University of Guelph – Peter Tremaine CRD

CRD Title: D20 Isotope Effects on Hydrolysis and Ionization Equilibria in High Temperature Water

Overview

Since Dr. Tremaine's appointment in 2001, the University of Guelph has sought to create a state-of-the-art research center for the development of high-precision instruments and theoretical tools to determine the thermochemical properties of aqueous systems under nuclear reactor operating conditions. Areas of particular importance to the industry are (i) the development of the Generation IV Supercritical Water CANDU reactor concept and hydrogen co-generation technology; (ii) lifetime extension of the current CANDU 6 and Advanced CANDU reactors; and (iv) the need for basic research under extreme conditions.

The grant to Guelph in 2006 was the first CRD grant awarded to a university by UNENE. The grant and UNENE's network of contacts, have proved to be key elements in establishing the university's expertise in this field. In addition to the targeted research projects funded by UNENE and other government/industry partnerships, the university has made significant progress towards its long-term goal of creating a state-of-the-art research center for high-temperature water chemistry in Ontario, with quantitative measurement capabilities for dealing with reactor chemistry problems at temperatures and pressures in excess of 450°C and 30 MPa. The $40,000/yr grant from UNENE has been leveraged with NSERC partnership program grants to provide operating funds of approximately $350,000/yr for nuclear-related R&D, that currently support five graduate students, two research associates and two postdoctoral fellows.

Research Program/Outcomes

Current Projects:

In addition to Dr. Tremaine's current UNENE CRD grant, the nuclear-related research at Guelph has been supported by four other grants.

(i) "D_2O Isotope Effects on Hydrolysis and Ionization Equilibria in High-Temperature Water" NSERC/UNENE CRD Grant: (2005-2009; renewed 2009-2012) ($87,000/yr x 3). UNENE has approved funds for a third, and final, stage of this project
(ii) "Chemistry in Near-Critical and Supercritical Water for the CANDU Generation IV Reactor Concept" NSERC/AECL Strategic Research Grant: (2007-2009; renewed 2009-2012) ($174,000/yr x3)
(iii) Aqueous Chemistry of Metals under Supercritical Water Reactor Conditions" NSERC/NRCan/AECL CRD Grant (2012-2016) ($80,000/yr x 4)
(iv) Aqueous Chemistry of Fission Products under Supercritical Water Reactor Conditions", NSERC/NRCan/AECL CRD Grant (2012-2016) ($50,000/yr x 4)

(v) "Aqueous Speciation and Liquid-Liquid Phase Separation of Boric Acid at Temperatures up to 350°C: Electric Power Res. Inst. (2012-2015) ($460,600 over 3 yrs)
(vi) “Aqueous Electrolytes and Non-Electrolytes under Hydrothermal Conditions” NSERC Discovery Grant: (2005-2011; renewed 2011-2016) ($45,000/yr x 5)

Research Results/Outcomes

CANDU nuclear reactors are a uniquely Canadian technology in that their design is based on the use of heavy water in a closed loop to transfer heat from the reactor core to the steam generator. Optimizing primary coolant chemistry requires detailed models for the chemical behaviour of metal oxides, dissolved gases and pH-control additives at temperatures as high as 300°C, using data determined in light water systems. The methods now used to correct these models for the differences between light-water and heavy-water systems are based entirely on room temperature studies. Tremaine’s UNENE CRD grant is for a definitive laboratory study to provide fundamental data and understanding for the difference in ionization constants between H_2O and D_2O, for simple acids and bases at the extreme temperatures and pressures encountered in nuclear reactors (250 to 300°C and 10 MPa). The first phase developed high precision AC conductance, densimetry, and UV-visible methods to measure the deuterium isotope effect on acid-base ionization. These state-of-the-art instruments, constructed of inert materials to withstand the corrosive conditions that exist in high temperature water, allow us to measure differences in the chemical equilibrium constants in H_2O and D_2O under identical conditions, directly. The second phase used these instruments, and a new custom-made Raman spectrometry system, to measure data for three model systems. The third, and final, phase will extend these studies to more systems and develop a practical model for estimating the magnitude of D_2O isotope effects on metal hydrolysis and metal oxide solubility, under CANDU operating conditions. The project will contribute to research aimed at extending the lifetime of existing reactors by providing criteria for optimizing primary circuit pH to reduce feeder tube thinning. It will make a long term contribution to Canada's leadership role in heavy water technology by providing a fundamental understanding of D_2O isotope effects on chemical equilibria under extreme conditions of temperature and pressure.

Tremaine’s other research uses state-of-the-art instruments to determine ionization and association constants for simple acids, bases, dissolved metals, and organic complexes under near-critical and super-critical conditions that will be encountered in the Generation IV CANDU Supercritical Water-cooled Reactor (“SCWR”). The projects include the construction of high-pressure cells and calibration of the equipment for operation in the supercritical region, measurements on several acids, bases and salts relevant to Gen IV steam generator chemistry, and the development of equations to predict the behaviour of aqueous species under these extreme conditions. The EPRI study applies these methods to understand and model PWR fuel deposition mechanisms, and provides synergy with PWR operating and R&D experience. The experimental equipment, models, and new research capabilities will all be directly applicable to the current CANDU reactor fleet.

Research Facilities

The current suite of high-precision instruments includes several with unique capabilities. The high-temperature platinum vibrating tube densimeter, constructed in 1997, is one of fewer than six worldwide that provide the precision ($\forall 1 \cong 10^{-5}$ g$\cong$cm^{-3}) needed to measure standard partial

molar properties up to 350°C. The UV-visible flow system constructed in 1999 has the stability needed for quantitative spectroscopic studies up to 275°C, and is being upgraded for operation up to 400°C. The AC flow conductance instrument, constructed at the University of Delaware, is one of only two such instruments in North America, with the capability to operate under supercritical conditions. These instruments all make use of inert cells fabricated from platinum, zirconium, titanium or Hastelloy C, and high-pressure liquid chromatography pumps with precise external pressure-control and sample injection systems. Recent CFI and NSERC Strategic Grants, supported by AECL and UNENE, have added a new high temperature (50 - 300^{o}C) solution calorimeter and state-of-the-art Raman spectrometer. Cells suitable for use under CANDU-6, CANDU ACR 1000, and CANDU SCWR reactor coolant conditions are being developed.

Research Team

In 2012, the hydrothermal chemistry group consisted of two PhD students, four MSc students, two research associates and two postdoctoral fellows. Research associate Dr. Jenny Cox (BSc U. Toronto, PhD, ETH, Zurich) is laboratory manager, and oversees our Quality Management System. Postdoctoral fellow Dr. Hugues Arcis, was promoted to research associate this year, and carries out or supervises all work with our flow conductivity cell. PhD students Kristy Erikson and Kwame Agbovi, and MSc student Mike Yacyshyn, work on our UNENE D_2O project. Postdoctoral fellow Lucas Applegarth, PhD student Chris Alcorn, and MSc students Katie Bissonette, Jeff Plumridge and Alex Lowe work on projects related to the supercritical water reactor or basic research. In 2010, we were honoured to have Professor Greg Zimmerman in our group from Bloomsberg University (USA), funded through a one-year award from the Fulbright Foundation, and he continues to collaborate on our SCWR and EPRI projects. The projects include collaboration with computational chemists Prof. Cory Pye (St. Mary's University), and Prof. Nela Mora-Diaz (Thompson River University).

Publications

Published Research Papers

1. Deuterium Water Chemistry in a Supercritical-Water-Cooled Pressure-Tube Reactor, D. Guzonas, F. Brosseau, P. Tremaine, J. Meesungnoen, J.-P. Jay-Gerin, *Nuclear Technol.* 179, 205-219 (2012).
2. Limiting Conductivities and Ion Association Constants of Aqueous NaCl under Hydrothermal Conditions: Experimental Data and Correlations. G. H. Zimmerman, H. Arcis, and P. R. Tremaine. *J. Chem. Eng. Data* 57, 2415-2429 (2012).
3. Limiting Conductivities and Ion Association in Aqueous $NaCF_3SO_3$ and $Sr(CF_3SO_3)_2$ from 298 to 623 K at 20 MPa. Is Triflate a Non-Complexing Anion in High Temp-erature Water? G. H. Zimmerman, H. Arcis, and P. R. Tremaine. *J. Chem. Eng.* 57, 3180–3197 (2012).

Published Proceedings from Conferences and Workshops

1. Ab Initio and Raman Investigation of Co(II) Complexes C. C. Pye, D. C. M. Whynot, L. Applegarth, J. Cox, P. Tremaine, *Proc. 3rd China-Canada Joint Workshop on Supercritical Water-cooled Reactors*, (CCSC 2012) (Xi'an, Shaanxi, China, April 18-20, 2012).

2. Ab initio and Raman Investigation of Ni(II) Complexes C. C. Pye, L. Cheng, J. P. Ferguson, K. Bissonette, L. Applegarth, J. Cox, P. R. Tremaine, *Proc. 3rd China-Canada Joint Workshop on Supercritical Water-cooled Reactors*, (CCSC 2012) (Xi'an, Shaanxi, China, April 18-20, 2012).
3. Acid Ionization Constants, Electrostriction and Ionic Transport in D_2O at Elevated Temperatures and Pressures: "How is heavy water solution chemistry different from light water?", P. Tremaine, Invited Speaker, Memorial University of Newfoundland, Dalhousie University, Acadia University, Univ. of Ontario Inst. Technol. (UOIT), Univ. of Western Ontario (January and February, 2012).
4. Ab Initio and Raman Investigation of Co(II) Complexes C. C. Pye, D. C. M. Whynot, L. Applegarth, J. Cox, P. Tremaine, *Proc. 3rd China-Canada Joint Workshop on Supercritical Water-cooled Reactors*, (CCSC 2012) (Xi'an, Shaanxi, China, April 18-20, 2012).
5. Ab initio and Raman Investigation of Ni(II) Complexes C. C. Pye, L. Cheng, J. P. Ferguson, K. Bissonette, L. Applegarth, J. Cox, P. R. Tremaine, *Proc. 3rd China-Canada Joint Workshop on Supercritical Water-cooled Reactors*, (CCSC 2012) (Xi'an, Shaanxi, China, April 18-20, 2012).

Oral Presentations (Abstract Only) from Conferences and Workshops

1. Partial Molar Volumes and Heat Capacities for Contact- and Solvent-Separated Ion Pairs of $MgSO_4$ and $NiSO_4$ under Hydrothermal Conditions. M. Madekufamba and P.R. Tremaine,95th Canadian Chemistry Conf.(Can. Soc. Chem., Calgary, May 26 - 30, 2012).
2. An Ab Initio and Raman Investigation of Aqueous Cu(I) and Cu(II) Chloride Complexes, L. Applegarth, C. Pye, J.S. Cox and P. Tremaine, Goldschmidt Conference. 2012, (Montreal, June 24 - 29, 2012).
3. Ionization Constants of Phosphoric Acid in H_2O and D2O from 25 ^oC to 300 ^oC at 20 MPa: Deuterium Isotope Effects under Hydrothermal Conditions, K.M. Erickson, H. Arcis, P.R. Tremaine, 18th Symp. Thermophysical Properties, (Boulder, CO, June 24 - 29, 2012).
4. Ion-Pair Formation in Strontium Chloride and Strontium Hydroxide Solutions at High Temperatures and Pressures, H. Arcis, G.H. Zimmerman, P.R. Tremaine, 18th Symp. Thermophysical Properties, (Boulder, CO, USA, June 24 - 29, 2012).
5. Deuterium Isotope Effects on the Limiting Molar Conductivities of Strong Aqueous Electrolytes from 25 ^oC to 300 ^oC at 20 MPa, J. Plumridge, K.M. Erickson, H. Arcis, G.H. Zimmerman, P.R. Tremaine, 18th Symp. Thermophysical Properties, (Boulder, CO, USA, June 24 - 29, 2012).Limiting Conductivities and
6. Ion Association of Aqueous Sodium Chloride Under Hydrothermal Conditions: New Experimental Data and New Correlations, H. Arcis, G.H. Zimmerman, P.R. Tremaine, 22nd Canadian Thermal Analysis Soc. (CTAS) Annual Workshop & Exhibition, (May 8-9, 2012, Mississauga, Ontario, Canada).

Interactions with Industry

Committees and Boards:

Dr. Tremaine serves on three industrial advisory committees for the nuclear industry, and on several committees charged with nuclear education, organizing conferences, and preparing large project proposals.
(i) Member, MULTEQ Database Advisory Committee, Electric Power Research Institute (EPRI).

(ii) Member of the Canadian National Committee, International Association for the Properties of Water and Steam (IAPWS). The CANDU Owners Group and the National Research Council provide funding and liaison, the University of Guelph provides the secretariat.
(iii) Chair, (with Jenny Cox), Symposium on Hydrothermal Chemistry and Geochemistry, 16th Int. Conf. on the Properties of Water and Steam, (Florence, Aug., 2013).
(iv) Member, Advisory Committee NSERC/AECL Chair in Radiation Chemistry held by Prof. Clara Wren, Univ. Western Ont. (2005 to present).

Project-related Interactions with Industry:

The UNENE Project Advisory Committee has visited Guelph on an annual basis, in December or January from 2006 to 2012. The UNENE Committee also provides technical advice for the Strategic and CRD grant funded projects. Co-op MSc student Katherine Bissonette has just returned from two 4 month semesters at Chalk River Labs, (May-Dec, 2012). A previous student, Francis Brosseau held a similar scholarship in (June-Dec, 2009). Tremaine is providing input on Canadian nuclear industry R&D needs to the EPRI MULEQ Database Committee, which published an updated database for magnetite and transition metal ferrite solubility in 2010. He is also a member of the Canadian National Committee of the International Association for the Properties of Water and Steam (Dr. D. Guzonas, AECL, was Canadian Committee Chair in 2012).

External Employment of Students, PDFs and Research Associates

PhD student Kristy Erickson began a tenure-track appointment at Red Deer College in September, 2012. She will defend her thesis this summer. Postdoctoral Fellow Dr. Melerin Madekufamba began an industrial postdoctoral fellowship at the Alberta Sulfur Research Institute in March 2011. MSc graduate Francis Brosseau has been employed as an Instrument Scientist with Bruker Scientific since July, 2010. Senior research associate, Dr. Liliana Trevani, was appointed to a tenure-track faculty position as Assistant Professor at the University of Ontario Institute of Technology January, 2009. PhD graduate Dr. Jana Ehlerova (University of Liberec, Czech Republic, 2009), who spent two 1 year exchange visits to Guelph (2006/07 and 2008/09) is now a Research Associate at U. Liberec.