectively reduce TcO_4^- to form soluble Tc(IV) species, because e_{aq}^- reacts with proton (H^+) to generate H radicals in acidic water.²¹ The soluble Tc(IV) species showed a strong absorption peak ($\epsilon = 6800 \text{ M}^{-1} \text{ cm}^{-1}$) at 320 nm and a weak peak ($\epsilon = 700 \text{ M}^{-1} \text{ cm}^{-1}$) at 500 nm in the UV-vis spectra.²⁵ These absorption peaks could be assigned to polymeric Tc(IV) species from the similarity of the spectra and of the molar extinction coefficients reported by Vichot et al.^{19, 22, 23}

No changes were observed in the spectra before and after ultra-filtration, indicating no colloid formation. When an NaOH solution was added to the solution containing polymeric Tc(IV) species, $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids appeared eventually. In the target solution with the initial pH at 2.7, both $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids and polymeric Tc(IV) species were formed by the irradiation (Figures 3(a) and 3(b)). It can be seen in the figures that the polymeric Tc(IV) species is produced early in the low dose region and followed by generation of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids. Namely, the polymeric Tc(IV) species partly changed to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids at pH 2.7 as the dose increases. Hence, it seems reasonable to consider that the polymeric Tc(IV) species should be a precursor of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids, although an exact stoichiometry of the polymeric species has not been clarified yet.

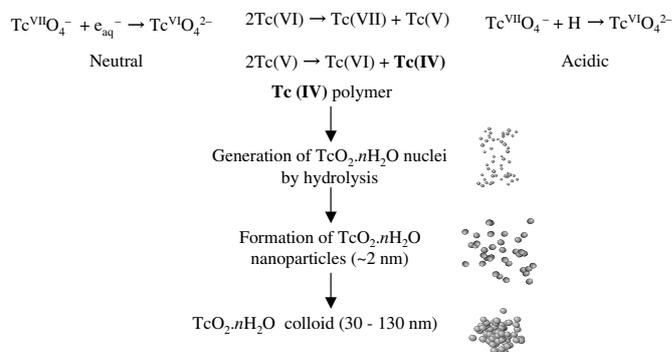
Reduction of TcO_4^- in the presence of colloidal $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ seed particles was also investigated. The own seed particles are known to enhance the rate of metal reduction in solution by γ -radiolysis. It is reported, for instance, that the reduction rate of Ag^+ was largely enhanced when colloidal silver seed particles are present in the solution, and larger colloidal silver particles with a narrow size distribution are produced.^{26,27,28} The reduction mechanism proposed is that reducing radicals transfer electrons to the seed particles, and the stored electrons finally reduce Ag^+ directly on the surface of the seeds. The metal nanoparticles in the solution principally work as a catalyst to enhance the coalescence to form larger particles. In the present experiment, however, no effects of colloidal $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ seed particles were observed as shown in Figure 4. The fact suggests that the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids are produced through solidification of Tc(IV) species in the solution, irrespective of the presence or absence of own seeds. Reoxidation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids by irradiation, as reported for the dissolution of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ by ^{60}Co γ -rays,¹⁶ might also occur.

As reported in the previous paper,¹⁷ a tiny $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ particle 2 nm in diameter must be a nanoparticle that is stabilized in the solution immediately after the colloid generation. The tiny particle generation can be explained by a mechanism proposed by LaMer.²⁹ The mechanism describes that solidification of solute in a solution is initiated at the solute concentration much higher than the solubility; so-called supersaturation.

Based on the LaMer's model, Sugimoto proposed a colloid generation mechanism that dealt with the emergence of nuclei with sizes distributed around a thermodynamically stable critical size under the supersaturation condition.³⁰ Nuclei smaller than the critical size quickly dissolve again, while larger nuclei grow through the Ostwald ripening, resulting in colloids with suitable sizes stabilized in the solution. In our experiment, amounts of the polymeric Tc(IV) species increased with an increase of absorbed dose, and 80% of TcO_4^- was converted to the polymeric Tc(IV) species at 6.5 kGy.²⁵ The stabilized colloids or nanoparticles of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (2 nm in diameter) appear through the solidification process of the colloid precursor, being followed by the growth of nuclei as mentioned above.

As pointed out in the previous section, the final concentration of TcO_4^- is 7.5×10^{-6} M. This should be a concentration where the solidification of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid is initiated. It means that only 90% of the TcO_4^- available in the target solution is converted to the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloid. The target solution below this concentration (7.5×10^{-6} M) would not afford colloids but soluble Tc(IV) species as can be seen in Table 1 for $[\text{TcO}_4^-]_{\text{initial}} = 2.56 \times 10^{-6}$ M. When the Tc(VII) reached 7.5×10^{-6} M in the irradiated solution, the Tc(IV) concentration is much higher than the reported solubility¹⁹ of $\text{TcO}(\text{OH})_2$, leading to the supersaturation condition.²⁹

The chemical structure of this highly soluble Tc(IV) species is unknown, and further investigation is required to elucidate more details for conversion of the polymeric Tc(IV) species to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids. At present, the overall formation pro-



Scheme 1. Formation processes of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids by bremsstrahlung irradiation.

cesses of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids by bremsstrahlung irradiation can be summarized in the Scheme 1.

5. Conclusions

Characteristic features of $^{99}\text{Tc}^{IV}\text{O}_2 \cdot n\text{H}_2\text{O}$ colloids formed by bremsstrahlung irradiation of aqueous pertechnetate ($\text{Tc}^{VII}\text{O}_4^-$) solution are as follows. The diameter of the colloids distributes around 30–130 nm. Irradiation at 40 °C gave round-shaped colloids, whereas irregular-shaped colloid particles composed of nanoparticles (2 nm in diameter) were formed at 17 °C. The colloid formation was observed only in the target solutions at pH higher than 3. At pH lower than 3, the dominant product was the polymeric Tc(IV) species that should be a precursor of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids as proved by its transformation to the colloid at higher pH.

The reduction of TcO_4^- to afford $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ colloids proceeded mainly through the processes involving a bimolecular reaction of TcO_4^- with hydrated electrons (e_{aq}^-) followed by the successive disproportionation reactions of Tc(VI) and Tc(V) to Tc(IV). In the acidic target solutions, TcO_4^- was effectively reduced by H radicals to produce polymeric Tc(IV) species. When the Tc(VII) reached 7.5×10^{-6} M in the irradiated solution, concentration of the polymeric Tc(IV) species should be much higher than the reported solubility of $\text{TcO}(\text{OH})_2$, leading to the supersaturation condition. The stabilized colloids or nanoparticles of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (2 nm in diameter) appear through the solidification process of the polymeric Tc(IV) species.

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