PCCP

High Temperature Gamma Radiation-Induced Chromium Redox Chemistry via in situ Spectroscopic Measurements

Journal:	*Physical Chemistry Chemical Physics*
Manuscript ID	CP-ART-10-2023-005296.R1
Article Type:	Paper
Date Submitted by the Author:	21-Nov-2023
Complete List of Authors:	Conrad, Jacy K; Idaho National Laboratory, Fox, Robert; Idaho National Laboratory Danaher, Emma; Idaho National Laboratory Horne, Gregory; Idaho National Laboratory, Center for Radiation Chemistry Research

High Temperature Gamma Radiation-Induced Chromium Redox Chemistry via in situ Spectroscopic Measurements

Jacy K. Conrad,[a],* Robert V. Fox,[b] Emma G. Danaher,[a] and Gregory P. Horne[a]

[a] *Center for Radiation Chemistry Research, Idaho National Laboratory, 1955 N. Fremont Ave., Idaho Falls, 83415, USA.*

[b] *Material Separations & Analysis, Idaho National Laboratory, 1955 N. Fremont Ave., Idaho Falls, 83415, USA.*

*Corresponding author e-mail: jacy.conrad@inl.gov

ORCID

Jacy K. Conrad	0000-0002-0745-588X
Robert V. Fox	0000-0003-0745-186X
Emma G. Danaher	0000-0003-3304-3229
Gregory P. Horne	0000-0003-0596-0660

Abstract

Chromium ions can make their way into the primary coolant of nuclear power reactors from the corrosion of stainless-steel reactor components, decreasing the material's corrosion resistance and resulting in increased transport of further corrosion products. Despite these potential effects, the radiation-induced redox speciation of chromium ions in aqueous solution is not well understood, especially at the elevated temperatures experienced by reactor coolants. In the present work, we report new experimental results demonstrating that in aerated aqueous solution, the radiolytic oxidation of Cr(III) to Cr(VI) occurs at pH 4, while the reduction of Cr(VI) to Cr(III) occurs at pH 2. The oxidation of Cr(III) is primarily attributed to the reaction of the hydroxyl radical ($^{\bullet}OH$) with the $Cr(OH)^{2+}$ species, while the reduction of Cr(VI) is attributed to reactions involving the hydrated electron (e_{aq}^{-}) and hydrogen atom ($H^{\bullet}$). Additionally, the steady-state equilibrium yield of Cr(VI) from the gamma irradiation of pH 4 Cr(III) solutions decreased with increasing temperature (over a range of 37–195 °C). This observation indicates that the activation energy of the Cr(VI) reduction reactions is higher than that for the Cr(III) oxidation reactions, such that it becomes relatively more favorable at higher temperatures. Overall, these data are important for the

development of complementary multiscale models for the prediction of metal ion speciation in high temperature radiation environments.

1. Introduction

Aqueous systems at elevated temperatures containing dissolved metal ions from the corrosion of stainless steels and other alloys are exposed to ionizing radiation fields throughout the nuclear fuel cycle. Understanding the aqueous radiation chemical behavior of metal ions released from key alloying materials, such as chromium (Cr) from stainless steels, is critical to model and monitor the performance of several industry processes, including: the corrosion of nuclear reactor materials, the extent of extraction in used nuclear fuel reprocessing systems, and the partitioning of materials for vitrification in nuclear waste storage. In addition, having this foundational understanding of chromium ion speciation under irradiation will help to shape the treatment of chromium-containing wastewaters to prevent excessive transport of toxic Cr(VI) through the environment.

Chromium is a well-known heavy metal that is a ubiquitous contaminant in wastewaters due to both natural and anthropogenic sources.[1] Chromium has a variety of available oxidation states; however, the three most stable forms are Cr(0), Cr(III), and Cr(VI).[2] Chromium metal, Cr(0), is valued for its high corrosion resistance and hardness, and therefore it is commonly used in industrial applications where it is incorporated into iron-based alloys such as stainless steels. During process applications, chromium can leach out of the stainless steels and make its way into wastewaters in the environmentally stable Cr(III) and Cr(VI) oxidation states.[3] Cr(III) is generally considered to be a micronutrient,[3] but Cr(VI) is highly toxic and carcinogenic,[4-5] resulting in strict regulations for its concentration limits in drinking water.[6]

At low concentrations, trivalent chromium ions, Cr(III), are present in aqueous solution as a variety of pH dependent hydrolysis species with relatively low solubility:[7]

$$Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+ \qquad pK_1 = 3.57 \text{ at } 25\ °C, \tag{1}$$

$$Cr(OH)^{2+} + H_2O \rightleftharpoons Cr(OH)_2^+ + H^+ \qquad pK_2 = 6.27 \text{ at } 25\ °C, \tag{2}$$

$$Cr(OH)_2^+ + H_2O \rightleftharpoons Cr(OH)_3^0 + H^+ \qquad pK_3 = 6.35 \text{ at } 25\ °C, \tag{3}$$

$$Cr(OH)_3^0 + H_2O \rightleftharpoons Cr(OH)_4^- + H^+ \qquad pK_4 = 11.46 \text{ at } 25\ °C. \qquad (\mathbf{4})$$

Hexavalent chromium ions, Cr(VI), are much more soluble, and therefore more mobile in environmental systems.[8] Aqueous Cr(VI) ions are present in dilute aqueous solutions in the form of chromic acid: [9-12]

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad pK_{1a} = -1.0\text{–}1.6 \text{ at } 25\ °C, \qquad (\mathbf{5})$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+, \qquad pK_{2a} = 6.472 \text{ at } 25\ °C. \qquad (\mathbf{6})$$

Polynuclear chromium species, such as the dimeric dichromate ion ($Cr_2O_7^{2-}$), also form with either oxidation state at higher concentrations or temperatures.[9, 12-14] The equilibrium constants (K) for the polynuclear species and for Cr(III) species at high temperatures are not as well-known as compared to other transition metal hydrolysis and polymerization reactions.[15-16] This knowledge gap is exacerbated by radiation fields, which can promote dynamic changes in the redox distribution of metal ions in aqueous solution. Radiation-induced changes in the distribution of chromium ion oxidation states ultimately affect its chemical properties, including solubility, complexation, and reactivity.

When ionizing radiation is absorbed by water, it undergoes excitation, ionization, and a series of subsequent radical reactions to liberate the primary products of water radiolysis:

$$H_2O \rightsquigarrow 2.73\ e_{aq}^- + 2.79\ {}^{\bullet}OH + 0.60\ H^{\bullet} + 0.45\ H_2 + 0.7\ H_2O_2 + 2.73\ H_{aq}^+, \qquad (\mathbf{7})$$

where the coefficients for each species represents its room temperature escape yield (G value, molecules/100 eV) from a pure water radiation track.[17] The hydrated electron (e_{aq}^-, E° = -2.9 V) and hydrogen atoms ($H^{\bullet}$, E° = -2.3 V) are powerful reducing agents, while the hydroxyl radical (${}^{\bullet}OH$, E° = 2.7 V) is a strong oxidant, all of which are capable of driving redox distribution changes in dissolved metal ions.[18] Hydrogen peroxide (H_2O_2), a molecular radiolysis product, is also capable of both reduction and oxidation depending on solution conditions and the metal ion redox potentials.[19-29] Recently, the reaction rates between several primary water radiolysis products and aqueous chromium ion species have been determined,[30-31] as summarized in **Table 1**. These experimental studies investigated many of these reactions to elevated temperatures, allowing for their activation energies (E_a) and pre-exponential factors (A) to be determined, also summarized in **Table 1**. Beyond these investigations, there are no reported studies of aqueous chromium ions irradiated at elevated temperatures.

Table 1. Reaction rates and Arrhenius parameters for reactions between aqueous chromium ion species and primary water radiolysis products at elevated temperatures from previous studies.

Reaction	k_o (25 °C, M^{-1} s^{-1})	**Activation Energy** (kJ mol^{-1})	**Preexponential Factor** (M^{-1} s^{-1})	**Reference**
$HCrO_4^- + e_{aq}^-$	$(3.28 \pm 0.58) \times 10^{10}$	12.87 ± 0.56	$(5.913 \pm 0.104) \times 10^{12}$	30
$CrO_4^{2-} + e_{aq}^-$	$(1.47 \pm 0.10) \times 10^{10}$	13.19 ± 0.12	$(3.001 \pm 0.130) \times 10^{12}$	30
$HCrO_4^- + H^\bullet$	$(1.19 \pm 0.17) \times 10^{10}$	12.98 ± 0.29	$(2.236 \pm 0.173) \times 10^{12}$	30
$Cr(V) + {}^\bullet OH$	$(4.80 \pm 0.52) \times 10^{9}$	7.03 ± 0.22	$(8.170 \pm 0.536) \times 10^{10}$	30
$Cr(III) + e_{aq}^-$	$(4.86 \pm 0.05) \times 10^{10}$	-[a]	-[a]	31
$Cr^{3+} + {}^\bullet OH$	0	-[b]	-[b]	31
$Cr(OH)^{2+} + {}^\bullet OH$	$(7.2 \pm 0.3) \times 10^{8}$	-[b]	-[b]	31

[a] High temperature measurements made, but behavior is not simple linear Arrhenius.

[b] Measurements only made to 50 °C.

With the above in mind, we report the steady-state gamma radiation-induced chemical behavior of chromium ions in aqueous solution by examining changes in the redox distribution of chromium ions over a wide range of temperatures (37–195 °C) with up to 12 kGy of absorbed gamma dose. These data are essential for benchmarking multiscale computational models for the prediction of the behavior of these metal ion systems from ambient to hydrothermal conditions in radiation environments.

2. Experimental

2.1. Solution Preparation

Chromium(III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%), iron(II) sulfate ($FeSO_4$, ≥ 99%), potassium dichromate ($K_2Cr_2O_7$, ≥ 99.5% Reagent Plus), perchloric acid ($HClO_4$, 99.999% trace metals basis), sodium chloride (NaCl, 99.999% trace metals basis), sodium hydroxide (NaOH, 50% in H_2O), sulfuric acid (H_2SO_4, 99.999%), ethylenediaminetetraacetic acid (EDTA) tetrasodium salt dihydrate (99.0–102.0% titration), ammonium acetate (NH_4OOCH_3, BioUltra, > 99%), and glacial acetic acid (CH_3COOH, ≥ 99% Reagent Plus) were purchased from Millipore Sigma (Burlington, MA, USA), and used without further purification.

All aqueous solutions were prepared in ambient air using ultra-pure water (18.2 MΩ cm) and NaOH or $HClO_4$ for pH adjustment.

2.2. Analytical Methods

UV-Visible spectrophotometry, as measured by an Agilent Technologies, Inc. (Santa Clara, CA, USA) Cary 60 UV-Vis spectrophotometer equipped with a fiber optic coupler, was used to quantify the concentrations of Fe(III), Cr(III), and Cr(VI) species in a given solution. Absorption spectra were recorded from 200–800 nm with a scan rate of 300 nm min^{-1}. Direct absorbances of Fe(III) (λ_{max} = 304 nm, ε = 2200 M^{-1} cm^{-1})[17], Cr(VI) (λ_{max} = 355 nm, ε = 1445 ± 5 M^{-1} cm^{-1}), and Cr(III) (λ_{max} = 408 nm, ε = 15.5 ± 0.5 M^{-1} cm^{-1}) were used for quantification, in addition to the Cr(III)-EDTA complex (λ_{max} = 544 nm, ε = 191 ± 1 M^{-1} cm^{-1}).[3, 11, 32]

2.3. Steady-State Gamma Irradiations

Aqueous chromium solutions were irradiated in either closed 8 mL screw-cap glass vials and analyzed post-irradiation in triplicate, or in a high temperature titanium vessel equipped with integrated in situ optical absorption monitoring via sapphire windows with coupled fiber optics, as described in detail elsewhere.[33] High temperature cell samples were intentionally pressurized to 2250 psi to avoid solution vaporization and studied at temperatures from 37–195 °C, with an uncertainty of ± 4 °C at the ambient irradiator temperature, and ± 1 °C at elevated temperatures. Closed glass vial samples were irradiated under ambient irradiator temperature conditions (37 ± 1 °C), as determined using a calibrated National Instruments (Austin, Texas, USA) USB-TC01 Single Channel Temperature Input Device equipped with a K-type thermocouple. All gamma irradiations were performed using the Idaho National Laboratory (INL) Center for Radiation Chemistry Research (CR2) Foss Therapy Services (Pacoima, CA, USA) Model 812 Cobalt-60 irradiator. Dose rates of 26–222 Gy min^{-1} were determined for each sample type using Fricke solution (1 mM $FeSO_4$, 1 mM NaCl, 0.4 M H_2SO_4) subsequently corrected for the natural decay of cobalt-60 ($\tau_{1/2}$ = 5.27 years: $E_{\gamma 1}$ = 1.17 MeV and $E_{\gamma 2}$ =1.33 MeV) throughout the duration of this study.[17] No dose rate effect on the Cr redox behavior was observed over this range.

3. Results and Discussion

3.1. Ambient Temperature Irradiations

Figure 1 shows the experimental oxidation state distribution of 0.6 mM Cr(III) or Cr(VI) from the gamma irradiation of aqueous solutions at 37 °C with room temperature pH values of 2 and 4. According to the equilibria presented by **Eq. 1–6**, at pH 2 Cr(III) is present primarily as the Cr^{3+} ion, whereas a mixture of $Cr(OH)^{2+}$ and Cr^{3+} species are expected at pH 4. Further, Cr(VI) should be present primarily as the bichromate species ($HCrO_4^-$) at both solution pH values. From the results shown in **Figure 1**, it is clear that regardless of the starting oxidation state of chromium, Cr(III) is favored at pH 2, while Cr(VI) is favored at pH 4. In similar ambient temperature irradiations of pH 6, 8.5, and 10.6 aqueous solutions, Alrehaily *et al.* reported no change in the oxidation state distribution of Cr(VI) irradiated under aerated conditions. However, they did observe the conversion of Cr(VI) to Cr(III) followed by colloidal precipitation under de-aerated conditions.[34] These observations are consistent with our findings, which are in aerated solutions.

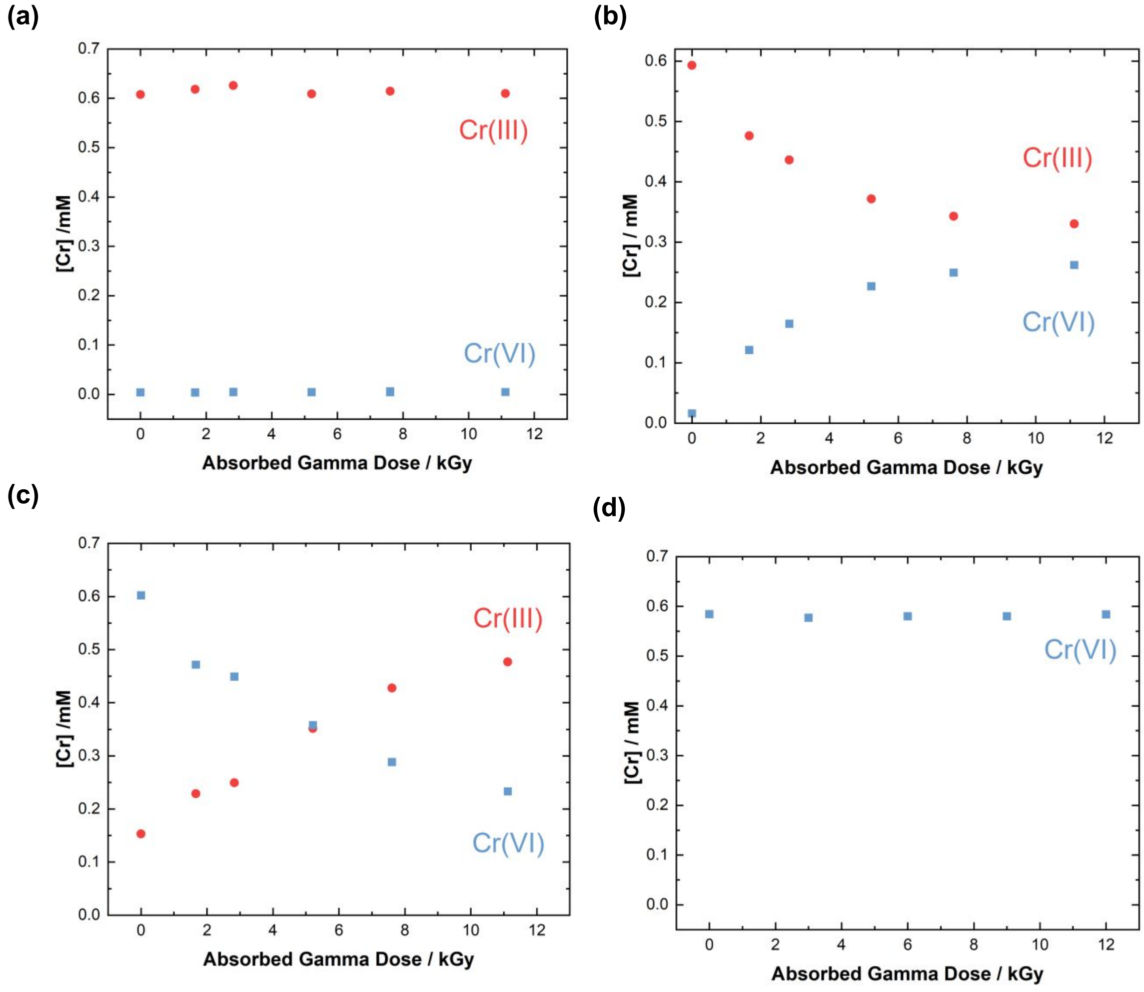

Figure 1. Oxidation state distribution of chromium ions from the ambient temperature (37 °C) gamma irradiation of aerated aqueous solutions of 0.6 mM Cr(III) at (**a**) pH 2 and (**b**) pH 4, and 0.6 mM Cr(VI) at (**c**) pH 2 and (**d**) pH 4.

When Cr(VI) species ($HCrO_4^-$ and CrO_4^{2-}) are present, they are reduced readily by the e_{aq}^- and $H^\bullet$ atoms at a rate of ~10^{10} M^{-1} s^{-1} (**Table 1**) to ultimately yield the corresponding Cr(III) species.[30] As stated in the introduction, the primary reducing water radiolysis product is the e_{aq}^-. Under aerated acidic conditions in the absence of other solutes, the e_{aq}^- is primarily consumed via the following reactions, whose kinetics have been measured in pure water up to 350 °C:[35]

$$e_{aq}^- + H^+ \rightleftharpoons H^\bullet \qquad K_8 = 3.6 \times 10^9, \quad k_{8f} = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}, \qquad k_{8b} = k_{8f}/K_8, \qquad \textbf{(8)}$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \qquad k_9 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}, \qquad E_a = 11.6\ kJ\ mol^{-1}, \qquad \textbf{(9)}$$

$$e_{aq}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- \qquad k_{10} = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}, \qquad E_a = 15.7\ kJ\ mol^{-1}, \qquad \textbf{(10)}$$

where K_i is the equilibrium constant and k_i is the rate coefficient of reaction i, all at 25 °C. The dominant pathway for the e_{aq}^- reactions depends on the pH of the solution. At pH 2, the concentration of H^+ is sufficiently high to scavenge the majority of the available e_{aq}^- via **Eq. 8** to yield $H^\bullet$ atoms, whereas at pH 4 a combination of all three reactions (**Eq. 8–10**) is expected. The $H^\bullet$ atom also reacts with O_2 at a rate of 1.3×10^{10} M^{-1} s^{-1} at 25 °C.[35] These fundamental reactions provide a mechanistic explanation as to why more Cr(VI) species are reduced in solutions that have been de-aerated, as there is less O_2 and H_2O_2 present to compete with Cr(VI) species for the reducing products of water radiolysis.

The primary oxidizing species in irradiated, acidic, aerated aqueous solutions is the $^\bullet OH$ radical. At pH 2, there was no net oxidation of Cr(III) to Cr(VI) species during gamma irradiation (**Figure 1a**). This is likely due to the slow rate of reaction between the Cr^{3+} ion and the $^\bullet OH$ radical (**Table 1**), thereby allowing other species to scavenge the available yield of $^\bullet OH$ radicals.[31] At pH 4 on the other hand, $Cr(OH)^{2+}$ becomes the dominant Cr(III) species and exhibits greater reactivity towards the $^\bullet OH$ radical (**Table 1**),[31] thereby facilitating the oxidation of Cr(III) to Cr(VI) species until a steady-state equilibrium is achieved, as shown in **Figure 1b**.

Beyond these transient radical species, H_2O_2 is another important water radiolysis product that can behave as either a reductant or an oxidant towards dissolved chromium ion species. Alrehaily *et al.* reported no detectable H_2O_2 in their irradiated solutions, indicating that it was consumed during the experiment by reaction with the various available chromium ion species.[34] Despite these observations, H_2O_2 chemistry is one of the main obstacles in the development of a comprehensive multiscale model for these chromium systems because of inconsistencies reported in the complicated kinetics and mechanisms for different chromium oxidation states reacting with H_2O_2.[19-29] These H_2O_2 reactions are currently being explored in more detail by follow-on studies.

3.2. High Temperature Irradiations

In addition to the above ambient temperature irradiations, a series of high temperature irradiation experiments were performed to study the speciation of Cr(III) ions in real time up to 195 °C. This temperature range was chosen to avoid chromium precipitation, polymerization, and ion pairing.[7, 9, 11-14]

Figure 2(a) shows the growth of the Cr(VI) optical absorbance peak at 375 nm with increasing absorbed gamma dose from the irradiation of a 0.5 mM Cr(III) ion solution at pH 4 and 37 ± 4 °C. **Figure 2(b)** shows the corresponding concentrations of Cr(VI) species detected, alongside the calculated concentration of remaining Cr(III) ions, as determined by mass balance. The average speciation data at particular absorbed gamma doses of the same solution formulation in closed 8 mL glass vials is also shown **Figure 2(b)** as solid circular symbols. The agreement between the two different experimental setups is excellent, with Cr(III) again being observed to be radiolytically converted to Cr(VI) in the form of the $HCrO_4^-$ species at pH 4.

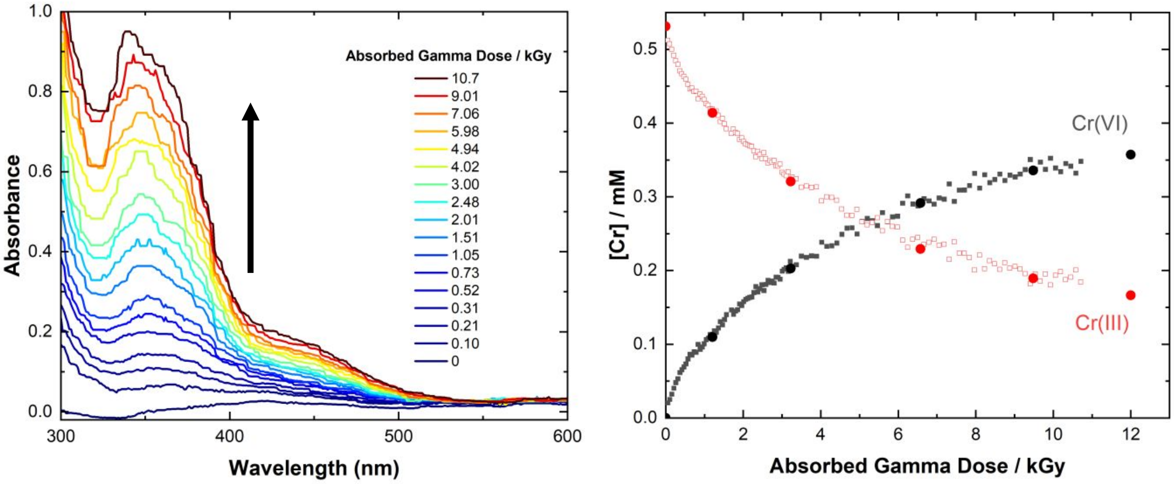

Figure 2. (a) Radiation-induced growth of the bichromate absorbance peak from the gamma irradiation of 0.5 mM Cr(III) ions in aqueous solution at pH 4 and 37 °C. **(b)** Concentration of aqueous chromium ion species as a function of absorbed gamma dose from experiments performed in the high temperature cell (□) and in closed 8 mL glass vials (●).

This experiment was repeated at 61, 101, 145, and 195 °C, where the uncertainty on the temperatures was ± 1 °C. A series of complementary benchtop heating studies were also performed to establish that the thermal conversion of Cr(III) to Cr(VI) ions does not occur appreciably over the timescale of our irradiation experiments. The yield of Cr(VI) ions determined here from optical absorbance measurements as a function of the absorbed gamma dose at each temperature is shown in **Figure 3**. The concentrations given in **Figure 3** have been corrected to account for the expansion of the aqueous solution with temperature. This was achieved by multiplying by the ratio of the density of water at the experimental temperature and room temperature. Overall, this correction removed the artificial decrease in Cr(VI) ion concentration resulting purely from the expansion of the aqueous solution with temperature.

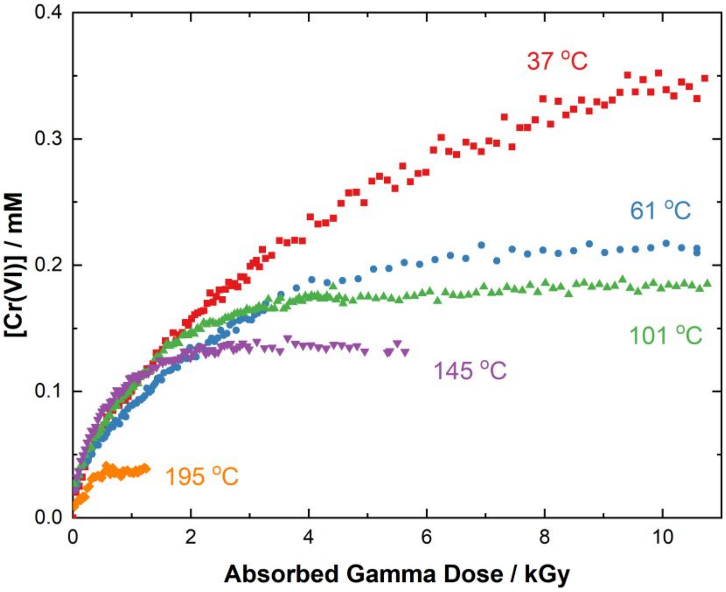

Figure 3. Radiation-induced growth of Cr(VI) ions from the gamma irradiation of 0.5 mM Cr(III) ion in aqueous solution at pH 4 as a function of temperature.

It is clear from the data in **Figure 3** that the steady-state yield of Cr(VI) decreases with increasing temperature, going from ~0.35 mM at 37 °C to 0.04 mM at 195 °C. This observation can be understood from the reactions previously discussed for ambient temperature conditions and their associated Arrhenius parameters (**Table 1**). The activation energy of a chemical reaction defines the extent to which its rate changes with temperature. As described above, Cr(III) ions are primarily converted to Cr(VI) ions via their reaction with the $^{\bullet}OH$ radical, while Cr(VI) is converted back to Cr(III) via its reaction with the e_{aq}^{-} and $H^{\bullet}$ atom. Under these conditions, the net rate for Cr(VI) reduction must be increasing more rapidly with increasing temperature than the rate of Cr(III) oxidation, resulting in the progressively lower steady-state Cr(VI) yield. Therefore, either the activation energy for the $Cr(OH)^{2+}$ hydrolysis product reaction with the $^{\bullet}OH$ is lower than the activation energies of the corresponding Cr(VI) reduction reactions (E_a = 13 kJ mol^{-1}, **Table 1**) , or the rates of H_2O_2-driven chromium reactions change significantly with temperature to favor reduction. Either way, additional reaction kinetics studies are necessary to unravel the observed radiation-induced behavior.

3. Conclusions

This study reports the radiation-induced oxidation state speciation of chromium ions in acidic aqueous solutions as a function of temperature (37–195 °C). To our knowledge, this is the first high temperature steady-state irradiation of an aqueous metal ion solution to be reported, and the first irradiation of this kind coupled with *in situ* UV-Vis spectroscopy measurements at any temperature. Our results demonstrate that Cr(III) ions are favored in pH 2 solutions and Cr(VI) ions are favored in pH 4 solutions. The oxidation of Cr(III) ions is believed to occur via the reaction of the $Cr(OH)^{2+}$ hydrolysis product with the $^{\bullet}OH$ radical, while Cr(VI) ions are reduced by reaction with the e_{aq}^{-} and $H^{\bullet}$ atom. Furthermore, we found that as the solution temperature was increased up to 195 °C, the steady-state yield of Cr(VI) from Cr(III) in pH 4 solutions decreased due to changes in the Arrhenius behavior of the respective reduction and oxidation reactions. It is likely that the activation energy of the $Cr(OH)^{2+} + {}^{\bullet}OH$ is < 13 kJ mol^{-1}. Thus, radiation-induced changes in chromium ion speciation are more significant at lower temperatures under the given conditions, which is fortuitous for nuclear reactor technologies.

Overall, these observations demonstrate the importance of the development of a predictive multiscale computer model for these chemical systems. Using the high temperature reaction rates measured in the literature as inputs, and the steady-state gamma irradiation behavior from this work as a benchmark test, a kinetic model for the reactions of chromium ions with water radiolysis products can be built. Currently, the reactions of H_2O_2 with the different chromium oxidation states have been identified as a key component missing from the known reaction set. Follow-on studies of these H_2O_2 kinetics, in addition to the measurement of the disproportionation reactions of the unstable intermediate oxidation states (Cr(IV) and Cr(V)) to high temperature, are required to complete model development for aqueous chromium systems.

4. Acknowledgements

This work was funded by the INL Laboratory Directed Research & Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517. E. Danaher was funded by the Department of Energy (DOE) Office of Science (SC) Science Undergraduate Laboratory Internship (SULI) Program. The authors would like to thank Dr. Dean Peterman for his assistance in setting up the cell inside the irradiator.

5. References

1. Uddin, M. K., A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chem. Eng. J.* **2017,** *308*, 438-462.

2. Bell, J.; Ma, X.; McDonald, T. J.; Huang, C.-H.; Sharma, V. K., Overlooked Role of Chromium(V) and Chromium(IV) in Chromium Redox Reactions of Environmental Importance. *ACS EST Water* **2022,** *2*, 932-942.

3. Gomez, V.; Larrechi, M. S.; Callao, M. P., Chromium speciation using sequential injection analysis and multivariate curve resolution. *Anal. Chim. Acta* **2006,** *571* (1), 129-135.

4. Deng, Y. J.; Wang, M.; Tian, T., et al., The Effect of Hexavalent Chromium on the Incidence and Mortality of Human Cancers: A Meta-Analysis Based on Published Epidemiological Cohort Studies. *Frontiers in Oncology* **2019,** *9*.

5. Pavesi, T.; Moreira, J. C., Mechanisms and individuality in chromium toxicity in humans. *Journal of Applied Toxicology* **2020,** *40* (9), 1183-1197.

6. Hausladen, D. M.; Alexander-Ozinskas, A.; McClain, C.; Fendorf, S., Hexavalent Chromium Sources and Distribution in California Groundwater. *Environ. Sci. Technol.* **2018,** *52* (15), 8242-8251.

7. Rai, D.; Sass, B. M.; Moore, D. A., Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorg. Chem.* **1987,** *26* (3), 345-349.

8. Peng, H.; Leng, Y. M.; Cheng, Q. Z.; Shang, Q.; Shu, J. C.; Guo, J., Efficient Removal of Hexavalent Chromium from Wastewater with Electro-Reduction. *Processes* **2019,** *7* (1).

9. Palmer, D. A.; Wesolowski, D.; Mesmer, R. E., A potentiometric investigation of the hydrolysis of chromate(VI) ion in NaCl media to 175 °C. *J. Solut. Chem.* **1987,** *16* (6), 443-463.

10. Bailey, N.; Carrington, A.; Lott, K. A. K.; Symons, M. C. R., Structure and reactivity of the oxyanions of transition metals 8. Acidities and spectra of protonated oxyanions. *J. Chem. Soc.* **1960,** (JAN), 290-297.

11. Chlistunoff, J. B.; Johnston, K. P., UV-vis spectroscopic determination of the dissociation constant of bichromate from 160 to 400 degrees C. *J. Phys. Chem. B* **1998,** *102* (20), 3993-4003.

12. Szabó, M.; Kalmár, J.; Ditrói, T.; Bellér, G.; Lente, G.; Simic, N.; Fábián, I., Equilibria and kinetics of chromium(VI) speciation in aqueous solution - A comprehensive study from pH 2 to 11. *Inorganica Chimica Acta* **2018,** *472*, 295-301.

13. Laswick, J. A.; Plane, R. A., Hydrolytic polymerization in boiled chromic solutions. *J. Am. Chem. Soc.* **1959,** *81* (14), 3564-3567.

14. Stunzi, H.; Spiccia, L.; Rotzinger, F. P.; Marty, W., Early stages of the hydrolysis of chromium(III) in aqueous solution. 4. Stability constants of the hydrolytic dimer, trimer, and tetramer at 25 °C and I = 1.0 M. *Inorg. Chem.* **1989,** *28* (1), 66-71.

15. Baes, C. F.; Mesmer, R. E., *The Hydrolysis of Cations*. Wiley-Interscience: New York, 1976.

16. Brown, P. L.; Ekberg, C., *Hydrolysis of Metal Ions*. Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2016.

17. Spinks, J. W. T.; Woods, R. J., *Introduction to Radiation Chemistry*. 3rd ed.; John Wiley & Sons Inc.: Canada, 1990.

18. Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O-) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988,** *17* (2), 513-886.

19. Bakac, A.; Espenson, J. H., Kinetics of the oxidation of chromium(II) by hydrogen peroxide: Flash-photolytic and stopped-flow studies based on radical-trapping reactions. *Inorg. Chem.* **1983,** *22* (5), 779-783.

20. Baloga, M. R.; Earley, J. E., Kinetics of oxidation of Cr(III) to Cr(VI) by hydrogen peroxide. *J. Am. Chem. Soc.* **1961,** *83* (24), 4906-&.

21. Al-Ajlouni, A. M.; Espenson, J. H.; Bakac, A., Reaction of hydrogen-peroxide with the oxochromium(IV) ion by hydride transfer. *Inorg. Chem.* **1993,** *32* (14), 3162-3165.

22. Dehghani, M. H.; Heibati, B.; Asadi, A.; Tyagi, I.; Agarwal, S.; Gupta, V. K., Reduction of noxious Cr(VI) ion to Cr(III) ion in aqueous solutions using H_2O_2 and UV/H_2O_2 systems. *J. Ind. Eng. Chem.* **2016,** *33*, 197-200.

23. Funahashi, S.; Uchida, F.; Tanaka, M., Reactions of hydrogen peroxide with metal complexes. 3. Thermodynamic and kinetic studies on the formation, dissociation, and decomposition of peroxochromium(VI) complexes in acid media. *Inorg. Chem.* **1978,** *17* (10), 2784-2789.

24. Perez-Benito, J. F.; Arias, C., A kinetic study of the chromium(VI) hydrogen peroxide reaction. Role of the diperoxochromate(VI) intermediates. *J. Phys. Chem. A* **1997,** *101* (26), 4726-4733.

25. Peng, H.; Guo, J.; Li, G.; Cheng, Q. Z.; Zhou, Y. J.; Liu, Z. H.; Tao, C. Y., Highly efficient oxidation of chromium (III) with hydrogen peroxide in alkaline medium. *Water Science and Technology* **2019,** *79* (2), 366-374.

26. Pettine, M.; Campanella, L.; Millero, F. J., Reduction of hexavalent chromium by H_2O_2 in acidic solutions. *Environ. Sci. Technol.* **2002,** *36* (5), 901-907.

27. Rao, L. F.; Zhang, Z. C.; Friese, J. I.; Ritherdon, B.; Clark, S. B.; Hess, N. J.; Rai, D., Oligomerization of chromium(III) and its impact on the oxidation of chromium(III) by hydrogen peroxide in alkaline solutions. *J. Chem. Soc.-Dalton Trans.* **2002,** (2), 267-274.

28. Rock, M. L.; James, B. R.; Helz, G. R., Hydrogen peroxide effects on chromium oxidation state and solubility in four diverse, chromium-enriched soils. *Environ. Sci. Technol.* **2001,** *35* (20), 4054-4059.

29. van Niekerk, W.; Pienaar, J. J.; Lachmann, G.; van Eldik, R.; Hamzaz, M., A kinetic and mechanistic study of the chromium(VI) reduction by hydrogen peroxide in acidic aqueous solutions. *Water Sa* **2007,** *33* (5), 619-625.

30. Conrad, J. K.; Lisouskaya, A.; Bartels, D. M., Pulse Radiolysis and Transient Absorption of Aqueous Cr(VI) Solutions up to 325 °C *ACS Omega* **2022,** *7* (43), 39071-39077.

31. Conrad, J. K.; Lisouskaya, A.; Barr, L.; Stuart, C. R.; Bartels, D. M., Reaction Kinetics of e_{aq}^- and •OH Radicals with Aqueous Cr(III) Ions. *J. Phys. Chem. A* **2023,** *127* (27), 5683-5688.

32. Soares, R.; Carneiro, M. C.; Monteiro, M. I. C.; Henrique, S. D.; Pontes, F. V. M.; da Silva, L. I. D.; Neto, A. A.; Santelli, R. E., Simultaneous speciation of chromium by spectrophotometry and multicomponent analysis. *Chemical Speciation and Bioavailability* **2009,** *21* (3), 153-160.

33. Conrad, J. K.; Rollins, H. W.; Peterman, D. R.; Fox, R. V., Design of a High-Temperature Cell for Cobalt-60 Irradiations of Aqueous Solutions with in situ UV-Visible Spectroscopy. *Rev. Sci. Instrum.* **2023**.

34. Alrehaily, L. M.; Joseph, J. M.; Musa, A. Y.; Guzonas, D. A.; Wren, J. C., Gamma-radiation induced formation of chromium oxide nanoparticles from dissolved dichromate. *Phys. Chem. Chem. Phys.* **2013,** *15* (1), 98-107.

35. Elliot, A. J.; Bartels, D. M. *The Reaction Set, Rate Constants and G-Values for the Simulation of the Radiolysis of Light Water Over the Range 20° to 350°C Based on Information Available in 2008*; 153-127160-450-001; AECL Nuclear Platform Research and Development: Ontario, Canada, 2009.