
IAPWS Canadian National Committee

Annual Report 2016

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CNC Executive: William Cook (Chair); Derek Lister; Peter Tremaine; Melonie Myszczyszyn; 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 (NRC). 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 an initial 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). An agreement with COG and the NRC for a third five-year term as the CNC's sponsor was signed in June 2016 providing continued involvement with IAPWS and the CNC through 21st June 2021. Thanks to Steve McGee for ensuring the renewal proceeded smoothly.

After two years acting as the IAPWS Vice President, Dr. Dave Guzonas transitioned to the role of IAPWS President for 2015-2016. Due to personal reasons, in March 2016, Dave Guzonas retired from the Canadian Nuclear Laboratories and as a result, resigned from his position as President of IAPWS. The CNC wishes Dave well in his retirement. The CNC is currently engaging COG and CNL to find a replacement for Dave Guzonas on our committee so that CNL and the Canadian nuclear industry's interests continue to be well represented within IAPWS.

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) wrapped up in March 2016. Seven water chemistry projects covering two main themes were investigated: a) corrosion product transport and deposition, and b) water radiolysis. The program developed chemistry control strategies for the SCWR as well as recommending realistic chemistry conditions for corrosion testing for materials selection. The program also funded eight projects examining materials degradation phenomena (e.g., corrosion, stress corrosion cracking, creep, ageing) at temperatures up to 800 °C. The chemistry program was 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) &: Reaction kinetics in SCW probed using muonium.
 K. Ghandi (Mount Allison University)

- 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; the recirculating water loop built for studying deposit formation on heat-exchange surfaces has been refurbished with a new test section (including a simulated heat exchanger tube with a high heat-flux heater) and control system. It is currently being commissioned prior to looking at the effects of a film-forming amine (FFA) on boiling heat transfer and the concomitant deposition of colloidal magnetite. The forces between magnetite particles and submerged surfaces with and without FFA additions are being investigated with atomic-force microscopy (AFM) in collaboration with CNL.

Flow-accelerated corrosion (FAC); experiments on the effects of FFA on FAC are proceeding in two recirculating water loops. Under feedwater conditions at 140°C, a commercial product is being investigated for its efficiency in mitigating FAC with no pH additive, while under two-phase steam-water conditions at 200°C another commercial product is undergoing similar testing.

Modelling reactor primary circuit contamination; inserting FAC mechanisms and in-core effects into models for material transport has led to predictions of the transport of radioactive corrosion products in a CANDU primary coolant system. The next task modelling the development of radiation fields around critical components.

Developing a robust probe for measuring FAC in-situ in operating plant; three probes have been successively installed downstream of the boiler feed pump in a coal-fired power station. After analysis of the results from the first probe, refinements were made to the system before the second probe was installed. The third probe was recently installed and analysis of the results from the second is continuing.

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 complete. The measured effects have been successfully described in terms of UNB's mechanistic model.

Modelling FAC under two-phase conditions; UNB's mechanistic model has been adapted to describing FAC in steam-water mixtures by applying the single-phase mechanisms to the conditions in the liquid film on piping surfaces, using vapour-liquid distribution parameters of additives such as ammonia to obtain the liquid phase chemistry and using standard correlations for predicting quantities such as mass transfer coefficient and fluid shear stress at the wall. Preliminary trials have indicated good agreement with experimental results.

Measuring the effusion rate of hydrogen through steel; in a collaborative project with UNB's Centre for Nuclear Energy Research, the development of an in-situ probe (HEPro) for monitoring FAC by measuring the rate of effusion of corrosion hydrogen through pipe walls is being supported by investigating the details of hydrogen diffusion around the probe structure.

Electrochemical influences in FAC; an in-situ FAC probe in a high-temperature water loop is made the working electrode of a three-electrode system and the corrosion characteristics are separately investigated by electrochemical techniques.

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 continuing to grow its consulting expertise and provides services to Canada's nuclear industry. The recommendation to formally appoint W. Cook as CNER's Director was made by the CNER Advisory Board in June 2016. The term will last four years.

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 in 2014 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 scavaging chemical to hydrazine is the primary goal. The experimental program is in full operation with a Master's student working full time at the Chalk River Nuclear Laboratories. Preliminary results are indicating that corrosion processes on carbon steel can significantly affect the reaction kinetics and production from water radiolysis.

W. Cook and David Addison (Thermal Chemistry Inc. – New Zealand) were awarded an IAPWS International Collaboration project 2015. The focus of the project was to establish capabilities at UNB / CNER's laboratories to measure, electrochemically, the effects of mixed contaminants on boiler materials. D. Addison visited UNB / CNER on three occasions between Nov. 2015 and June 2016 and the test rig was designed and commissioned. Further funding for the project was secured from Thermal Chemistry and from Swan (thanks to David Addison and Lukas Staub).

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

Peter Tremaine was appointed to a newly created NSERC/UNENE Senior Industrial Research Chair in High Temperature Aqueous Chemistry in June 2016. The objective is to expand mission-oriented basic research and modelling expertise at Guelph in areas related to primary coolant chemistry, moderator chemistry, steam generator chemistry and nuclear waste management, and to recruit a tenure-track junior faculty member to address succession planning issues. In addition to UNENE, the industrial partners are the CANDU Owners Group, the Nuclear Waste Management Organization and the Electric Power Research Institute. The site visit took place in October, 2015, and the Chair was approved by NSERC on December 20, 2015, subject to receiving signed agreements from the four sponsoring organizations. Legal negotiations were completed in late May 2016.

Other current and recent projects include (i) Solvation and Equilibria of Ions and Organic Solutes in Water up to Near-Critical Conditions (ii) CANDU Nuclear Reactor Chemistry: D₂O Isotope Effects on Acidbase Ionization and Metal Hydrolysis (UNENE/NSREC CRD Grant), (iii) Generation IV Nuclear Reactor Chemistry: Ion Pairs and Complexes in Sub-critical and Supercritical Water (NRCan/AECL/ NSERC CRD Grants), (iv) 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) Measurements of river anomalies were made in the Canadian Arctic Archipelago as part of a Canadian GEOTRACES rivers project (with H. Uchida and K. Brown) (2) Measurements were made (again) on the ocean "Line-P" section (run by the Canadian Department of Fisheries and Oceans) in the northeast Pacific, to try and understand and replicate some unusual features of interest.

A major milestone for JCS was the publication 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); they are now (8 months after publication) among the most "downloaded" (or read) articles in that journal, with more than 10,000 downloads (Pawlowicz is an author or co-author on 3 of the 4).

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.

IAPWS CNC Workshop – October 2015

On October 19th, 2016 the CNC held a Workshop at the COG offices in Toronto with 16 attendees from both industry and academia. The following presentations were made:

Background on IAPWS and the CNC-IAPWS structure Current IAPWS Working Groups and activities Candu Owners Group (COG) – synergies between the nuclear and fossil industries Value of Robustness in Water Plant Treatment, in Design, Operation, Monitoring and Maintenance Challenges with Plant Layup During Flexible Operations Summary of Current and Planned IAPWS Technical Guidance Documents Coolant sampling in power generating systems D₂O isotope effects on transport properties and ionization constants in high temperature water by AC conductivity Water Challenges Associated with Hydraulic Fracturing FAC in power generating circuits IAPWS Initiative – Corrosion Product Sampling for Plants with Flexible Operation (discussion) Round Table / Panel Discussion: Engaging Canadian Industry in IAPWS activities

CANDU Industry-IAPWS Engagement

The presentations "HEPro and its Use at PLGS" and "Extending Studies of FAC under Single-Phase Conditions to Two-Phase Steam Water Conditions" were made by Dr. William Cook and Dr. Derek Lister respectively, at the COG FAC Workshop in May 2016.

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.

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" which was formally approved in May 2016. 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 five year period (2014 – 2019). 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

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).

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 concluded Phase II in 2016 but may have more focused research beginning in Phase III, potentially beginning in 2017.

A IAPWS CNC workshop for Canadian industry and academic stakeholders is in the planning stages for Winter/Spring 2017. The goal would be to raise the profile of the Canadian National Committee and IAPWS activities with researchers in Canada doing complementary research within the fossil and HRSG community. A working topic is FAC in steam raising systems.

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 of great interest to Canada and provided contacts with the CANDU community to support the work.

5. Select List of Publications

- Pawlowicz, R., Electrical Properties of Seawater: Theory and Applications, Reference Module in Earth Systems and Environmental Sciences, Elsevier, 11pp, doi:10.1016/B978-0-12-409548-9.09578-6 (2015)
- R Feistel, R Wielgosz, S A Bell, M F Camões, J R Cooper, P Dexter, A G Dickson, P Fisicaro, A H Harvey, M Heinonen, O Hellmuth, H-J Kretzschmar, J W Lovell-Smith, T J McDougall, R Pawlowicz, P Ridout, S Seitz, P Spitzer, D Stoica and H Wolf: EP Metrological challenges for measurements of key

climatological observables: ^[1] Oceanic salinity and pH, and atmospheric humidity. Part 1: Overview. REVIEW PAPER. Metrologia, 53 (2016) R1–R11, doi:10.1088/0026-1394/53/1/R1

- R Pawlowicz, R Feistel, T J McDougall, P Ridout, S Seitz, H Wolf: Metrological challenges for measurements of key climatological observables, Part 2: Oceanic salinity. REVIEW PAPER. Metrologia, 53 (2016) R12–R25, doi:10.1088/0026-1394/53/1/R12
- A G Dickson, M F Camões, P Spitzer, P Fisicaro, D Stoica, R Pawlowicz and R Feistel: Metrological challenges for measurements of key climatological observables, Part 3: Seawater pH. REVIEW PAPER. Metrologia, 53 (2016) R26–R39, doi:10.1088/0026-1394/53/1/R26
- Fandiño, O.; Yacyshyn, M.; Cox, J. S.; Tremaine, P. R., Speciation in Liquid-Liquid Phase- Separating Solutions of Aqueous Amines for Carbon Capture Applications by Raman Spectroscopy. In Acid Gas Extraction for Disposal and Related Topics, Ying Wu, J. J. C., and Weiyao Zhu, eds. Scrivener Publishing.: 2016; pp 81-94.
- H. Arcis, J. Ferguson, G. Zimmerman, L. Applegarth, C. Pye, S. Sasidharanpillai, J. Cox, D. Hussey, D. Wells and P. Tremaine, Speciation and Thermodynamic Stability of Boric Acid, Borate and Polyborates under PWR Primary Coolant Conditions by AC Conductivity and Raman Spectroscopy, Nuclear Plant Chemistry NPC 2016, Brighton, UK, Oct. 2 to 7 (2-16) Accepted.
- Guzonas, D.A., Penttilä, S., Cook, W.G., Zheng, W., Novotny, R., Sáez-Maderuelo, A., Kaneda, J., "The Reproducibility of Corrosion Testing in Supercritical Water – Results of an International Interlaboratory Comparison Exercise", Corrosion Science, vol.106, pp.147-156, May 2016.
- 8. 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.
- 9. Swift, R. and Cook, W.G., *Validation of Constant Load C-ring Apex Stresses for SCC Testing in Supercritical Water*, accepted to Journal of Nuclear Engineering and Radiation Science, in press.
- 10. Steeves, G. and Cook, W.G., *Development of Kinetic Models for the Long-term Corrosion Behaviour of Candidate Alloys for the Canadian SCWR*, accepted to Journal of Nuclear Engineering and Radiation Science, in press.
- 11. Cook, W., Brown, G., Smith, B. and Stuart, C., *Evolution of Radiation Fields in the Point Lepreau CANDU Reactor Following Refurbishment*, accepted to Nuclear Plant Chemistry Conference (NPC 2016), Brighton, UK, October 2016 (accepted).
- 12. Stuart, C., Lee, J., Gardner, E. and Cook, W., *Steam Cycle Contamination and Remediation following the Refurbishment Outage at the Point Lepreau Generating Station*, accepted to Nuclear Plant Chemistry Conference (NPC 2016), Brighton, UK, October 2016 (accepted).
- 13. Lyons, J., Cook, W., Stuart, C. and Gardner, E., *Synergistic Effects Between Radiation Chemistry and Carbon Steel Corrosion in the Calandria Vault and End Shield Cooling System of a CANDU Reactor*, accepted to Nuclear Plant Chemistry Conference (NPC 2016), Brighton, UK, October 2016 (accepted).
- L.M.S.G.A. Applegarth, C. Alcorn, K. Bissonette, J. Nöel, P. Tremaine. Non-complexing Anions for Quantitative Speciation Studies by Raman Spectroscopy in Fused-silica High Pressure Optical Cells under Hydrothermal Conditions, Appl. Spectroscopy 8: 972-983 (2015).
- Coulier, Y.; Lowe, A.; Tremaine, P. R.; Coxam, J. Y.; Ballerat-Busserolles, K., Absorption of CO2 in aqueous solutions of 2-methylpiperidine: Heats of solution and modeling. Int. J. Greenhouse Gas Control 2016, 47, 322-329.
- H. Arcis, J.P. Ferguson, G. H. Zimmerman, and P. R. Tremaine, The Limiting Conductivity of the Borate Ion and its Ion-Pair Formation Constants with Sodium and Potassium Ions in Aqueous Solutions up to Near-Critical Conditions by AC Conductivity Methods Phys. Chem. Chem. Phys.(Accepted)

- D.E. Nieto Roca, C.M. Romero and P.R. Tremaine, Ionization constants of DL-2-aminobutyric acid and DL-norvaline under hydrothermal conditions by UV-visible spectroscopy, J. Solution Chem. (Submitted)
- Fandiño, O.; Yacyshyn, M.; Cox, J. S.; Tremaine, P. R., Speciation in Liquid-Liquid Phase- Separating Solutions of Aqueous Amines for Carbon Capture Applications by Raman Spectroscopy. In Acid Gas Extraction for Disposal and Related Topics, Ying Wu, J. J. C., and Weiyao Zhu, eds. Scrivener Publishing.: 2016; pp 81-94.
- H. Arcis, J. Ferguson, G. Zimmerman, L. Applegarth, C. Pye, S. Sasidharanpillai, J. Cox, D. Hussey, D. Wells and P. Tremaine, Speciation and Thermodynamic Stability of Boric Acid, Borate and Polyborates under PWR Primary Coolant Conditions by AC Conductivity and Raman Spectroscopy, Nuclear Plant Chemistry NPC 2016, Brighton, UK, Oct. 2 to 7 (2-16) Accepted
- 20. M. Edwards, J. Semmler, D. Guzonas, H.Q. Chen, A. Toor, S. Hoendermis, Aluminum corrosion product release kinetics, Nuclear Engineering and Design, v 288, p 163-174, July 1, 2015.
- 21. Y. Jiao, W. Zheng, D. Guzonas, J. Kish, Microstructure Instability of Candidate Fuel Cladding Alloys: Corrosion and Stress Corrosion Cracking Implications, JOM, v 68, n 2, p 485-489, February 1, 2016.
- 22. L. Qiu, D. Guzonas, J. Qian, Corrosion of silicon nitride in high temperature alkaline solutions, Journal of Nuclear Materials, v 476, p 293-301, August 1, 2016.
- 23. W. Zheng, D. Guzonas, K. Boyle, J. Li, S. Xu, Materials Assessment for the Canadian SCWR Core Concept, JOM, v 68, n 2, p 456-462, February 1, 2016.
- S. Mahboubi, Y. Jiao, W. Cook, W. Zheng, D. Guzonas, G. Botton, J. Kish, Stability of Chromia (Cr2O3)-Based Scales Formed During Corrosion of Austenitic Fe-Cr-Ni Alloys in Flowing Oxygenated Supercritical Water, Corrosion, v 72, n 9, p 1170-1180, September 2016.
- K. Choudhry, D. Guzonas, D. Killikragas, I. Svishchev, On-line monitoring of oxide formation and dissolution on alloy 800H in supercritical water, Corrosion Science, v 111, p 574-582, October 1, 2016.
- 26. Y. Zeng, D. Guzonas, Corrosion Assessment of Candidate Materials for Fuel Cladding in Canadian SCWR, JOM, v 68, n 2, p 475-479, February 1, 2016.
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- 29. Lister, D.H. (2015). "Reporting Radiation Risks". Comment letter to the Editor, The Chemical Engineer, Issue 86, April.
- Jack, M., Weerakul, S. and Lister, D., (2015) "The Interaction of a Film-Forming Amine with Surfaces of a Recirculating Experimental Water Loop". International Conference on Heat Exchanger Fouling and Cleaning XI-2015. Enfield, Dublin, Ireland, June 7-12.
- Lister, D.H., Weerakul, S. and Caravaggio, M. (2015). "Laboratory Tests on the Effects of Amines on FAC in Single-Phase and Two-Phase Flows". IAPWS 2015 Annual Meeting, Stockholm, Sweden. June 26-July 3.
- 32. Lister, D.H., Mohajery, K. and Uchida, S. (2015). "The Controlling Mechanism in FAC: Protective Oxide Dissolution or Fluid Flow". Ibid

- Briggs, M. and Lister, D.H. (2015). "Mechanistic Modelling of Flow-Accelerated Corrosion". Proc. 11th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators. EPRI. St. Louis, MO, July 14-16.
- Lister, D.H., Weerakul, S. and Caravaggio, M. (2015). "Laboratory Tests on the Effects of Amines on FAC in Single-Phase and Two-Phase Flows". IAPWS 2015 Annual Meeting, Stockholm, Sweden. June 26-July 3.
- 35. Lister, D.H., Weerakul, S. and Caravaggio, M. (2016). "The Effects of a Film-Forming Amine on Flow-Accelerated Corrosion in Single- and Two-phase Flows". 2016 International Conference on Flow Accelerated Corrosion, Lille, France. May 24-27.
- 36. Weerakul, S., Moed, D., and Lister, D.H., (2016). "Further investigation on Flow-Accelerated Corrosion under Two-Phase Flow Conditions: Effects of a Film-Forming Amine and Effects of Amine Degradation Products in the Presence of Ammonia and Ethanolamine". 36th Annual Conference of the Canadian Nuclear Society, Toronto, ON, June 19-22.
- 37. Santiwiparat, T. Rirksomboon, T., Steward, F.R., Lister, D.H. and Cook, W.G. (2016). "Modelling Hydrogen Permeation in a Hydrogen Effusion Probe for Monitoring Corrosion of Carbon Steel". 36th Annual Conference of the Canadian Nuclear Society, Toronto, ON, June 19-22.
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