Project Summary Report (Project ID Number 55171)

Development of Advanced In-Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments

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Super Critical Water Oxidation (SCWO) is a promising technology for destroying highly toxic organic waste (including physiological agents) and for reducing the volume of DOE's low-level nuclear waste. The major problem inhibiting the wide implementation of SCWO is the lack of fundamental knowledge about various physico-chemical and corrosion processes that occur in SCW environments. In particular, the lack of experimental techniques for accurately monitoring important parameters, such as pH, corrosion potential and corrosion rate, has severely hampered the development of a quantitative understanding of the degradation of materials in this extraordinarily aggressive environment. Accordingly, the principal objective of the present program has been to develop new, innovative methods for accurately measuring parameters that characterize corrosion processes under super critical conditions.

As a result of our three-year effort, we have developed new chemical and corrosion sensors for use in high subcritical and supercritical aqueous environments. The precision and readability of the sensors have been significantly improved over previous systems and the fundamental thermodynamic and corrosion properties of supercritical aqueous system can now be properly measured over wide ranges of temperature and pressure. In particular, the novel flow-through yttria-stabilized zirconia (YSZ) pH electrode and flow-through external reference electrode have been developed and evaluated. Potentiometric measurements have been carried out to determine the pH of dilute hydrochloric acid (from 0.001 to 0.01 mol kg^{-1}) at temperatures up to 400°C (Figure 1). High precision potential data were obtained with an uncertainty of ± 3 mV. The isothermal diffusion (liquid junction) potential was determined using available thermodynamic and conductivity data found in literature. The diffusion potential was then employed to correct the potential of the YSZ pH electrode measured against the reference electrode. The association constant of hydrochloric acid was evaluated from the corrected potential data and used to judge the accuracy of the pH measuring system. The results have been compared with available literature data and good agreement between experimentally measured and literature data is obtained. The data demonstrate that the reference electrode is capable of providing potential measurements of sufficient accuracy that quantitative potentiometric studies on aqueous solutions at temperatures above the critical temperature are now possible.

Three-electrode electrochemical noise (EN) sensors have been developed for measuring corrosion rate in subcritical and supercritical environments. The EN sensors were tested in flowing aqueous solutions containing NaCl and HCl at temperatures ranging from 150° to 390°C, at a pressure of 25 MPa, and at flow rates from 0.375 ml/min to 1.00 ml/min. The noise records in the potential and coupling current from Type 304 stainless steel were recorded simultaneously. The inverse noise resistance ($1/R_n = \sigma_I / \sigma_E$) was calculated from the standard deviations in the current (σ_I) and potential (σ_E) and was compared with the corrosion rate determined via mass loss measurements. The inverse noise resistance correlated very well with the measured corrosion rate measured at various temperatures and flow rates (Figure 2). At temperatures higher than 150°C, the corrosion rate was found to be proportional to the inverse noise resistance as required by the Stern-Geary relationship. Accordingly, noise resistance can be used to evaluate corrosion rate in these aggressive, low density (super critical) environments. Good agreement was found between the Stern-Geary constant evaluated via electrochemical noise analysis (ENA) and that determined via polarization measurements. To our knowledge, the work reported here represents the first determination of corrosion rate using electrochemical noise techniques in super critical aqueous solutions.

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A phenomenological model that was previously developed to account for the dependence of corrosion rate on temperature, and in particular to account for the passing of the corrosion rate through a maximum in the vicinity of the critical temperature, has been further developed to describe the variation of corrosion rate with pressure. This model incorporates three effects of pressure: (1) That due to the volume of activation of the reaction, (2) that due to the change in volumetric concentrations of the reactants (e.g. O_2), and (3) that due to the compressibility of the medium. The model has been used for Stone & Webster Engineering Co. to estimate corrosion rates of materials in the US Army's SCWO program for the destruction of chemical agents. In particular, the model was used to correct the corrosion rates measured at MIT for differences in pressure between the laboratory studies and the MOC (Materials of Construction) work that was being carried out at General Atomics in La Jolla, CA.

The current project has been completed, and we are now preparing a follow on proposal to expand the work that was carried out during the first three years. The follow on will propose to continue the development of chemistry and corrosion sensors, but will also explore the corrosion of noble metals in SCWO environments (platinum has now been selected as the liner material for the Army's program to destroy VX hydrolysate) and will seek to develop novel cathodic protection technologies for use in these systems.

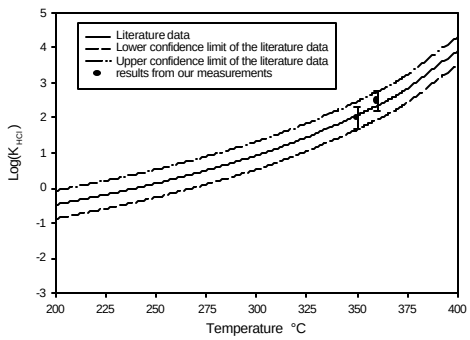

Figure 1. Comparison of log (K_{HCl}) obtained in this work and the values derived from the literature for a pressure of 33.8 MPa.

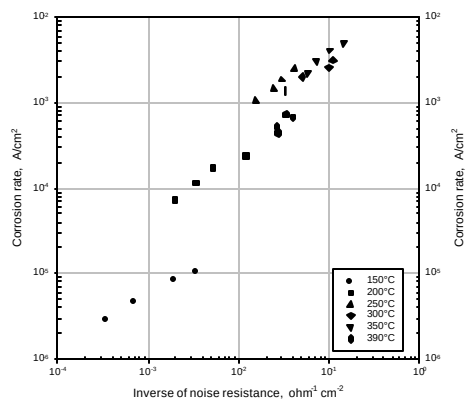

Figure 2. Relation between corrosion rate and inverse noise resistance for Type 304 SS in 0.1 M NaCl + 0.01 M HCl..

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Publications and Presentations

Papers in press or in print:

1. Lvov S.N., Zhou X.Y, Macdonald D.D. Flow-Through Electrochemical Cell for Accurate pH measurements at Temperatures up to 400°C. *J. Electroanal. Chem.,* 1999, v. 463, p.146-156.

2. Lvov S.N., Zhou X.Y., Ulyanov S.M., Macdonald S.N. Potentiometric Measurements of Association Constant and pH in High Temperature HCl (aq) solutions, In: "Steam, Water, and Hydrothermal Systems: Physics and Chemistry. Meeting the Needs of Industry", Eds. P. P.R. Tremaine, P.G. Hill, D.E. Irish, and P.V. Palakrishnan, NRC Press Ottawa, 2000 (in press).

Papers in preparation:

1. Macdonald, D. D., "Effect of Pressure on the Rates of Corrosion Processes in Super Critical Aqueous Systems", Corrosion Science, (in preparation).
2. Zhou X.Y., Wei X.J., Lvov S.N., Benning L., and Macdonald D.D. Measuring Corrosion Rate of Type 304 Stainless Steel in Subcritical and Supercritical Aqueous Solutions Via Electrochemical Noise Analysis. *J. Electroanal. Chem.,* (in preparation)

Conference presentations and invited seminars:

1. Macdonald D. D. "Chemistry Sensors for the Universal Solvents-Supercritical Aqueous Solutions." Proceedings of the 4th International Symposium on Supercritical Fluids, p.861-864, May 11-14, 1997, Sendai, Japan.
2. Lvov S.N. (1), Zhou X.Y., Macdonald S.N. "Potentiometric pH Measurements in Supercritical Aqueous Solutions", The 193rd Meeting of The Electrochemical Society, Inc., Abstracts No. 1016, May 3-8, 1998.
3. Macdonald D.D., Lvov S.N., Kriksunov L.B. "The chemical and Electrochemical Properties of Supercritical Aqueous Solutions". The 193rd Meeting of The Electrochemical Society, Inc., Abstract No. 1012, May 3-8, San Diego, 1998.
4. Lvov S.N., Zhou X.Y., Wei X.J., Ulyanov S.M., and Macdonald D.D. "Electrochemical Corrosion Studies in High Temperature Subcritical and Supercritical Aqueous Environments". The 218th American Chemical Society Meeting, Abstract No. 129, August 22-26, New Orleans, 1999.
5. D. D. Macdonald, "The Chemistry and Electrochemistry of High Subcritical and Supercritical Aqueous Systems", Distinguished Lecturer Series, University of Toronto, Toronto, Canada, November 10, 1999.

Invention Disclosures

1. Zhou X.Y., Lvov S.N., Ulyanov S.M. "Safe Yttria-Stabilized Zirconia (YSZ) pH Sensing Electrode for High Temperature Aqueous Systems" Invention Disclosure No. 98-1989, November 11, 1998.

Degrees Granted

Mr. Ulyanov is expected to defend his MS thesis ("pH Measurements and Potential-pH Diagram Calculations in High Temperature Subcritical and Supercritical Aqueous Solutions") in the fall of 2000.