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Radiation-Induced Formation of Co₃O₄ Nanoparticles from Dissolved Co²⁺ in Aqueous Solution: Probing the Kinetics Using Radical Scavengers

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Abstract

The effects of the Co^{2+} content and different radical scavengers on the kinetics of γ radiation-induced $\text{Co}_{3}\text{O}_{4}$ nanoparticle formation and growth were investigated. There are four
distinct stages of particle formation with different oxidation rates. Scavengers and $[\text{Co}^{2+}]_{0}$ affect
the oxidation kinetics in the different stages and consequently the final size of the particles
formed. Radiolysis model calculations were performed to obtain the time-evolution of the
concentrations of key oxidants and reductants, and the effect of scavengers on those
concentrations. Based on the model results and experimental data a reaction mechanism for $\text{Co}_{3}\text{O}_{4}$ particle formation by γ -irradiation of solutions containing $\text{Co}^{2+}(\text{aq})$ is proposed. The main
cobalt oxidation reaction changes with time. Oxidation of $\text{Co}^{2+}(\text{aq})$ to $\text{Co}^{3+}(\text{aq})$ by radiolytically
produced •OH occurs first in the solution phase. This is followed by spontaneous coprecipitation of mixed $\text{Co}^{II}/\text{Co}^{III}$ hydroxide nucleate particles. Adsorption of $\text{Co}^{II}(\text{ad})$ followed by
surface oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH(ad) by H_2O_2 grows particles with a solid CoOOH(s)
phase. In parallel, the solid-state transformation of CoOOH(s) and $\text{Co}^{II}(\text{ad})$ to form $\text{Co}_3\text{O}_4(\text{s})$ occurs.

Key words: Co₃O₄ nanoparticles, radical scavengers, gamma-radiolysis, particle growth kinetics

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Transition metal oxide nanoparticles (such as iron oxide, chromium oxide and cobalt oxide) have many potential useful applications. The magnetic, catalytic, optical, and electronic properties of these metal oxides are determined by the size, structure and shape of the particles that they form.^{1,2} For example, spinel-type cobalt oxide (Co_3O_4) nanoparticles have been used as heterogeneous catalysts, selective absorbers of solar radiation,³ and anode materials for rechargeable Li ion batteries.¹ The properties of Co_3O_4 nanoparticles make them promising materials for electronic devices,⁴ gas sensors,⁵ magnetic materials,⁶ electrochromic devices,⁷ and electrochemical anodes for sensors.⁸

Cobalt oxide nanoparticles have been synthesized by several physical and chemical methods including spray pyrolysis,⁹ chemical vapour deposition,⁵ sol-gel techniques,¹⁰ pulsed laser deposition,¹¹ thermal decomposition of solid cobalt nitrate,¹² microwave-assisted synthesis, ¹³⁻¹⁵ laser ablation synthesis,¹⁶⁻¹⁷ and hydrothermal synthesis.¹ These methods are either complex, or require chemically harsh conditions and/or high processing temperatures. Additional drawbacks of some of these methods include a low level of control over particle size and composition, and a difficulty in generating a pure, single-phase product. Radiation-induced nanoparticle synthesis is a promising alternative technique that addresses these drawbacks.

When exposed to ionizing radiation, water decomposes to yield a range of chemically reactive species. For γ -radiolysis at room temperature, the primary radiolysis products (formed within ~ 100 ns following the absorption of radiation energy) and their yields per unit absorbed radiation energy (in brackets in units of μ mol·J⁻¹) are:^{18,19}

$$H_2O \stackrel{\gamma}{\checkmark} \{H_2O^+, e^-, H_2O^*\} \rightarrow \rightarrow$$

•OH(0.26), •
$$e_{aq}(0.26)$$
, •H(0.06), H₂(0.045), H₂O₂(0.075), H⁺(0.26) (1)

These chemical yields per unit energy input are very high. Such high yields, particularly for the radicals, cannot be obtained by thermal processes and gamma-radiolysis is the most effective way of producing these reactive species. Due to the long penetration depth of a typical γ -ray in water (~20 cm for a half reduction in intensity), these species can be produced uniformly within a reasonably large volume of water. The combination of high densities of redox reactive species and their uniform production and distribution in solution can provide ideal conditions for promoting homogeneous redox reactions.

If the product of a reaction of a dissolved metal ion with a radiolysis-generated species has a significantly different solubility from that of the reactant, then a solid product can be formed. Rapid condensation can create homogeneously distributed nucleation sites onto which the radiolysis-induced oxidation or reduction product can continue to deposit and grow the particle size. Because a very large number of nucleation sites are generated simultaneously and homogeneously, this process leads to the formation of nanoparticles with a narrow, uniform size distribution. This principle has been applied in making noble metal nanoparticles (of silver and gold) from dissolved metal ions, taking advantage of the strong reducing power of $\cdot e_{aq}$ produced by radiolysis.²⁰⁻²⁴

We have recently reported on the formation of nanometer-sized Cr₂O₃, γ -FeOOH and Co₃O₄ particles by continuous γ -irradiation of solutions containing dissolved Cr^{VI} (added as K₂Cr₂O₇), Fe²⁺ (added as FeSO₄) and Co²⁺ (as CoSO₄) respectively without any other chemical additives.²⁵⁻²⁷ The formation of chromium oxide nanoparticles takes advantage of the reducing power of $\bullet e_{aq}^{-}$. On the other hand, for the iron and cobalt oxide nanoparticles the oxidizing

power of •OH and H_2O_2 is used. In all cases a large difference in the solubilities of the initially dissolved metal ions and their reduction or oxidation products is necessary. The low solubility of the product leads to precipitation of metal oxide nanoparticles.

In our previous work on cobalt we investigated nanoparticle formation as a function of pH and dissolved O_2 concentration, and found that the nanoparticles were formed only under conditions that promote Co^{II} adsorption on the growing particles. Based on the observed effects of pH and dissolved oxygen on the oxidation kinetics of Co^{II} to Co^{III} , and the final size of the particles, we proposed a mechanism in which Co^{II}/Co^{III} hydroxide condensates act as nucleation sites on which radiolytically-induced heterogeneous oxidation processes can occur. The particles grow as a solid CoOOH phase that, in the presence of Co^{II} , slowly transforms to thermodynamically more stable Co_3O_4 with time.

In this study we investigate the effects of the initially dissolved Co^{2+} concentration and the presence of radical scavengers (*t*-butanol, N₂O and O₂) on γ -radiation-induced cobalt oxide nanoparticle formation. The cobalt oxidation kinetics were followed by chemical analysis of Co^{II} and Co^{III} dissolved and/or dispersed in solution, light-absorbance (at 400 nm), analysis of Co_3O_4 dispersed in solution, and analyses of the particles by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy as a function of irradiation time. The experiments were augmented by radiolysis model calculations which provided the time evolution of the concentrations of key oxidants and reductants during long-term continuous irradiation.

2. Experimental

Cobalt solutions were prepared by dissolving high-purity cobalt (II) sulfate obtained from Sigma-Aldrich (purity \geq 99%). The *t*-butanol obtained from Sigma-Aldrich was of high purity (purity \geq 99%). Gas containing 50% N₂O in Ar was purchased from Praxair (impurities < 0.001%). All solutions were freshly prepared with water purified using a NANOpure Diamond UV ultrapure water system, with a resistivity of 18.2 MΩ·cm. The pH was adjusted to 10.6 using a concentrated NaOH solution. The pH value was chosen based on the solubilities of Co^{II} and Co^{III} hydroxides.²⁸ The solubility of Co^{III} hydroxide is less than 10⁻¹³ M at this pH, many orders of magnitude lower than that of Co^{II} hydroxide (~10⁻⁶ M). The solubility of Co^{II} hydroxide is at a minimum at this pH and this facilitates nucleation of particles and the adsorption of Co^{II} species on the nucleates.²⁷ The solutions were either aerated by purging with high purity air (Praxair) or de-aerated by purging with high purity Ar for one hour prior to a test. Using a syringe, 10 ml of the test solution was transferred to a pre-sealed 20-ml vial.²⁹ All experiments were performed with a gas headspace in the test vial. For experiments performed with N₂O, the test solutions were purged with N₂O gas for about 15-20 min. The test vials were irradiated in a ⁶⁰Co gamma cell (MDS Nordion) as described in reference 29. The gamma source provided a uniform absorption dose rate of 4.5 kGy·h⁻¹ in the vials at the time of this study. All experiments were conducted at room temperature (25 °C).

Following irradiation for a desired period, a series of analyses were performed: $H_2(g)$ present in the headspace by GC-MS, dispersed Co_3O_4 in the water by light absorbance at 400 nm, and dissolved and dispersed Co^{II} and Co^{III} species, and H_2O_2 in the irradiated solution by colorimetric analyses. Colloid particles were then collected for particle analyses by TEM, XPS and Raman spectroscopy. For H_2 measurements a gas sample extracted from the headspace in a test vial using a gas-tight syringe with a Luer lock (Agilent Technologies) was analyzed using gas chromatography with a thermal conductivity detector (GC-TCD, 6580 Agilent Technologies) as discussed elsewhere in detail.²⁹

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A liquid sample removed from the vial using a syringe was first analyzed by UV-Vis absorption spectroscopy (BioLogic Science Instruments). We have previously reported on a reference UV-Vis spectrum of dispersed Co₃O₄ taken using a standard Co₃O₄ power sample with diameter ranging from 8-20 nm (purchased from Alfa Aesar).²⁷ The Co₃O₄ spectrum shows two absorption bands with peaks at ~ 270 nm and 400 nm, while the other Co^{III} species expected to be present, CoOOH, does not show any appreciable absorbance in the 200 to 700 nm range. The UV-Vis spectra of the irradiated solutions show similar absorption bands to the reference spectrum with peaks at 270 nm and 400 nm, see Figure 1. The peak intensities in the spectra of the irradiated solutions increase with irradiation time indicating that the concentration of colloidal (dispersed) Co_3O_4 is increasing. We have used the intensity of background-subtracted light absorbance at 400 nm (A_{400nm}) to follow changes in the reaction kinetics. A quantitative conversion of an absorbance to a concentration of colloidal Co_3O_4 particles is not possible because the absorbance depends on the size of the colloidal particles and the particle size changes with time in our experiments. Nevertheless, an increase in A_{400nm} corresponds qualitatively to an increase in $[Co_3O_4]$.

The solution cobalt species and H_2O_2 content were quantified by colorimetric analyses. The total concentration of dissolved or dispersed Co^{III} present in the test solution was determined by reacting a sample from the solution with 4-(2-pyridylazo) resorcinol (PAR) to form a coloured complex that absorbs light at 510 nm with a molar extinction coefficient of $5.6 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$.³⁰ To determine the concentration of Co^{II} present, any Co^{II} in the sample was oxidized to Co^{III} by adding some 3% hydrogen peroxide solution, allowing it to react with the Co^{II} and then heating the sample to 100 °C in a boiling water bath to remove any unreacted hydrogen peroxide. The Co^{III} concentration of this oxidized solution was then determined again by the PAR method described above. The difference between the total cobalt concentration (determined after oxidation) and the concentration of Co^{III} determined prior to the hydrogen peroxide treatment was taken to be the concentration of Co^{II} in the solution phase. Using this method, the detection limits for both Co^{II} and Co^{III} were 1 μ M.³⁰ The concentrations determined by the PAR method are referred to as simply [Co^{II}] and [Co^{III}] although these 'concentrations' may include dissolved as well as adsorbed or solid species. The micro-syringe sampling method would not detect large particles or any cobalt species present that could have settled on the bottom or sides of the test vials.

The concentration of hydrogen peroxide in the test solution was determined by the Ghormley tri-iodide method³¹ in which Γ is oxidized to I_3^- by H_2O_2 in the presence of ammonium molybdate as a catalyst, followed by spectrophotometric measurement of the I_3^- concentration; I_3^- has a maximum absorption at 350 nm with a molar extinction coefficient of 25500 M⁻¹·cm⁻¹.³² We tested for and observed no oxidation of Γ to I_3^- by Co^{III} in our test solutions.

Particles were collected from the sample vials for analyses by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. For TEM the particles were collected by dipping a carbon-coated copper grid into the irradiated test solution and drying the sample grid in air. Samples for the XPS and Raman analyses were collected by centrifuging the solution and then drying the precipitate on a glass plate in air. The sizes and shapes of the particles were measured using TEM with the microscope operating at 80 keV. X-ray photoelectron spectra were acquired with a KRATOS Axis Nova spectrometer using monochromatic Al K (alpha) radiation and operating at 210 W, with a base pressure of 10⁻⁸ Pa. The high-resolution XPS Co-2p and O-1s bands were deconvoluted to obtain the oxidation-state and chemical composition in the outermost particle layer, 6-7 nm in depth (the estimated XPS analysis depth for solid cobalt oxide particles). The deconvolution followed the method established by Biesinger et al. ³³ and used in our previous studies on cobalt oxides formed on a

Co-Cr alloy (Stellite-6)^{34,35}. Raman spectra of the particles were obtained using a Renishaw model 2000 Raman Spectrometer with a laser excitation wavelength of 633 nm.

3. **RESULTS**

The kinetics of the radiolytic conversion from dissolved Co^{2+} to cobalt oxide nanoparticles were investigated for solutions initially aerated and containing two different $[\text{Co}^{2+}]_0$ (0.1 mM and 0.3 mM), and for 0.1 mM $[\text{Co}^{2+}]_0$ solutions containing different scavengers, O₂, N₂O and t-butanol. The conversion kinetics were followed by analyzing as a function of irradiation time: (1) the concentrations of Co^{II} and Co^{III} dispersed in solution, (2) the UV-Vis absorbance by Co_3O_4 dispersed in the solution, (3) the concentration of H₂ in the head space ([H₂(g)]), (4) the sizes and shapes of the particles, and (5) the oxidation-state and chemical composition of the particles. We also determined the concentration of the molecular radiolysis product H₂O₂.

3.1 Effect of $[Co^{2+}]_0$ on the Kinetics

The results of the solution and gas analyses obtained for the initially aerated solutions containing 0.1 mM $[Co^{2+}]_0$ at pH 10.6 and room temperature are shown in Figure 2. All experiments were repeated at least three times and the scatter in the data from different experiments was much less than a factor of two in concentration (or absorbance).

Four distinct stages are observed in Figure 2. Stage 1 represents the delay period prior to the onset of a steady linear increase in $[Co^{III}]$ in Stage 2. During the transition from Stage 1 and Stage 2, mass balance was not always observed, i.e., $-\Delta[Co^{II}] \neq \Delta[Co^{III}]$. This mass imbalance is attributed to the production of solid precipitates that escaped the sampling for the PAR analysis. For tests with a given initial $[Co^{2+}]_0$ the mass imbalance was consistent and reproducible, and hence is not attributed to the experimental errors. This type of mass imbalance has also been observed in our other studies on radiation-induced formation of metal oxide nanoparticles.²⁵⁻²⁷ It

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is not surprising for Co because the initial concentrations of the Co^{2+} solutions are well above the solubility limit for $\text{Co}(\text{OH})_2$.

In Stage 2 $[Co^{II}]$ increases linearly with time and this is accompanied by a linear decrease in $[Co^{II}]$ at the same rate:

$$rate = \frac{\Delta [Co^{III}]}{\Delta t} = -\frac{\Delta [Co^{II}]}{\Delta t}$$
(2)

However, the rate of increase in $[Co^{III}]$ (or the rate of decrease in $[Co^{II}]$) changes after about 1-h irradiation, and Stage 3 follows. In Stage 3 $[Co^{III}]$ increases at a slower linear rate and this rate again matches the rate of decrease in $[Co^{II}]$. The same change between Stage 2 and Stage 3 can be also seen in the time-dependent behaviour of A_{400nm} and $[H_2(g)]$. Stage 4 starts after the oxidation of Co^{II} to Co^{III} is completed.

The time dependent results obtained for 0.3 mM $[Co^{2+}]_0$ solutions are compared with those for 0.1 mM $[Co^{2+}]_0$ solutions in Figure 3. For the higher $[Co^{2+}]_0$ the decrease in $[Co^{II}]$ in Stage 1 is faster and the delay in the onset of the linear increase in $[Co^{III}]$ is shorter. Once $[Co^{II}]$ reaches 0.1 mM the data matches that seen for a 0.1 mM $[Co^{2+}]_0$ test. The rates of increase in $[Co^{III}]$ in Stage 2 and Stage 3 and the final $[Co^{III}]$ reached are also independent of $[Co^{2+}]_0$. Figure 3 also contains a graph of the time-dependence of A_{400nm} . For the 0.3 mM $[Co^{2+}]_0$ test A_{400nm} is initially higher than that seen for a 0.1 mM $[Co^{2+}]_0$ test, but it reaches the same value at ~ 1 h. It remains at this value until ~ 3 h after which it starts increasing again while A_{400nm} measured in a 0.1 mM $[Co^{2+}]_0$ test remains the same. As discussed in Section 4, this increase in A_{400nm} at longer times (with no accompanying cobalt oxidation can be attributed to formation of Co_3O_4 via a process that does not require additional Co^{II} oxidation.

The TEM, XPS and Raman results for the particles collected after irradiating 0.3 mM $[Co^{2+}]_0$ solutions for different times are shown in Figures 4 to 6. Some of these results have been

reported previously²⁷ and are reproduced here for comparison with the additional new data. The TEM images show two different shapes and sizes of particles; thin hexagonal crystals that are 300 - 400 nm wide and smaller spherical nanoparticles, 8-20 nm in diameter, with a small fraction into needle-shaped particles.

Examples of the high resolution XPS Co-2p band spectra with deconvoluted peaks and the deconvolution analysis results are presented in Figure 5. The XPS results presented in Figure 5 show the presence of three cobalt oxides/hydroxide species, $Co(OH)_2$, CoOOH and Co_3O_4 . The number of particles collected from the unirradiated solution (0 min) is very small and do not have The XPS intensity of these particles was small and the distinct crystalline structures. deconvolution had a large uncertainty. These particles are identified mostly as $Co(OH)_2$ by the XPS and they are attributed to the precipitation of Co²⁺ species during drying of the sample solution on the TEM carbon grid. For the particles collected from the irradiated solutions, three different crystalline shapes, hexagonal, spherical and needle-shape, are present. For these particles, the XPS shows that the $Co(OH)_2$ contribution to the Co-2p band decreases slowly with time in Stage 2 while that of CoOOH increases with time. The fraction of Co_3O_4 in the outer 6 nm layer of a particle in Stage 2 is initially small and soon disappears, possibly due to increasing thickness of CoOOH in the outer layer. However, the Co_3O_4 content increases again in Stage 3 and it constitutes near 100% of the particle after 5-h irradiation (Stage 4). The same morphological features, hexagonal crystals of β -Co(OH)₂ and spherical nanoparticles of Co₃O₄, were reported by Hu et al. in their study of the synthesis of nanostructured cobalt hydroxides and oxide by laser ablation.¹⁶ The needle-shaped particles seen after 5-h irradiation are assigned to CoOOH that has not been transformed to Co_3O_4 .

The Raman spectra of the particles (Figure 6) show peaks at 200, 480-500 and 700 cm⁻¹. Also shown in the figure are the reference spectra taken for standard powder samples of

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 $Co(OH)_2$, CoOOH and Co_3O_4 . The reference spectra all exhibit similar Raman shifts but with the ratio of the intensities at 700 cm⁻¹ to 480-500 cm⁻¹ higher for Co_3O_4 than for CoOOH. For the particles formed in this study the intensities of all three peaks increase with irradiation time, possibly due to the presence of more particles with time. The intensities of the three peaks in the Raman spectra for the particles formed after 5 h most closely resemble the Co_3O_4 spectrum.

The TEM images of particles collected after irradiating 0.1 mM $[Co^{2+}]_0$ solutions for different times are shown in Figure 7. In this case we did not observe any hexagonal crystals and saw only spherical particles even at short times. The TEM images also show that the spherical particles grow with irradiation time and the particles formed at 5 h have a size (8-20 nm) similar to that of particles formed from 0.3 mM $[Co^{2+}]_0$ solutions. This observation, combined with the $[Co^{II}]$ and $[Co^{III}]$ time dependent behaviour indicates that the initial sharp decrease in $[Co^{II}]$ in the first 10 min observed for the 0.3 mM $[Co^{2+}]_0$ solutions (Figure 3) is due to the precipitation of the initially dissolved Co^{2+} as hexagonal $Co(OH)_2$ crystals (Figure 4).

3.2 Effect of Scavengers

Tertiary butanol and N₂O are well-known scavengers for •OH and • e_{aq}^{-} , respectively.^{36,37} Dissolved O₂ also reacts very effectively with • e_{aq}^{-} while the product of this reaction, •O₂⁻, reacts with •OH.^{29,38,39} These radical scavengers are often used to influence the concentrations of water radiolysis products. The effect of adding these radical scavengers to Co^{II} solutions was investigated for 0.1 mM [Co²⁺]₀ at pH 10.6 and room temperature. The tests included: no scavengers ((1) deaerated only), only one type of scavenger ((2) deaerated & 0.1 M *t*-butanol, (3) purged with N₂O/Ar, and (4) aerated only), and two different scavengers ((5) aerated & 0.1 M *t*butanol). The concentration of dissolved O₂ in an air-saturated solution is ~ 0.25 mM at 25 °C.¹⁸ The concentration of N₂O in the 50% N₂O/Ar purged solution is estimated to be ~ 12.5 mM, half of the solubility of N₂O at 1 atm at 25 °C.⁴⁰

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Particle analyses were not performed as a function of irradiation time for these tests (except for the aerated only tests discussed above); particles were examined after 5-h irradiation. No detectable particles were formed after 5 h of irradiation for two cases, deaerated only or deaerated & 0.1 M *t*-butanol. The TEM images and Raman spectra of the particles formed after 5 h of irradiation in the other three scavenging environments are presented in Figure 8. The TEM images show that the particle diameters are very different for the different scavenger additions: 8-20 nm in the aerated only solutions, 10-30 nm in the aerated & 0.1 M *t*-butanol solutions, and 60-80 nm in the N₂O/Ar purged solutions. The Raman spectra from all cases are essentially identical and match the reference spectrum of Co_3O_4 very well. The deconvolution analysis of the high-resolution XPS Co-2p and O-1s bands of the particles formed after 5-h irradiation confirms that the particles are all Co_3O_4 .

The concentrations of Co^{II} and Co^{III} as a function of time for the tests with different scavengers are compared in Figure 9. In a given scavenging environment mass balance for the cobalt species is not always achieved in Stage 1. The time for the transition from Stage 1 to Stage 2 depends on the scavenging environment; this occurs faster in the order N₂O, O₂, (O₂ + 0.1 M t-butanol), no scavenger (deaerated) and 0.1 M t-butanol. With only 0.1 M *t*-butanol present no changes in $[Co^{II}]$ or $[Co^{III}]$ were observed after 5-h irradiation while in the absence of any scavenger (deaerated) a small reduction in $[Co^{II}]$ was observed after 3-h irradiation with no visible production of Co^{III} . Consistently, no particles were found in these latter two case by TEM.

For the other scavenger cases the time-dependent behaviour of $[Co^{II}]$ and $[Co^{III}]$ consistently show the four kinetic stages described in Section 3.1. In all solutions the decrease in $[Co^{II}]$ matches the increase in $[Co^{III}]$ in Stage 2. The rate of decrease in $[Co^{II}]$ in Stage 2 depends on the scavenging environment; it is faster in the aerated only or the aerated & 0.1 M t-butanol

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solutions than in the N₂O/Ar purged solution. The duration of Stage 2 appears to be independent of the scavenging environment and Stage 3 is reached in ~ 1 h in all cases. In Stage 3 the rate of increase in $[Co^{III}]$ equals the rate of decrease in $[Co^{II}]$ and is independent of the scavenging environment (the rate is $4.5 \times 10^{-9} \text{ M} \cdot \text{s}^{-1}$). The conversion from Co^{II} to Co^{III} continues at this rate until the $[Co^{II}]$ becomes negligible.

Comparison of Figure 8 and Figure 9 suggests that the more Co^{II} that is converted to Co^{III} before Stage 3 begins, the smaller the final Co_3O_4 particles. The conversion of Co^{II} to Co^{III} in Stage 3 is not controlled by the rate of cobalt oxidation (either in solution or on a particle surface) by radiolytically-produced oxidants, but by other processes such as mass transport or solid phase transformation. Faster oxidation in Stage 2 may produce more particles and this leaves less Co^{2+} to continually adsorb on these particles. The net result is smaller particles.

4. **DISCUSSION**

The experimental data show that there is a complex mechanism involved in radiolysismediated Co nanoparticle formation. There appear to be four stages involved. The presence of different radical scavengers affects the processes that occur in the different stages. A reaction mechanism consisting of four kinetic stages is proposed for the Co_3O_4 particle formation by γ irradiation of solutions containing initially dissolved Co^{2+} . A schematic of the mechanism is shown in Figure 10. The main processes in the four stages can be summarized as follows.

<u>Stage 1</u>: The main reaction is the oxidation of $\text{Co}^{2+}(\text{aq})$ to $\text{Co}^{3+}(\text{aq})$ by radiolytically produced •OH in the solution phase. This is followed by spontaneous co-precipitation of mixed $\text{Co}^{II}/\text{Co}^{III}$ hydroxide nucleate particles.

<u>Stage 2:</u> The main reaction is the surface oxidation by H_2O_2 of $Co^{II}(ad)$ adsorbed onto the nucleate particles to CoOOH(ad). Formation of nucleates may continue during this phase. The

nucleates provide sites for continuous adsorption of $\text{Co}^{II}(\text{ad})$. The rate of oxidation in this stage is controlled by the rate of radiolytic production of H₂O₂. The CoOOH(ad) that is created incorporates into a solid CoOOH phase, growing the oxide particles. As the oxide grows, the CoOOH + Co^{II}(ad) slowly transforms to Co₃O₄. This results in particles consisting of an inner Co₃O₄ core and a thin outer film of CoOOH.

<u>Stage 3</u>: The main processes are the surface oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH and the transformation of CoOOH with additional $\text{Co}^{II}(\text{ad})$ to Co_3O_4 . The surface oxidation reaction is the same as that occurs in Stage 2, but at a slower rate. In this stage there are more, larger particles and the amount of CoOOH available on the particles to react with $\text{Co}^{II}(\text{ad})$ to form Co_3O_4 is larger. This transformation reaction becomes faster and competes for $\text{Co}^{II}(\text{ad})$ with the surface oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH. The rate of surface oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH in Stage 3 is limited by the net rate of formation of $\text{Co}^{II}(\text{ad})$ and not by the rate of radiolytic production of H_2O_2 .

<u>Stage 4:</u> No more net cobalt oxidation occurs, but the solid-state transformation of $Co^{II}(ad)$ and CoOOH(s) to $Co_3O_4(s)$ may continue.

In the following sections we examine the behaviour of the reacting radiolysis products and the experimental data to show how they support this mechanism.

4.1 Radiolytic Production of Oxidants and Reductants

The effects of different scavengers on the behaviour of irradiated cobalt solutions suggest that different redox species control the cobalt oxidation and particle growth at different times. To explore this, we first consider the radiolytic production of oxidants and reductants, and the hydrolysis and phase equilibria of cobalt species that can occur. Radiolysis kinetics model calculations were performed to determine the time evolution of the concentrations of key radiolytically-produced oxidants and reductants, and the effects of dissolved N₂O and O₂ on them. As noted above γ -radiation decomposes water molecules to a range of redox active species (reaction 1). The water decomposition products are homogeneously distributed almost immediately (< 100 ns) upon irradiation.^{18,19} The chemical yields per absorbed radiation energy at this stage are referred to as the primary radiolysis yields or the g-values. The primary radiolysis yields are not affected by the presence of a solute at a concentration less than ~ 10 mM since the probability of solute species present at a low concentration directly interacting with gamma photons or Compton scattered electrons is very small and can be neglected.^{18,19,29,38,39}

Under continuous irradiation the primary radiolysis products are continuously produced at rates proportional to the radiation energy deposition rate into the water. However, as they accumulate, these primary products participate in chemical reactions in the solution phase. They react with each other, solvent water molecules and their dissociated ions and, if present, solute species (cobalt ions and scavengers in this study). Compared to the primary radiolysis product formation, these chemical reactions are much slower.^{41,42} With continuous irradiation lasting longer than a few milliseconds, the solution reactions of the radiolysis products must be taken into account to determine their concentrations.

The chemical kinetics of water radiolysis are very complex. Not counting the reactions with any added solute species, about 45 reactions involving more than 10 chemical species are required to adequately describe the radiolysis kinetics in pure water under long-term continuous radiation.^{29,38,39} We have developed a radiolysis chemistry kinetic model that has been validated against experimental data obtained under a wide range of solution conditions.^{29,38,39,43-45} The impacts of added N₂O and O₂ on key radiolytically-produced oxidants and reductants were

calculated using this model plus the additional reactions and rate constants needed to address the presence of N_2O (the O_2 reactions are in the base model).

The results of the radiolysis model calculations for deaerated, aerated and N₂O/Ar purged solutions at pH 10.6 are shown in Figure 11. For a given scavenging condition the concentrations of the radiolysis products at short times (< 1 ms) increase linearly with time (i.e., the slope of the log-log plot is 1), except for $\bullet e_{aq}^{-}$ in the aerated and N₂O/Ar purged solutions. At such short times when solution reactions do not yet occur at any substantial rates, the net production rate of a radiolysis product is determined mainly by the primary radiolysis yield, e.g.,

$$\frac{d[\bullet OH]_t}{dt} \approx 10^{-6} \cdot g_{\bullet OH} \cdot D_R \cdot \rho_{H2O}$$
(3)

$$[\bullet \text{ OH}]_t \approx 10^{-6} \cdot g_{\bullet \text{OH}} \cdot D_R \cdot \rho_{H2O} \cdot t \tag{4}$$

where $g_{\bullet OH}$ is the g-value for $\bullet OH (\mu M \cdot J^{-1})$, D_R is the radiation dose rate $(J \cdot kg^{-1} \cdot s^{-1})$, and ρ_{H2O} is the density of water (kg/L).

Similarly, $[\bullet e_{aq}]$ increases linearly with time in a deaerated solution at pH 10.6 where the $[H^+]$ is low:

$$\left[\bullet \ \mathbf{e}_{aq}^{-}\right]_{t} \approx 10^{-6} \cdot g_{\bullet \mathbf{e}_{aq}} \cdot D_{R} \cdot \rho_{H20} \cdot t \tag{5}$$

where $g_{\bullet e_{aq}}$ is the g-value for $\bullet e_{aq}^-$. The hydrated electron reacts very fast with O₂ and N₂O and their reactions can influence the $[\bullet e_{aq}^-]$ even at very short times:

$$O_2 + \bullet e_{aq} \to \bullet O_2^ k_6 = 2.2 \times 10^{10} \,\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$$
 (6)

$$N_2O + \bullet e_{aq}^- + H_2O \rightarrow N_2 + \bullet OH + OH^- \qquad k_7 = 0.86 \times 10^{10} \,\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$$
 (7)

The rate equations for $[\bullet e_{aq}^{-}]$ and $[\bullet O_2^{-}]$ in an aerated solution at early times when the aqueous reaction of $\bullet O_2^{-}$ is not yet significant are

$$\frac{d[\cdot \mathbf{e}_{aq}^{-}]_{SS}}{dt} \approx 10^{-6} \cdot g_{\cdot \mathbf{e}_{aq}} \cdot D_R \cdot \rho_{H20} - k_{\cdot \mathbf{e}_{aq}^{-}\mathbf{O}_2} \cdot [\mathbf{O}_2] \cdot \left[\cdot \mathbf{e}_{aq}^{-} \right]_{SS} \approx 0$$
(8)

$$\frac{d[\bullet O_2^{-}]}{dt} \approx k_{\bullet e_{aq} - O_2} \cdot [O_2] \cdot \left[\bullet e_{aq}^{-}\right]_{SS} = k_{\bullet e_{aq} - O_2} \cdot [O_2] \cdot \left[\bullet e_{aq}^{-}\right]_{SS}$$
(9)

where $k_{\bullet e_{aq}-O_2}$ is the rate constant for the reaction of O_2 and $\bullet e_{aq}^-$. The analytical solutions to the rate equations are:

$$\left[\bullet e_{aq}^{-}\right]_{SS} \approx \frac{10^{-6} \cdot g_{\bullet e_{aq}} \cdot D_R \cdot \rho_{H2O}}{k_{\bullet e_{aq} - O_2} \cdot [O_2]} \tag{10}$$

$$[\bullet 0_2^{-}]_t \approx 10^{-6} \cdot g_{\bullet e_{aq}} \cdot D_R \cdot \rho_{H20} \cdot t \tag{11}$$

Similar approximations can be made for an N₂O/Ar purged solution, resulting in.

$$\left[\bullet \mathbf{e}_{aq}^{-}\right]_{SS} \approx \frac{10^{-6} \cdot g_{\bullet \mathbf{e}_{aq}} \cdot D_R \cdot \rho_{H2O}}{k_{\bullet \mathbf{e}_{aq} - \mathbf{N}_2O} \cdot [\mathbf{N}_2O]}$$
(12)

The analytical solutions in equations (10) and (12) predict that $[\bullet e_{aq}^{-}]$ in an aerated or N₂O/Ar purged solution reaches a very low steady-state concentration, 6×10^{-14} M and 3×10^{-15} M, respectively. These analytical approximations are consistent with the full computational model results (Figure 11). The analytical equations also predict that at short times $[\bullet O_2^{-}]$ increases at a linear rate determined by D_R and the g-value for $\bullet e_{aq}^{-}$ in the aerated solution (equation 11). Thus, at short times the $[\bullet O_2^{-}]$ in an aerated solution is the same as the $[\bullet e_{aq}^{-}]$ in a deaerated solution. In an N₂O/Ar purged solution it is the $[\bullet OH]$ (produced by reaction 7) that increases at the expense of $\bullet e_{aq}^{-}$ and hence, the $[\bullet OH]$ at short times is the same as the sum of $[\bullet OH]$ and $[\bullet e_{aq}^{-}]$ in a deaerated solution:

$$[\bullet \text{ OH}]_t \approx 10^{-6} \cdot \left(g_{\bullet \text{OH}} + g_{\bullet e_{aq}}\right) \cdot D_R \cdot \rho_{H2O} \cdot t \qquad \text{at } t < 1 \text{ ms}$$
(13)

At times longer than 1 ms, other aqueous-phase reactions of radiolysis products become important in controlling the concentrations of primary radiolysis products, and secondary radiolysis products such as O_2 and $\bullet O_2^-$ can accumulate to substantial levels (Figure 11). Eventually the rates of reactions consuming a radiolysis product increase and approach the primary radiolysis production rate and concentrations approach steady state. The more chemically reactive a radiolysis product is, the faster its concentration reaches steady state and the lower the steady-state concentration that is reached. The $[\bullet e_{aq}^{-}]$ reaches steady state nearly immediately (less than μ s) and the concentration of the less reactive radical, \bullet OH, reaches steady state in 10 ms, while less reactive molecular species such as $[H_2O_2]$ reach steady state at longer times.

In deaerated or aerated water at pH 10.6 the [•OH] first rises and then decreases with time until it reaches steady state at 5 – 10 min. By then the concentrations of all the other radiolysis products also approach steady state. The decrease in [•OH] in a deaerated solution is due to reactions of •OH with secondary radiolysis products such as O_2 and $•O_2^-$. A catalytic cyclic with the reaction of O_2 with $•e_{aq}^-$ (reaction 6) and the reaction of $•O_2^-$ with •OH (reaction 14) is established:²⁹

•
$$O_2^- + \bullet OH \to O_2 + OH^ k_{14} = 8.0 \times 10^9 \,\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$$
 (14)

The consequence is a decrease in [•OH] and [• e_{aq}^{-}] and an increase the production of the oxygen species.^{29,38,39} The reduction in [•OH] and [• e_{aq}^{-}] also leads to increases in [H₂O₂], [O₂] and [H₂] at longer times. In an aerated solution, the catalytic cycle is responsible for the decrease in [•OH] after [•OH] and [•O₂⁻] reach sufficiently high concentrations (~ 10⁻⁹ M).

In an N₂O/Ar purged solution $[\bullet e_{aq}^{-}]$ reaches steady state very early and its concentration is very low. By the time $[O_2]$ and $[\bullet O_2^{-}]$ reach significant levels the concentrations of other molecular radiolysis products (such as H₂O₂ and H₂) have increased to levels where they can compete for reactions with \bullet OH and $\bullet e_{aq}^{-}$ more effectively than the oxygen species. This prevents the catalytic cycle of reactions (6) and (14) from being established with N₂O present and consequently the steady-state concentration of \bullet OH is higher.

At times longer than ~10 ms the concentrations of the molecular radiolysis products have a quasi-inverse relationship with the concentrations of radical products.^{29,38,39} The reason for this

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is that the main removal path of a molecular species is its reactions with a radical and vice versa. For example, $[H_2O_2]$ increases with decreasing [•OH] and [•e_{aq}⁻] since the main removal reactions for H_2O_2 are:

$$\bullet OH + H_2 O_2 \rightarrow \bullet HO_2 + H_2 O \tag{15}$$

$$\bullet e_{aq}^{-} + H_2 O_2 \rightarrow \bullet OH + OH^{-}$$
(16)

In particular, when $[\bullet e_{aq}]$ is very low a decrease in $[\bullet OH]$ increases $[H_2O_2]$ at long times.

The radiolysis model calculations were not performed for the 0.1 M t-butanol solution because of the lack of kinetic data for some intermediate reaction products. However, using the same steady-state approximation described above, an analytical expression for [•OH] in a 0.1 M t-butanol solution at short times can be derived (times when the reactions of the intermediate products are negligible). The addition of t-butanol has a negligible effect on [• e_{aq}] at short times because it does not react rapidly with • e_{aq} . However, t-butanol does react fast with •OH (rate constant from ³⁶):

$$(CH_3)_3COH + \bullet OH \rightarrow \bullet CH_2(CH_3)_2COH + H_2O \qquad k_{17} = 6 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$$
 (17)

The [•OH]_{SS} can then be approximated by

$$[\bullet \text{ OH}]_{SS} \approx \frac{10^{-6} \cdot g_{\bullet \text{OH}} \cdot D_R \cdot \rho_{H2O}}{k_{\bullet \text{OH}-\text{tB}} \cdot [t-butanol]_0} \qquad \text{at } t < 1 \text{ ms}$$
(18)

The $\bullet e_{aq}^{-}$ scavengers, N₂O and O₂, have relatively small direct effects on [•OH] but tbutanol has a strong effect on [•OH] at short times (< 1 ms). The result is that, for an irradiation time t < 1 ms, [•OH]_t will be higher with scavangers in the order

N₂O/Ar purged > aerated \approx deaerated >> t-butanol solution.

The scavengers affect [•OH] and $[H_2O_2]$ at longer times (> 10 ms) more strongly and for an irradiation time t > 10 ms, [•OH]_t will be higher in order:

 N_2O/Ar purged > deaerated > aerated solution

while $[H_2O_2]_t$ would be the higher in order of,

aerated > deaerated > N_2O/Ar purged solution.

Again we did include t-butanol in that ranking because we did not have full modeling results. We have focused on the radiolytic production of $\bullet e_{aq}^{-}$, $\bullet OH$ and H_2O_2 because these are the most important species that control the oxidation and reduction of Co ions in solution and on particle surfaces.

4.2 Reactions of Dissolved Cobalt Ions

Radiolysis model calculations were also performed with Co^{2+} present in solutions containing different scavengers (Figure 8, bottom panel). In these calculations, only the homogeneous solution reactions of cobalt ions are included (rate constants from ^{46,47}):

•OH + Co²⁺
$$\rightarrow$$
 Co³⁺ + OH⁻ $k_{19} = 1.6 \times 10^{6} \,\mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$ (19)

The oxidation of Co^{2+} by H_2O_2 is known to be negligible at room temperature.⁴⁶ Hydrolysis reactions of the cobalt species, precipitation of hydroxide particulates and oxidation of solid particles were not included in the model calculations.

Because reactions (19) and (20) are slow compared to the rates of other reactions the addition of 0.1 mM $[\text{Co}^{2+}]_0$ has a negligible impact on the behaviour of •OH and •e_{aq}⁻. However, the [•OH] and [•e_{aq}⁻] affect the rates of reactions (19) and (20) and hence the rate of Co³⁺ production. For a given scavenging environment, it was shown above that [•OH] increases linearly with *t* at short times (< 1 ms) but reaches (pseudo-) steady state at longer times. Consequently, $[\text{Co}^{3+}]$ initially increases with t^2 (i.e., the slope of the log-log plot is 2):

$$\frac{d[\mathrm{Co}^{3+}]_t}{dt} \approx k_{\bullet\mathrm{OH-Co}^{2+}} \cdot [\mathrm{Co}^{2+}]_0 \cdot [\bullet \mathrm{OH}]_t$$
(21)

$$[Co^{3+}]_t \propto [Co^{2+}]_0 \cdot t^2 \qquad \text{at } t < 1 \text{ ms}$$
(22)

After [•OH] reaches steady state [Co³⁺] increases linearly with t.

The model calculations predict that the $[\text{Co}^{3+}]$ reaches the Co^{3+} solubility limit (10⁻¹³ M) in less than 0.1 ms in all of the irradiated solutions. The time scale is too short for the cobalt ions $(\text{Co}^{2+} \text{ and Co}^{3+}))$ to hydrolyze and precipitate as solid hydroxide particles. Gamma-irradiation thus induces supersaturation of the solutions with Co^{3+} very quickly and homogeneously. This promotes rapid homogeneous nucleation and a uniform distribution of nucleate particles. The calculated $[\text{Co}^{3+}]$ at ~1 min is about 10⁻⁵ M in an N₂O/Ar purged solution, about 4 × 10⁻⁷ M in an aerated solution, and less than 10⁻⁷ M in a deaerated solution. The calculated Co^{3+} production at short times is inversely related to the delay times for the onset of Stage 2 (deaerated shortest, then aerated and finally N₂O/Ar purged (Figure 11)).

The model calculations show that Co^{2+} to Co^{3+} oxidation (for conversion of initially dissolved Co^{2+} to Co_3O_4 particles) should occur faster in an N₂O/Ar purged solution than in an aerated or deaerated solution because the [•OH] is highest for the N₂O case. In addition, because the reduction of Co^{3+} back to Co^{2+} by reaction with $\bullet e_{aq}^{-}$ (reaction 20) can become important after a prolonged irradiation time, the yield of Co^{3+} would be lower in an aerated solution than in a N₂O/Ar purged solution. However, we observed faster conversion of Co^{II} to Co^{II} in Stage 2 in an aerated solution than in a N₂O/Ar purged solutions. These differences suggest that the oxidation processes occurring in Stage 2 and Stage 3 are not the only important redox reactions. Liquid-solid interfacial and surface reactions must play a role.

4.3 Hydrolysis and Precipitation of Cobalt Species

For a given oxidation state, cobalt will exist in a number of different chemical forms in solution. The Co^{2+} ions that are released during dissolution of CoSO_4 will be hydrolyzed: ³⁰

$$Co^{2+} + 3 H_2O \leftrightarrows Co(OH)^+ + H^+ + 2 H_2O$$
$$\leftrightarrows Co(OH)_2 + 2 H^+ + H_2O$$
$$\leftrightarrows Co(OH)_3^- + 3 H^+$$
(23)

Dissolved Co^{II} (referred to as $Co^{2+}(aq)$ hereafter) thus includes Co^{2+} , $Co(OH)^+$, $Co(OH)_2$ and $Co(OH)_3^-$. While these cobalt species are in hydrolysis equilibria, the neutral $Co(OH)_2$ molecule can aggregate and precipitate as a gel or a solid Co^{II} hydroxide ($Co(OH)_2(s)$) and establish liquid-solid phase equilibriums:

$$Co^{2+}(aq) \leftrightarrows Co(OH)_{2}$$

n Co(OH)_2 \IP (Co(OH)_2)_n \IP Co(OH)_2(s) (24)

Similarly, Co^{III} will exist as a number of dissolved species (collectively $Co^{3+}(aq)$) (Co^{3+} , $Co(OH)^{2+}$, $Co(OH)_2^+$ and $Co(OH)_4^-$). For Co^{III} , the neutral species, $Co(OH)_3$, is not stable and quickly dehydrates to form CoOOH:²⁸

$$Co^{3+}(aq) \leftrightarrows Co(OH)_3$$

$$n \operatorname{Co}(OH)_3 [\leftrightarrows (\operatorname{Co}(OH)_3)_n \leftrightarrows (\operatorname{Co}OOH)_n + n \operatorname{H}_2O] \leftrightarrows \operatorname{Co}OOH(s) + n \operatorname{H}_2O$$
 (25)

The solubility of $Co^{3+}(aq)$ is very low and Co^{III} prefers to be present as a solid species for a wide range of pH.

The distribution of the cobalt species, particularly Co^{II} , between the solution phase and the solid state is sensitive to the pH of the solution because the pH can shift the hydrolysis equilibria. At a pH where the solubility of $\text{Co}^{2+}(\text{aq})$ is high the phase equilibrium will shift to the left and the precipitation of solid Co^{II} hydroxide will be negligible. This explains the negligible conversion of $\text{Co}^{2+}(\text{aq})$ to solid Co^{III} particles at pH 6.0 even after a prolonged irradiation.²⁷

In pure water (no SO_4^{2-} present) the solubilities of Co^{III} and Co^{II} species at pH 10.6 are ~10⁻¹³ M and ~10⁻⁶ M, respectively.²⁸ The concentration of Co^{2+} in water immediately after dissolution of $CoSO_4$ to make a 0.1 mM solution is higher than the saturation limit of $Co^{2+}(aq)$ in

pure water. Hydrolysis of the Co^{2+} will occur rapidly, but precipitation of $Co(OH)_2$ takes some time at room temperature. No precipitation of $Co(OH)_2$ was seen in less than 1 d without irradiation. Even with irradiation the hexagonal $Co(OH)_2$ crystals were observed only for a 0.3 mM solution where the supersaturation is greater. Gamma-irradiation of a Co^{2+} solution more rapidly converts $Co^{2+}(aq)$ to $Co^{3+}(aq)$ leading to much greater supersaturation with $Co^{3+}(aq)$. The very low solubility of Co^{3+} promotes earlier condensation and particle nucleation (mixed $Co(OH)_3$ and CoOOH) (reaction 25). These Co^{III} particles provide adsorption sites for $Co^{2+}(aq)$ enabling precipitation of $Co(OH)_2$ on the Co^{III} particles. Thus, the radiolytic formation of $Co^{3+}(aq)$ triggers co-precipitation of Co^{II}/Co^{III} hydroxides. The adsorbed Co^{II} can grow either as solid $Co(OH)_2$ crystals, or be oxidized while on the surface to form Co^{III} hydroxides and oxyhydroxides. Heterogeneous surface oxidation typically has a lower activation energy than homogeneous oxidation (because of the participation of the solid in stabilizing the system) and hence less powerful oxidants than •OH (H₂O₂ and O₂) can react.

The decrease in $[Co^{II}]$ measured during Stage 1 far outweighs the increase in $[Co^{III}]$ at the same time (Figure 3). This is likely due to condensation of $Co^{2+}(aq)$ in addition to Co^{2+} oxidation. The large hexagonal $Co(OH)_2(s)$ particles that can form¹⁶ may have eluded the PAR analysis technique that we used. Interestingly, we note that the rate of Co^{II} oxidation in Stage 2 is the same for our two different $[Co^{2+}]_0$ (with different degrees of supersaturation). The onset of Stage 2 is delayed longer in the lower $[Co^{2+}]_0$ solution.

The importance of the adsorption of Co^{II} on the oxidation rate in Stage 2 can be seen in the effect of pH on particle formation found in our previous study.²⁷ The solubility of Co^{2+} is much higher at lower pHs and we did not observe any production of solid cobalt species at pH 6.0. While conversion of Co^{2+} to Co^{3+} can still occur, there is no particle growth through Co^{2+} precipitation and the solid Co^{3+} species are reduced back to Co^{2+} in solution. This prevents the growth of CoOOH and Co₃O₄ particles.

4.4 Reactions of Adsorbed and Solid Cobalt Species

The standard redox potential for the oxidation of $\text{Co}^{2+}(\text{aq})$ to $\text{Co}^{3+}(\text{aq})$ ($\text{E}^{\circ}(\text{Co}^{2+}/\text{Co}^{3+})$) is 1.81 V_{SHE}.⁴⁹ This oxidation does not occur without the participation of a very strong oxidant. Dissolved oxygen and H₂O₂, whose standard redox potentials are 1.229 V_{SHE} and 1.763 V_{SHE}, are not sufficiently strong oxidants to oxidize $\text{Co}^{2+}(\text{aq})$.⁴⁸ The •OH radical has a standard redox potential of 2.3 V_{SHE} ⁴⁹ and can support this oxidation in solution. The standard redox potential for conversion of a Co^{II} hydroxide/oxide to a Co^{III} hydroxide/oxide is lower. For example, that for Co(OH)₂(s) \leftrightarrows CoOOH(s) is -0.695 V_{SHE}⁴². This allows the weaker oxidants H₂O₂ and O₂ to participate in the oxidation of adsorbed Co^{II}:

$$2 \operatorname{Co}(OH)_2(ad) + H_2O_2 \rightarrow 2 \operatorname{Co}OOH(ad) + 2 H_2O$$

$$\tag{26}$$

$$2 \operatorname{CoOOH}(\mathrm{ad}) + (\operatorname{CoOOH})_{\mathrm{n}}(\mathrm{s}) \to \to (\operatorname{CoOOH})_{\mathrm{n+2}}(\mathrm{s})$$

$$(27)$$

The conversion of adsorbed Co^{II} ions to CoOOH stabilizes the nucleate particles and promote the continuing adsorption of $Co^{II}(ad)$ on the nucleates. Once sufficient nucleates with sufficient surface area are formed the oxidation of adsorbed $Co^{II}(ad)$ to CoOOH(ad) becomes the main cobalt oxidation path.

The oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH(ad) is initially limited by the rate of radiolytic production of H₂O₂. Hence, the rate of cobalt oxidation in Stage 2 can depend on the impact of radical scavengers on H₂O₂ production. This explains why the rate of cobalt oxidation is higher in the aerated solutions than in the N₂O/Ar purged solutions in Stage 2; the H₂O₂ concentration is higher in the former (see Figure 11).

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The CoOOH(ad) incorporates into a solid CoOOH phase, growing the oxide particles (reaction 27). As the CoOOH particles are formed they slowly transform to thermodynamically more stable $Co_3O_4(s)$:

$$Co(OH)_2(ad) + 2 CoOOH(s) \rightarrow Co_3O_4(s) + 2 H_2O$$
 (28)

This results in particles with an inner core of Co_3O_4 and a thin outer film of CoOOH. The transformation reaction competes for $Co^{II}(ad)$ with the surface oxidation of $Co^{II}(ad)$ to CoOOH. At long irradiation times when the $[H_2O_2]$ becomes high the rate of the surface oxidation of $Co^{II}(ad)$ to CoOOH (Stage 3) is limited by the rate of adsorption of $Co^{II}(ad)$ and not by the rate of radiolytic production of H_2O_2 . The solid-state conversion of CoOOH to Co_3O_4 is seen in the XPS results for particles formed as a function of irradiation time (Figure 5). Reaction (28) could also continue in Stage 4 when the surface oxidation becomes negligible if sufficient Co^{2+} and CoOOH(s) remain. This can then explain the increase in A_{400nm} in Stage 4 in the 0.3 mM [Co^{2+}] solutions.

The particle growth mechanism that we have proposed is consistent with the observed effect of scavengers on the kinetics of oxidizing species as a function of time. Due to its dependence on the H_2O_2 production rate, the net rate of oxidation of Co^{II} to Co^{III} in Stage 2 depends on how a scavenging environment affects the production of H_2O_2 . The model calculations presented in Figure 11 show that without cobalt present the $[H_2O_2]$ at times longer than 1 s is higher in aerated water than in N₂O/Ar purged water. Thus, the rate of Co^{II} to Co^{III} oxidation in Stage 2 will be expected to be higher in aerated water than in N₂O/Ar purged water. This is what we observed.

Figure 12 presents the $[H_2O_2]$ as a function of time in the irradiated solutions with and without initially dissolved Co²⁺. The $[H_2O_2]$ in the aerated solutions free of Co²⁺ at pH 6.0 and pH 10.6 reaches about 0.1 mM, the level predicted by the radiolysis model. As discussed above,

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no cobalt particles form at pH 6.0 and they are not present to react with H_2O_2 , so the $[H_2O_2]$ as a function of time is the same for aerated solutions with and without added Co^{2+} . However, at pH 10.6 where particles are formed $[H_2O_2]$ is below the detection limit; all of the radiolytically-produced H_2O_2 is consumed by the reactions with the adsorbed Co^{2+} species.

In Stage 3 after enough CoOOH(s) has formed, the net oxidation of Co^{II} to Co^{III} will be determined by the rate of reaction (28). As the adsorbed Co^{II} is incorporated into the growing Co_3O_4 oxide lattice, less Co^{II} is oxidized to form CoOOH that can convert to Co_3O_4 . The net rate of reaction (31) is independent of the scavenging environment. This explains why Stage 3 starts at nearly the same time (~ 1 h) for all systems and the rate of conversion of Co^{II} to Co^{III} in Stage 3 is the same with different scavengers present (Figure 6).

5. CONCLUSIONS

The effects of $[\text{Co}^{2+}]_0$ and different radical scavengers on the kinetics of γ -radiationinduced Co_3O_4 nanoparticle formation and growth were investigated. The experimental study shows that there are four distinct stages of particle formation. Scavengers and $[\text{Co}^{2+}]_0$ affect the oxidation kinetics in different stages differently, and consequently can influence the final size of the particles that are formed. Radiolysis model calculations on the time-evolution of the concentrations of key oxidants and reductants and the effect of scavengers provide insights into the role of key oxidants in controlling particle formation.

Based on the model calculations and experimental results a mechanism for Co_3O_4 particle formation is proposed. The main processes in the four stages are: (1) the oxidation of $\text{Co}^{2+}(\text{aq})$ to $\text{Co}^{3+}(\text{aq})$ by radiolytically-produced •OH in the solution phase, followed by spontaneous coprecipitation of mixed $\text{Co}^{II}/\text{Co}^{III}$ hydroxide nucleate particles, (2) adsorption of Co^{II} on the nucleates followed by surface oxidation of $\text{Co}^{II}(\text{ad})$ to CoOOH(ad) by H₂O₂, growing particles as a solid CoOOH(s) phase, (3) continuing adsorption and surface oxidation of $Co^{II}(ad)$ to CoOOH(ad) to grow CoOOH(s) and solid-state transformation of CoOOH(s) + $Co^{II}(ad)$ to $Co_3O_4(s)$, and (4) completion of cobalt oxidation and continuing solid-state transformation of CoOOH(s) + $Co^{II}(ad)$ to $Co_3O_4(s)$.

This study shows how steady-state water radiolysis kinetics, metal ion hydrolysis, and phase equilibria of cobalt species are linked. It also shows how appropriate adjustment of solution conditions and radical scavenger concentrations can be used to produce Co_3O_4 nanoparticles with tailored sizes. We found that particles as small as 8-20 nm can be formed by using O_2 to enhance H_2O_2 generated by radiolysis and particles as large as 20-80 nm can be formed by using N_2O to enhance •OH generated by radiolysis.

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Figure Captions:

- **Figure 1:** Examples of the UV-Vis spectra of irradiated solutions: (a) raw spectra and (b) background-subtracted spectra. The reference spectrum of Co_3O_4 is shown as the dashed curve. These figures are adopted from ref. [27].
- **Figure 2:** Solution and gas analysis results obtained for a $0.1 \text{ mM} [\text{Co}^{2+}]_0$ aerated solution as a function of irradiation time: (a) concentrations of Co^{II} (solid symbols) and Co^{III} (half-filled symbols) determined by the PAR method, (b) background-subtracted absorbance at 400 nm of the irradiated solution (A_{400nm}), and (c) the concentration of H₂ in the head space ([H₂(g)])]. The error bars represent the scatter in the data from different experiments.
- **Figure 3:** Comparison of the results obtained for 0.1 mM $[Co^{2+}]_0$ and 0.3 mM $[Co^{2+}]_0$ aerated solutions: the concentrations of (a) Co^{II} and (b) Co^{III} determined by the PAR method, and (c) the background-subtracted absorbance at 400 nm of the irradiated solution (A_{400nm}).
- **Figure 4:** TEM images of the particles collected after irradiation of a $0.3 \text{ mM} [\text{Co}^{2+}]_0$ aerated solution for different durations.
- **Figure 5:** XPS results of the particles collected after irradiation of a 0.3 mM $[Co^{2+}]_0$ aerated solution for different durations: (a) the high resolution XPS Co-2p spectra after 5 min, (b) the high resolution XPS Co-2p spectra after 5 h (the inset shows the Co₃O₄ spectrum consisting of multiple peaks) and (c) a summary of the deconvolution analysis results.
- **Figure 6:** (a) Raman spectra of the particles collected after 5-h irradiation of a $0.3 \text{ mM} [\text{Co}^{2+}]_0$ aerated solution for different durations. This figure is reproduced from ref. [27]. (b) Reference spectra taken using standard powder samples of cobalt oxides
- **Figure 7:** TEM images of the particles collected after irradiation of a $0.1 \text{ mM} [\text{Co}^{2+}]_0$ aerated solution for different durations.
- **Figure 8:** TEM images of the particles formed after 5-h irradiation of a $0.1 \text{ mM} [\text{Co}^{2+}]_0$ solution: (a) aerated only, (b) aerated & 0.1 M *t*-butanol, and (c) N₂O/Ar purged. The graph shows the Raman spectra of the particles.
- **Figure 9:** Concentrations of Co^{II} (solid symbols) and Co^{III} (open symbols) as a function of irradiation time for a 0.1 mM CoSO₄ solution with different scavenger: aerated only (\bigstar &), aerated and 0.1 M *t*-butanol (\blacksquare $\&\square$), purged with N₂O/Ar (\bigcirc & \bigcirc), deaerated only (\bigstar &), and deaerated and 0.1 M *t*-butanol (\blacklozenge).

- Figure 10: Schematic of the proposed mechanism for radiation-induced formation and growth of Co_3O_4 nanoparticles from initially dissolved Co^{2+} .
- Figure 11: Calculated time evolution of radiolysis product concentrations during irradiation of deaerated, aerated (dissolved $[O_2] = 0.25 \text{ mM}$) and N₂O/Ar purged (dissolved $[N_2O] = 12.5 \text{ mM}$) solutions at pH 10.6 at a dose rate of 4.5 kGy·h⁻¹, (top panel) free of Co²⁺, and (bottom panel) with 0.1 mM $[Co^{2+}]_0$.
- **Figure 12:** Concentration of H_2O_2 formed as a function of time during irradiation of an aerated solution free of Co^{2+} (\blacklozenge) at pH 10.6, and aerated solutions with and without 0.3 mM [Co^{2+}]₀, respectively, at pH 6.0 (\bigstar , \Box). The [H_2O_2] was below the detection limit of 3 μ M for the aerated solution with 0.3 mM [Co^{2+}]₀.



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