# Impact of Metal Ion Complexation on the Radiation Chemistry of Acetohydroxamic Acid in Aqueous Solutions

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## Background

As the world population continues to grow, increasing global energy demands necessitate high power density and low carbon emission solutions such as nuclear power. Reprocessing used nuclear fuel (UNF)—for the recovery and re-use of uranium in new fuel—is key to achieving a sustainable and secure nuclear fuel cycle that could meet the base load for these energy demands. Currently, a major reprocessing research focus is on the development of next generation solvent extraction technologies that promote the efficient recovery of high purity uranium product streams from UNF.

Acetohydroxamic acid (AHA) has been proposed as a safer and more effective substitute for hydrazine-stabilized reductants for the selective separation of plutonium and neptunium from co-extracted uranium [1]. Under typical UNF reprocessing conditions, AHA would be dissolved in concentrated aqueous nitric acid ($HNO_3$) and exposed to the intense multicomponent ionizing radiation fields resulting from the radioactive constituents of the dissolved UNF. These conditions ultimately promote hydrolytic and radiolytic degradation processes that limit the effectiveness and longevity of AHA. The hydrolytic behavior of AHA has been well documented [2-,3,4,5,6], and our knowledge of its radiation chemistry is maturing [7-8,9,10,11,12,13].

The radiolysis of water and aqueous $HNO_3$:

$$\mathrm{H2O} \rightsquigarrow e_{aq}–, \mathrm{H}^{\bullet}, {}^{\bullet}\mathrm{OH}, \mathrm{H_2O_2}, \mathrm{H_2}, \mathrm{H_{aq}}+, \qquad \textbf{(1)}$$

$$\mathrm{HNO3} \rightsquigarrow e_{aq}–, {}^{\bullet}\mathrm{NO_3}, \mathrm{HNO_2}, \mathrm{O}^{\bullet}, \mathrm{H_{aq}}+, \qquad \textbf{(2)}$$

lead to the formation of reactive radical (eaq–, $H^{\bullet}$, $^{\bullet}OH$, and $NO_3^{\bullet}$) and molecular ($H_2O_2$ and $HNO_2$) species that exhibit chemistry with AHA that ultimately leads to its conversion into acetic acid, hydroxylamine, and nitrous oxide gas [11,12]. This foundational radiation chemistry can now be modeled and predicted in the presence and absence of hydrolytic contributions [11,12].

However, this current understanding of AHA radiation chemistry is limited to aqueous solutions in the absence of metal ions, whereas, under envisioned UNF reprocessing conditions, AHA will be present as a mixture of the "free" ligand and its neptunium/plutonium ion complexes, the radiation chemistries of which can be significantly different [14-, 15,16,17,18,19,20,21,22,23,24]. For example, the complexation of trivalent iron ions, Fe(III), by ethylenediaminetetraacetic acid (EDTA), has been shown to enhance the steady-state rate of EDTA radiolysis [15-,16,17,18]. This has been explained by the Fe(III) ion center providing additional reaction pathways for the products of water radiolysis (**Equation 1**) [17,19]. Similar behavior is expected for the metal ion complexes of AHA, and thus this knowledge is essential for the accurate assessment and prediction of the effectiveness and longevity of AHA under envisioned UNF reprocessing conditions.

## Research Scope

The proposed research aims to use a combination of steady-state gamma and time-resolved electron pulse irradiation techniques, coupled with multiscale computer modeling calculations, to determine the impact of metal loading on the radiation chemistry of AHA in aqueous solutions (water, nitrate, and perchloric and nitric acids). For this work, Fe(III) is the metal ion chosen for evaluating the impact of complexation on the rate of AHA radiolysis, and the subsequent distribution of AHA degradation products, as compared to previously reported metal-free AHA systems [11,12]. Iron has been chosen for this project because it is typically found as a solute from the corrosion of steel-based alloy systems, it is readily complexed by AHA [5], non-radioactive, and its impact on AHA hydrolysis has been well studied [5]. To achieve this research goal, the Visiting Young Scientist will execute three parallel research objectives over the course of 9 months, beginning in October 2023:

1. ***Steady-State Gamma Irradiations***. The *Idaho National Laboratory* (INL) *Center for Radiation Chemistry Research* (CR2) cobalt-60 gamma irradiators and wet chemistry laboratories will be used for the preparation, irradiation, and subsequent analysis of 0.5 M AHA samples. Gamma irradiated samples will be interrogated by a series of previously benchmarked analytical techniques and methods [11-,12,13], including UV-visible-nIR absorption spectroscopy, and ion and gas chromatography, all of which the Visiting Young Scientist will be trained in. The steady-state irradiation results will provide the necessary data to begin multiscale model expansion and evaluation.

2. ***Time-Resolved Electron Pulse Irradiations***. The reaction kinetics of metal ion complexes of AHA and its degradation products are currently unknown, and yet needed to construct an accurate reaction set for multiscale model development. Therefore, chemical kinetics will be measured using the *Brookhaven National Laboratory* (BNL) *Laser Electron Accelerator Facility* (LEAF)—of which both Conrad and Horne hold visiting scientist status—for the reaction of Fe(III) AHA complexes (and where possible Fe(III) complexes of AHA degradation products) with the transient radical products from water and aqueous nitrate radiolysis, specifically $e_{aq}$–, $H^{\bullet}$, $^{\bullet}OH$, and $NO_3^{\bullet}$. Isolation of these radicals is trivial, the

methods for which have been previously reported [**Error! Bookmark not defined.**,**Error! Bookmark not defined.**]. The resulting second-order rate coefficients from these kinetic data will be used to expand the current AHA multiscale model reaction sets for the impact of metal ion complexation.

3. ***Multiscale Model Development***. The data acquired by the two previous experimental research objectives will be used to expand and evaluate current multiscale models for AHA radiolysis in aqueous solutions [**Error! Bookmark not defined.**,**Error! Bookmark not defined.**]. The multiscale modeling approach uses a combination of stochastic [25,26] and deterministic modeling methods, which leverage the INL *High Performance Computing Center* resources and desktop kinetic modeling software (MCPA *FACSIMLE* [27]), respectively.

**Visiting Young Scientist**

Ms. Elen Clayton (*Dalton Nuclear Institute, The University of Manchester, Manchester, M1 7HF, UK*) is a graduate student in the second year of her Ph.D. on the "*Development of a New UK Radiolysis Flow Loop for Determination of Radiolytic Solvent Stability*," which entails the construction and evaluation of a recirculation loop with capability to investigate the irradiation of biphasic mixtures—as seen in processes for the recovery of uranium from UNF. Elen is uniquely qualified to carry out this work because she has excellent knowledge of the radiation chemistry of water, AHA, and other components of next generation UNF reprocessing technologies due to her previous work towards her Master's degree dissertation: "*Development of a Kinetic Model for the Hydrolytic and Radiolytic Degradation of Acetohydroxamic Acid.*" Elen's master's project focused on the computer simulation of AHA decomposition *via* hydrolytic and radiolytic pathways in a UNF recycling process. The research proposed here would provide Elen with the opportunity to be involved in the experimental study of the radiation chemistry of AHA. This presents an opportunity for Elen to network internationally and learn from specialists in the field of radiation chemistry, and to develop and hone laboratory skills; both of which are essential for a future career in radiation chemistry research. Overall, this project will contribute to the mentorship and comprehensive radiation chemistry training of Ms. Elen Clayton, essential to the completion of her Ph.D. thesis.

**Deliverable**

At the end of this 9-month project, the proposed research will lead to the expansion of current predictive modeling of AHA radiolysis capabilities to include metal-loaded systems. This project aligns well with the goals of the IAPWS Physical Chemistry of Aqueous Systems Working Group. A report of completed research activities will be delivered to the IAPWS and could directly contribute to the publication of IAPWS documents, such as Guidelines on the anticipated lifetime of AHA in the extreme environments found in UNF reprocessing flowsheets. Further, results will be disseminated through publication of a peer-reviewed journal manuscript (at a minimum *Radiation Physics and Chemistry*, Impact Factor = 2.858 as of 2022) and presentation of our findings at the 2024 *Actinide Separations Conference* and the *18th International Conference on the Properties of Water and Steam.*

**Budget (£20,000.00)**

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| • Student Travel Support (return flights from the UK to Idaho Falls, USA): | £3,000.00 |
| • Student Travel Support (research trip to BNL): | £800.00 |
| • Student Housing/Accommodation Support (£200 per week): | £7,200.00 |
| • Student Living Expenses (£250 per week): | £9,000.00 |

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(27) MCPA Software FACSIMILE Kinetic Modeling Software Package

# Proposal for IAPWS International Collaborative Project

## Towards a replacement for the IAPWS Formulation 1995: Detailed analysis of available data

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November 18, 2022

## Abstract

Support is requested for an IAPWS Fellowship for a young scientist to pursue research "Towards a replacement for the IAPWS Formulation 1995: Detailed analysis of available data".

## Introduction

For more than two decades, the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use [1,2] (IAPWS-95) served to a broad public as a reference equation for computing thermodynamic properties of ordinary water. For a variety of reasons, notably the availability of new experimental data and recognition of some shortcomings in the IAPWS-95 functional form, such as poor extrapolation into metastable regions and problematic performance in mixture models, IAPWS intends to replace IAPWS-95 in the coming decade. One of the reasons is that new experimental data are available for various thermodynamic properties in different regions. Also, new accurate statistical mechanical computations are available for the gas phase and molecular simulations have been performed providing the approximate course of thermodynamic properties in metastable regions and at extreme conditions. Beyond this, there have been efforts to arrive at realistic uncertainty statements for the computed properties complying with the present best practice of uncertainty assessment. The multitude of available thermodynamic data makes water prominent among other fluids. However, the fact that the data exist in the form of partially overlapping clouds of measurements for various thermodynamic properties makes the question of the most likely location of the thermodynamic surface highly non-trivial. In order to properly asses the value of individual datasets and to judge their mutual consistency, one needs to study the original experimental reports and, preferably based on the assessor's experimental background, identify the decisive sources and magnitudes of uncertainties, and to transform gained information into a form suitable for data correlation.

The Lehrstuhl für Thermodynamik at Ruhr-Universität Bochum (RUB) and the Applied Chemicals and Materials Division of the National Institute of Standards and Technology (NIST), Boulder, are world-wide leaders in the area of development of reference multi-parameter equations of state and in reference thermodynamic measurements. The Institute of Thermomechanics of the Czech Academy of Sciences (IT CAS) possesses experimental and data-handling expertise based on the running program of accurate experimental determination of density of cold and supercooled aqueous systems.

## Young investigator

Young scientist Aleš Blahut graduated from the University of Chemistry and Technology in Prague, has working experience from the Czech Metrology Institute, and currently performs research of thermodynamic properties of supercooled water and aqueous systems at the Institute of Thermomechanics. He is uniquely qualified to pursue this research. A Curriculum Vitae of Aleš Blahut is presented in Attachment I.

## Implementation of project

The project is to be done during 2023 and 2024. During this period, the young scientist will be employed at the Institute of Thermomechanics in Prague and he will collaborate with colleagues at the

National Institute of Standards and Technology (NIST) in Boulder and at Ruhr-Universität Bochum (RUB). IAPWS support is requested for several short research stays of the young scientist abroad. We plan 4 one-week stays at RUB (two in 2023, two in 2024) and one two-week stay at NIST. A final Report will be provided at the 2025 IAPWS Meeting.

The specific goals of the Young Scientist Project will be:

- For a selected range of parameters, tentatively the whole liquid and supercritical region, including metastable regions of supercooled, superheated, and stretched water, develop a complete database of relevant experimental or simulated data (i.e., data with significant information content) with a brief characterization of each dataset in terms of the experimental methods, sources of uncertainty, and uncertainty estimates, in particular concerting various systematic effects.
- Participate in the development of a preliminary thermodynamic formulation aiming at a replacement of IAPWS-95. The developed model will provide intimate know how and required partial derivatives for the data analysis and it will be useful as an intermediate step helping to identify ways of improvement of IAPWS-95 shortcomings.

By completing this project, the young scientist will learn modern methods of development of reference equation of state. For IAPWS, the results should bring significant progress towards a new and advanced “flagship” formulation of thermodynamic properties of ordinary water.

**Budget (in GBP)**

Support for a one-week stay at RUB: 1,200 GBP. Support for a two-week stay at NIST: 4,500 GBP. The project includes 4 stays at RUB and one stay at NIST.
Total Young Scientist Grant: 9,300 GBP.

**References**

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**Attachment:** Curriculum Vitae of Aleš Blahut