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

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INTRODUCTION

- Supercritical Water Oxidation (SCWO) is a promising technology for destroying highly toxic organic waste (including physiological agents) and for reducing the volume of low-level nuclear waste.

- SCWO offers a number of unique advantages over other waste destruction technologies, such as incineration and pyrolysis (e.g., in plasmas). These advantages include:

  1. Zero emissions to the environment.
  2. Very high destruction efficiencies (> 99.99 %), for even the most resilient waste.
  3. Relatively low cost.
  4. Remote siting through minimal need for services (electricity, etc.).
  5. Scalable to almost any size, hence may be portable. Thus, the unit can be taken to the problem rather than the problem being taken to the unit. This is important for highly toxic materials, such as PCBs (poly-chlorinated biphenyls).

- Greatest challenges are the selection of materials that can withstand the harsh oxidizing conditions that exist in the reactor and in downstream components and the development of effective, *in situ* chemical (pH, $[O_2]$, $[H_2]$), electrochemical (corrosion potential), and corrosion rate monitoring techniques.

TYPICAL SCWO PROCESS CONDITIONS

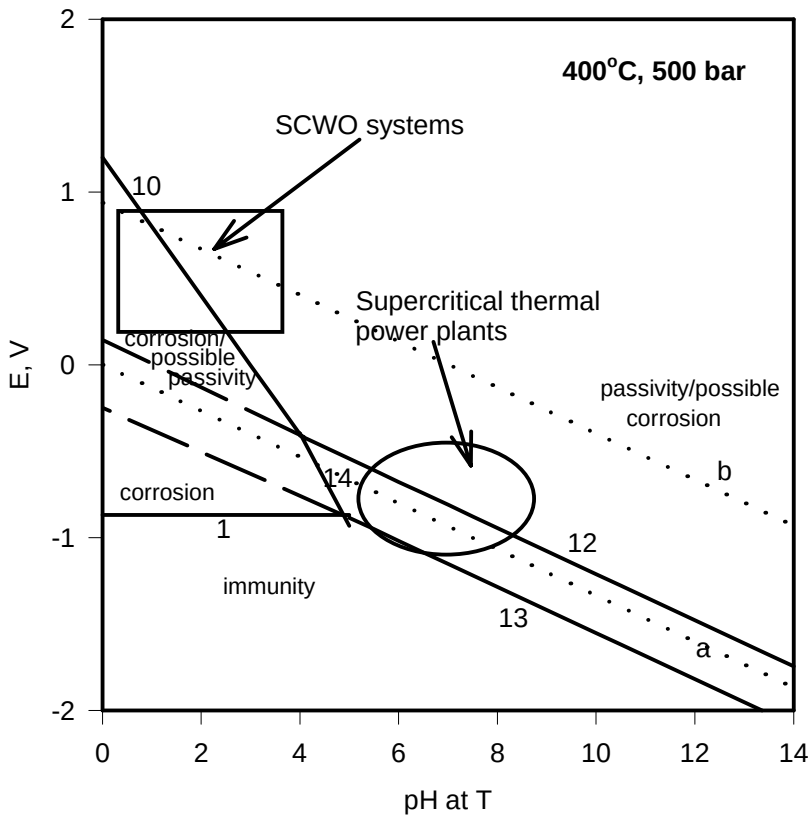
Conditions within the reaction zone in SCWO systems vary widely depending upon the nature of the feed and the resiliency of the waste and upon the desired conversion efficiencies. Typical conditions are as follows:

- T = 600 to 650 ^{o}C in the reaction zone, sub critical in much of the downstream regions.
- P = 200 to 400 bar.
- Partial pressure of oxygen = 150 % to 500 % of the stoichiometric requirement for the oxidation of the organic.
- Flow rates – highly variable depending upon location.
- Salts – depending upon the composition of the feed, may contain high concentrations of chloride, sulfate, nitrate, phosphate, etc. The trend is toward acidification due to oxidation, e.g.

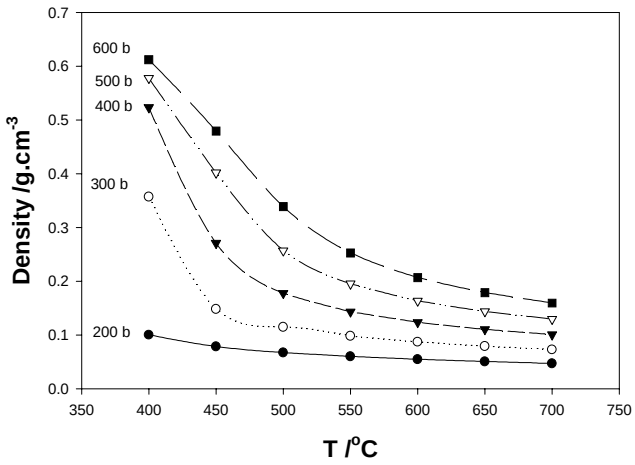
$$C_xH_yCl_z + O_2 + H_2O = xCO_2 + (y/2)H_2O + zHCl$$

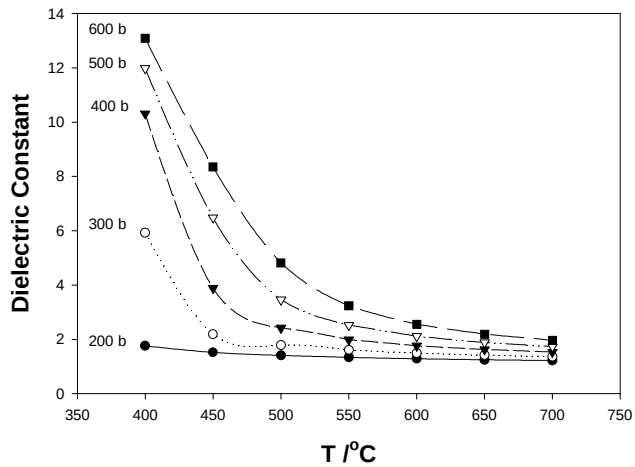
$$CO_2 + H_2O = HCO_3^- + H^+$$

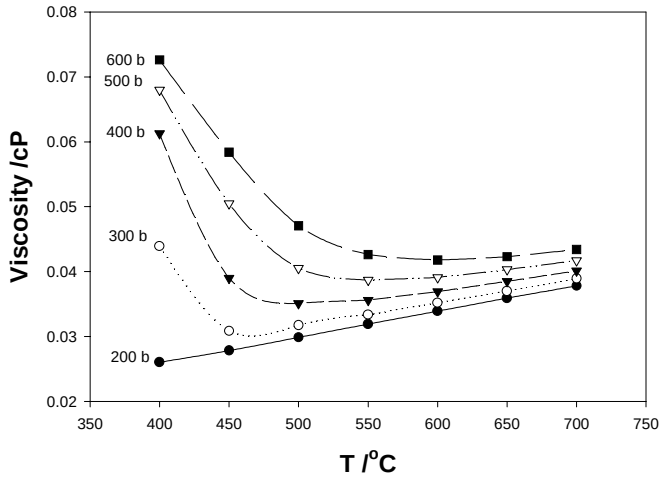
$$HCl = H^+ + Cl^-$$



Location of SCWO conditions in potential-pH space. Note that the E-pH diagram corresponds to that for iron at 400 ^{o}C.







Properties of the fluid in a SCWO reactor. Note that in the reaction zone the density, dielectric, and viscosity are similar to those of a gas at the same pressure.

OBJECTIVES

- Develop methods for accurately measuring pH in high sub critical and super critical aqueous environments.

- Define the pH scale for super critical aqueous systems.

- Explore Electrochemical Emission Spectroscopy (“electrochemical noise”) as a quantitative means of monitoring corrosion rate in prototypical SCWO environments.

- Develop a theoretical understanding of the dependence of corrosion rate on important independent variables, in particular on pressure and temperature.

BACKGROUND

pH Sensors

- $Hg/HgO/ZrO_2(Y_2O_3)/H_2O$, H^+ electrode with a theoretical potential of

$$E = E^0_{Hg/HgO} - (2.303RT/2F)\log(a_{H2O}) - (2.303RT/F)\,pH$$

or

$$pH = (F/2.303RT)\,(E - E^0_{Hg/HgO}) - 0.5\log(a_{H2O})$$

1. The YSZ sensor is a pH primary electrode.
2. Thermodynamically well understood in terms of the potential-determining reactions.
3. No redox response.
4. Major problem is fragility and chemical stability of the ceramic membrane.
5. Used previously by us to make quantitative pH measurements at temperatures up to 325 ^oC and more recently (partly in this work) to make semi-quantitative pH measurements at temperatures as high as 528 ^oC.

- $H_2(Pt)/H^+$ electrode with a theoretical potential of

$$E = -(2.303RT/2F)\log(f_{H2}) - (2.303RT/F)\,pH$$

or

$$pH = -(F/2.303RT)\,E - 0.5\log(f_{H2})$$

1. pH primary electrode
2. Thermodynamically well understood in terms of the potential-determining reaction.
3. Redox response – must know accurately f_{H2}.
4. Rugged and easily handled.
5. Used in this work for the first, quantitative potentiometric determination of the dissociation constant of HCl at high subcritical temperatures.

- $W/WO_3/H_2O, H^+$ electrode with an empirically derived potential of

$$E = E'_{W/WO3} - (2.303RT/2F)\log(a_{H2O}) - (2.303RT/F)\,pH$$

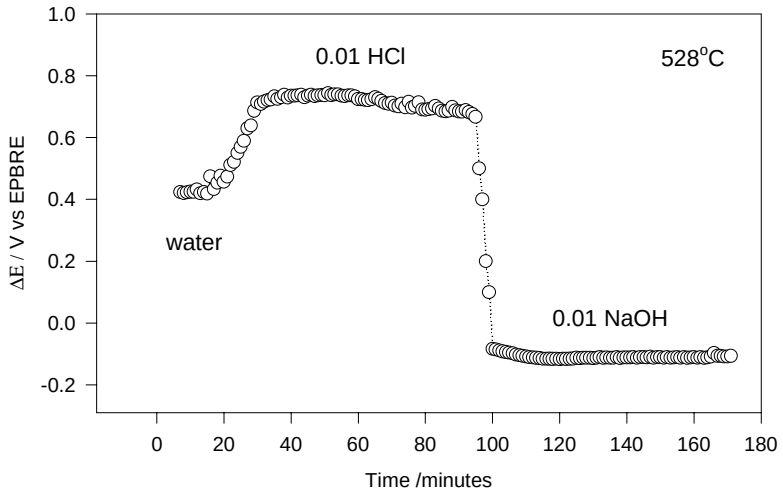
or

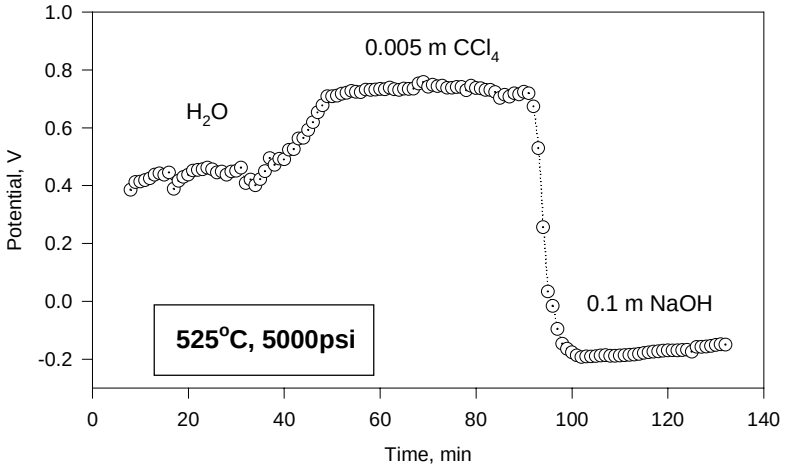
$$pH = (F/2.303RT)\,(E - E'_{W/WO3}) - 0.5\log(a_{H2O})$$

1. A secondary pH electrode that needs calibrating.
2. Potential determining reactions not well understood.
3. No redox response detected in experiments but a response is possible.
4. Rugged.
5. Used recently (partly in this work) to make semi-quantitative pH measurements at temperatures as high as 525 ^{o}C.

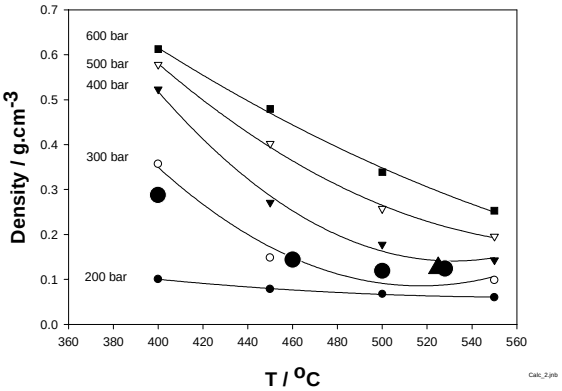
Reference Electrodes

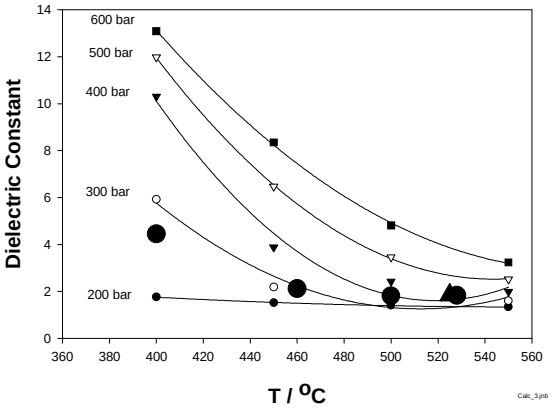
- Must provide a constant reference potential on a thermodynamic scale (e.g., the Standard Hydrogen Scale) over wide ranges of temperature and pressure.
- Previous work employed "External Pressure Balanced Reference Electrodes" at temperatures up to 528 ^{o}C. The EPBRE is capable of providing quantitative reference potentials (± 2-3 mV) at T < 300 ^{o}C, but considerably higher uncertainties (± 20 mV) are experienced in super critical environments. This level of uncertainty renders the EPBRE unsuitable for precise ("research grade") potentiometric measurements at super critical temperatures. The principal source of uncertainty has been traced to the phenomenon of thermal diffusion, which causes the movement of electrolyte (KCl) to the cold end of the non-isothermal bridge that connects the high temperature test system with the Ag/AgCl electroactive element at ambient temperature.
- We have developed a new reference electrode in which a reproducible thermal liquid junction potential, corresponding to the Soret initial state, is established by slowly flowing electrolyte along the non-isothermal bridge. This "Flow Through External Pressure Balanced Reference Electrode (FTEPBRE)" is based on previous work by M. Danielson at PNL. We have demonstrated in this program that the FTEPBRE, when combined with a $H_2(Pt)/H^+$ pH sensor, is capable of measuring pH to better than ± 0.03 at temperatures up to 410 ^{o}C. To our knowledge, these are the first "research grade" pH measurements to have been ever performed in supercritical aqueous systems.

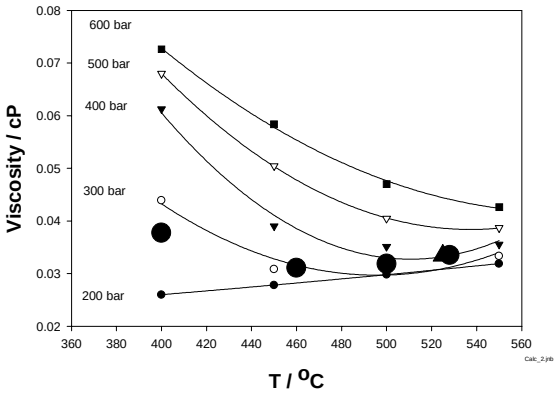




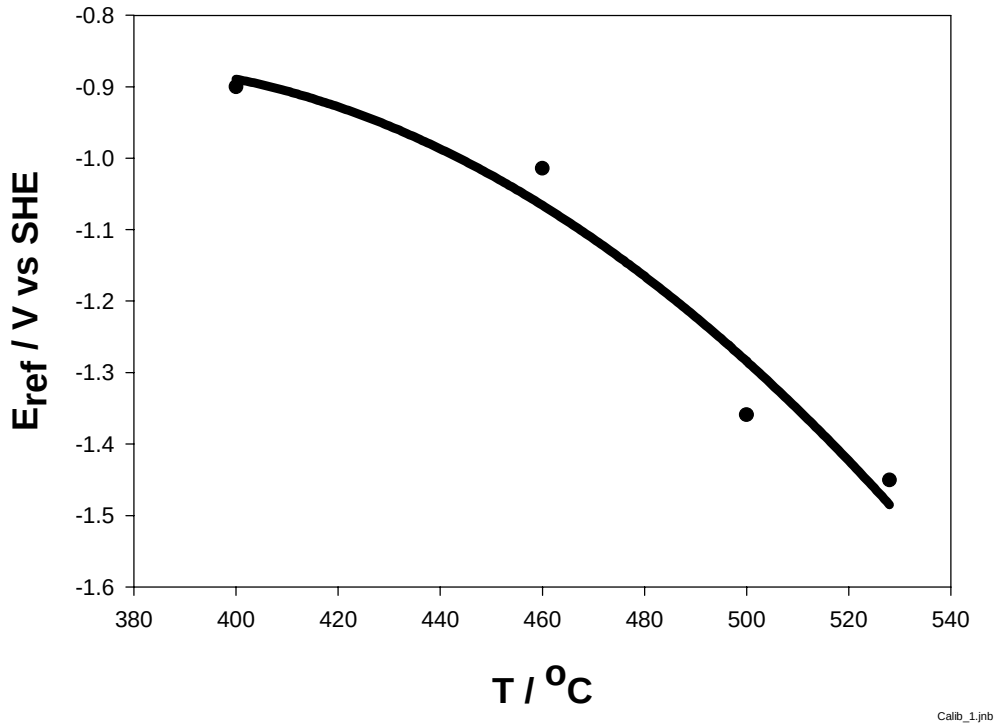
Previous studies in our laboratory sponsored by DOE and ARO established the feasibility of making pH measurements in super critical aqueous solutions using W/WO_3 and $Hg/HgO/ZrO_2(Y_2O_3)$ sensors coupled with an External Pressure Balanced Reference Electrode. However, the accuracy was not “research grade”.







Plots of density, dielectric constant, and viscosity vs. temperature for super critical HCl-H_2O as a function of pressure. The conditions employed in the experimental determination of pH for the HCl calibrating solutions are indicated by the large filled circles, whereas those for the CCl_4 solution are depicted by the filled triangle.



Calibration plot of the potential of an external pressure balanced reference electrode vs. temperature for super critical HCl-H_2O solutions. Calibration was carried out against a Hg/HgO/YSZ pH sensor and by calculating the pH of the solution using a thermodynamic speciation model. The resulting calibration function is:

$$E_{ref} = -4.3369 + 0.01867\ T_c - 2.5132e\text{-}5\ T_c^{\ 2}$$

MAJOR PROBLEMS

- At super critical temperatures, the potential of the external pressure balanced reference electrode becomes highly sensitive to small changes in pressure.

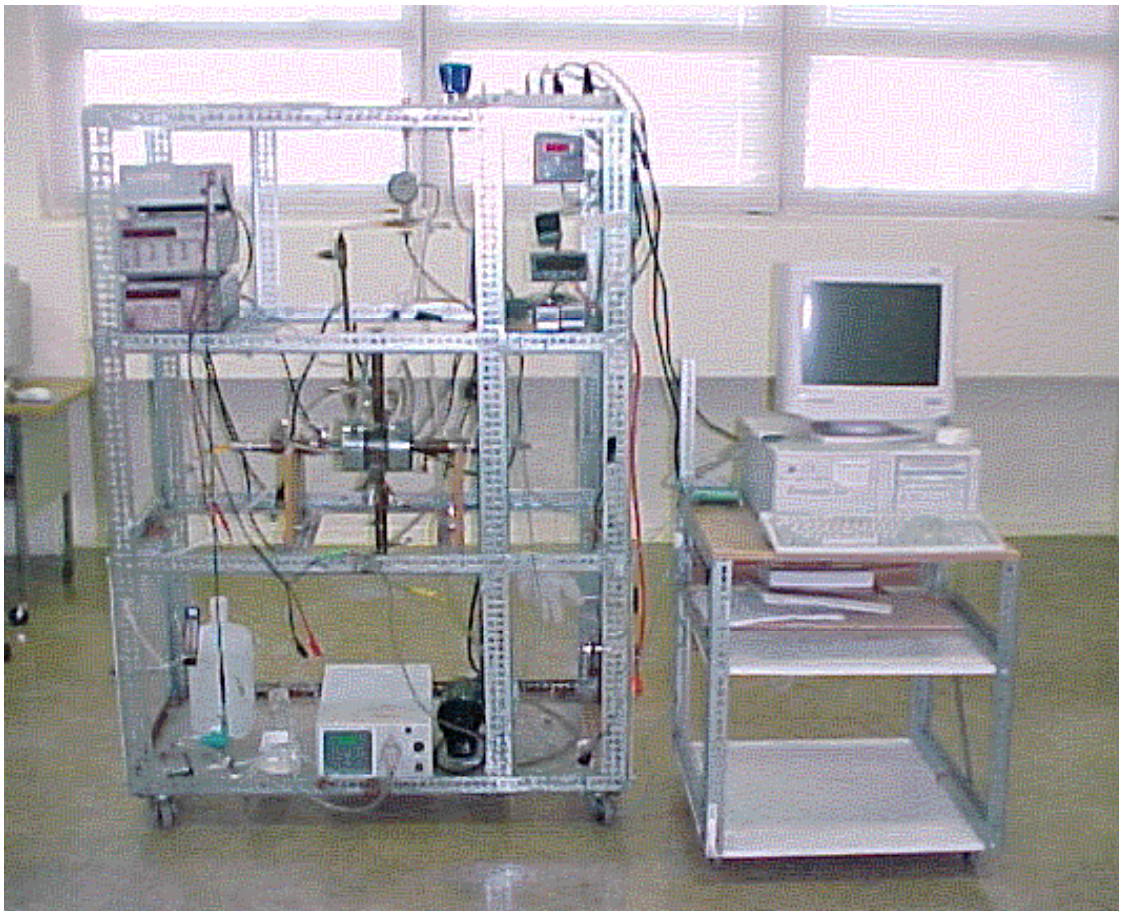
- Thermal diffusion within the non-isothermal electrolyte bridge of the EPBRE causes potential drift as the system evolves from the Soret initial state towards the Soret steady state.

- Corrosion of the loop material (stainless steel, nickel alloys, etc.) changes the pH in a manner that makes comparison with theory (thermodynamic speciation models) impossible.

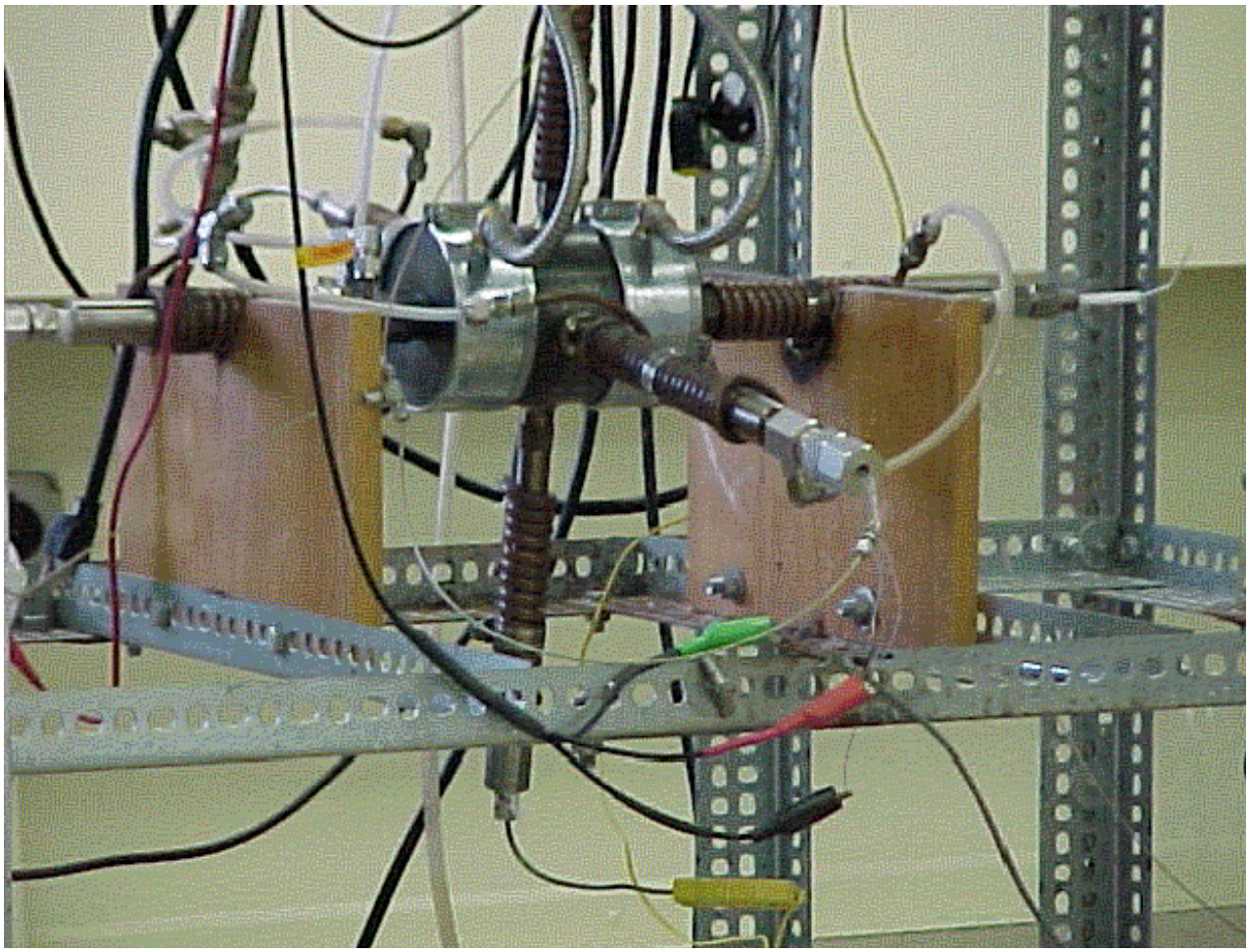
These problems reflect the unusual properties of SCW (highly pressure dependent transport properties) and the fact that all metals and alloys (including the noble metals) corrode in super critical aqueous systems. Accordingly, the problems had to be overcome largely by design.

EXPERIMENTAL SYSTEMS

Flow Loops and Test Cells

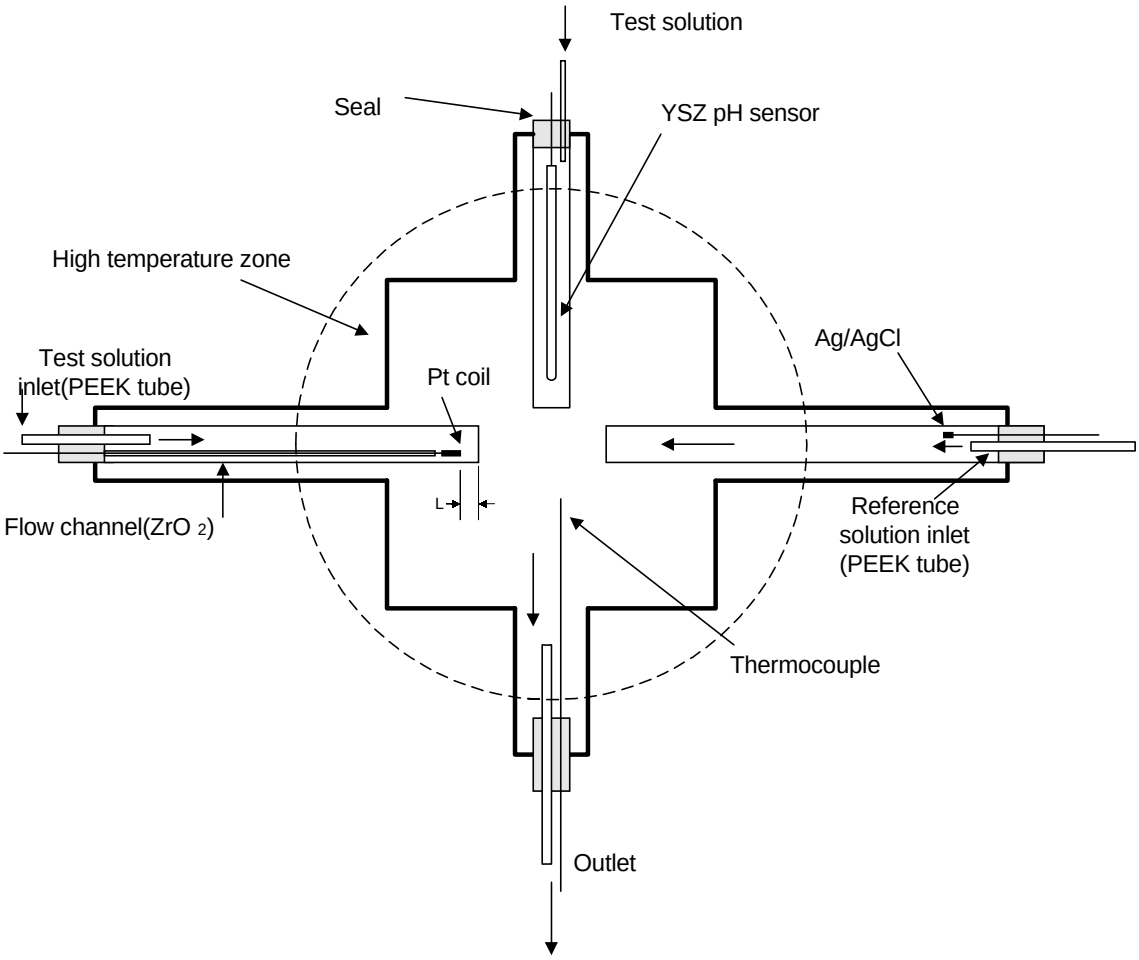


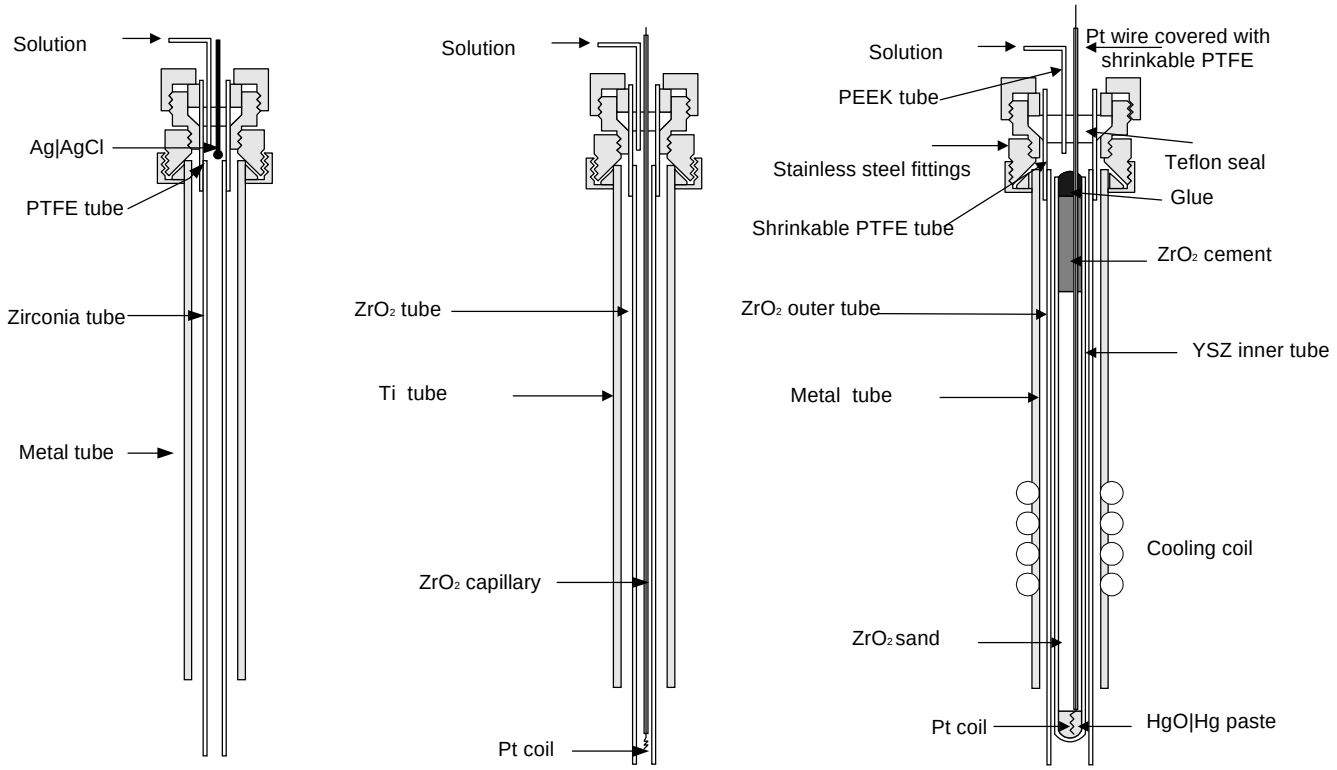
Apparatus for pH and electrochemical noise measurements in high temperature subcritical and supercritical aqueous solutions.



Titanium cell for pH and electrochemical noise measurements in high temperature subcritical and supercritical aqueous solutions.

Test Cell


Test solution
Seal
YSZ pH sensor
High temperature zone
Ag/AgCl
Test solution
inlet(PEEK tube)
Pt coil
L
Flow channel(ZrO 2)
Reference
solution inlet
(PEEK tube)
Thermocouple
Outlet



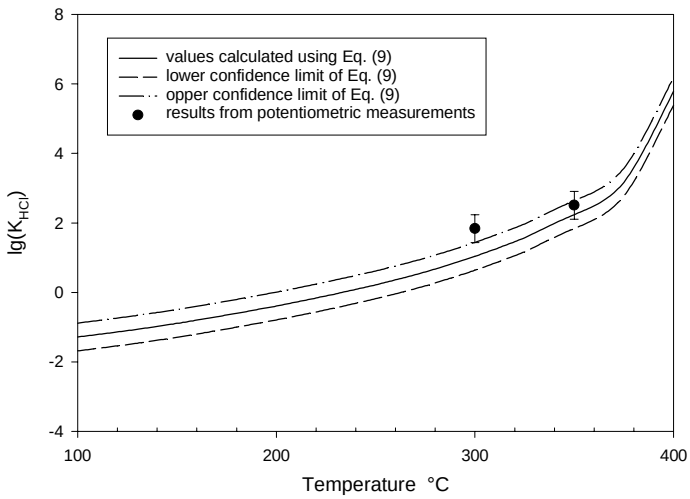
Reference Electrode $H_2(Pt)/H^+$ $Hg/HgO/ZrO_2(Y_2O_3)$

“Flow-through Reference Electrode, $H_2(Pt)/H^+$ pH sensor, and $Hg/HgO/ZrO_2(Y_2O_3)$ pH Sensor.

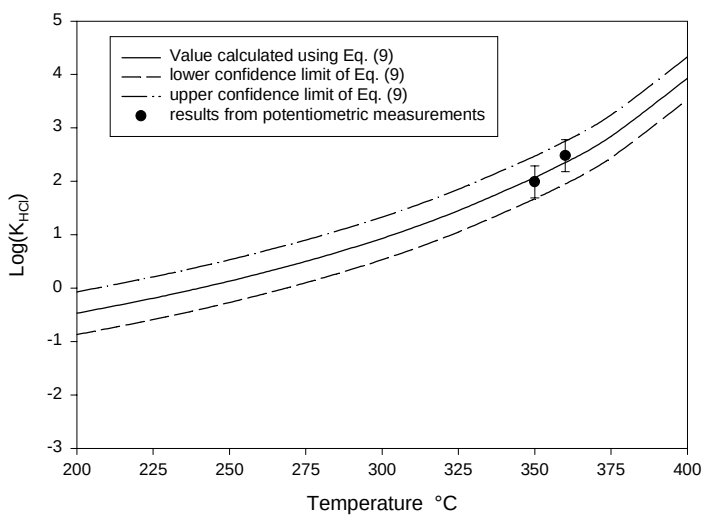
Experimentally measured potential differences, $\Delta E_{1,2}$ [13], and the calculated diffusion potentials, association constants, and pH of aqueous HCl solutions at temperatures between 25 to 360°C and pressure of 27.5 and 33.8 MPa.

T °C	P MPa	$E_{d,1}$- $E_{d,2}$ mV	$\Delta E_{1,2}$ mV	log(K_{HCl})	pH	
					0.01 mol/kg HCl	0.001 mol/kg HCl
25	27.5	-2.9	64.5*	-	2.04	3. 02
25	33.8	-3.9	61.4	-	2. 04	3. 02
100	27.5	2.8	81.0	-	2. 05	3. 02
200	27.5	4.5	97.8	-	2. 07	3. 02
300	27.5	4.4	100.3	1.84±0.4	2.21±0.10	3.06±0.03
350	27.5	3.8	93.4	2.51±0.3	2.40±0.09	3.13±0.03
350	33.8	3.6	97.4	1.99±0.3	2.26±0.06	3.07±0.02
360	33.8	3.6	91.7	2.48±0.3	2.39±0.09	3.13±0.04

(*) The experimental precision of measurements was estimated in Ref. [13] to within ± 3-10 mV (±6.5 mV average).



Comparison of lg(K_{HCl}) obtained in this work and the values calculated by Eq. (9) at a pressure of 27.5 MPa.

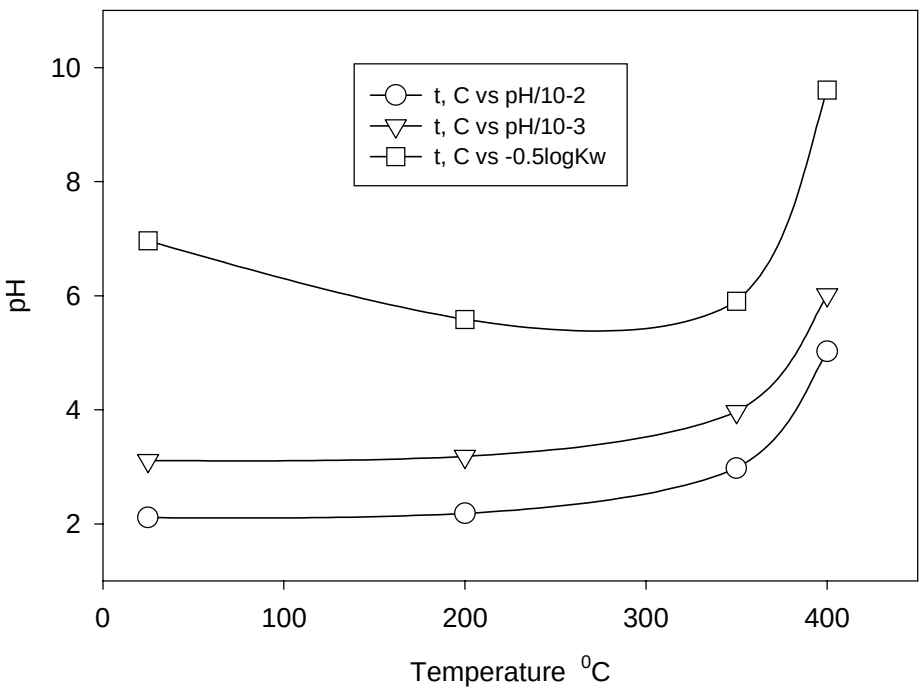


Comparison of lg(K_{HCl}) obtained in this work and the values calculated by Eq. (9) at a pressure of 33.8 MPa.

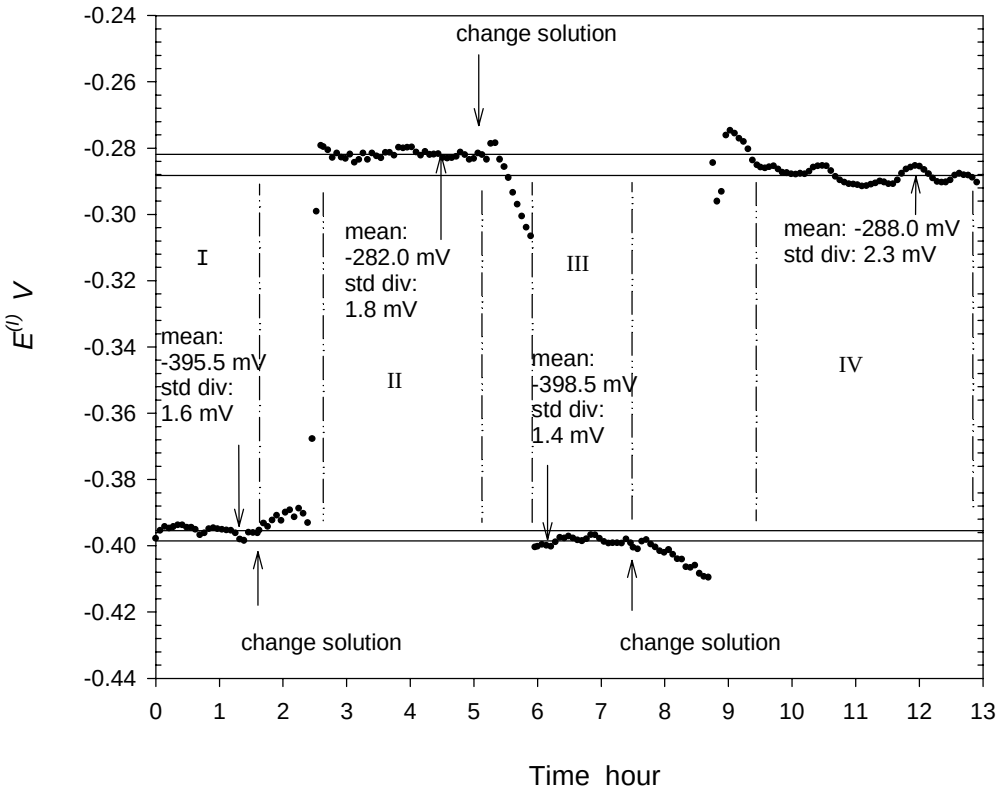
$$\lg K_{\mathrm{HCl}} = \rho(255.63 - 192.62 \times \tilde{T}) + \rho^2(-385.80 + 295.00 \times \tilde{T}) + \rho^3(162.46 - 135.20 \times \tilde{T}) + 42.16 \times [\exp(-31.202 \times \rho \times \tilde{T}) - 1] + 1.652 + 35.6 \times \tilde{T} - 0.221 \times \lg \tilde{T} - 1.744 \quad (9)$$

HCl-NaCl Solutions

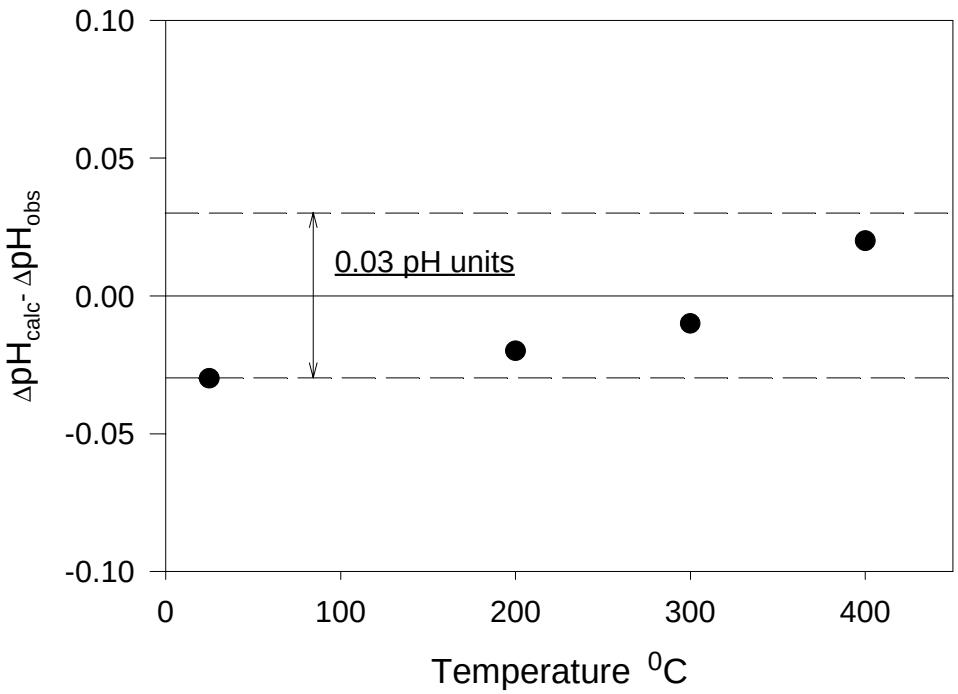
- Using known association constants for HCl and NaCl (values obtained from conductiometric studies) we can calculate the speciation and hence calculate the pH.
- Compare the measured and calculated pH.
- Have done this for temperatures up to 400 ^{o}C.



Calculated pH values of Solution 1 (10^{-3} mol kg^{-1} HCl + 10^{-1} mol kg^{-1} NaCl), Solution 2 (10^{-2} mol kg^{-1} HCl + 10^{-1} mol kg^{-1} NaCl) and pure water over a wide temperature range from 25 to 400°C and pressures between 18.7 and 25.3 MPa.



An example of emf, $E^{(I)}$, measurements for temperature of 400°C (P=25.3 MPa) and flow rate of 0.5 cm^3 min^{-1}. In regions I and III the Solution 1 (10^{-3} mol kg^{-1} HCl + 10^{-1} mol kg^{-1} NaCl) was used and in regions II and IV the Solution 2 (10^{-2} mol kg^{-1} HCl + 10^{-1} mol kg^{-1} NaCl) was used for measuring $E^{(I)}$ values.



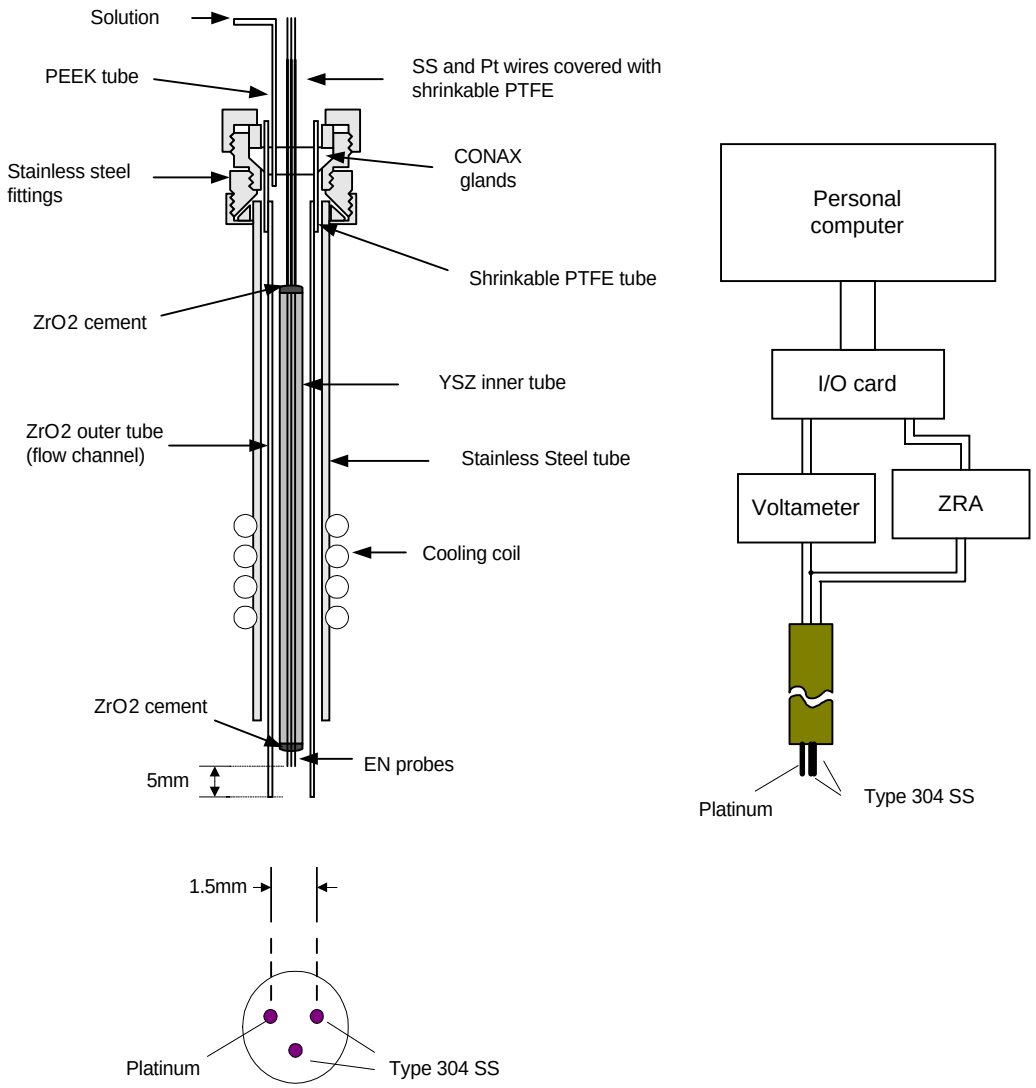
Comparison between theoretically calculated and observed differences in pH, [$\Delta pH_{CALC} - \Delta pH_{OBS}$] of the Thermocell (I).

ELECTROCHEMICAL EMISSION SPECTROSCOPIC DETERMINATION OF CORROSION RATE

- EES is the "electrocardiogram of corrosion science" in that we record spontaneous electrical emissions from the system and then deduce the rate of accumulation of corrosion damage.

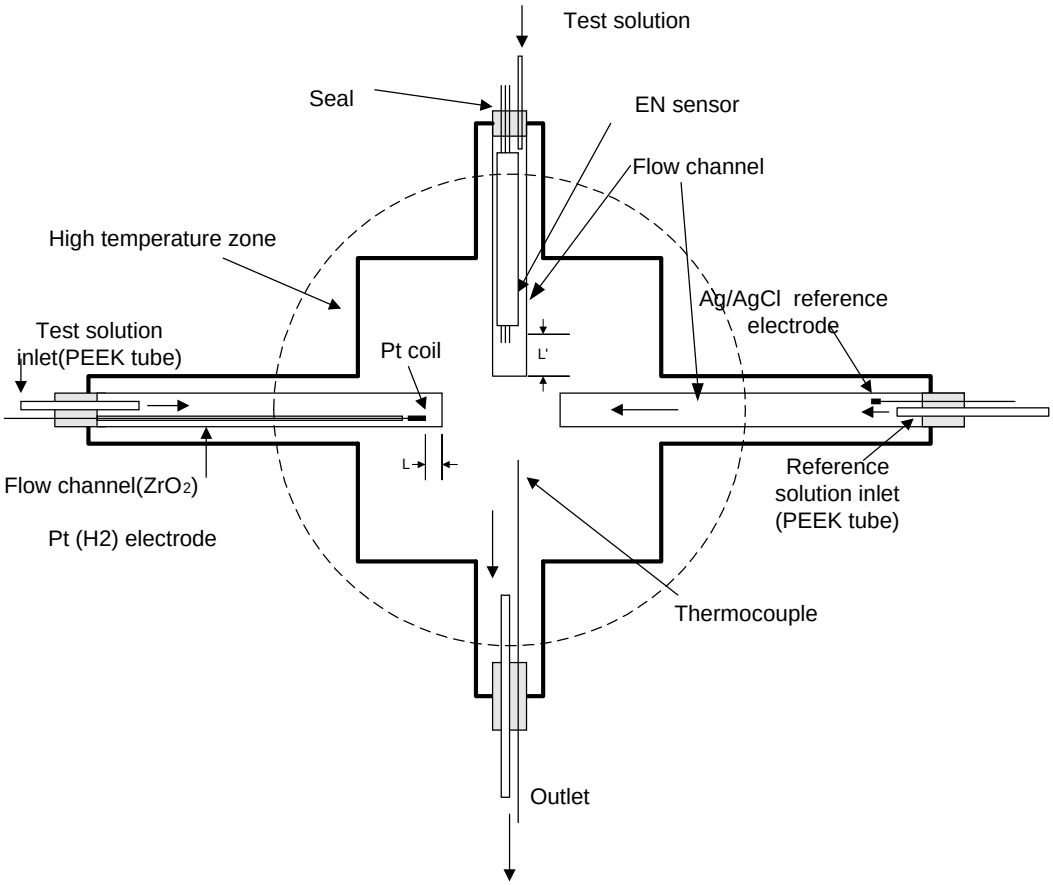
- Previous work in this laboratory sponsored by Union Electrica Fenosa (a Spanish utility), ARO, and DOE (INEL) established the feasibility of recording "electrochemical noise" from steels in SCW at temperatures in excess of 500 ^{o}C. The goal of that previous work was to develop a simple, two-electrode "corrosion activity" sensor. This goal was met successfully.

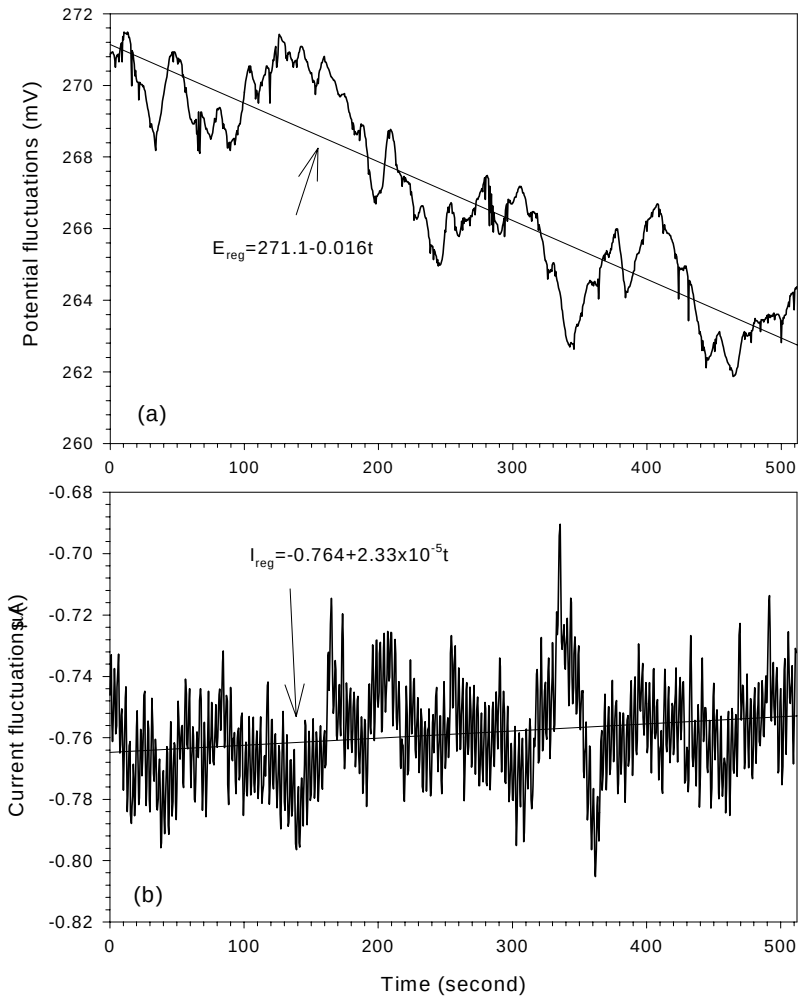
- The goal of the present work was to determine whether three electrode EES techniques could be used to quantitatively measure corrosion rate at high subcritical and supercritical temperatures. This goal has also been met successfully.



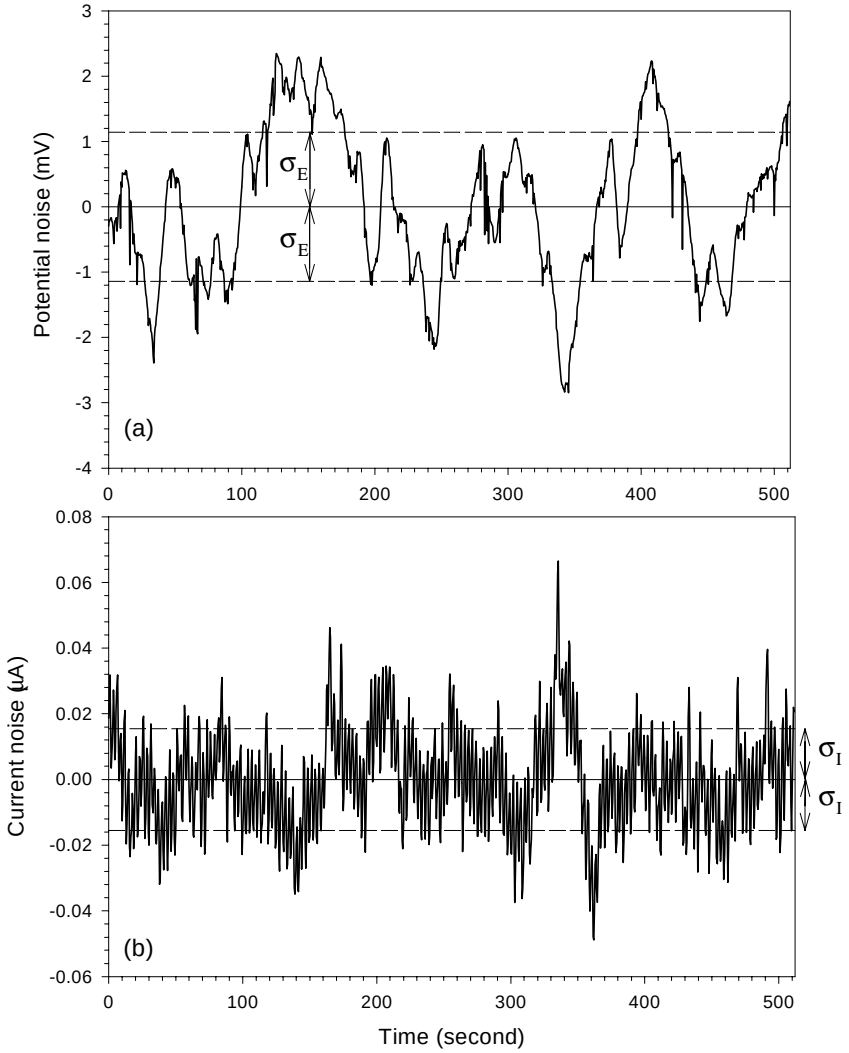
EES Sensor for Corrosion Rate Measurement Using Electrochemical Emission Spectroscopy.

EES Test Cell

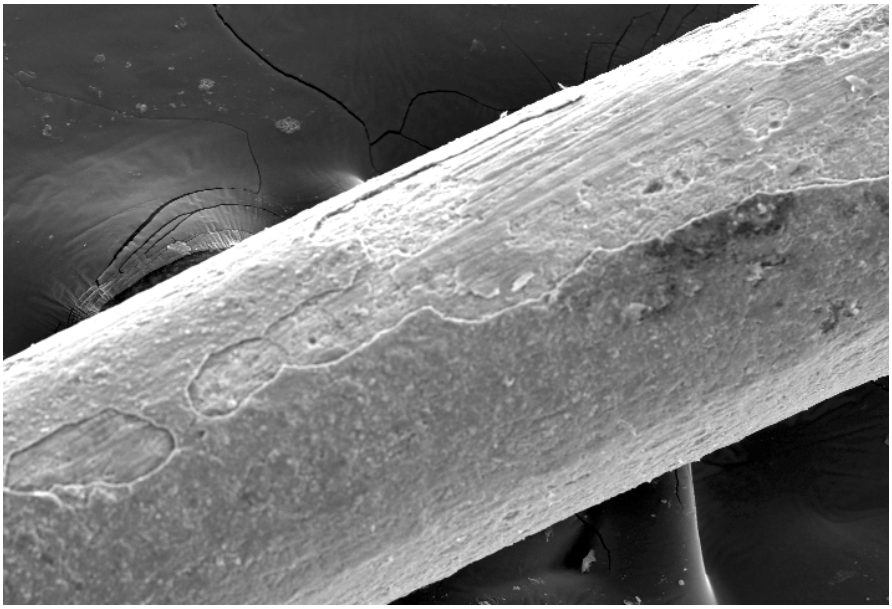




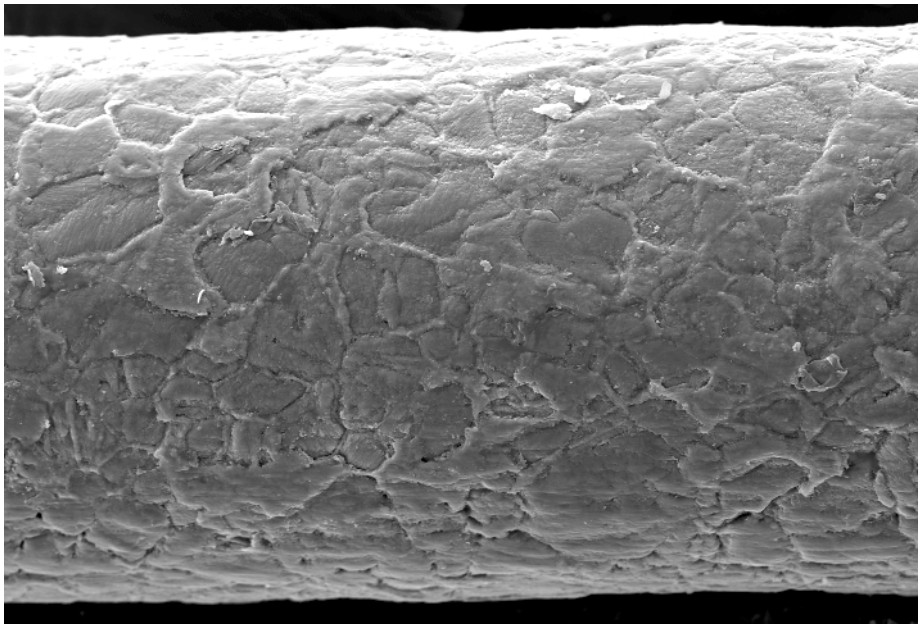
Original records of potential and coupling current acquired from an EN sensor at a temperature of 350°C, pressure of 25 MPa, and flow rate of 0.5 ml/min in hydrogenated 0.01 mol kg^{-1} HCl + 0.1 mol kg^{-1} NaCl.



Potential and coupling current records after removing drifts and DC components.

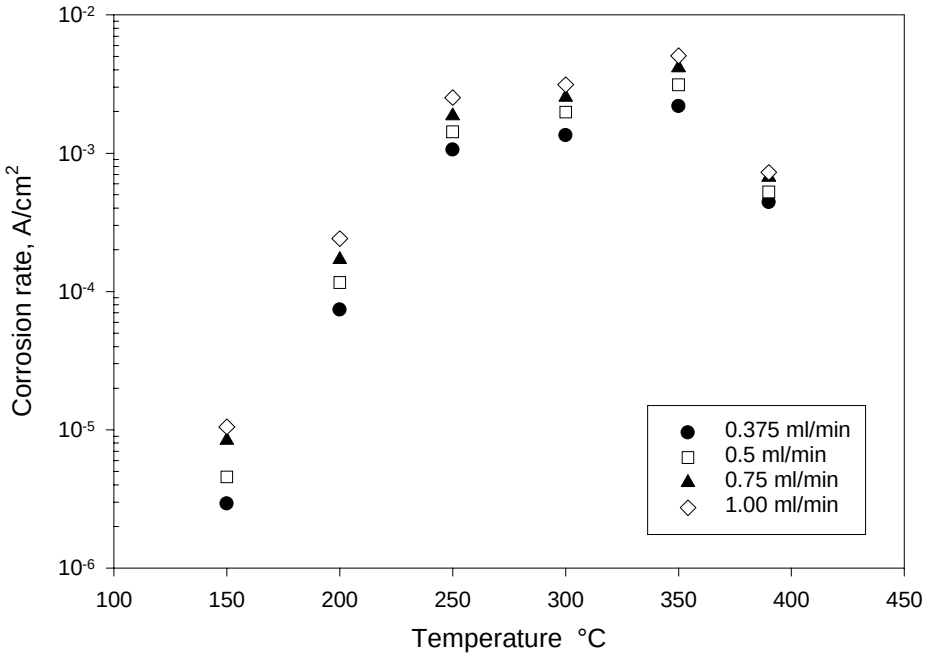


(a)



(b)

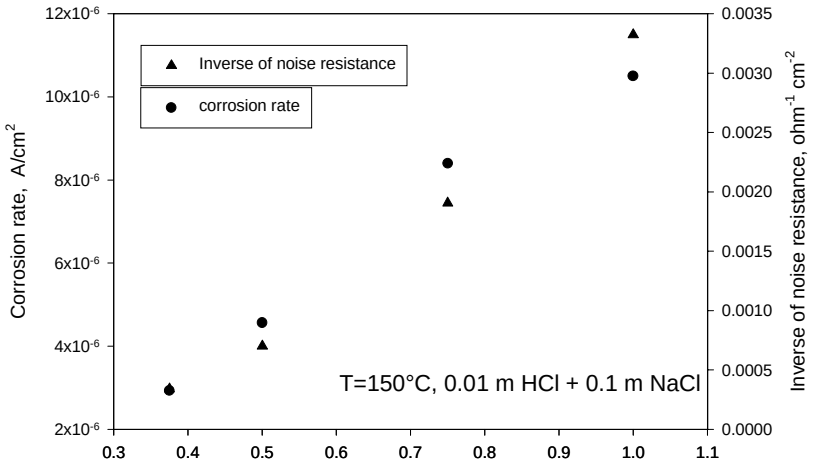
SEM micrographs: (a) sample tested at 150°C for 168 hours; (b) sample tested at 390°C for 1 hour.

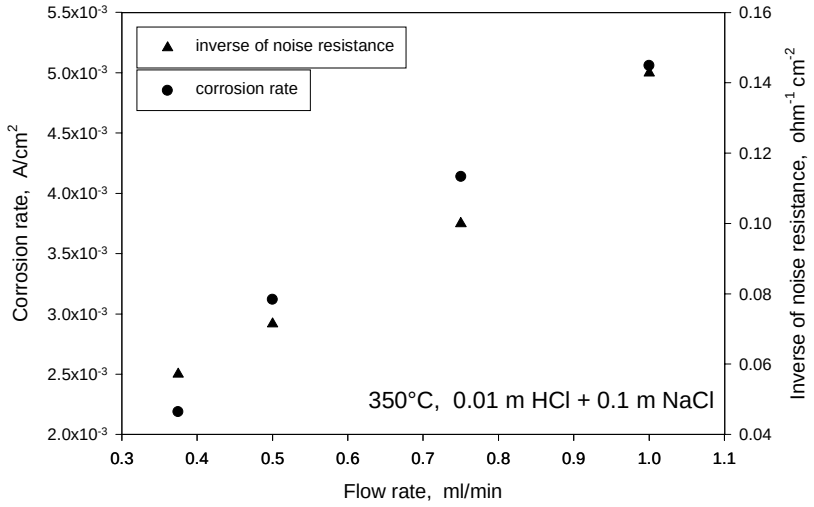


Corrosion rate (current) evaluated using mass loss tests is plotted as a function of temperature.

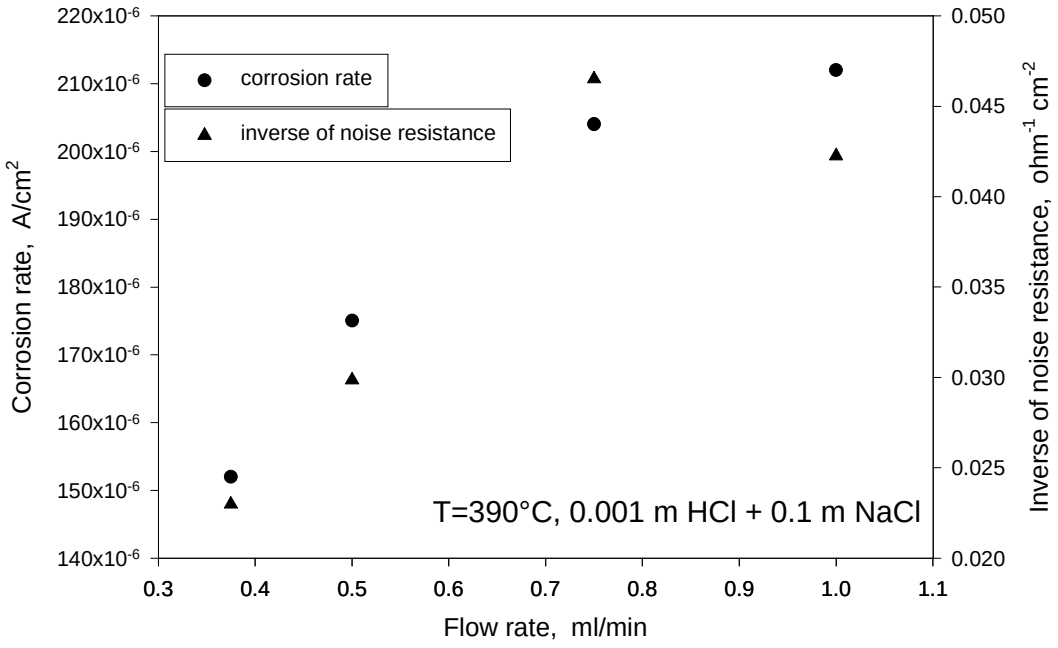
Summary of the results of SEM and EDAX studies. The diameter was measured directly under SEM. The ratio of elements was obtained from EDAX analysis.

		Average wire diameter	Cr : Fe	Cr: Ni	Fe : Ni
(a)	uncorroded	490 ± 3 μm	0.46 : 1	4.7 : 1	10.0 : 1
(b)	150°C (1 week)	480 ± 5 μm	15.5 : 1	48.7 : 1	3.1 : 1
(c)	390°C (1 h)	350 ± 5 μm	8.6 : 1	19.9 : 1	2.3 : 1

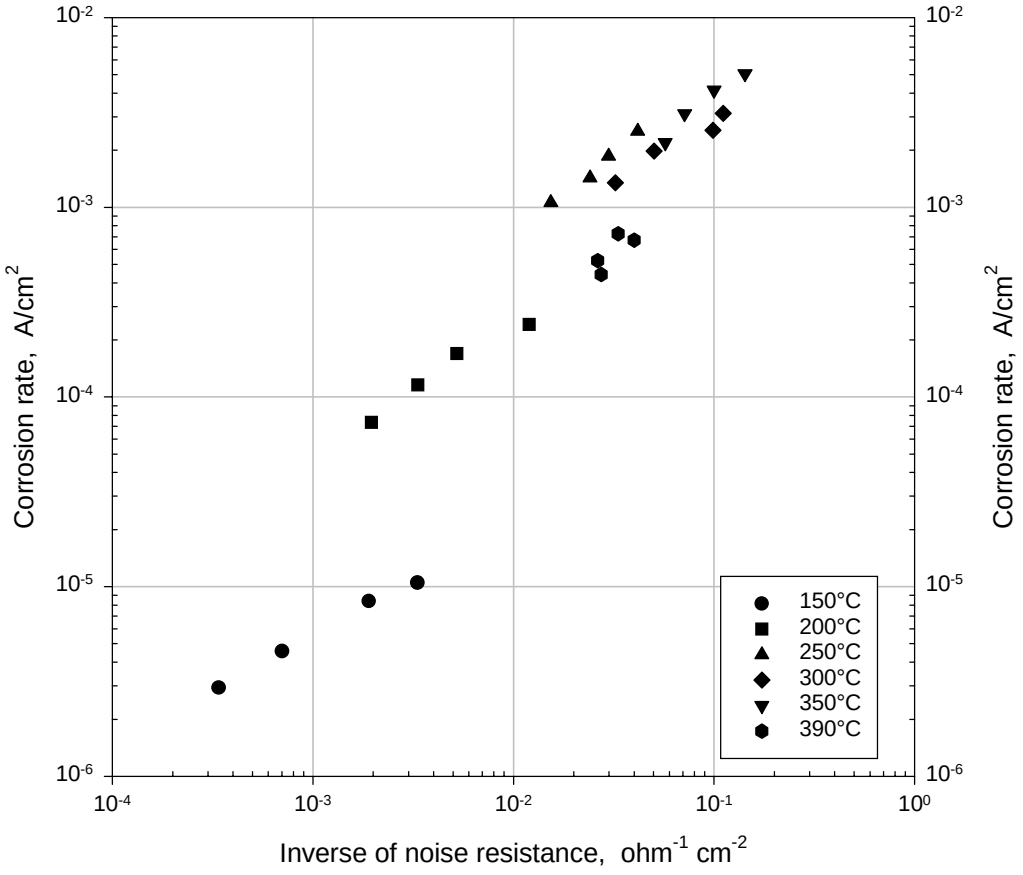




Inverse noise resistance and corrosion rate are plotted as functions of flow rate.



Inverse noise resistance and corrosion rate as functions of flow rate for supercritical conditions.



Relation between corrosion rate and inverse noise resistance.

Stern-Geary Relationship

- Provides relationship between the polarization resistance and the corrosion current.
- Faraday's law provides the relationship between the corrosion current and the corrosion rate (rate of mass loss).
- Assume that $R_n = R_p$.

$$\mathbf{I_{corr} = B/R_p}$$

$$\mathbf{B = b_a b_c / 2.303(b_a + b_c)}$$

b_a and b_c are respectively Tafel parameters for the anodic and cathodic reactions.

- Stern - Geary relationship does not take into account mass transfer effects correctly. We have modified the theory to include mass transport effects, yielding

$$\frac{1}{R_p} = I_{corr}\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial E}\right)_{E=E_{corr}} + I_{corr}\frac{2.303(b_a+b_c)}{b_a b_c} - I_{corr}^2\frac{2.303}{b_c I_{l,c}}$$

where

- α is the fraction of the surface upon which the anodic reaction occurs
- $I_{l,c}$ is the mass transfer limited cathodic current.

- Limiting cases

1) If the cathodic reaction is charge transfer controlled, i.e. $I_{l,c} >> I_{corr}$,

$$\frac{1}{R_p} = I_{corr} \frac{2.303(b_a + b_c)}{b_a b_c}$$

which is exactly the Stern-Geary relationship.

2) If, however, the cathodic reaction is purely mass transport controlled, i.e. $I_{corr} = I_{l,c}$,

$$\frac{1}{R_p} = I_{corr} \frac{2.303}{b_a}$$

For both above cases, the ratio of R_p to I_{corr} does not depend on flow rate.

3) If the entire surface of the electrode is in passive state and the anodic current is a constant with respect to potential:

$$\frac{1}{R_p} = I_{corr} \frac{2.303}{b_c}$$

Stern Geary constant, B* (I_{corr}=B*/R_n), evaluated via ENA and B {B=$b_a b_c/(b_a+b_c)$} evaluated via polarization measurements.

Temperature °C	B* (ENA), volts	b_c, volts	b_a, volts	B (polarization), volts
150	0.007	0.07	0.17	0.022
200	0.02	0.17	0.19	0.039
250	0.07	0.60	0.21	0.068
300	0.04	0.40	0.23	0.063
350	0.045	No data	No data	No data
390	0.008	No data	No data	No data

SUMMARY

In-situ potentiometric measurement of pH

Advanced electrodes and sensors for in-situ potentiometric monitoring of pH in high subcritical and supercritical aqueous solutions were developed. An experimental flow-through thermocell was fabricated to test the flow-through reference electrode, the flow-through hydrogen electrode, and the flow-through YSZ pH sensor.

An approach was developed for experimentally evaluating the association constant of 1-1 aqueous electrolytes using a flow-through electrochemical thermocell. The thermocell consists of a flow-through Pt(H_2) electrode and a flow-through external reference electrode. The viability of this method is verified using the previously obtained emf data for aqueous HCl solutions at temperatures from 300 to 360°C and pressures of 27.5 and 33.8 MPa. The derived values of the association constant of HCl(aq) are in good agreement with literature data. pH values of the 0.01 and 0.001 mol kg^{-1} aqueous HCl solution are determined at temperatures and pressures of interest.

In-situ measurement of corrosion rate via EES

An Electrochemical Emission Spectroscopic sensor has been developed for in-situ measurement of corrosion rate in high subcritical and supercritical conditions. The sensor was evaluated in a contamination-free, flow-through hydrothermal electrochemical cell. We found that:

1) By measuring potential and coupling current of a pair of identical metal electrodes, the corrosion rate can be evaluated quantitatively.
2) The corrosion rate of Type 304 SS is a function of temperature and flow rate and that the corrosion rate passes a maximum at 350°C as predicted by theory.
3) The proportionality between the inverse noise resistance and corrosion rate evaluated from mass loss tests exists over a wide range of conditions, i.e. temperature from 150 to 390°C and flow rate from 0.375 to 1.00 ml/min.
4) The Stern-Geary relationship is valid for temperatures higher than 150°C and that the Stern-Geary constant can be evaluated from the proportionality between the corrosion rate and the inverse noise resistance.
5) More information on electrochemical parameters is needed to clarify the mechanisms of corrosion in subcritical and supercritical aqueous environments, which is a topic for our future work.