University of Guelph – Peter Tremaine CRD

NSERC/UNENE Collaborative Research and Development Grant on D20 Isotope Effects on Hydrolysis and Ionization Equilibria in High Temperature Water

Overview

Since its establishment with Dr. Tremaine's appointment in 2001, the University of Guelph has sought to develop a state-of-the-art research program to develop high-precision instruments and theoretical tools for determining the thermochemical properties of aqueous systems at extremes of temperature and pressure. Areas of particular importance to the nuclear 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 UNENE CRD grant to Guelph was the first funding to the center from the nuclear industry. The grant, and UNENE's network of contacts, have proved to be a key element establishing the center. 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 to create 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..

Research Program/Outcomes

Current Projects:

In addition to Dr. Tremaine's UNENE CRD grant, the nuclear-related research at Guelph is 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 k/yr x 3).(ii) "Chemistry in Near-Critical and Supercritical Water for the CANDU Generation IV Reactor Concept" NSERC/AECL Strategic Research Grant: (2007-2009).
(iii) Aqueous Electrolytes and Non-Electrolytes Under Hydrothermal Conditions" NSERC/NRCan/AECL CRD Grant (2009-2011) ($100 k/yr x 3).
(iv) "Thermomechanical Design of Nuclear-Based Hydrogen Production: Thermochemical Measurements on the Copper Chloride Cycle" UOIT/AECL Ontario Research Fund Grant: (2007-2009) ($42 k/yr x 2).
(v)"Aqueous Electrolytes and Non-Electrolytes Under Hydrothermal Conditions" NSERC Discovery Grant: (2006-2011) ($60 k/yr x 5).

Research Results

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 detailled 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 will use these instruments, and a new custom-made Raman spectrometry system, to measure data for a number of model systems and to develop an improved, 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 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 include 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 (1□10^{-5} g□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 Canadian Fund for Innovation (CFI) and NSERC Strategic Grants, supported by AECL and UNENE, have added new 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 2006/07, the hydrothermal chemistry group consisted of four PhD students, two MSc students, one postdoctoral fellow and our Research Associate, Dr. Liliana Trevani. Postdoctoral fellow Dr. Diego Raffa (PhD Univ. Buenos Aires), PhD student Kristy Erikson (MSc Lethbridge) and summer student Sarah Moore joined the group this year, specifically to work on our UNENE D_2O project. PhD students Ephraim Bulemela and Melerin Madekufamba, will work on projects related to the supercritical water reactor. A new MSc student Vanessa Mann will work on underlying research, as will MSc student Erik Balodis and visiting PhD student Jana Ehlerova (Univ. Liberec, Czech Republic).

Publications

Published Research Papers

1. Apparent and Standard Partial Molar Volumes of NaCl, NaOH, and HCl in Water and Heavy Water at 523 K and 573 K at p = 14 MPa", L.N. Trevani, E. Balodis, and P.R. Tremaine, *J. Phys. Chem. B* 111, 2015-2024 (2007).
2. Standard Partial Molar Volumes of Aqueous 2- and 3-Hydroxypropionic Acid from 100 to 325□C: Functional Group Additivity in Isomers with Closely Spaced Polar Groups, E. Bulemela and Peter R. Tremaine, *J. Solution Chem.* 36, 1525-1546 (2007).
3. Spectrophotometric Determination of the Ionization Constants of Aqueous Nitrophenols at Temperatures up to 225°C, J. Ehlerova, L.N. Trevani, J. Sedlbauer and Peter.R. Tremaine, *J. Solution Chem.* 37, 854-857 (2008).
4. Standard Partial Molar Volumes of Some Aqueous Alkanolamines and Alkoxyamines at Temperatures up to 325□C: Functional Group Additivity in Polar Organic Solutes under Hydrothermal Conditions. E. Bulemela and Peter R. Tremaine, *J. Phys. Chem. B* 112, 5626-5645 (2008).
5. D_2O Isotope Effects on the Ionization of ¸-Naphthol and Boric Acid at Temperatures from 225 to 300□C using UV-Visible Spectroscopy. E. Bulemela and Peter R. Tremaine, *J. Solution Chem.* 38, 805-826 (2009).
6. Recent Canadian Advances in Nuclear-Based Hydrogen Production and the Thermochemical Cu-Cl Cycle, G. Naterer, S. Suppiah, M. Lewis, K. Gabriel, I. Dincer, M. Rosen, M. Fowler, G. Rizvi, E.B. Easton, B.M. Ikeda, M.H. Kaye L.Lu, I. Pioro, P. Spekkens, P. Tremaine, J. Mostaghimi, J.Avsec, J. Jiang, *Int J. Hydrogen Energy* 34, 2901-2917 (2009).
7. Chemistry Control Challenges in a Supercritical-Water-Cooled Reactor, D. Guzonas, P. Tremaine, J.-P. Jay Gerin, *Power Plant Chemistry* 11, 284-291 (2009).

8. Complexation in the Cu(II)-LiCl-H_2O System at Temperatures to 423 K by UV-Visible Spectroscopy, L.N. Trevani, J. Ehlerova, J. Sedlbauer, and P.R. Tremaine., *Int J. Hydrogen Energy* 96, 117-124 (2009).

Published Proceedings from Conferences and Workshops

9. Chemistry Challenges for the Gen IV Supercritical Water Cooled Reactor. Workshop on the CANDU SCWR Research Program, Natural Resources Canada (Ottawa, July, 2007) Invited Speaker
10. Deuterium Isotope Effects on the Ionization Constants of -Naphthol in High-Temperature Water by UV-Visible Spectroscopy, E. Bulemela and P.R. Tremaine, *Proc. 15th International Conf. on the Properties of Water and Steam, ICPWS XV*, Berlin, September 8–11, 2008.
11. Deuterium Isotope Effects on the Ionization Constants of Acetic Acid in High-Temperature Water by AC Conductance Measurements, D. Raffa, R. H. Wood, and P. R. Tremaine, *Proc. ICPWS XV*, Berlin, September 8–11, 2008.
12. Calorimetric and Ionization Properties of Aqueous Nitrophenols, J. Ehlerova, L.N. Trevani, J. Sedlbauer, K. Ballerat-Busserolles and P.R. Tremaine, *Proc. ICPWS XV,* Berlin, September 8–11, 2008.
13. Chemistry Control Challenges in a Supercritical Water-Cooled Reactor, D. Guzonas, P.R. Tremaine and J.P. Jay-Gerin, *Proc. Int. Conf. on Water Chemistry of Nuclear Reactor Systems* (Berlin, Sept 15-18, 2008).
14. Predicting Activity Transport in a Supercritical Water Cooled Pressure Tube Reactor. Guzonas, F. Brosseau and P.R. Tremaine, *Proc. 4th Int. Conf. on Supercritical Water-Cooled Reactors*, (Heidelburg Mar. 8 - 11, 2009).

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) Vice-Chair, R&D Advisory Panel Atomic Energy of Canada Ltd. The Panel reports to the Board of Directors through its Science & Technology Sub-Committee.
(ii) Member, MULTEQ Database Advisory Committee, Electric Power Research Institute (EPRI).
(iii)Chair 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.
(iv) Chair, (with Ian Hey, COG), IAPWS Workshop on Water and Steam Chemistry, Toronto, May 11-12, 2009.
(v) Member, Proposal Committee for a CFI Regional Platform for Sustainable H_2 Production (2008 -2009) (Chaired by Greg Naterer, UOIT): $19 M request, LOI approved, application unsuccessful)
(vi)Member representing UNENE (J. Luxat, Chair) NCE “Nucleus” Proposal Committee, (2009); The LOI approved, application unsuccessful).

(vii) Member, Advisory Committee NSERC/AECL Chair in Radiation Chemistry held by Prof. Clara Wren, Univ. Western Ont. (2005 to present).
(viii) External Consultant, Province of Ontario Undergraduate Program Review, Univ. Ont. Inst. Technology (UOIT) BSc (Chemistry) Program, November, 2009.

Project-related Interactions with Industry:

The UNENE Project Advisory Committee visited Guelph on an annual basis, in December 2006 and January 2008 and 2009. The UNENE Committee also provides technical advice for the Strategic and CRD grant funded projects. One of his students Francis Brosseau, has been awarded an NSERC AECL Industrial Postgraduate Scholarship, and spent two 10 week terms at Chalk River Labs, (June-Aug, 2008 and 2009). He will graduate in 2010.

External Employment of Students, PDFs and Research Associates

Senior research associate, Dr. Liliana Trevani, started a tenure-track faculty position as Assistant Professor at the University of Ontario Institute of Technology January, 2009. Postdoctoral Fellow Dr. Diego Raffa (2005-2007) is now employed by Quest Oil Ltd. (Calgary). Postdoctoral Fellow Dr. Ephraim Bulemela, started work as a Research Officer in the Analytical Chemistry Department at AECL (Chalk River Labs) in June 2008. MSc student Erik Balodis (2007) accepted a position as Staff Scientist, R&D Division, Bank of Canada. PhD student Jana Ehlerova (University of Liberec, Czech Republic) spent two 1 year exchange visits to Guelph (2006/07 and 2008/09), and graduated in 2009.