



# IAPWS Canadian National Committee

## Annual Report 2015

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**CNC Executive:** *William Cook (Chair); David Guzonas (IAPWS President); Derek Lister; Peter Tremaine; Melonie Myszczyzyn; Rich Pawlowicz; Steve McGee (CANDU Owners Group Representative, Treasurer).*

**1. Canadian National Committee:** Dues for the Canadian National Committee (CNC) of IAPWS are supported by the National Research Council of Canada. This arrangement requires support and participation by a national organization representing industry. In 2004 the CANDU Owners Group took on this role on a trial basis, and in 2007 the CANDU Owners Group accepted this role for a five-year term, including travel support for the academic members of the CNC. In December 2012, COG agreed to another five-year term as the CNC's industrial sponsor (2013-2017).

After two years acting as the IAPWS Vice President, Dr. Dave Guzonas transitioned to the role of IAPWS President for 2015-2016.

### **2. NSERC/NRCan/AECL Generation IV Energy Technologies Program**

A major university-based program to study water chemistry in support of the development of the Canadian Supercritical Water-cooled Reactor concept (NSERC/NRCan/AECL Generation IV Energy Technologies Program) is currently in the final year of its Phase II funding and includes seven water chemistry projects that cover two main themes: a) corrosion product transport and deposition, and b) water radiolysis. The goal is to develop chemistry control strategies for the SCWR as well as to recommend realistic chemistry conditions for corrosion testing for materials selection. The program also funds eight projects examining materials degradation phenomena (e.g., corrosion, stress corrosion cracking, creep, ageing) at temperatures up to 800 °C.

The chemistry program is co-ordinated by D. Guzonas (CNL). Research on high-temperature water chemistry being funded by this program includes:

- P. Tremaine (U. of Guelph):** Aqueous chemistry of metals and fission product under SCWR conditions.
- C. Pye (St. Mary's University):** Ab initio calculations on ionic hydration and complexation.
- W. Cook (U. of New Brunswick):** Corrosion product transport and deposition under SCWR conditions.
- I. Svishchev (Trent University):** Water chemistry, pH control and particle formation process in an SCWR.
- A. Anderson (St. F. X. University):** Time-resolved investigations of metal oxide-water systems under conditions of extreme temperature, pressure and radiation.
- P. Percival (Simon Fraser University) & K. Ghandi (Mount Allison University):** Reaction kinetics in SCW probed using muonium.
- J.-P. Jay-Gerin (U. of Sherbrooke):** Computational modelling of water radiolysis in high temperature water (including SCW).
- C. Wren (U. of Western Ontario):** Water radiolysis effects on materials degradation in high temperature water (including SCW).

### 3. CNC Member Activities

#### 3.1 Activities at the University of New Brunswick

##### Derek Lister

Heat exchanger fouling; analysing the adsorption/desorption of film-forming amines (FFAs) on the surfaces of bench-scale apparatus and high-temperature water loops under single- and two-phase flow conditions has provided kinetic constants that can be used to plan experiments examining the effects of FFAs on the deposition of corrosion products on heat-exchange surfaces (in collaboration with CNL).

Flow-accelerated corrosion (FAC); predicting the characteristics of scallops (the sculpting of surfaces undergoing FAC). Computational-fluid-dynamic analysis of characteristic scallop shapes has provided insights into the mechanisms of flow-accelerated corrosion.

Modelling reactor primary circuit contamination. Inserting FAC mechanisms and in-core effects into models for material transport has led to predictions of radioactivity transport. The resulting model been applied to the Point Lepreau CANDU to estimate the effect of the core refurbishment and the associated equipment lay-up on the development of fields due to common corrosion products.

Sampling high-temperature water systems; modelling hold-up of corrosion products in coolers and introducing precipitation kinetics provide information relevant to the IAPWS technical guidance document.

Characterising the effects of film-forming amines on FAC in two-phase flow. Scoping studies in single-phase flow are complete and similar experiments under two-phase flow at 200°C have also been completed. The results show the effect of the multi-layer nature of the FFA on FAC as its concentration is varied.

Developing a robust probe for measuring FAC in-situ in operating plant. A probe has been designed and an agreement negotiated with a power utility to install it in a coal-fired station. The probe has been manufactured and is awaiting bench trials before installation in the plant.

Verifying the effects of dissolved iron on FAC. Experiments injecting iron into a coolant stream by promoting FAC upstream of an in-situ FAC probe are almost complete. The measured effects have been described in terms of UNB's mechanistic model preliminary to its incorporation into a commercial code.

Measuring the dissolution kinetics of coolant-system corrosion products. The rate of dissolution of magnetite under a range of coolant conditions has been measured and the kinetic constants derived. Under the conditions of power-system coolants, the dissolution is much slower than mass transfer, indicating that the conventional description of flow-accelerated corrosion is invalid. Similar measurements have been made on nickel ferrite, indicating that nickel release from steam generators is not via dissolution of the in-situ oxide film.

##### Willy Cook

W. Cook has been acting as the Director of the Centre for Nuclear Energy Research (CNER), a research institute on UNB's campus. CNER has over two-decades of research / collaboration with the nuclear industry and has developed and patented online sensors for monitoring corrosion of plant piping in-situ. Additional field trials to show the utility of the sensors for nuclear power plants are currently in preparation. CNER is growing its consulting expertise and continues to provide service to Canada's nuclear industry, most recently in evaluating post-refurbishment radiation fields at the Point Lepreau CANDU through detailed analysis of plant data and predictions of activity transport by modifications to UNB's corrosion product and activity transport model.

Involvement in the Generation IV Technologies Program for development of the SCWR. The major focus is corrosion-product transport and deposition in the core of a SCWR where both experimental techniques and modeling are employed to elucidate material corrosion and the deposition kinetics of the “fall-out” from solution that occurs upon traversing the critical point.

Hydrogen control in CANDU cooling systems is a project initiated last year in conjunction with industrial collaborators. Current CANDUs have several nuclear auxiliary light water systems that are exposed to intense radiation fields. Suppression of water radiolysis and mitigation of hydrogen production in these systems using alternate oxygen scavenging chemical to hydrazine is the primary goal.

### **3.2. Activities at the University of Guelph (Peter Tremaine)**

#### **Research Themes**

1. Ions and Organic Solutes in Very High Temperature Water
2. Origins of Life: Pre-Biotic Chemistry under Deep Ocean Hydrothermal Vent Conditions
3. CANDU Nuclear Reactor Chemistry: the Next Generation
4. Thermal Power Generation, Carbon Capture, and Hydrogen Co-Generation

#### **Current and Recent Funders**

The following companies and granting agencies contributed to our research during the past five years: NSERC, Atomic Energy of Canada Ltd. (now Canadian Nuclear Laboratories – CNL), Ontario Power Generation Ltd., The Electric Power Research Institute (EPRI), Inco, IAPWS, UNENE, Natural Resources Canada.

#### **Specific Projects**

Solvation and Equilibria of Ions and Organic Solutes in Water up to Near-Critical Conditions  
Origins of Life: Pre-Biotic Chemistry under Deep Ocean Hydrothermal Vent Conditions

CANDU Nuclear Reactor Chemistry: D<sub>2</sub>O Isotope Effects on Acid-base Ionization and Metal Hydrolysis (UNENE/NSERC CRD Grant)

Generation IV Nuclear Reactor Chemistry: Ion Pairs and Complexes in Sub-critical and Supercritical Water (NRCan/AECL/ NSERC CRD Grants):

Carbon Capture and Sequestration by Novel Phase-Separating Solvents (NSERC International Strategic Grant with University Blaise Pascal, France)

### **3.3. Activities at the University of British Columbia (Rich Pawlowicz)**

IAPWS-related activities continue to concentrate on investigations into the effect of chemical composition changes in seawater on its physical properties, and coordination of international activities in supporting and extending the seawater standard TEOS-10 through chairmanship of the Joint SCOR/IAPWS/IAPSO Committee on the Properties of Seawater (JCS).

Field measurements of “density anomaly”: (1) Interpretation of measurements undertaken Feb 2014 in the North-East Pacific as part of the Canadian Department of Fisheries and Ocean “Line-P” program, in collaboration with JCS member Frank J. Millero (U. Miami), continues now that more comprehensive (independent) chemical analyses of the seawater samples are available. (2) Measurements were taken in Oct 2014 in the Salish Sea in collaboration with H. Uchida (JAMSTEC). Upcoming activities include (1) measurements taken in Arctic coastal areas, in collaboration with H.

Uchida and K. Brown (WHOI), and (2) measurements of highly supersaturated gas concentrations in the anoxic ancient seawater of Powell Lake, B.C.

Numerical modelling of “density anomaly” effects when river waters are mixed with seawaters has been published. This work will continue by extending this work to investigate effects of composition variations from hydrothermal vent plumes.

A major milestone for JCS was the submission of 4 linked papers to the journal *Metrologia*. These papers discuss proposed plans for developing traceability of seawater salinity, salinity pH, and relative humidity to the International System of Units (SI).

### **3.4. CANDU Owner’s Group (COG) Activities (Steve McGee)**

COG is a not-for-profit corporation with voluntary funding from international CANDU-owning utilities and Canadian National Laboratories. The COG mission is to improve the performance of CANDU stations worldwide through member collaboration. COG Canadian R&D program members include Ontario Power Generation, Bruce Power Limited Partnership, New Brunswick Power and Canadian Nuclear Laboratories.

#### *CANDU Industry-IAPWS Engagement*

The presentation “International Association for the Properties of Water and Steam” was made by Dr. William Cook at the CANDU Chemistry Workshop in June 2015. This presentation informed the audience of approximately 65 CANDU industry chemists about IAPWS and the available IAPWS information.

Dr. Peter Tremaine, Dr. William Cook and Dr. Derek Lister have participated in the COG R&D Chemistry Working Group meetings and have informed Working Group members of the research activities at the University of Guelph and the University of New Brunswick. IAPWS activities and their benefits have been presented to the COG Chemistry Working Group by Dr. Tremaine, Dr. Cook, Dr. Lister and also by Dr. Dave Guzonas who is a member of this Working Group.

The COG R&D Chemistry Working Group has made a five-year commitment to fund the University of Guelph Industrial Research Chair in the field of “High Temperature Aqueous Chemistry”. COG members are also funding the Collaborative Research and Development Grant “Chemistry and Corrosion in Nuclear and Conventional Power System Coolants” at the University of New Brunswick for the next five years. Plans are under development to formally incorporate university research programs with the COG industry Working Groups, which should further integrate and leverage the value of IAPWS activities with the COG R&D program.

#### *CANDU Industry-Technology Implementation*

COG members are actively implementing technologies presented at IAPWS conferences. An example is the presentation “Optimized pH Strategy Combined with Application of Film-Forming Amine for Improved Water Chemistry Treatment in Steam-Water Cycle of PWR” made by Dr. Andreas Drexler (Areva) at the 16th International Conference on the Properties of Water and Steam in London-Greenwich 2013.

There is ongoing research at Chalk River Laboratories to investigate the thermal resistances and fouling rates prior to and after the application of the Areva Film-Forming Amine. This project is to provide an independent technical basis for using Areva Film-Forming Amine during the upcoming CANDU station refurbishment outages. COG Joint Project 4494 “Qualification of Film Forming Amine (FFA) Preservation of Steam Generators” is underway to qualify the process for the participating CANDU stations. A presentation about implementing the Areva Film-Forming Amine process were made at the June 2015 CANDU Chemistry Workshop by Dennis Moghul (OPG) (Film Forming Amine Application for Darlington Refurbishment Lay-up Protection).

### 3.5 Activities within Canadian Natural Resources Ltd. (Melonie Myszczyszyn)

Melonie Myszczyszyn is a regular participant and session chair at the annual ASME International Water Conference, specifically for the produced water sessions. She also participates as chair of the Task Group within the ASME for the development of the produced water consensus document with 60 participants from Canada and USA. She filed two patents on 8<sup>th</sup> April 2015 with CNRL (#45353-201 and #45353-202) for treating Polymer Flood Produced Water specifically for use during polymer flooding, alkaline surfactant polymer flooding, and future Steam Assisted Gravity Drainage after polymer flooding applications.

## 4. Activities Planned to Next ICPWS (2017/18)

The CNC activities over the next few years will continue the work that is currently ongoing, as described above. The supercritical water-cooled reactor project is a focus for much of the current research activities of the CNC. This university-government-industry program focused on fundamental research will conclude Phase II in 2016 but may have more focused research beginning in Phase III.

A workshop on the IAPWS TGD's to Canadian industry and academic stakeholders is in the planning stages for October 2015. The goal would be to raise the profile of the Canadian National Committee and IAPWS activities with researchers in Canada doing complementary research and within the HRSG community.

Each of the CNC members and IAPWS-involved researchers in Canada are involved in industry-sponsored research with organizations such as EPRI and the CANDU Owners Group pertinent to topics of interest to IAPWS.

The CNC identified that the reformulation of the properties of heavy water is still of great interest to Canada and provided contacts with the CANDU community to support the work.

## 5. Select List of Publications

1. D. Guzonas; W. Cook, "Chemistry Control Strategy for the Canadian SCWR Concept", Canadian Nuclear Laboratories report 217-127120-REPT-001, Revision 0, February 2015
2. V. Subramanian; J.M. Joseph; H. Subramanian; J.J. Noël; D.A. Guzonas; J.C. Wren "Steady-State Radiolysis of Supercritical Water: Model Development, Predictions and Validation", 7th International Symposium on Supercritical Water-Cooled Reactors (ISSCWR-7), 2015 March 15-18, Helsinki, Finland.
3. D.T Kallikragas; A. Yu. Plugatyr; D.A. Guzonas; I.M. Svishchev "Effect of Confinement on the Hydration and Diffusion of Chloride at High Temperatures", J. of Supercritical Fluids 97, 22-30.
4. D. Guzonas, "Extreme Water Chemistry – How Gen IV Water Chemistry Research Improves Gen III Water-Cooled Reactors", The 19th Pacific Basin Nuclear Conference (PBNC 2014), Hyatt Regency Hotel, Vancouver, British Columbia, Canada, August 24-28, 2014.
5. D. Guzonas; W. Cook "Water Chemistry Specifications for the Canadian Supercritical Water-Cooled Reactor Concept", The 7th International Symposium on Supercritical Water-Cooled Reactors (ISSCWR-7), 15-18 March 2015, Helsinki, Finland
6. D. Guzonas; M. Edwards; W. Zheng, "Assessment of Candidate Fuel Cladding Alloys for the Canadian Supercritical Water-cooled Reactor Concept", The 7th International Symposium on Supercritical Water-Cooled Reactors (ISSCWR-7), 15-18 March 2015, Helsinki, Finland
7. D. Guzonas; L. Qiu; S. Livingstone; S. Rousseau, "Fission Product Release under Supercritical Water cooled Reactor Conditions", The 7th International Symposium on Supercritical Water-Cooled Reactors (ISSCWR-7), 15-18 March 2015, Helsinki, Finland

8. O.S. Bakai; D.A. Guzonas; V.M. Boriskin; A.M. Dovbnya; S.V. Dyuldya “Combined Effect of Irradiation, Temperature, and Water Coolant Flow on Corrosion of Zr-, Ni–Cr-, and Fe–Cr-based Alloys” The 7th International Symposium on Supercritical Water-Cooled Reactors (ISSCWR-7), 15-18 March 2015, Helsinki, Finland
9. M. Briggs & D. Lister, “Mechanistic Modelling of Flow-Accelerated Corrosion”, 11th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generator, St. Louis, USA, 2015.
10. Palazhchenko, O.Y. and Lister, D.H., “Modelling the Transport of Corrosion Products and Radionuclides in the CANDU Primary Heat Transport System,” 35th Annual CNS Conference, Saint John, NB, May 31-June 3, 2015.
11. Palazhchenko, O.Y. and Lister, D.H., “Modelling Material and Radioactivity Transport in the Primary Circuit of CANDU Reactors,” Proceedings of the International Nuclear Plant Chemistry Conference, Sapporo, Japan, October 27-31, 2014.
12. M. Jack, S. Weerakul, D.H. Lister, “The interaction of a film-forming amine with surfaces of a recirculating experimental water loop”, International Conference on Heat Exchanger Fouling and Cleaning XI, Dublin, Ireland, 2015.
13. Uchida, S., Koshizuka, S. and Lister, D.H., “Evaluation of the Effects of pH and Oxygen on Mitigation of Wall Thinning of Carbon Steel due to Flow-Accelerated Corrosion.” Proc. EUROCORR 2014, Pisa, Italy, September 8-12.
14. Lister, D.H. and Uchida, S., “Determining Water Chemistry Conditions in Nuclear Reactor Coolants”. J. Nucl. Sci. Techn. Invited Review for 50th Anniversary Edition, vol. 52, no. 4, pp. 451-466, June 2015.
15. Solution Calorimetry Under Hydrothermal Conditions, P.R. Tremaine and H.Arcis, . Rev. Mineralogy Geochem. Vol 76, Chapt. 7 (Geochem Soc. & Mineral. Soc. Amer., 2013).
16. A Raman and Ab Initio Investigation of Aqueous Cu(I) Chloride Complexes from 25 to 80 °C. L.M.S.G.A. Applegarth, C.R. Corbeil, D.J.W. Mercer, C.C. Pye and P. R. Tremaine, J. Phys. Chem. B 118, 204–214 (2014).
17. Ion-Pair Formation in Aqueous Strontium Chloride and Strontium Hydroxide Solutions under Hydrothermal Conditions by AC Conductivity Measurements, H. Arcis, G.H. Zimmerman and P.R. Tremaine, Chem. Phys. Phys. Chem. 16, 17688-17704 (2014).
18. Standard Partial Molar Heat Capacities and Enthalpies of Formation of Aqueous Aluminate under Hydrothermal Conditions from Integral Heat of Solution Measurements. Y. Coulier and P. R. Tremaine, J. Chem. Thermodynamics 78, 79-92 (2014).
19. Limiting Conductivities of Univalent Cations and the Chloride Ion in H<sub>2</sub>O and D<sub>2</sub>O under Hydrothermal Conditions, J. Plumridge, H. Arcis and P. R. Tremaine, J. Solution Chem. (Special issue honouring Prof. R.H. Wood). 44,1062–1089 (2015).
20. Non-complexing Anions for Quantitative Speciation Studies by Raman Spectroscopy in Fused-silica High Pressure Optical Cells under Hydrothermal Conditions. L.M.S.G.A Applegarth, C. Alcorn, K. Bissonette, J. Noël, P. Tremaine. Appl. Spectroscopy (In Press, MS Number 14-07825).
21. Theoretical Study of Deuterium Isotope Effects on Acid-Base Equilibria under Ambient and Hydrothermal Conditions, N. Mora-Diez, Y Egorova, H. Plommer, P. R. Tremaine, JCS Advances 5, 9097-9108 (2015).
22. Thermodynamics of the Sodium–Iron–Phosphate–Water System Under Hydrothermal Conditions: The Gibbs Energy of Formation of Sodium Iron(III) Hydroxy Phosphate, Na<sub>3</sub>Fe(PO<sub>4</sub>)<sub>2</sub>·(Na<sub>4</sub>/3H<sub>2</sub>/3O), from Solubility Measurements in Equilibrium with Hematite at 498–598 K, S. Quinlan, D. Chvedov, L.N. Trevani and P. R. Tremaine, J. Solution Chem. 44, 1121–1140 (2015).

23. Boiling Points and Speciation of Aqueous Electrolyte Solutions Under “Hideout” Conditions in Supercritical Water-cooled Reactor Coolant by Raman Spectroscopy, L. Applegarth and P. Tremaine, Proc. 19th Pacific Basin Nucl. Conf. (Can. Nucl. Soc., Vancouver, Aug. 24-28, 2014).
24. Overview on Investigation of Metal Speciation under Supercritical Water-Cooled Reactor Coolant Conditions by Ab Initio Calculations, Spectroscopy, and Conductivity Measurements, C.C. Pye, L. Cheng, P.R. Tremaine, Proc. 19th Pacific Basin Nuclear Congress (Vancouver, BC, Canada, August 24-28, 2014).
25. Validity Range of the Meissner Activity Coefficient Model used in MULTEQ. S. Dickinson, M. Bachet, R. Eaker, J. Henshaw, C. Marks, P. Tremaine, D. Wells. Proc. Nuclear Plant Chemistry Conference 2014 (NPC2014), (Sapporo, Japan, October 26-31, 2014 )
26. Pawlowicz, R., “The Absolute Salinity of seawater diluted by riverwater”. Deep Sea Research I, 101, 71-79 (2015)
27. Jiao, Y. Zheng, W., Guzonas, D. and Cook, W., Kish, J., “Effect of Thermal Treatment on the Corrosion Resistance of Type 316L Stainless Steel in Supercritical Water”, Journal of Nuclear Materials, vol. 464, pp. 356-364, September 2015.
28. Swift, R. and Cook, W.G., “Validation of Constant Load C-ring Apex Stresses for SCC Testing in Supercritical Water”, Proceedings ISSCWR7, Helsinki, Finland, March 2015.
29. Steeves, G. and Cook, W.G., “Development of Kinetic Models for the Long-term Corrosion Behaviour of Candidate Alloys for the Canadian SCWR”, Proceedings ISSCWR7, Helsinki, Finland, March 2015.
30. Cook, W.G., Gardner, E., Lee, J., and Stuart, C.R., “Secondary System Return to Service Following the Refurbishment Outage at the Point Lepreau Generating Station”, Proceedings NPC 2014 - Nuclear Plant Chemistry 2014, Sapporo, Japan, October 2014.
31. Stuart, C.R, Cook, W.G. and Gardner, E., “Primary Heat Transport System Return to Service Following the Refurbishment Outage at the Point Lepreau Generating Station”, Proceedings NPC 2014 - Nuclear Plant Chemistry 2014, Sapporo, Japan, October 2014.