

## *University of Toronto – Roger C. Newman IRC*

NSERC-UNENE Senior Industrial Research Chair in Corrosion and Materials Performance in Nuclear Power Systems (formerly Nano-engineering of Alloys for Nuclear Power Systems)



The primary focus of research in this chair program is corrosion and protection of alloys used in CANDU systems. Model alloys are also used, along with atomistic simulation, to interpret the more complex behaviour of industrial alloys. A fundamental understanding of corrosion mechanisms is vital for plant life prediction, guidance for remedial measures, and materials selection for new and refurbished plants. The UofT chair has a particular focus on Steam Generator (SG) materials, and also covers some aspects of nuclear waste management such as dry storage. Research activities include mechanisms of stress corrosion cracking in high-temperature aqueous environments, intergranular corrosion of Monel, lead effects in nickel-alloy corrosion, theory of alloy corrosion and stress corrosion, properties of nanoporous metals formed during corrosion, and electrochemical monitoring in concrete.

### Overview

Prof. Roger Newman joined the Department of Chemical Engineering and Applied Chemistry in June, 2004, after spending 20 years in the Corrosion and Protection Centre, UMIST, Manchester, UK. He has pursued research in corrosion and nanostructuring of metals, and has interacted extensively with the UNENE partners through contract research and review as well as through the main UNENE research program.

Corrosion prediction and control are ever-present concerns in nuclear power generation, and cannot be achieved reliably and cheaply without a deeper scientific understanding of the mechanisms involved. Accordingly, the research program addresses corrosion mechanisms from the atomistic to the component level. The materials involved are mainly nickel base alloys used in steam generators, with some work on carbon steel in the context of CANDU feeder degradation, and stainless steel as a possible future feeder material. Model alloys are also being used, to idealize or simulate particular processes that occur on small length scales in engineering alloys. The chair-holder's extensive experience of corrosion mechanisms in a wide range of metallic materials, from aluminum alloys to stainless steels to noble metal alloys, is providing novel and useful insights into the behavior of nuclear-industry materials. Such insights will lead naturally to improvements in corrosion prediction and control. Alongside these main themes of the research, smaller projects are being conducted, such as a study of electrochemical monitoring in concrete relevant to dry storage of used fuel, and a project on electroplating of exotic metals from ionic liquids.

### Research Facilities

The group has excellent electrochemical instrumentation, autoclaves for corrosion and stress corrosion studies, slow strain rate testing, optical microscopy, electrochemical hydrogen sensing, and a state-of-the-art atomic force microscope system. The department, together with Materials and Chemistry, has state-of-the-art surface analysis and electron microscopy facilities.

### Research Team

The following PhD holders worked in the group during this reporting period:

Dr. Anatolie Carcea – Senior Research Associate, 2004-present

Dr. David He – Postdoctoral Fellow, 2005-2007

Dr. Dorota Artymowicz – Research Associate, 2006-present

Dr. Steve Wang – Research Associate, 2007-present

Dr. Smruti Parida – Postdoctoral Fellow, 2008-present

Dr. Yin Huang – Postdoctoral Fellow, 2008-2009

As befits the wide range of disciplines needed to understand corrosion, these senior people have brought expertise in materials science, physics and chemistry to the group, as well as chemical engineering.

As of September 2009, the research group comprised Dr. Carcea, 2 Research Associates, 2 Postdoctoral Fellows, 4 PhD students and 5 MASc students, as well as MEng students and undergraduate thesis students.

The group's research has been mainly funded by the NSERC-UNENE program, but also by other sources including NSERC (Discovery), NWMO, SKB (Sweden), COG, USDOE and OCE.

Projects under way during this reporting period included:

#### PhD

Stress corrosion cracking mechanisms in reducing hot water  
Intergranular corrosion and pitting of steam generator tubing alloys  
Localized corrosion in thin particulate layers (DOE funding)  
Elucidation of the role of cold work in stress corrosion cracking  
Catalysis by nanoporous metals (Discovery funding)

#### MASc

Simulation of low-temperature underdeposit corrosion of steam generator tubing  
Kinetics of alloy corrosion  
Properties and applications of nanoporous metals (Discovery funding)  
Electroplating of exotic metals from ionic liquids  
Small stress corrosion cracks and the effect of surface mechanical treatment (COG-EMK-OCE funding)  
Modification of oxide films for improved corrosion resistance  
Stress corrosion cracking of copper in sulfide solutions (SKB funding)

Electrochemical monitoring of dry storage containers for used nuclear fuel  
Stress corrosion cracking prediction of nickel-base alloy weldments

#### Postdoctoral and Research Associate

Atomistic simulation of alloy corrosion

Anaerobic atmospheric corrosion kinetics of steel (NWMO funding)

Properties and applications of nanoporous metals (Discovery funding)

Stress corrosion cracking of copper in sulfide solutions (SKB funding)

Stability of localized corrosion in nickel-base alloys (DOE funding)

Drs Carcea, Artymowicz and Newman were active in a wide range of other research involving summer students, MEng students, and local and international collaborators.

#### Interaction with Industry and Other Collaborations

Interaction with industry is based around a Technical Advisory Group with representation from OPG, AECL and Bruce Power that meets several times annually.

Roger Newman led a number of short-term contract projects for industry, including OPG (Pickering Unit 7 return to service; hydrogenation of pressure tube material; monitoring of dry storage containers), AECL (aspects of NRU return to service) and Bruce Power (low-temperature corrosion in steam generators).

Collaboration is extensive worldwide. The most active collaborations during this period were with Johns Hopkins University and Imperial College.

Roger Newman serves on the Scientific Advisory Board of the Max Planck Institute for Iron and Steel Research and is a member of the Proactive Aging Management Committee, a nuclear materials expert group based in Tohoku University, Japan. He was a member of the ROCSE (Research Opportunities in Corrosion Science and Engineering) committee of the National Academies, Washington DC, whose report will be issued in 2010. He was Vice Chair of the 2008 Gordon Research Conference on Corrosion (aqueous) and will be the Chair of the 2010 Conference. He continues to chair the Education Advisory Committee of UNENE.

Students and postdoctoral staff have lively interactions with industry and with collaborators worldwide.

#### Research Results

##### Conferences, workshops and seminars

In 2008 Roger Newman was invited to address a special symposium in memory of Norman Hackerman, *The Corroding of America's Infrastructure*, at the James Baker Institute for Public Policy, Rice University, Houston. Later he gave a plenary lecture at Eurocorr 2008 in Edinburgh. He and other members of the group have attended and made presentations at many other international and local events. William Zhang continued the tradition of winning a prize at the NACE student poster session.

### Publications

The following list gives all papers published by the Chairholder, students and colleagues in the 2007-2009 period, to bring the list up to date from the last Annual Report. This list includes both UNENE and non-UNENE funded research and scholarship. Roger Newman made a significant contribution to the 4<sup>th</sup> Edition of Shreir's 'Corrosion', including a major chapter on Stress Corrosion Cracking.

### Journals

1. A. Barnes, J. Deakin and R.C. Newman, Stress corrosion cracking of Monel 400 in copper sulfate solution. *Corrosion*, 63, 416-418 (2007).
2. T.J.R. Leclere, A.J. Davenport and R.C. Newman, Enhancement of localized corrosion in aluminum alloys by weak acids. *Corrosion*, 63, 338-345 (2007).
3. I.L. Liakos, R.C. Newman, E. McAlpine and M.R. Alexander, A study into the resistance of SAMs on aluminium to acidic and basic solutions using dynamic contact angle measurement, *Langmuir*, 23, 995-999 (2007).
4. P. Ernst and R.C. Newman, Explanation of the effect of high chloride concentration on the Critical Pitting Temperature of stainless steel, *Corros. Sci.*, 49, 3705-3715 (2007).
5. R.C. Newman and C. Healey, Stability, validity, and sensitivity to input parameters of the slip-dissolution model for stress corrosion cracking, *Corros. Sci.*, 49, 4040-4050 (2007).
6. R.C. Newman, Dependence of stress corrosion crack velocity on strain rate for a binary noble-metal alloy, *Corrosion*, 63, 1048-1050 (2007).
7. P. Ernst and R.C. Newman, A kinetic interpretation of the peculiar interaction between alloyed molybdenum and dissolved bromide in the pitting corrosion of stainless steels, *Electrochemical and Solid State Letters*, 11, C1-C4 (2008).
8. D.L. Engelberg, R.C. Newman and T.J. Marrow, Effect of thermo-mechanical process history on grain boundary control in austenitic stainless steel, *Scr. Materialia*, 59, 554-557 (2008).
9. R.C. Newman, Stress corrosion cracking of noble metals and their alloys in solutions containing cations of the noble metal: Review of observations relevant to competing models of SCC, *Corros. Sci.*, 50, 1807-1810 (2008).
10. R.C. Newman, Review and hypothesis for the stress corrosion mechanism of carbon steel in alcohols, *Corrosion*, 64, 819-823 (2008).
11. R.C. Newman and F. Scenini, Another way to think about the critical oxide volume fraction for the internal to external oxidation transition? *Corrosion*, 64, 721-726 (2008).

12. F. Scenini, R.C. Newman, R.A. Cottis and R.J. Jacko, Effect of surface preparation on intergranular stress corrosion cracking of Alloy 600 in hydrogenated steam, *Corrosion*, 64, 824-835 (2008).
13. A. Barnes, N.A. Senior and R.C. Newman, Film-induced cleavage of AgAu alloys, *Metall. Trans. A*, 40, 58-68 (2009).
14. I.L. Liakos, E. McAlpine, X. Chen, R.C. Newman and M.R. Alexander, Assembly of octadecyl phosphonic acid on air annealed alumina; evidence for termination dependent adsorption to the  $\alpha\text{-Al}_2\text{O}_3$  (0001) surface, *Appl. Surf. Sci.*, 255, 3276-3282 (2008).
15. D.M. Artymowicz, R.C. Newman and J.D. Erlebacher, The relationship between the parting limit for de-alloying and a geometric high-density percolation threshold, *Philos. Mag.*, 89, 1663-1693 (2009).
16. Jörg Weissmüller, Roger C. Newman, Hai-Jun Jin, Andrea M. Hodge and Jeffrey W. Kysar, Nanoporous metals by alloy corrosion: Formation and mechanical properties, *MRS Bulletin*, special issue, 34, 577-586 (2009).
17. R.C. Newman and N.A. Senior, A revised interpretation of ultra-fast stress corrosion cracking experiments by Serebrinsky and Galvele, *Corros. Sci.*, discussion article, in press (2010).
18. J. Ulaganathan and R.C. Newman, Thermodynamic control of iron reactivation from the passive state in mild acid, *Electrochemical and Solid State Letters*, in press (2010).
19. Zoe Coull, Roger Newman, Neil Coombs, and Julia Huang, Dealloying and its relationship to stress corrosion cracking in FeNiCr alloys exposed to hot caustic environments, *Metall. Trans. A*, submitted (2009).

#### Conferences and book chapters

20. A. Barnes, N.A. Senior and R.C. Newman, Revisiting the film-induced cleavage model of SCC, *Environment-Induced Cracking of Materials*, eds S.A. Shipilov, R.H. Jones, J.-M. Olive and R.B. Rebak, Vol 1, pp 47-58, Elsevier, Amsterdam (2008).
21. D.L. Engelberg, T.J. Marrow, R.C. Newman and L. Babout, Grain boundary engineering for crack bridging, a new model for intergranular stress corrosion crack propagation, *Environment-Induced Cracking of Materials*, eds S.A. Shipilov, R.H. Jones, J.-M. Olive and R.B. Rebak, Vol 1, pp 69-80, Elsevier, Amsterdam (2008).
22. T.J. Marrow, L. Babout, B.J. Connolly, D. Engelberg, G. Johnson, J.-Y. Buffiere, and R.C. Newman, High-resolution, in-situ, tomographic observations of stress corrosion cracking, *Environment-Induced Cracking of Materials*, eds S.A. Shipilov, R.H. Jones, J.-M. Olive and R.B. Rebak, Vol 2, pp 439-448, Elsevier, Amsterdam (2008).

23. Z. L. Coull and R.C. Newman, Selective dissolution and oxidation zones in Ni-Cr-Fe space and their relationship to SCC, Corrosion/2007, paper #487, NACE, Houston (2007).
24. F. Scenini, R.C. Newman, R.A. Cottis and R.J. Jacko, Dependence of PWSCC of Ni base alloys on their oxidation behaviour, Corrosion/2007, paper #611, NACE, Houston (2007).
25. D.M. Artymowicz, R.C. Newman and J. Erlebacher, Insights into the parting limit for de-alloying from revision of atomistic considerations, ECS Transactions Volume, Vol 3, issue 31, Critical Factors in Localized Corrosion, a Symposium in Honor of Hugh S. Isaacs, pp 499-506 (2007).
26. Zoe L. Coull, Roger C. Newman, Anatolie G. Carcea and Dorota M. Artymowicz, Fundamental reasons for the good performance of Alloy 800 in nuclear steam generators, Proc CNS Annual Conference, St John, New Brunswick (2007).
27. G. Kwong, A.G. Carcea and R.C. Newman, Apparent inversion of the effect of alloyed molybdenum for corrosion of ordinary and enhanced 316L stainless steel in sulfuric acid, Proc. E-MRS Spring Meeting, Strasbourg, 2007.
28. W. Zhang and R.C. Newman, The effects of reduced sulfur compounds in chloride-free solutions on steam-generator tubing alloys, Proc. Conf. Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, in press (2010).
29. R.C. Newman, Dealloying, Shreir's Corrosion, 4<sup>th</sup> Edition, Elsevier, 2010.
30. R.C. Newman, Environment-Assisted Cracking – Overview, Shreir's Corrosion, 4<sup>th</sup> Edition, Elsevier, 2010.
31. R.C. Newman, Stress Corrosion Cracking, Shreir's Corrosion, 4<sup>th</sup> Edition, Elsevier, 2010.
32. W. Zhang and R.C. Newman, Localized corrosion of nickel-based steam generator tubing alloys in sodium sulfate solutions containing thiosulfate ions, Proc 6<sup>th</sup> CANDU Steam Generator Conference (Toronto, 2009), in press.

### Teaching

Until 2008, Roger Newman taught introductory nuclear physics and basic reactor concepts in one half of the Nuclear Engineering 4<sup>th</sup> year Chemical Engineering elective course. He taught the second half of a 3<sup>rd</sup> year Materials course for Chemical Engineers, and teaches a graduate course in Corrosion, both of which have used many nuclear examples. He also teaches a 500-level course on Electrochemistry which has used examples such as pH measurement in high-temperature water.

This period was marked by a noticeable upsurge of interest among undergraduates in nuclear matters, and UofT began plans for new nuclear courses based in Mechanical and Industrial Engineering as well as Chemical Engineering and Applied Chemistry. It can be expected that by 2012 there will be 3-4 times the number of nuclear offerings in UofT that existed in 2007. As part of this renaissance of nuclear teaching, Roger Newman revived a graduate course on 'Nuclear Chemical Engineering' in 2009.