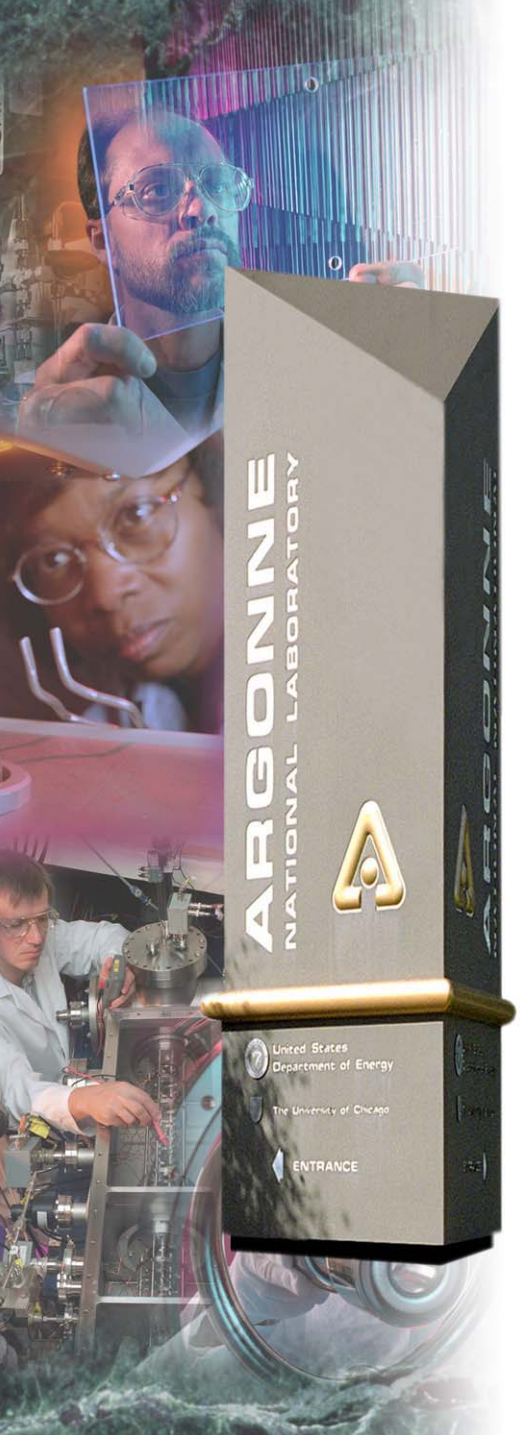


Degradation of RPV Boundary Components in Concentrated Boric Acid Solutions

Tasks 4:
Measurement of ECP of A600, A182 & A533B in Concentrated Boric Acid Solutions

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

Project Goals *(TASK #4)*

Measurement* of ECP and conduct of PD-tests on A600, A308 and A533Gr.B materials to define the specific environmental conditions for corrosion/wastage test in Task#3.

I. Establish the test facilities for various tests

II. ECP measurements & PD tests

a) High T (100 to 316°C) and P (1,300-1,800 psi)

b) Ambient environment, P = 1 atm and T = 100°C, and

c) Molten H-B-O conditions

Note*

ECP = electrochemical corrosion potential

PD-test = potentiodynamic (anodic) polarization test

Team/Resources

- **Team members**
  K. Natesan, J.-H. Park, O. K. Chopra, R. Clark, E. Listwan, W. Shack, and W. Soppet

- **Resources allocated to this project**
  - Wastage-test: Installed/assembled ANL ET(212) G-137
  - Hi-T&P-test: Installed/assembled ANL ET(212) G-137
  - PD-test: Installed/assembled ANL ET(212) E-214L
  - Molten-test: Installed/assembled ANL ET(212) E-214L
  - Samples fabricated by ANL Central Shop (212 and 372)
  - X-ray crystallography by ANL Anal. Lab (205)
  - Bulk chem. anal by Conam Kawin Inc., Glendale Hts, IL

Phases present in the B-O-H system

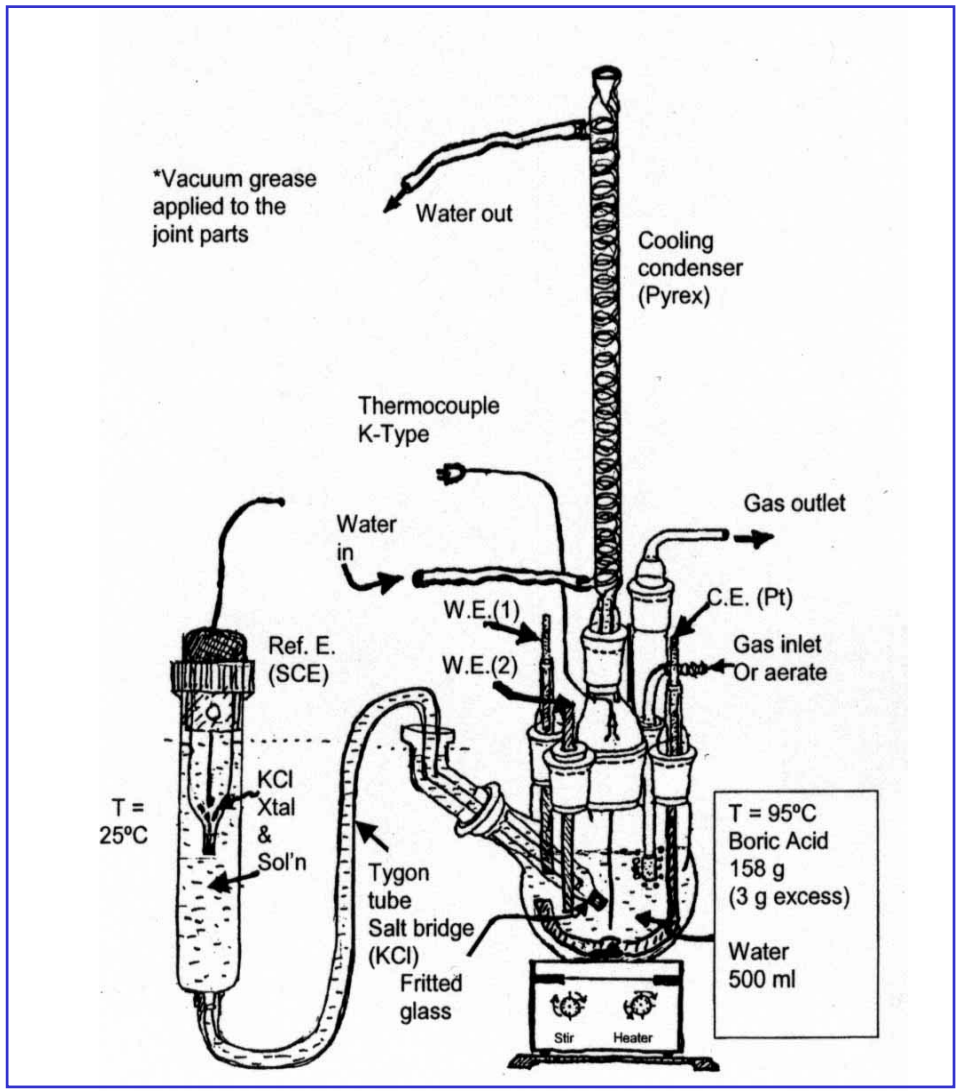
Phases	T (°C)	Reaction with H_2O
H_3BO_3 $B(OH)_3$	169 (tr)	$B(OH)_3 + H_2O = [B(OH)_4]^- + H^+$
HBO_2	236(mp) 300(tr)	$B(OH)_3 - H_2O = HBO_2$
B_2O_3	450(mp)	$HBO_2 - ½ H_2O = ½ B_2O_3$

ECP measurement at T ≈100°C at P = 1 atm in the BA solution

Experimental Electrochemical Cell for ECP Measurements & Potentiodynamic test

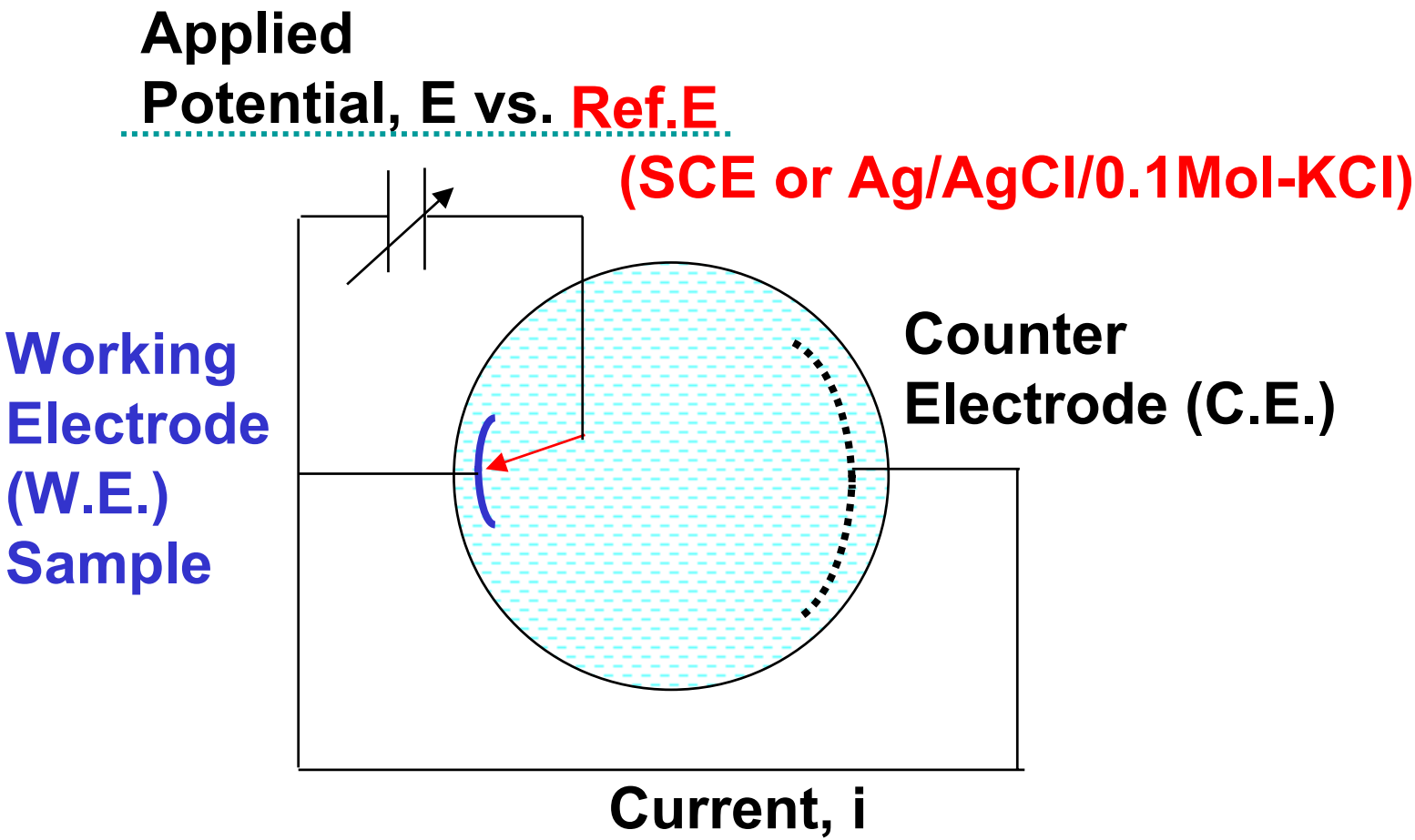
Tests were performed in BA solution at ≈100°C

- **Measured ECPs and performed PD-test**
  -Specimen (bar shape)
  -Sol'n stirred (magnetic stirrer)
- **PH measurement on the Sat'd BA solution at rt to 100°C**
- ***PH measured in (de/ae)rated BA solutions**



Electrochemical Cell for ECP Measurements & Potentiodynamic test

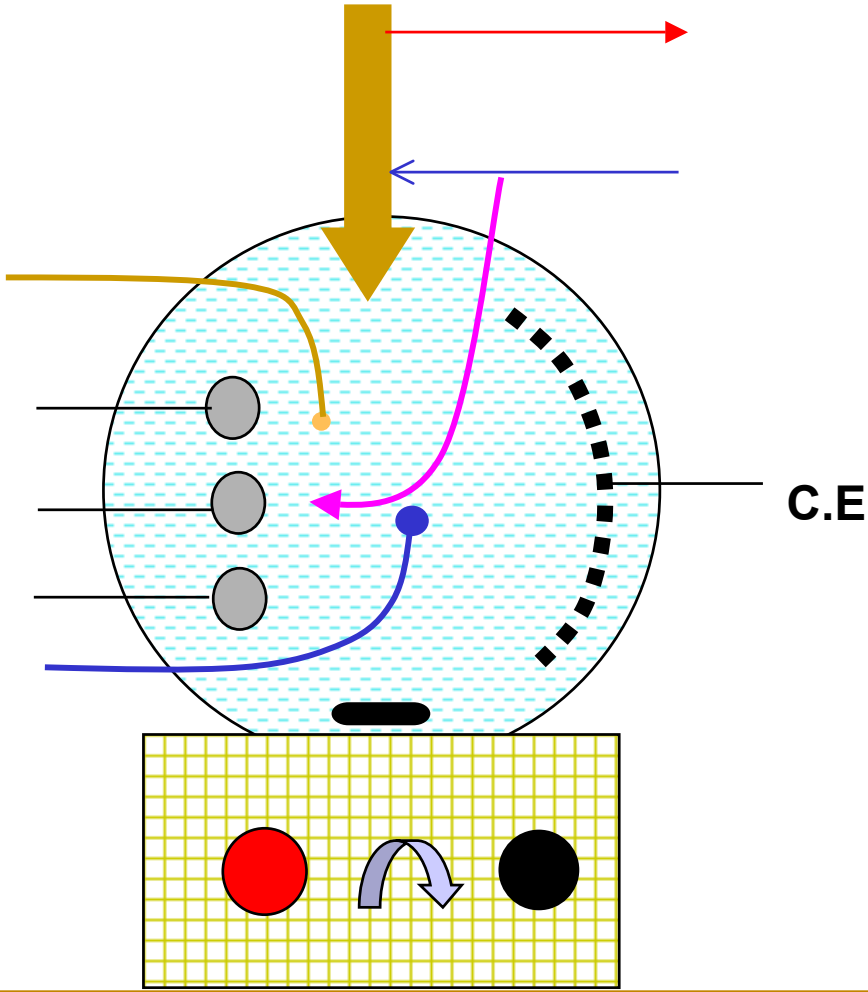
3-electrodes cell: W.E.(sample), Ref. E., and C. E. (Pt)



Details of the cell

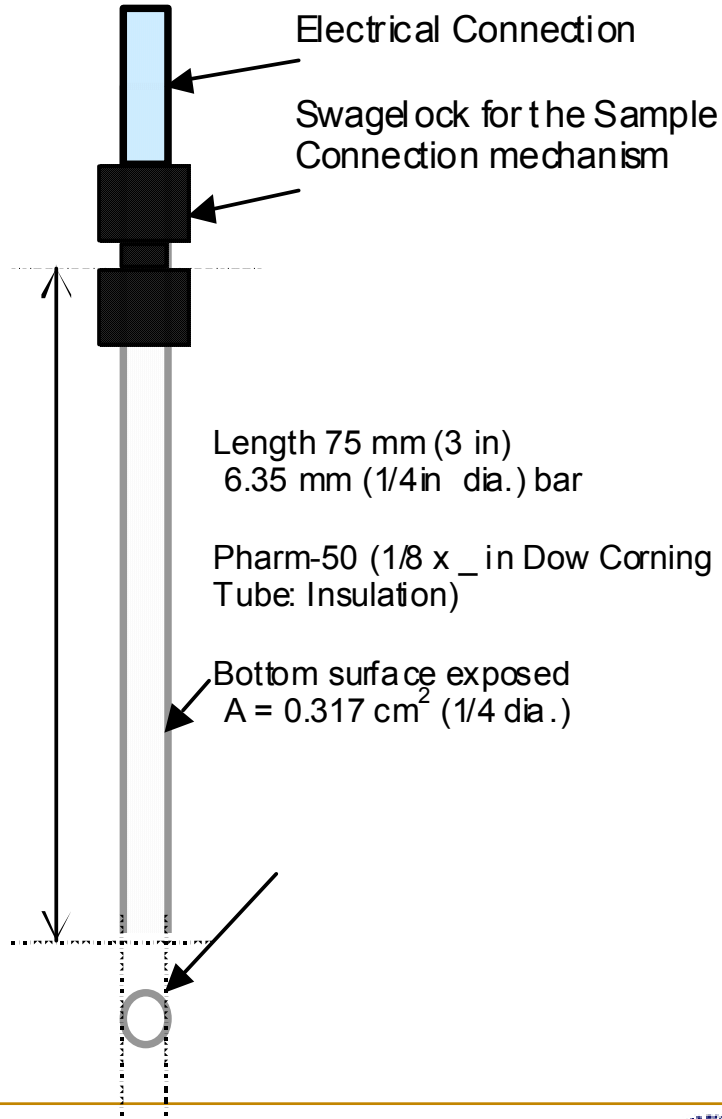
Electrochemical Test Cell (Pyrex) Sat'd BA solution

- W.E.1 (A533B)
- W.E.2 (A600)
- W.E.3 (SS-308)
- Ref. E. (SCE)
- C.E. (Pt)
- pH-probe
- T.C. (K-type)
- (De/ae)ration
- Stirrer (magnetic)
- Heating
- Cooling condenser
  Water (in/out)

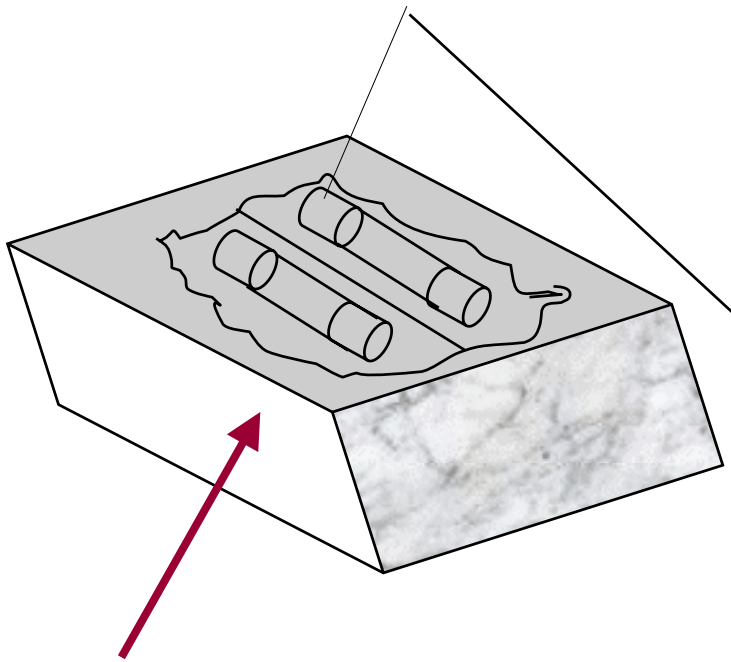


Structure of the working electrodes (which are the specimens)

- **Reference electrode: SCE**
- **Counter electrode (Pt: foil or 20-mil wire)**
- ***Sample bottom ~1mm cut after the PD-test for examination and for the continuation of the test**



Schematic drawing of the E308–16 SMA weld samples overlay on A533Gr B plate



308 SS welding metal

A533Gr B

Heat: A5466-2

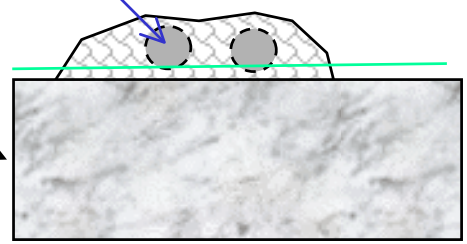
(Midland reactor)

308 SS welding metal

Two ¼“ dia x 3” long

Samples taken 1/16” above the fusion line

A533Gr B: 5¼ ” x 3” x 1”

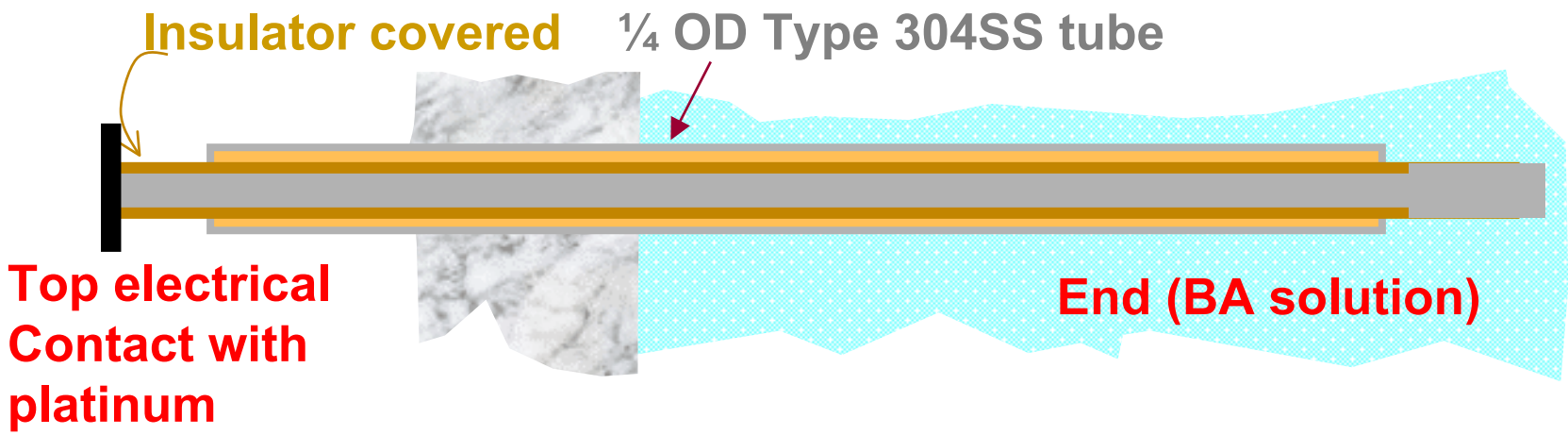


ECP measurement and PD-Test at T up to 316°C at P up to 1800 psi

Hi-T & P test: Structure of Working Electrode-I

- **Working electrodes : Samples A533B, A600, &SS304**

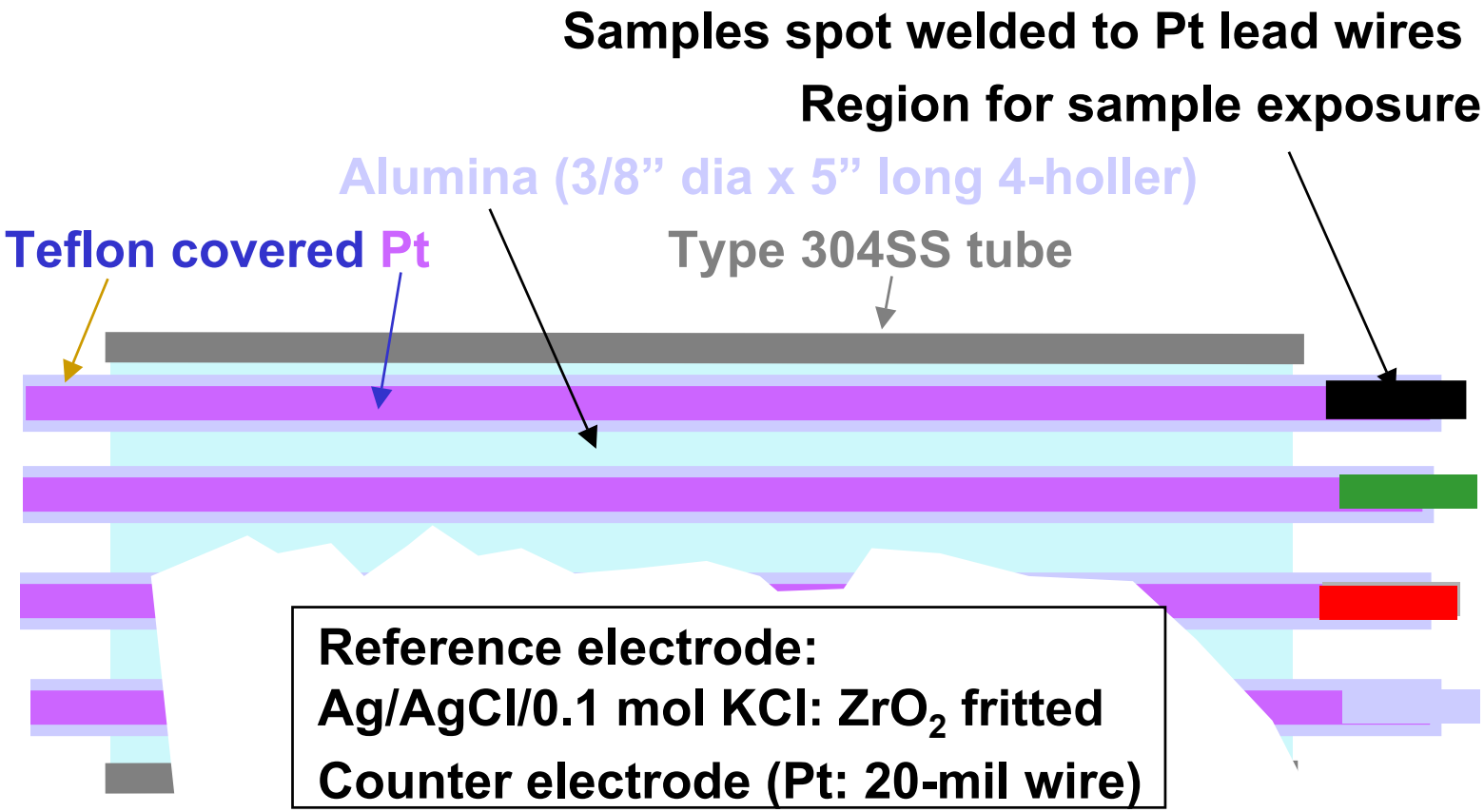
1/8" dia x 5-6" long bar: open at the bottom*



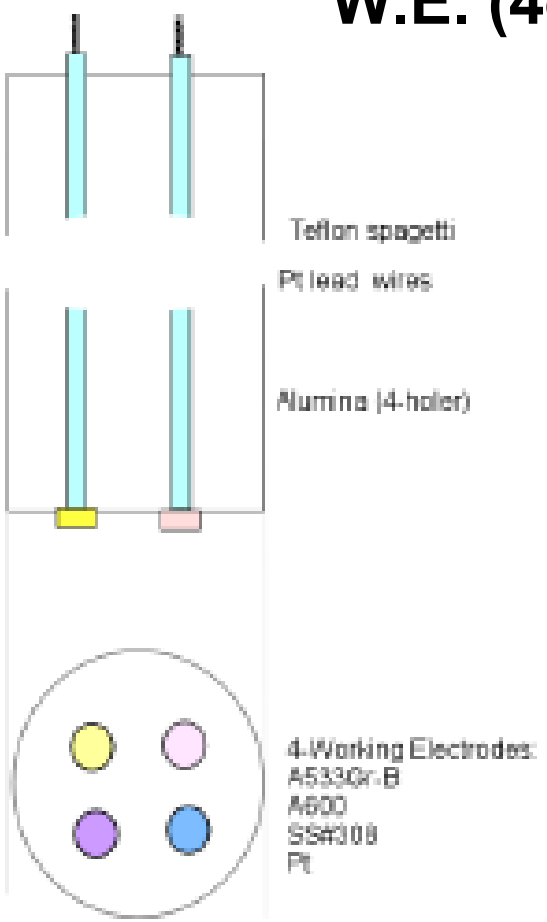
- **Reference electrode: Ag/AgCl/0.1 mol KCl: ZrO_2 fritted tip**
- **Counter electrode (Pt: 20-mil wire)**

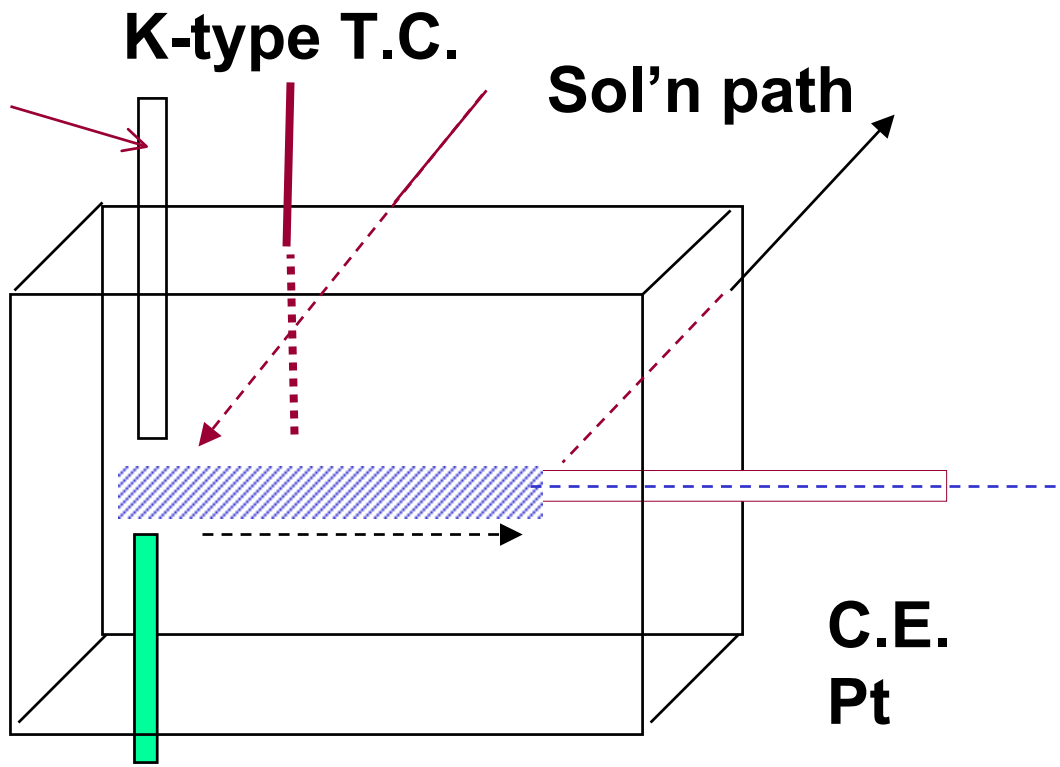
Hi-T & P test: Structure of Working Electrode-II

- **Working electrodes : A533B, A600, SS308 & Pt**



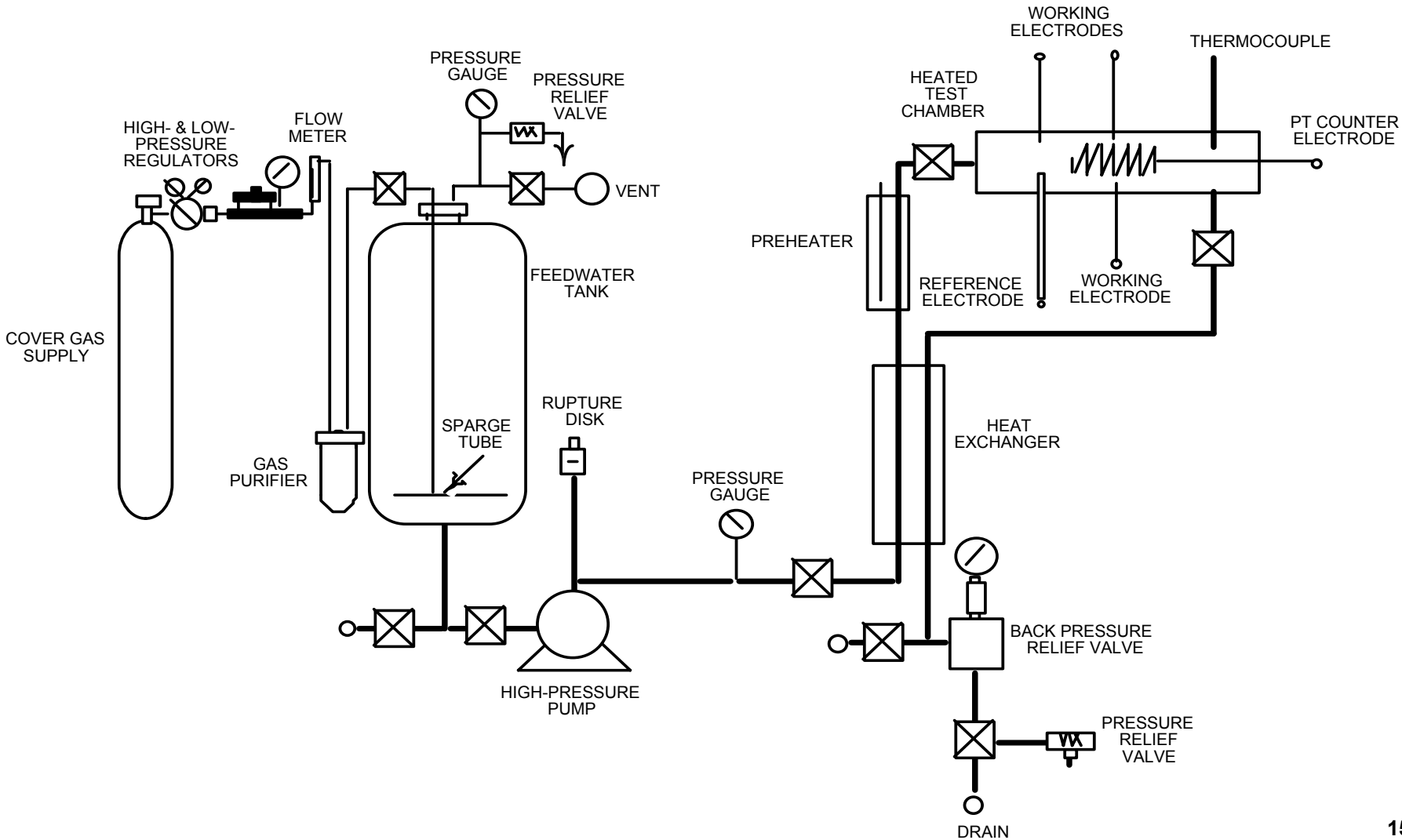
ECP measurement at High T & P



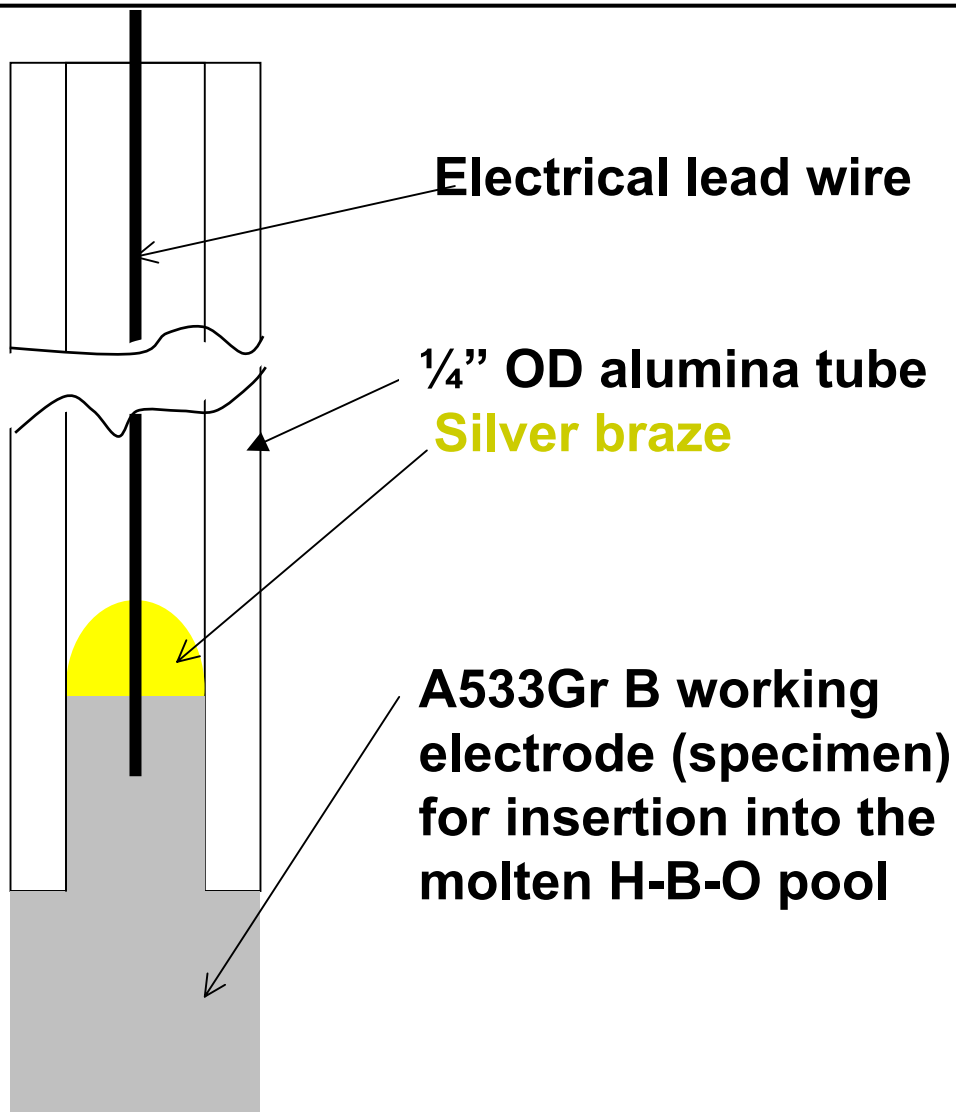


Ref. E
Ag/AgCl-0.1 Mol KCl

Corrosion test facility in High–T & P of BA solutions at T up to 316°C and P up to 1800 psi



Molten H-B-O test: Specimen (Working Electrode)

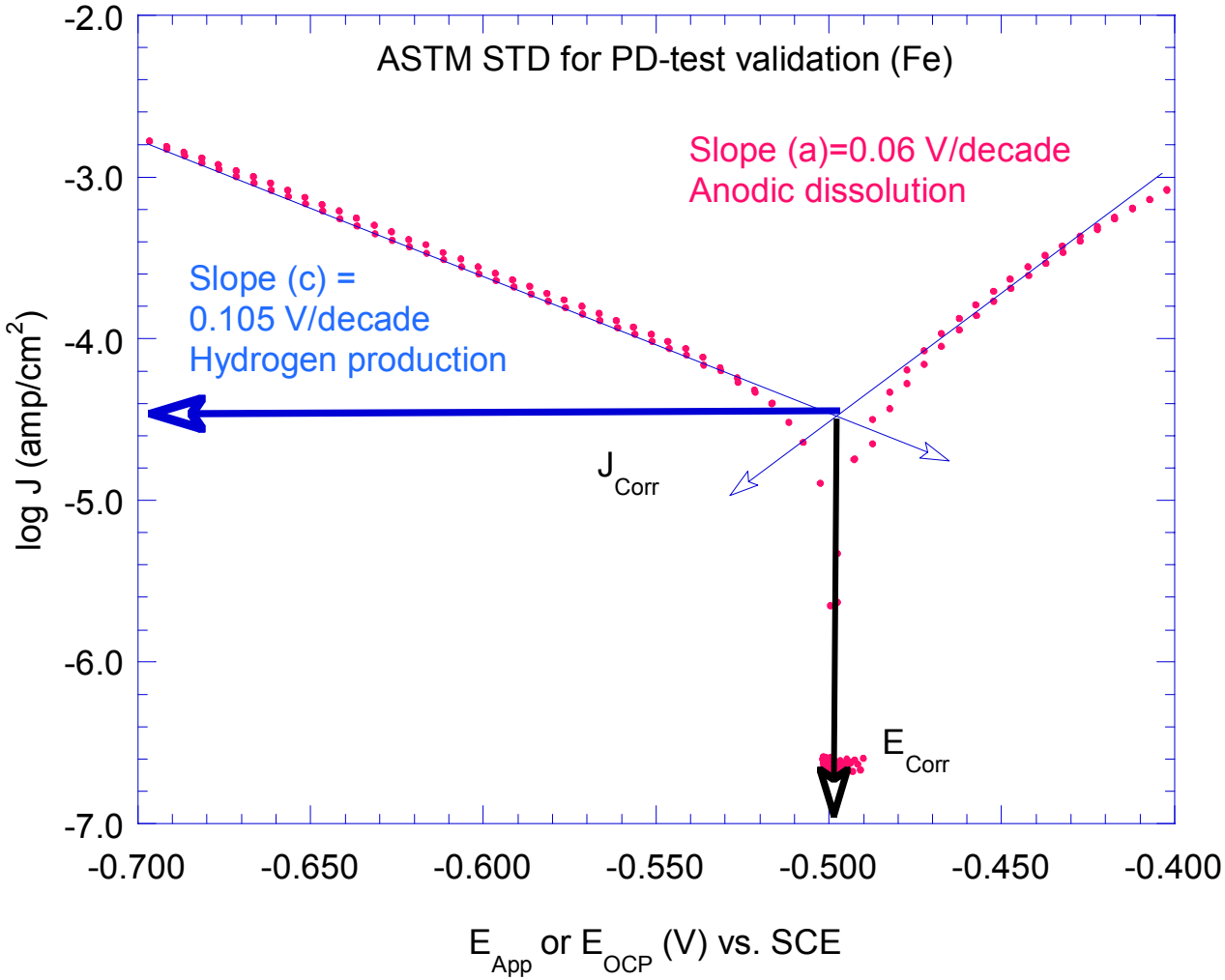


Experimental Procedure

- **Made a solution of BA at 95°C in a 1-liter Pyrex glass test chamber (BA concentration ≈ 153 g)**
- **Bar sample covered with an insulator except at the bottom exposed to the BA solution : ECP measurement & PD-test***
- **Sample was taken out and ~1 mm from the exposed bottom was cut and the remaining specimen was re-exposed for continuing the run**

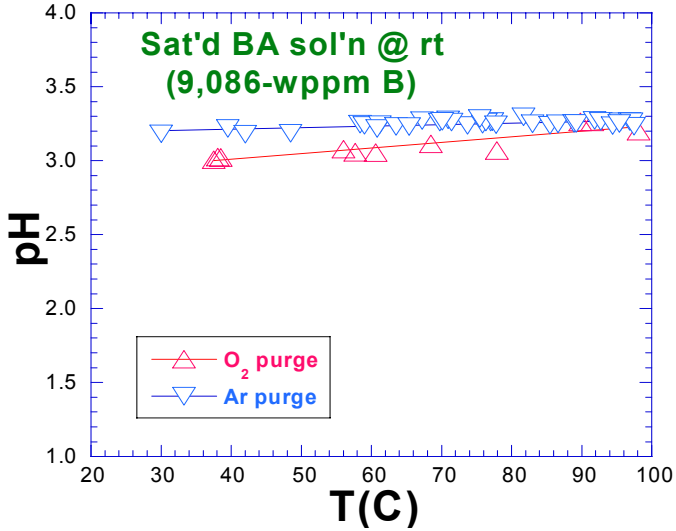
*PD-test was done by following the **ASTM Standard: G5-94**

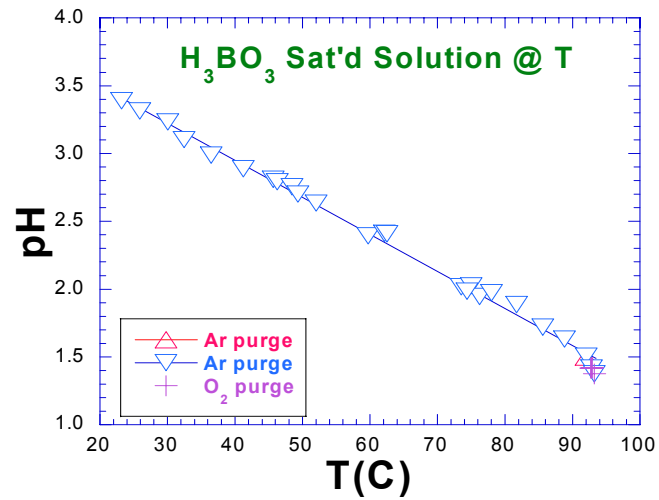
PD-test Calibration of Apparatus with ASTM 5G-94

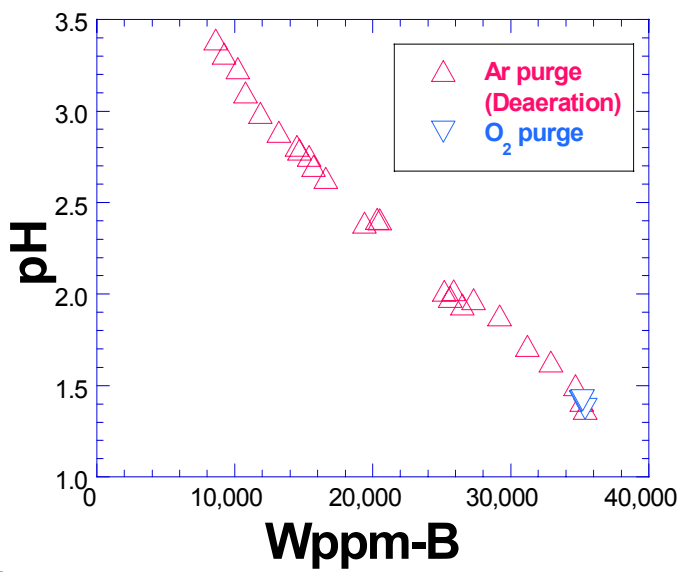


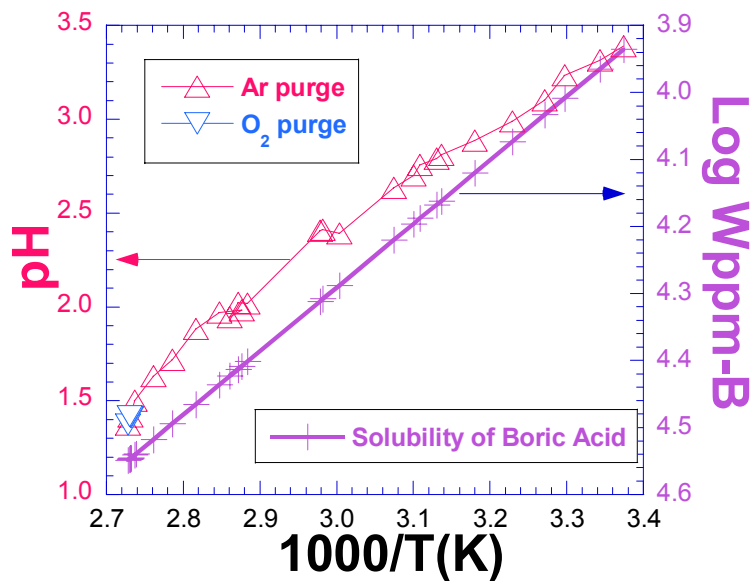
Results on the Task #4 ECP & PD-test

pH for BA & Sat'd BA (rt < T < 100°C)

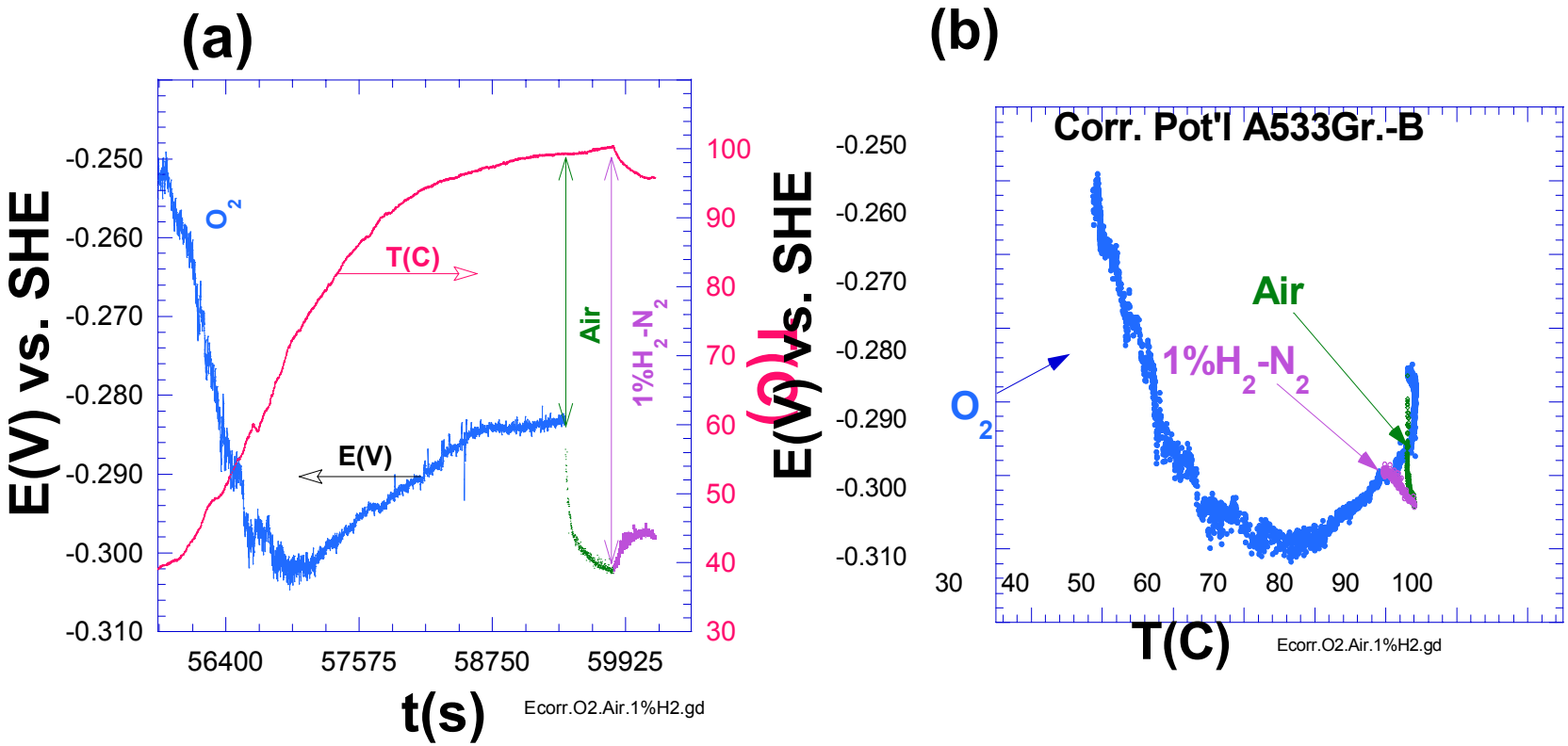








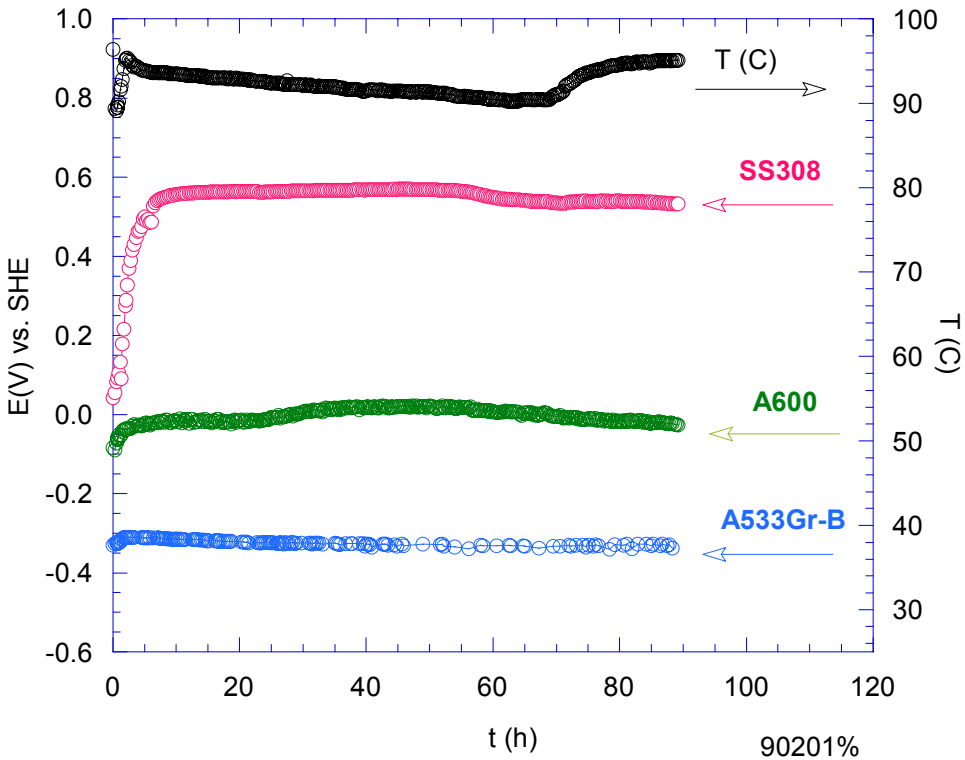
ECP: A533Gr B in the SBA solution



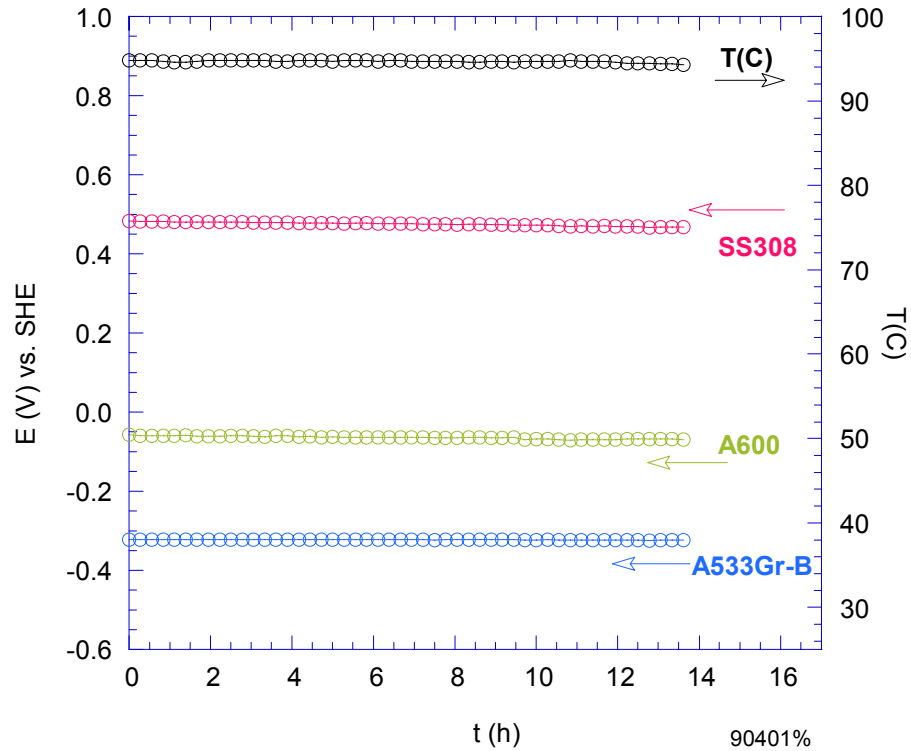
(a) E & T vs. t

(b) E vs. T

E(V) vs. t in the Sat'd BA sol'n @97.5°C

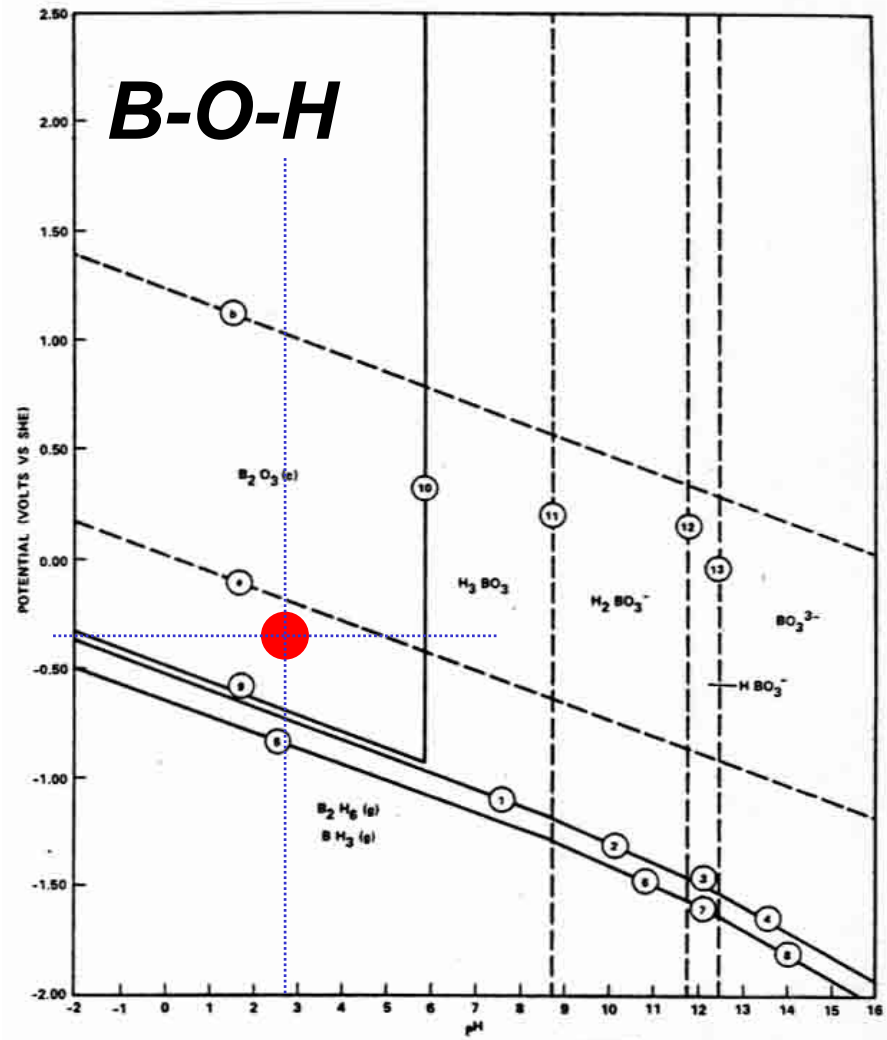


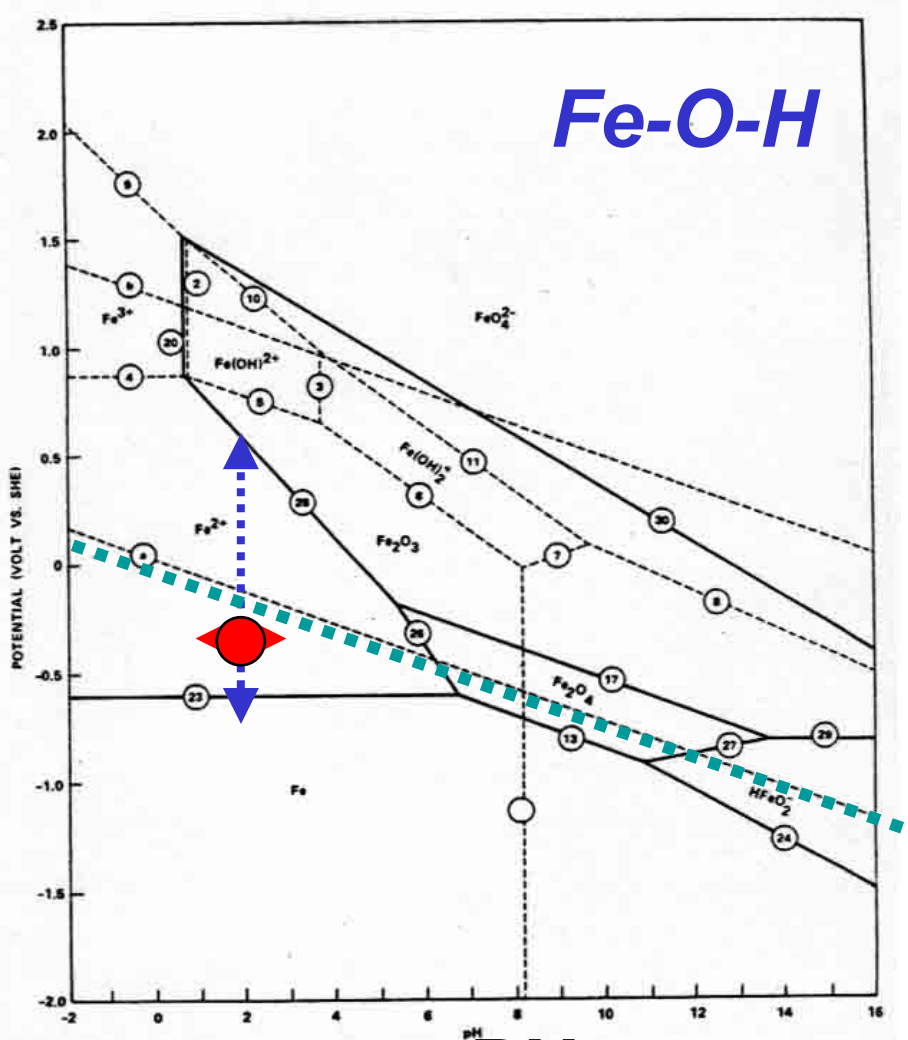
For the initial 90 hrs exposure



After the initial 90 hrs exposure

EH vs. PH for B-O-H and Fe-O-H @ 100°C (Ref. EPRI)





PH →

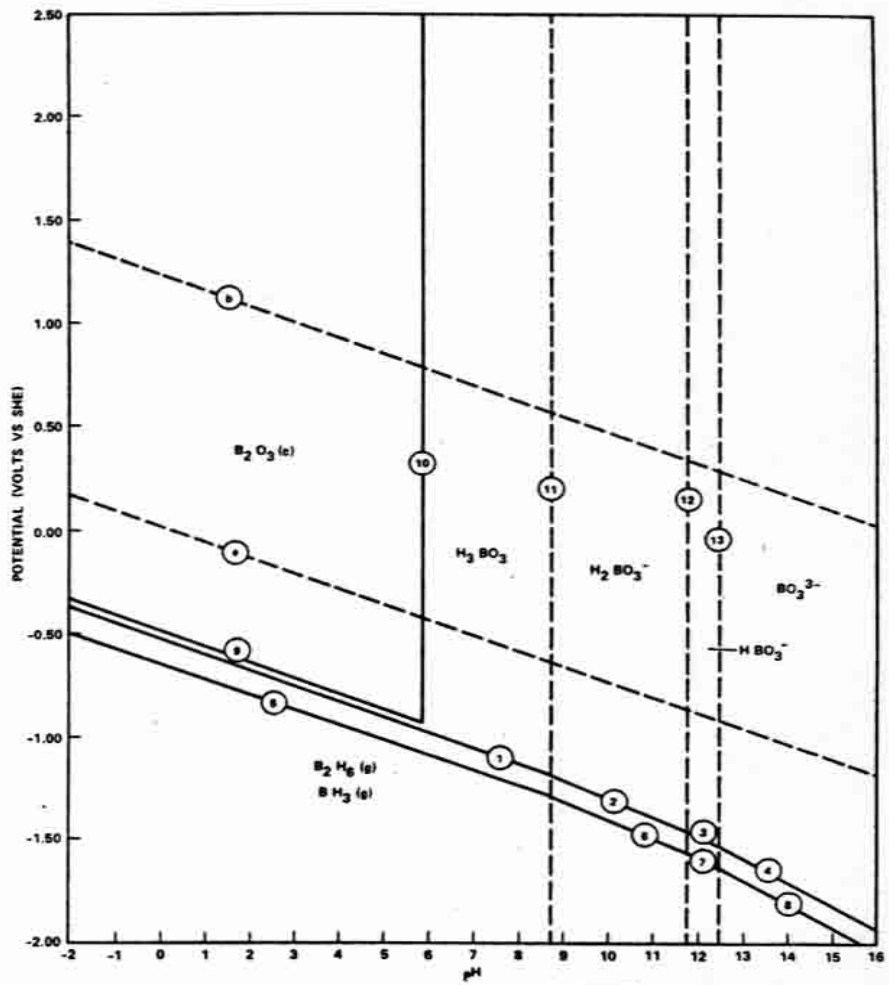
Pioneering Science and Technology

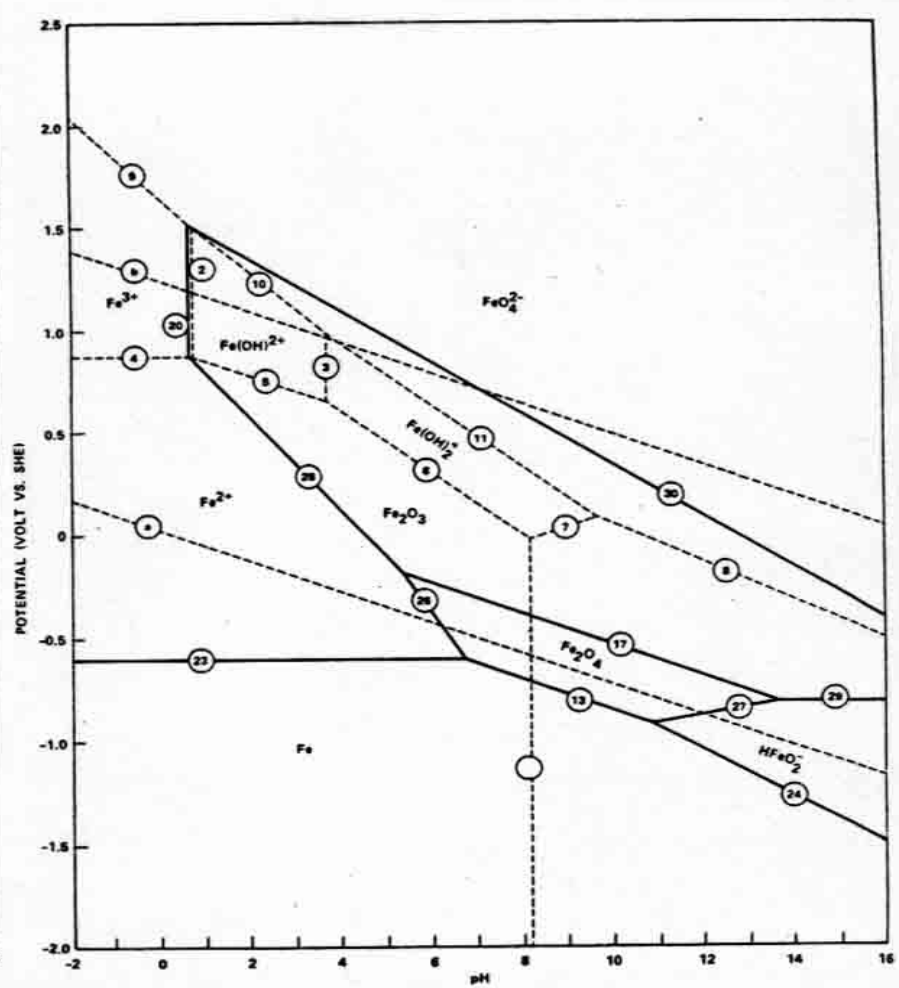
ECP for different alloys in Sat'd BA @95°C

Alloy	ECP (V) vs. SCE (measured) →	ECP (V) vs. SHE (converted)
*A533Gr B	-0.52 to -0.49	-0.35 to -0.30
304 SS	+0.125	+0.314
A600	-0.039	+0.151

*Note: ECP values collected in both aerated and deaerated solutions.

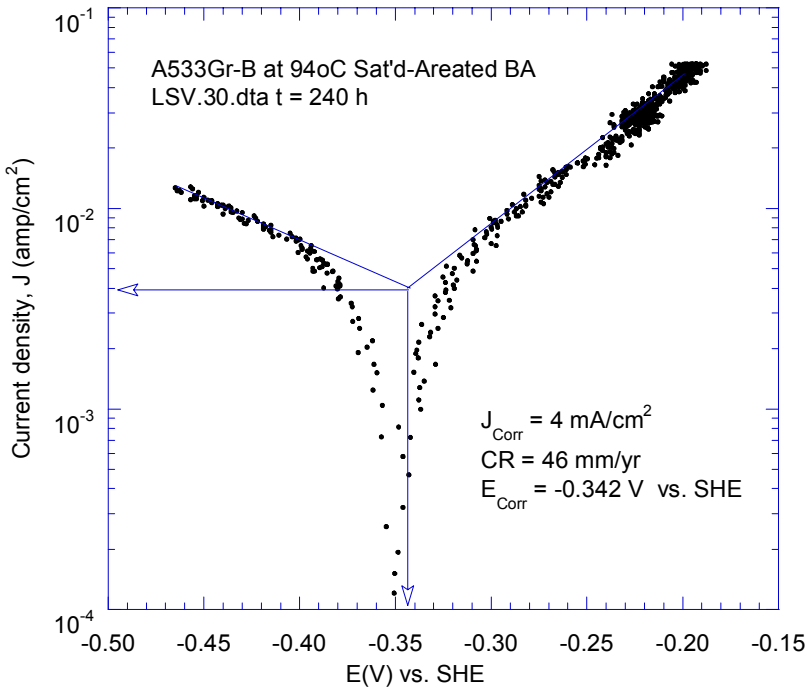
EH vs. PH for B-O-H and Fe-O-H @ 250°C (Ref. EPRI)

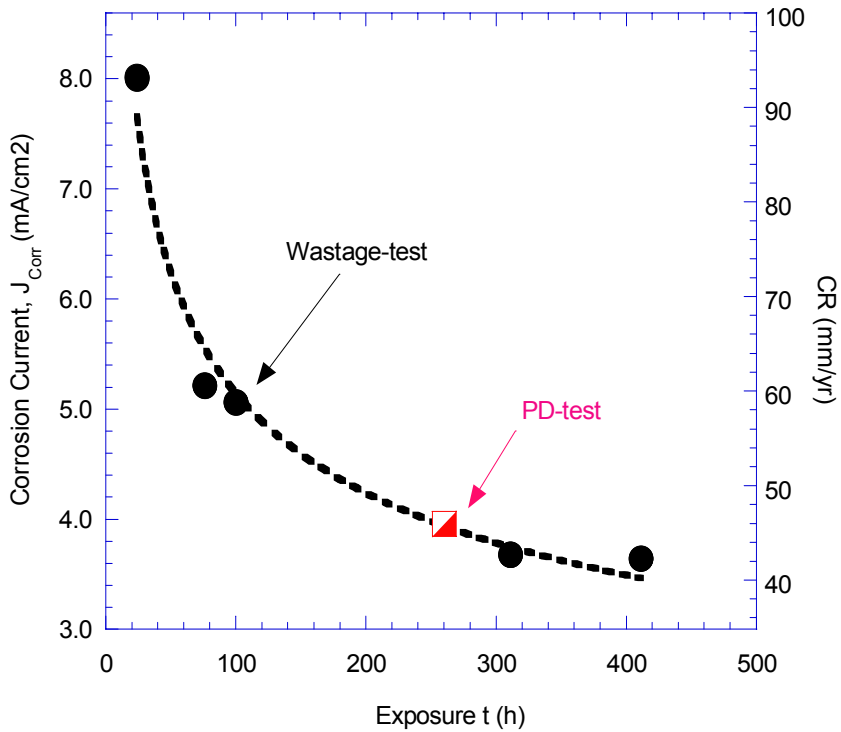




PD-test of A533Gr B in Sat'd BA soln at 97.5°C

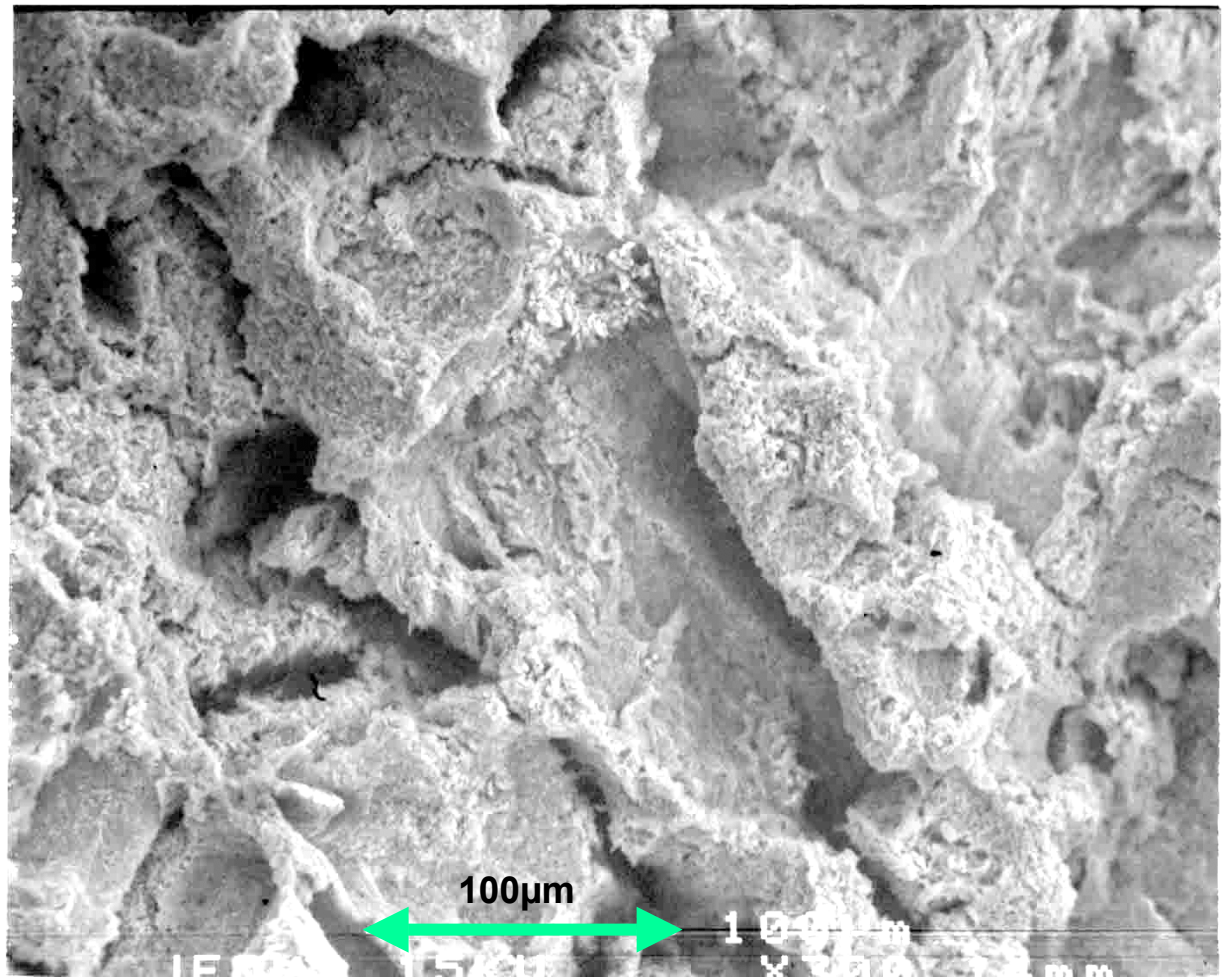
- **42,000-ppm B (Sat'd BA)**





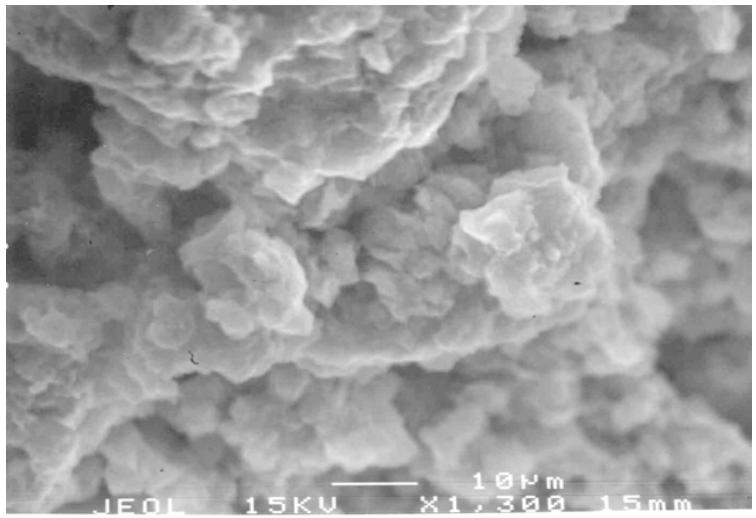
SEM surface view the post PD-test at 95°C of A533Gr B

A533Gr B
Heavily reacted porous dark surface



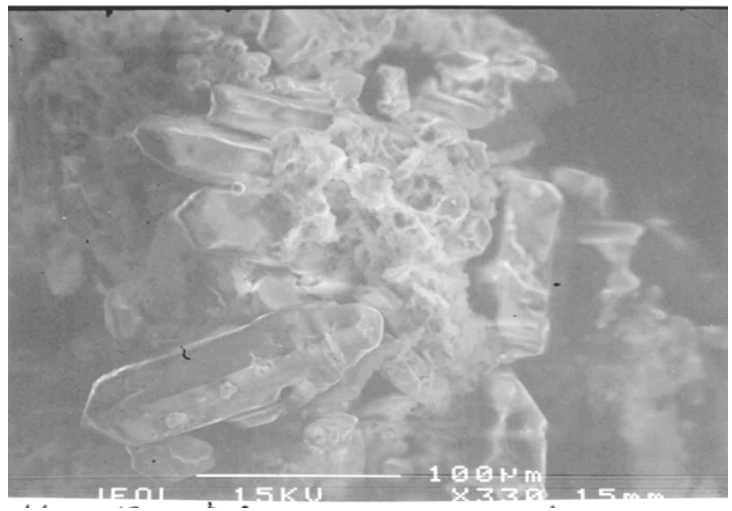
Electrochemical Corrosion Products for the A533Gr B in Sat'd BA at 95°C

(a)



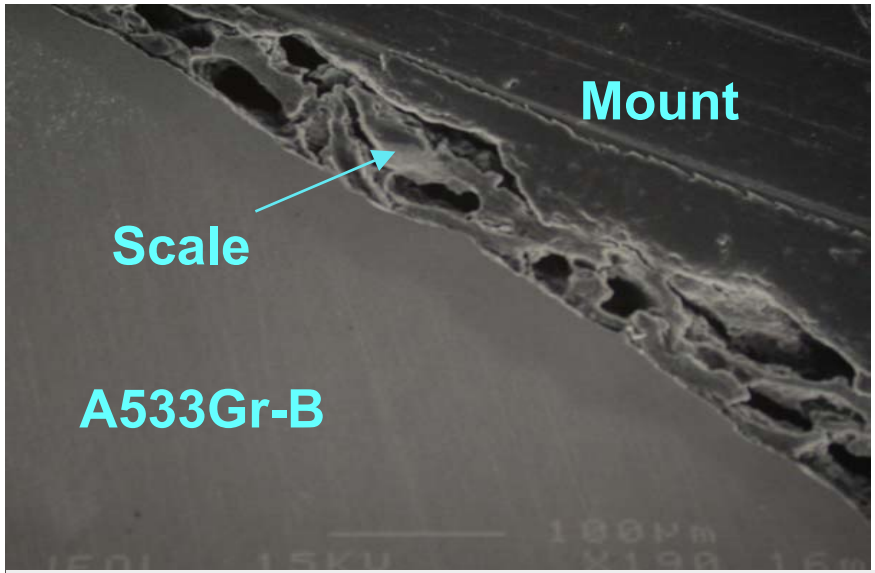
(a) Darker brown color precipitates bottom of the test chamder: X-ray analysis shows iron borate ($FeBO_3$)

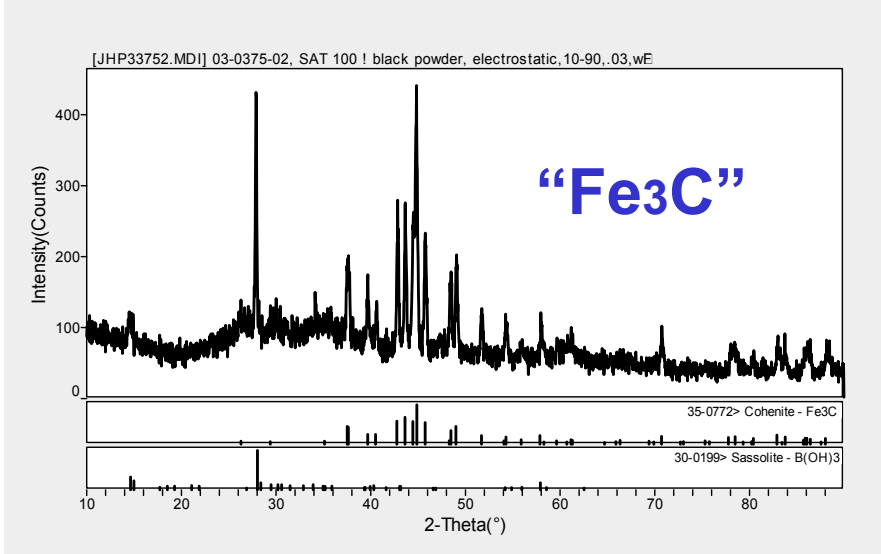
(b)

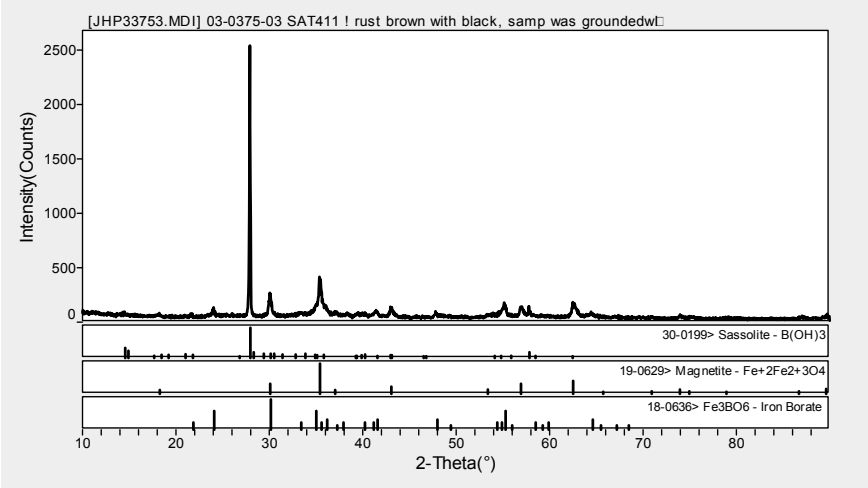


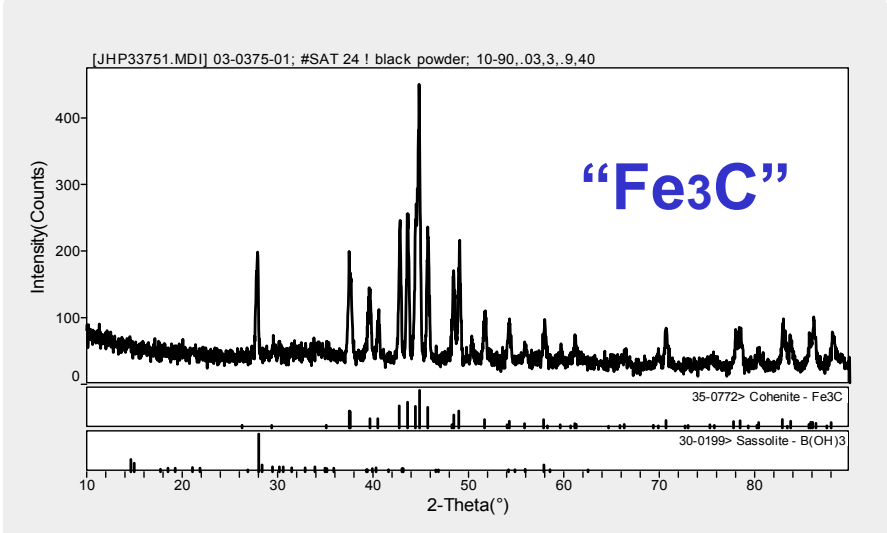
(b) Brown color slurry deposited around the A533B: X-ray diffraction shows boric acid (H_3BO_3)

Wastage product from A533Gr-B in the BA corrosion at 97.5ºC (SEM and X-Ray)



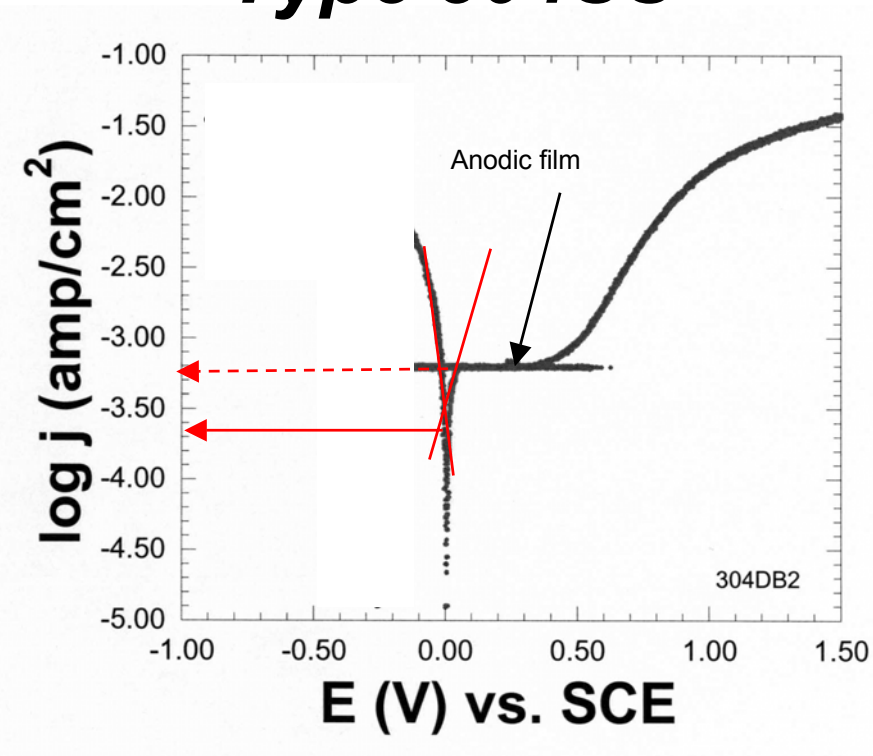




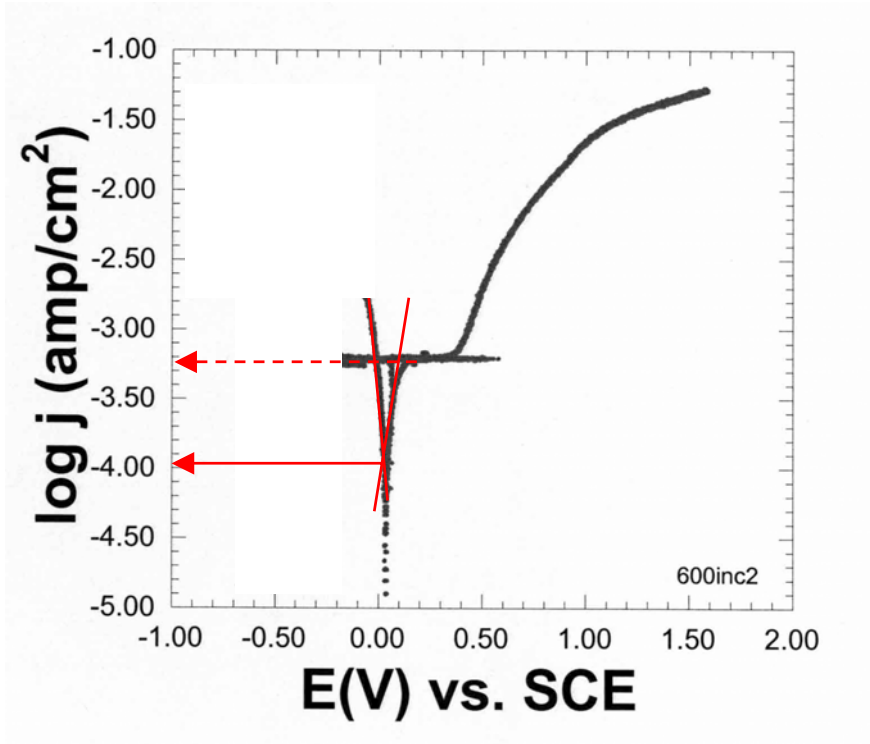


PD-test Curves SS304 and A600 in SBA @95°C

Type 304SS



A600



Corrosion Rate Conversion: $Fe \rightarrow Fe^{2+} + 2e'$

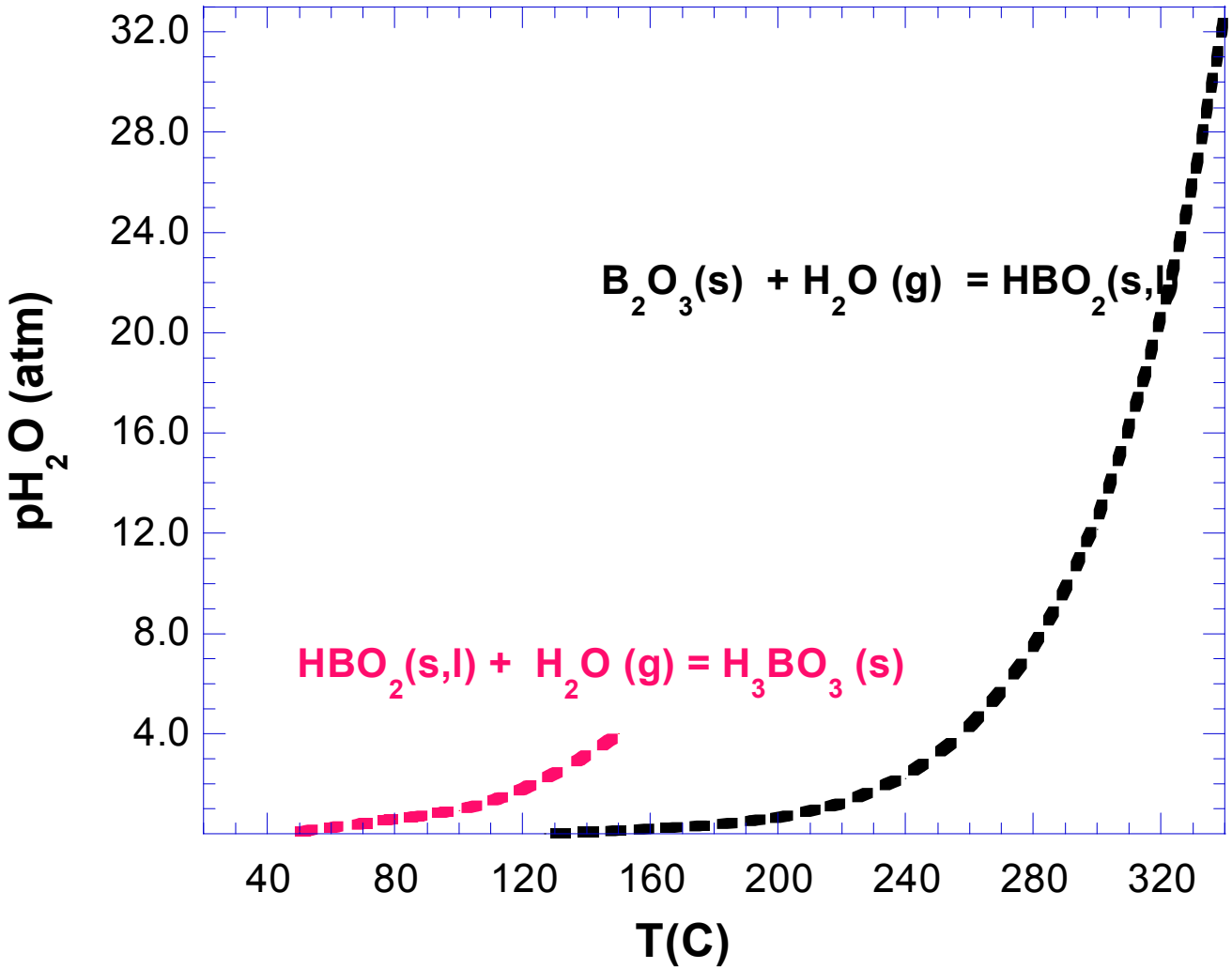
$$CR\ (mm/yr) = [0.306\ nd/M] * J_{Corr}$$

- CR (mm y^{-1}) =Corrosion rate
- J_{corr} (mA cm^{-2}) =Corrosion current
- n = # of electrons freed by the corrosion reaction
- M = atomic mass, d = density

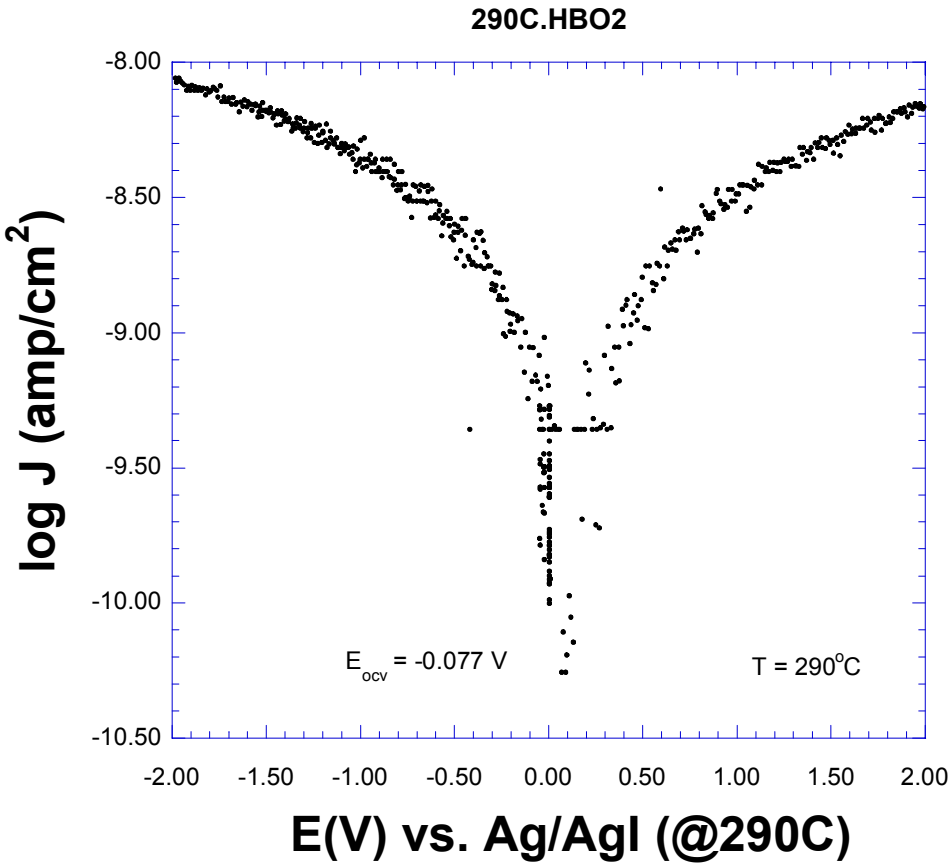
For steel:

- n =2, M = 55.85 g and d = 7.88 g cm^{-3}
- $CR\ (mm/yr) = 11.6 * J_{Corr}$

Equilibrium p_{H2O} vs. T in the H-B-O system



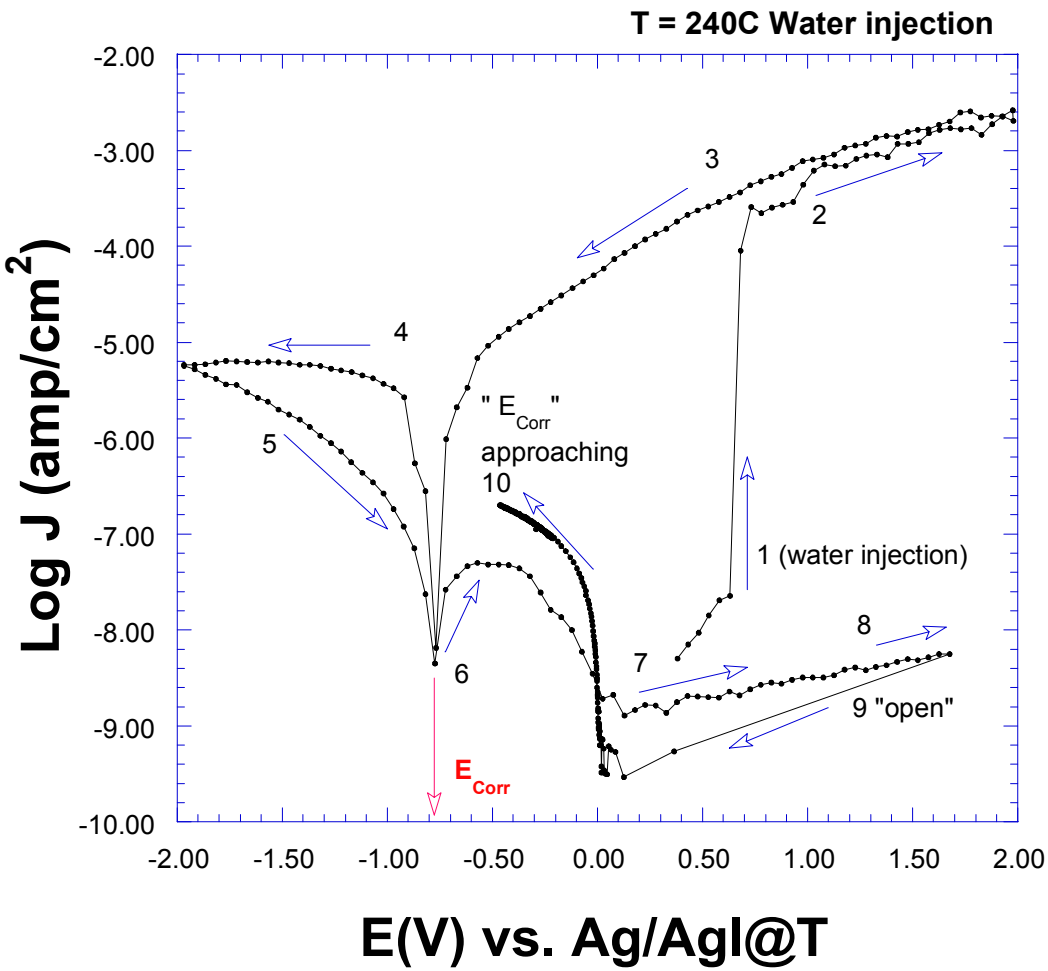
PD-test in the molten $HBO_2 + B_2O_3$



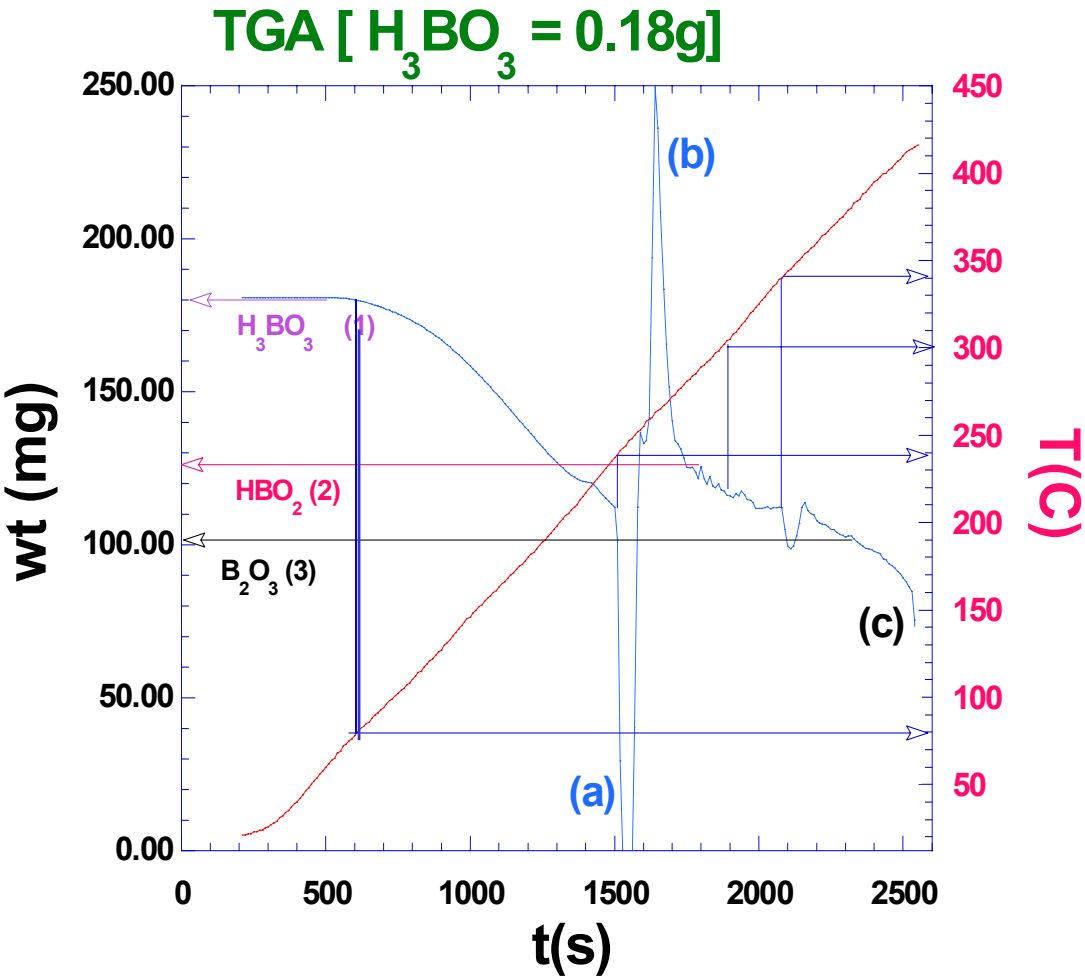
Overnight air equilibrium @ 290ºC.
Measured current density indicates that A533Gr B is highly protective. **Equilibrium pH_2O in the air is 2-3%.**

PD-test in the molten $HBO_2 + B_2O_3$

- ***Adding water into the test cell***



TGA test at 1 atm in air (10ºC/min heating rate)



(a) Bubble forming
(b) Bubble pop out
(c) All B_2O_3 phase

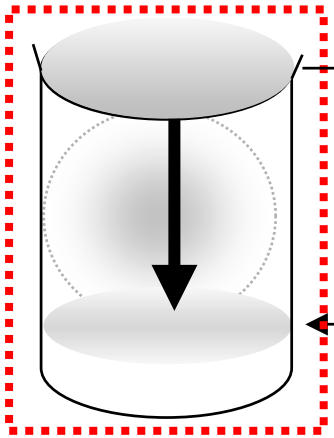
(1) $2H_3BO_3 - 2H_2O = 2HBO_2$

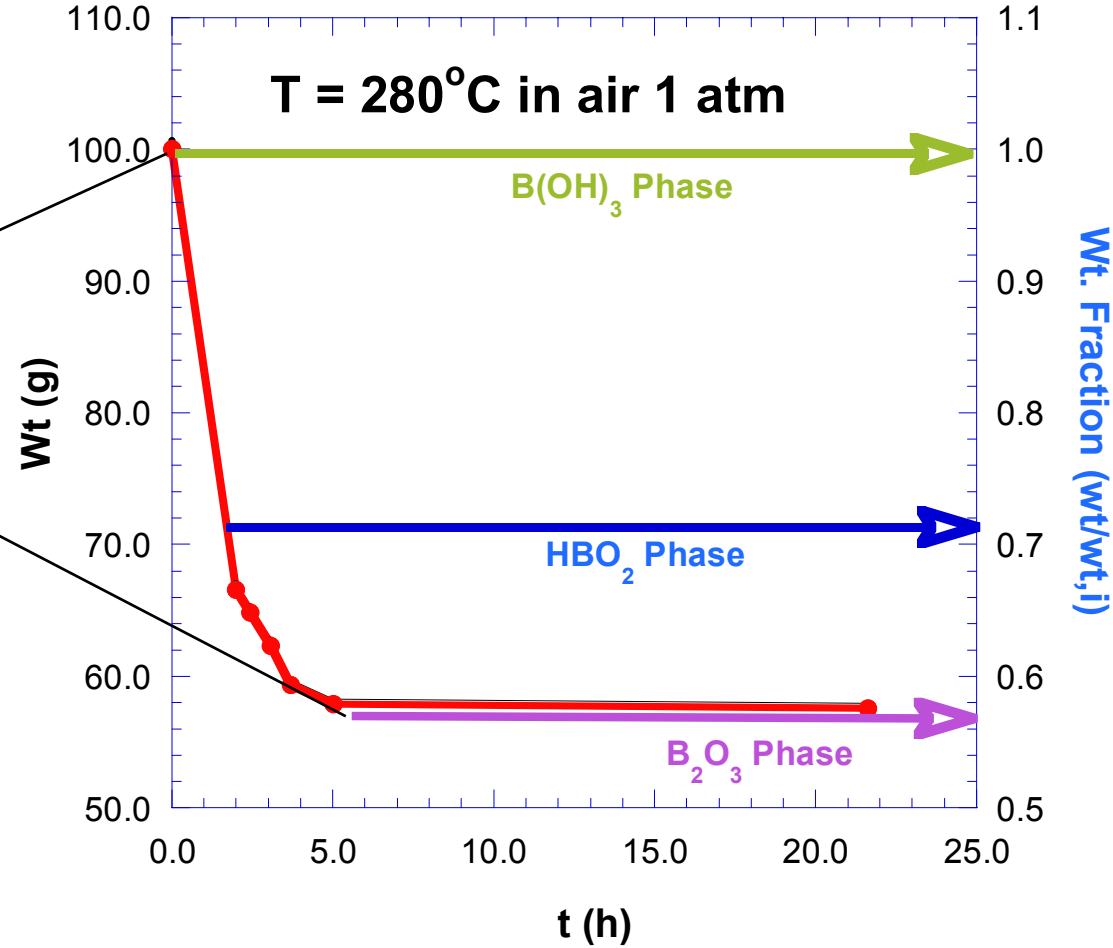
(2) $2HBO_2 - H_2O = B_2O_3$

(3) All B_2O_3 phase

Boric acid heated in air at 280°C

Boric acid turned to snow-ball shape and then glass like transparent boric oxide collected in the bottom of the beaker by loosing water.

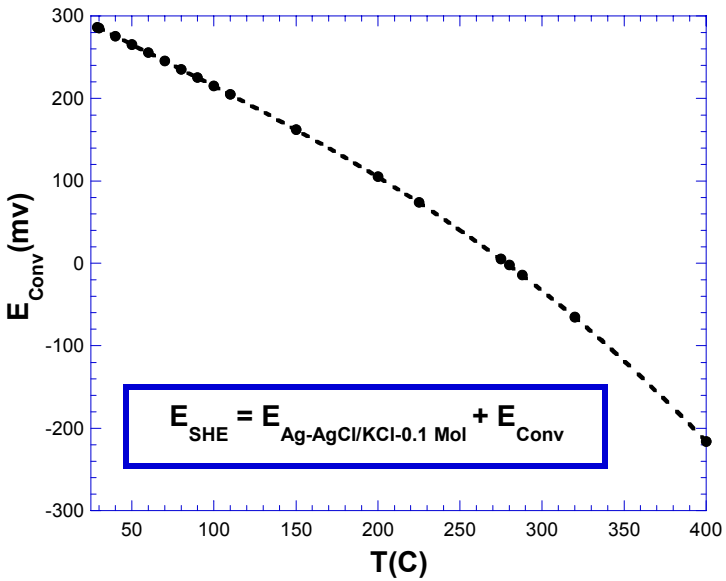


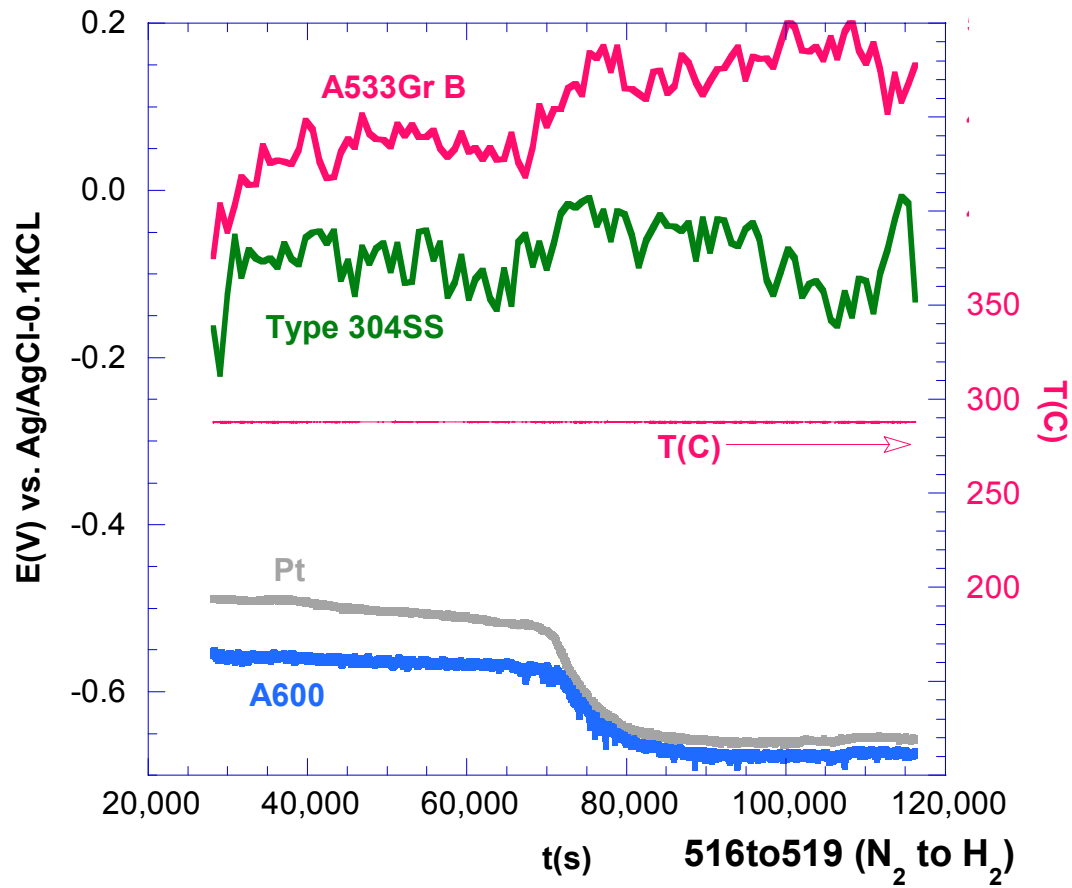


Note:100-g Boric acid heated in air (pH_2O = 3%) at 280°C

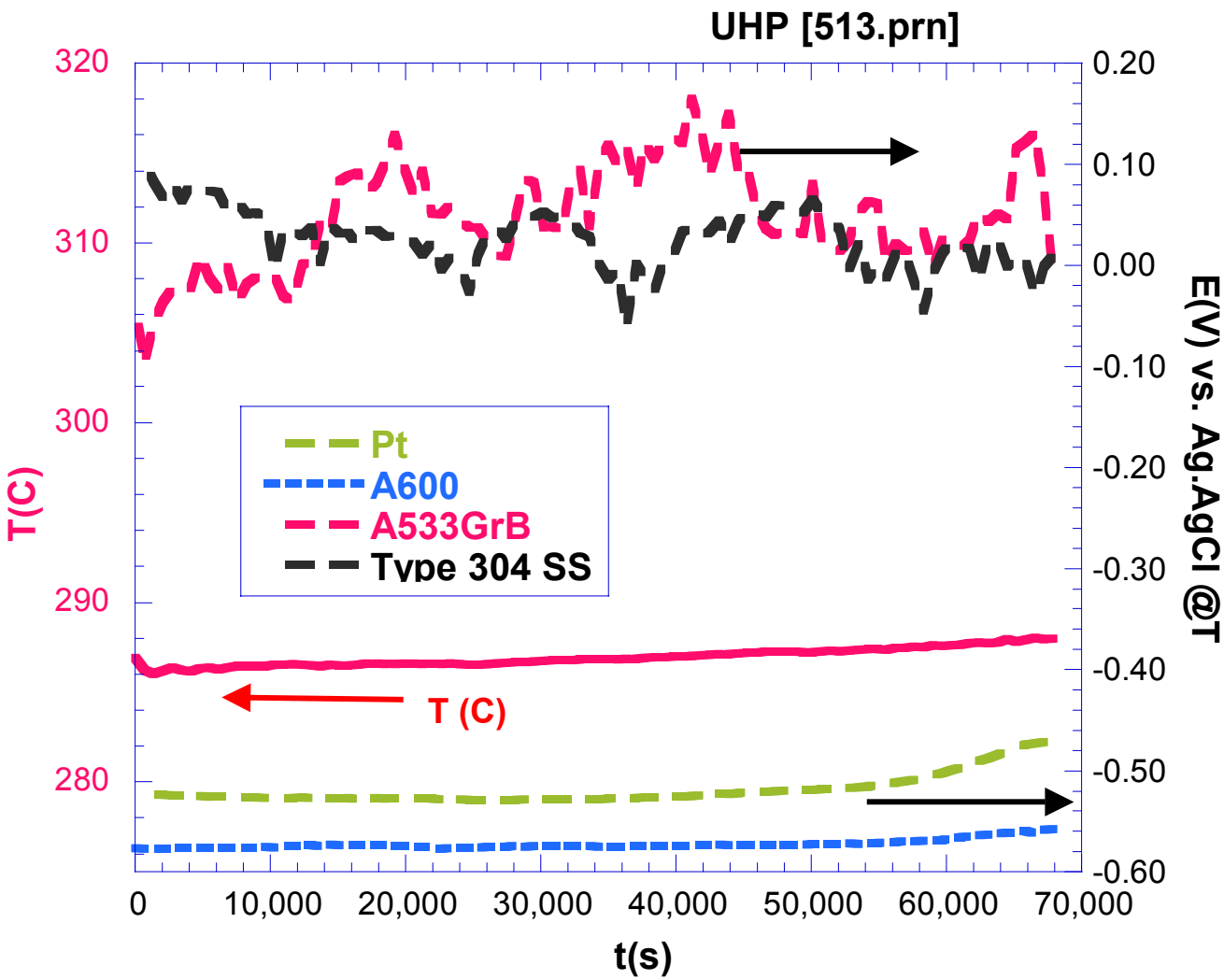
ECP vs. t: Hi-T & P cell in UHP-water
$N_2 \rightarrow H_2$ Cover gases @288°C and 1300 psi

Conversion to E_{SHE}



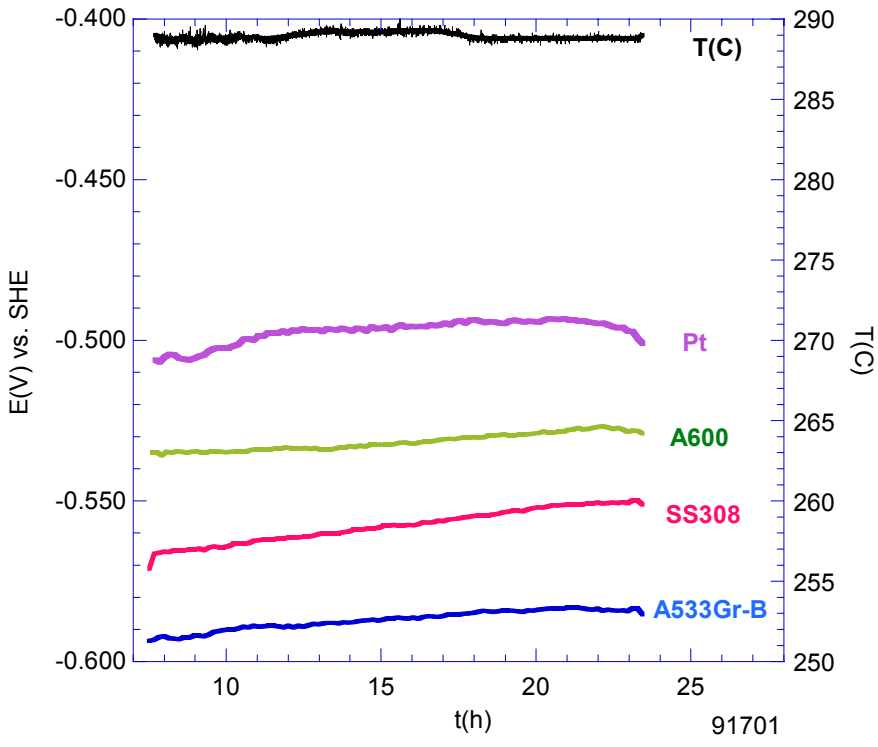


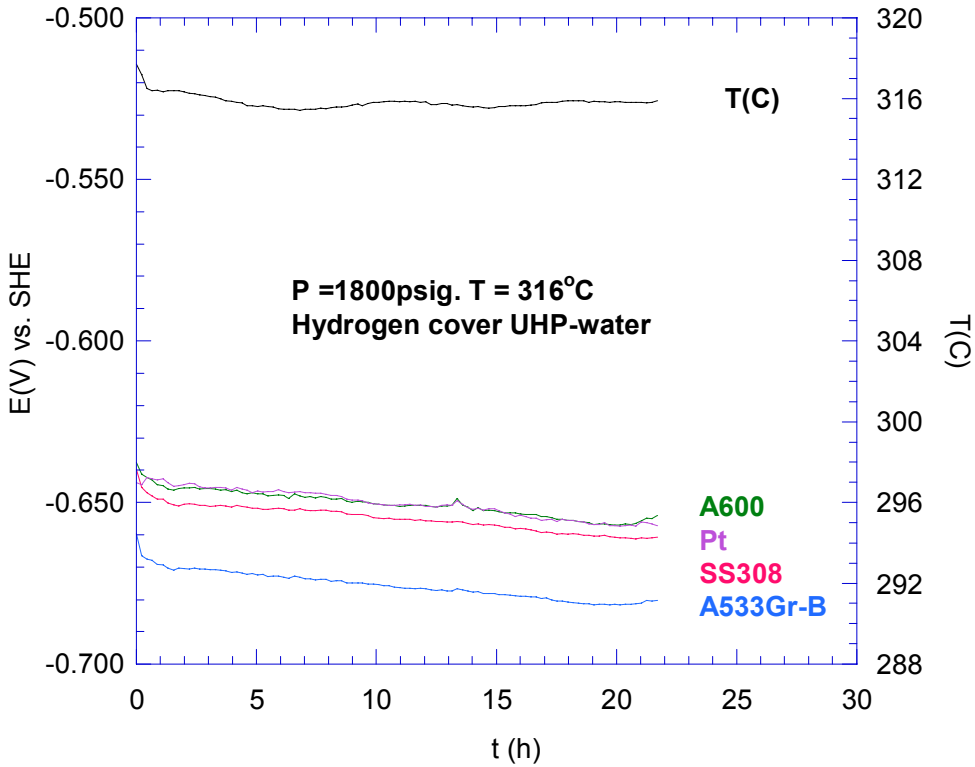
ECP vs. t: Hi-T & p cell in UHP-water @288°C and 1300 psi



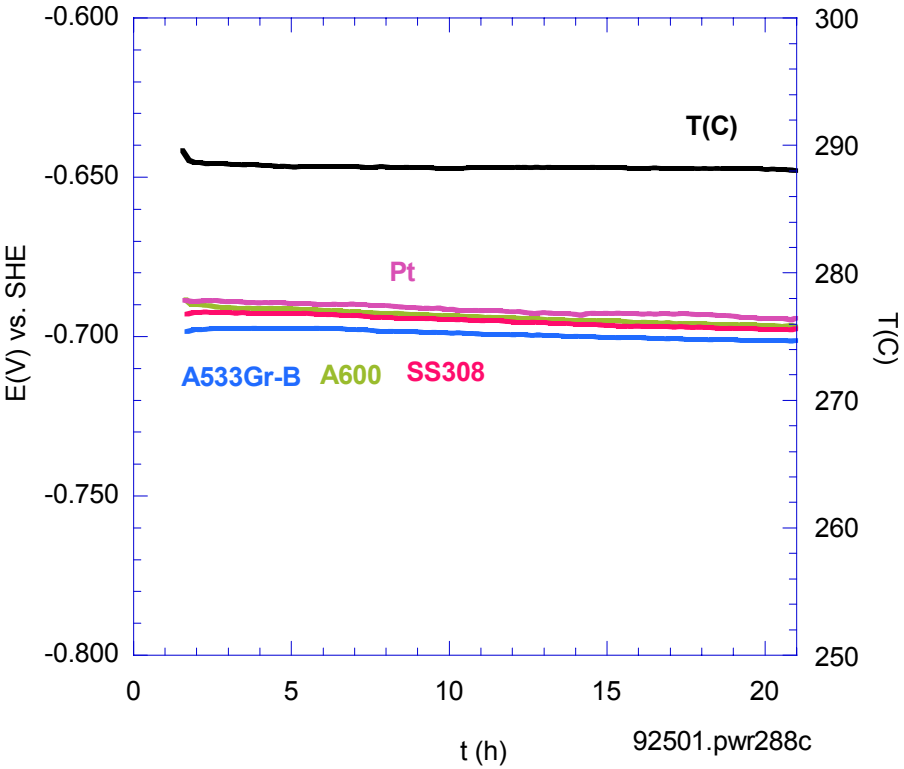
***Note**
Water flow rate = 4.5 ml/min
UHP only
not covered gas
only for the Hi-T&P system checking.

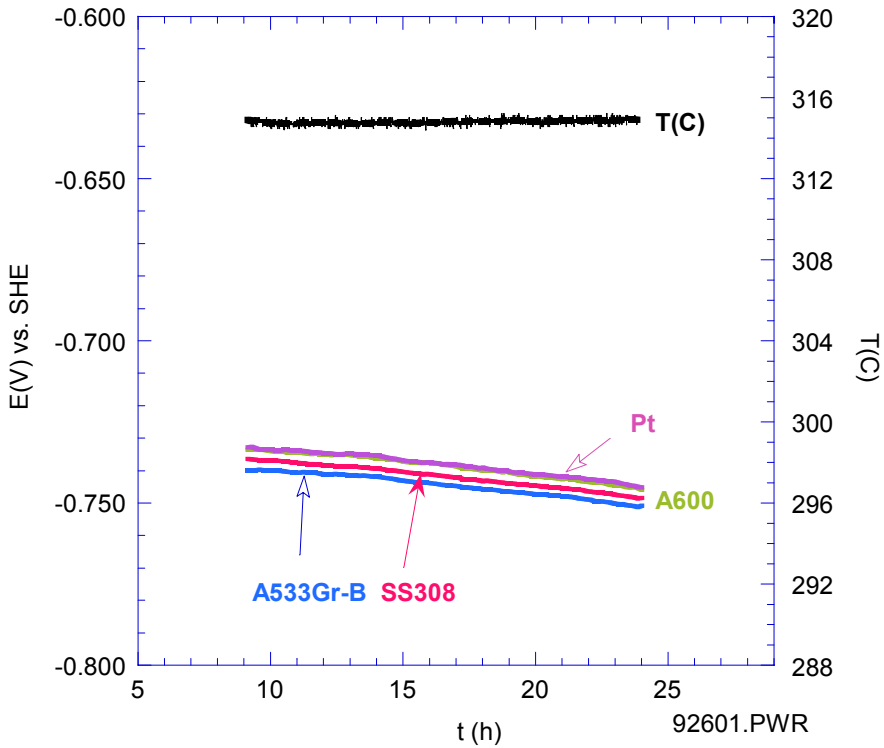
ECP for A533Gr-B, A600, SS308, and Pt in the hydrogen covered UHP-water at 288 &316ºC



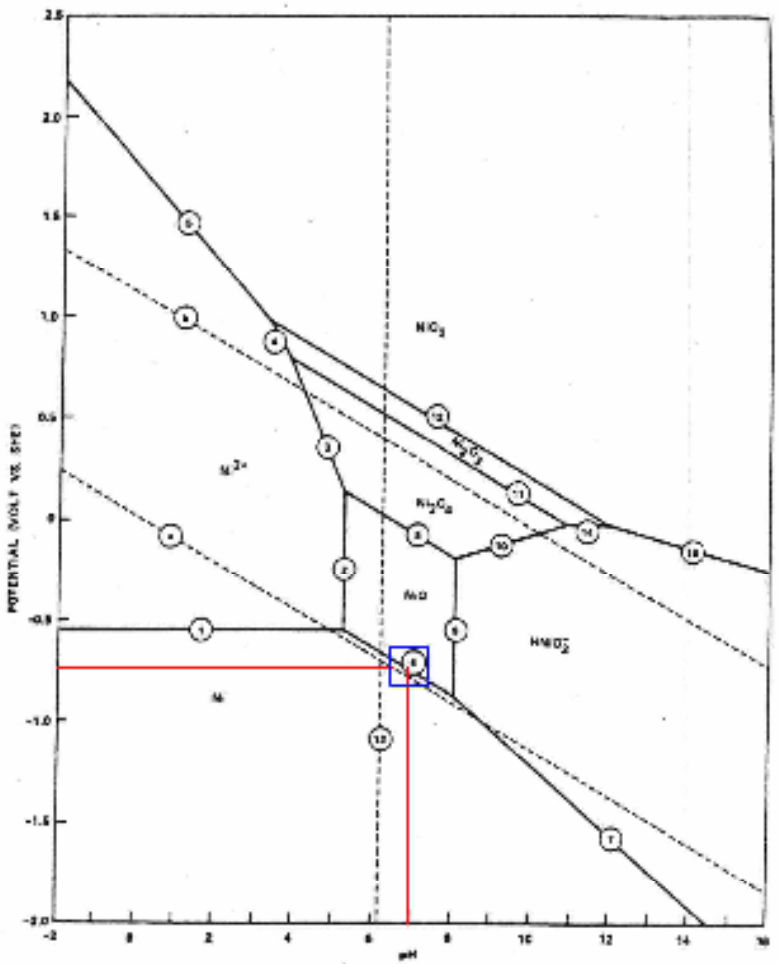


ECP for A533Gr-B, A600, SS308, & Pt in the hydrogen covered PWR-water at 288 & 316ºC

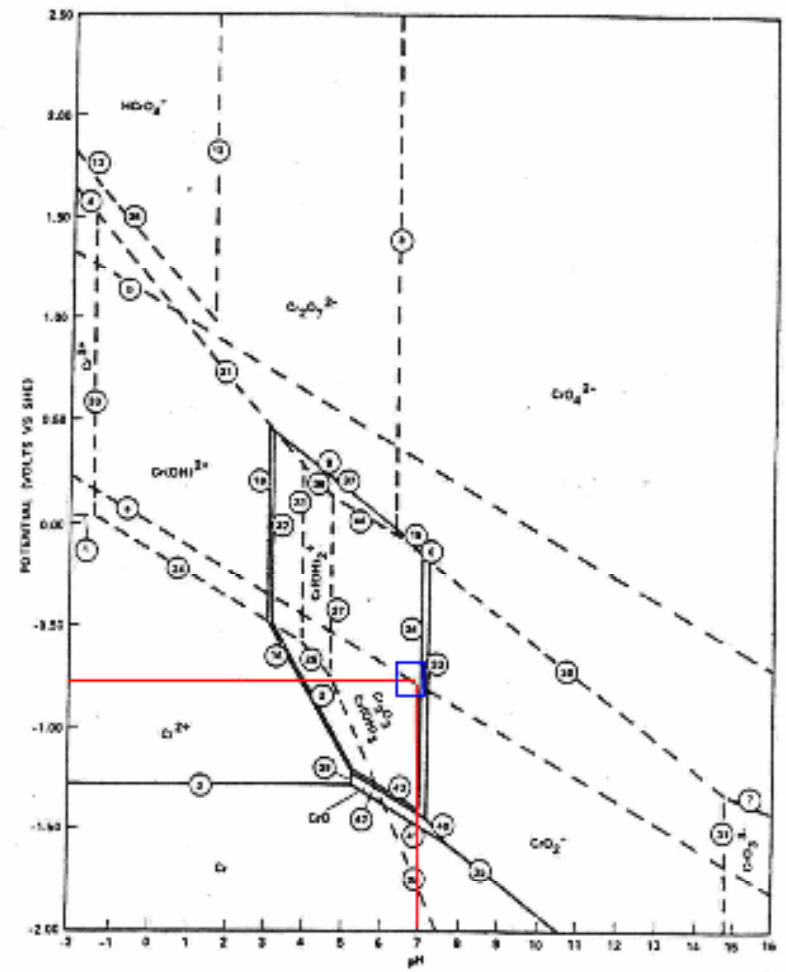




EH vs. PH diagram for Ni-O-Hand Cr-O-H @300ºC

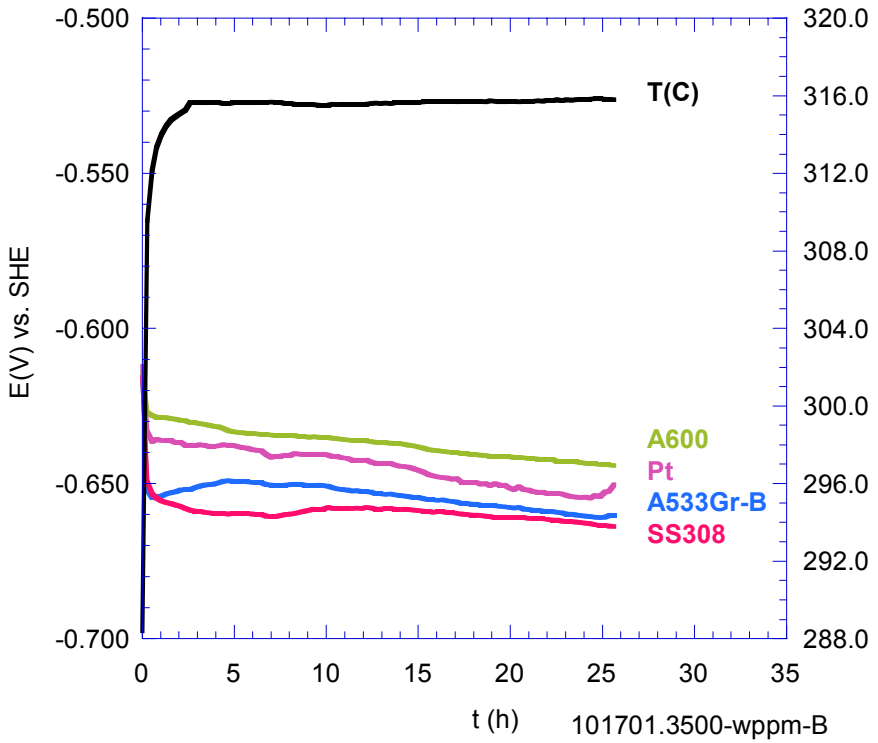


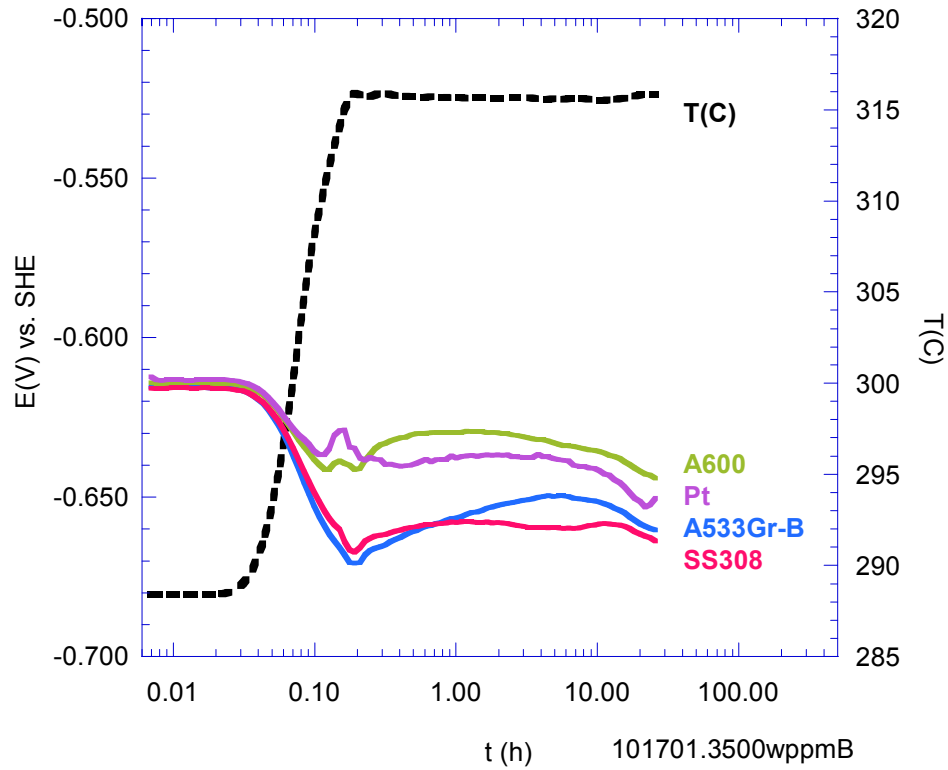
(d) @ 300°C



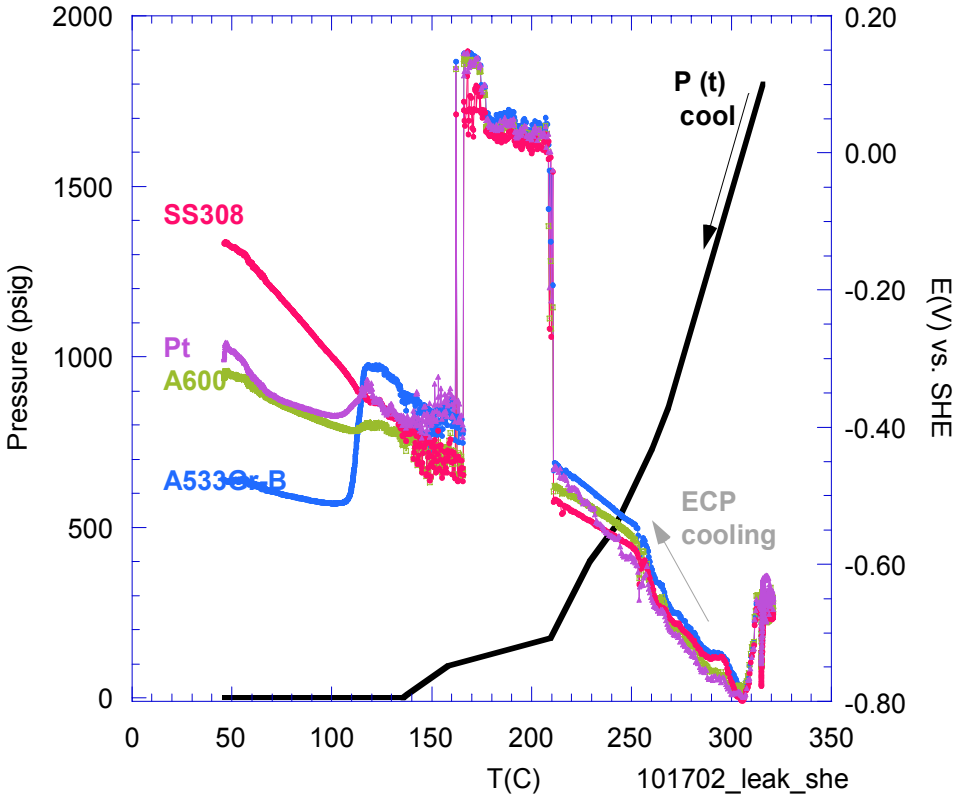
(d) @ 300°C

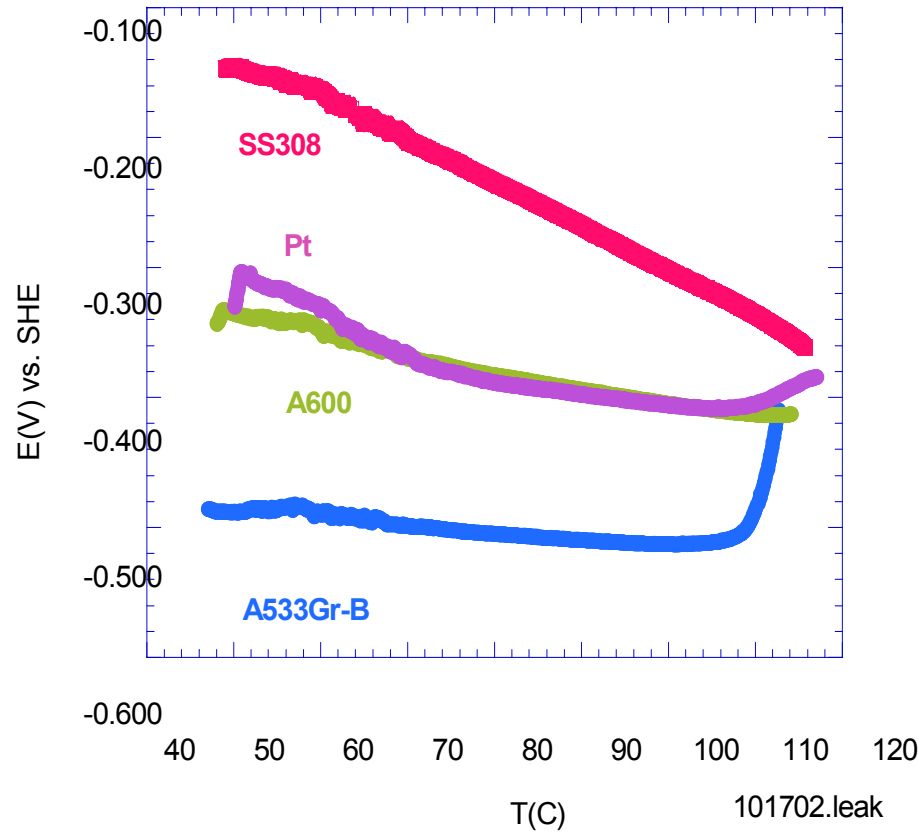
ECP for A533Gr-B, A600, SS308, and Pt :hydrogen covered 3500-wppm-B, 2-wppm-Li at 288/316 ºC



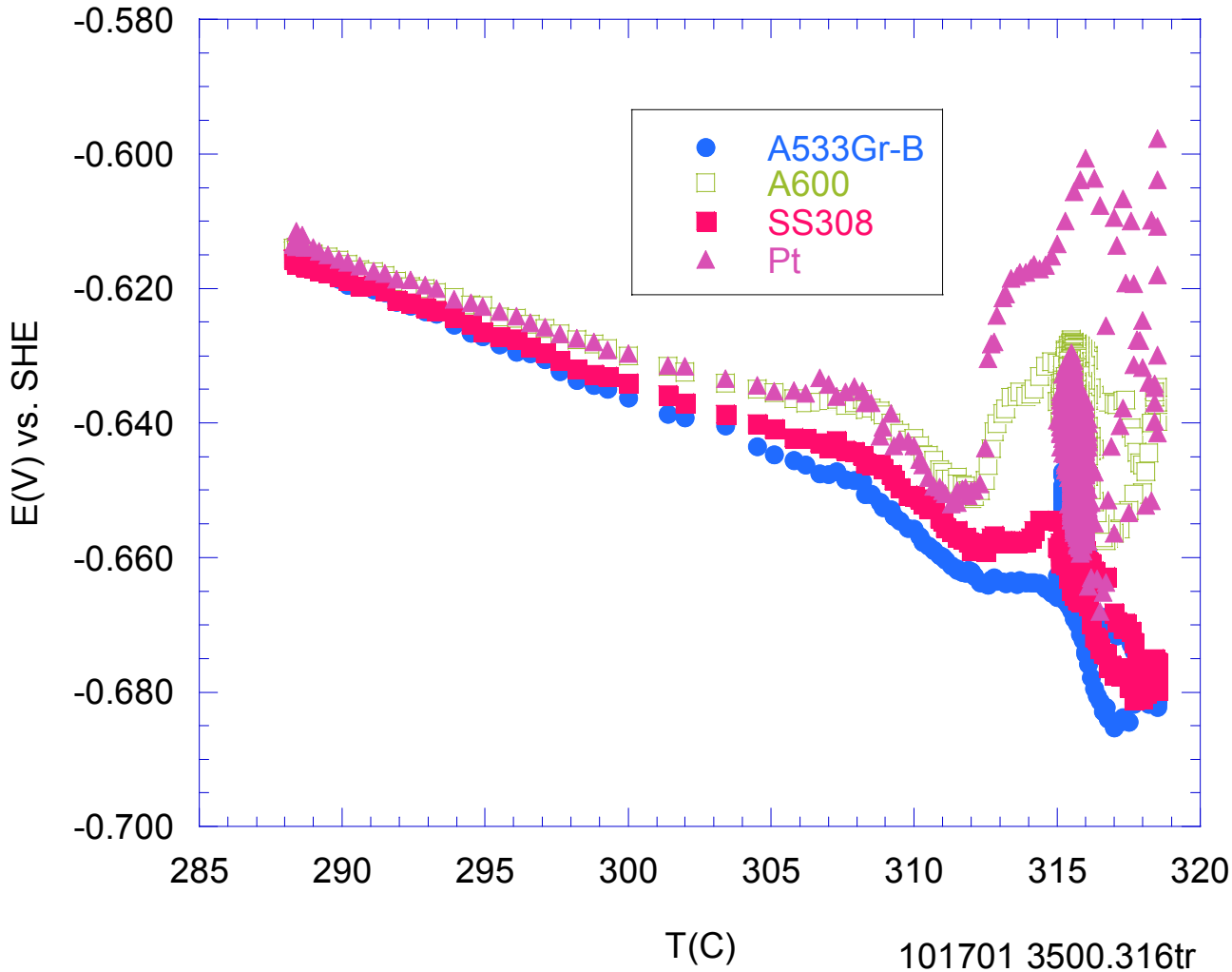


ECP in the hydrogen covered 3500-wppm-B, 2-wppm-Li solution leakage/tighten at 316°C and shutdown

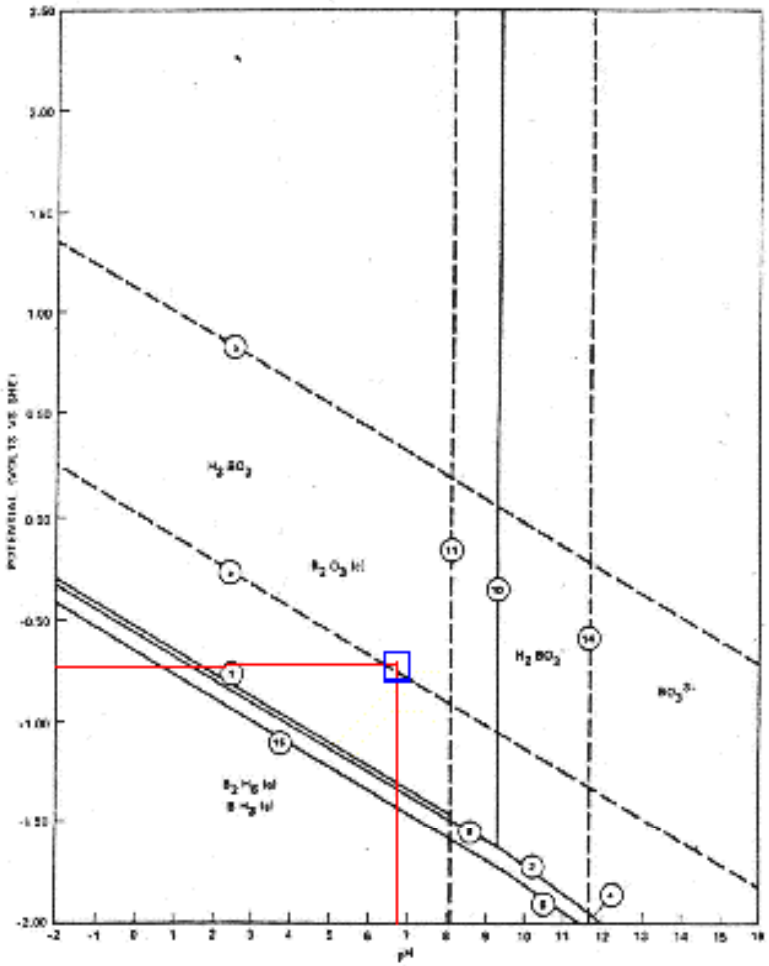


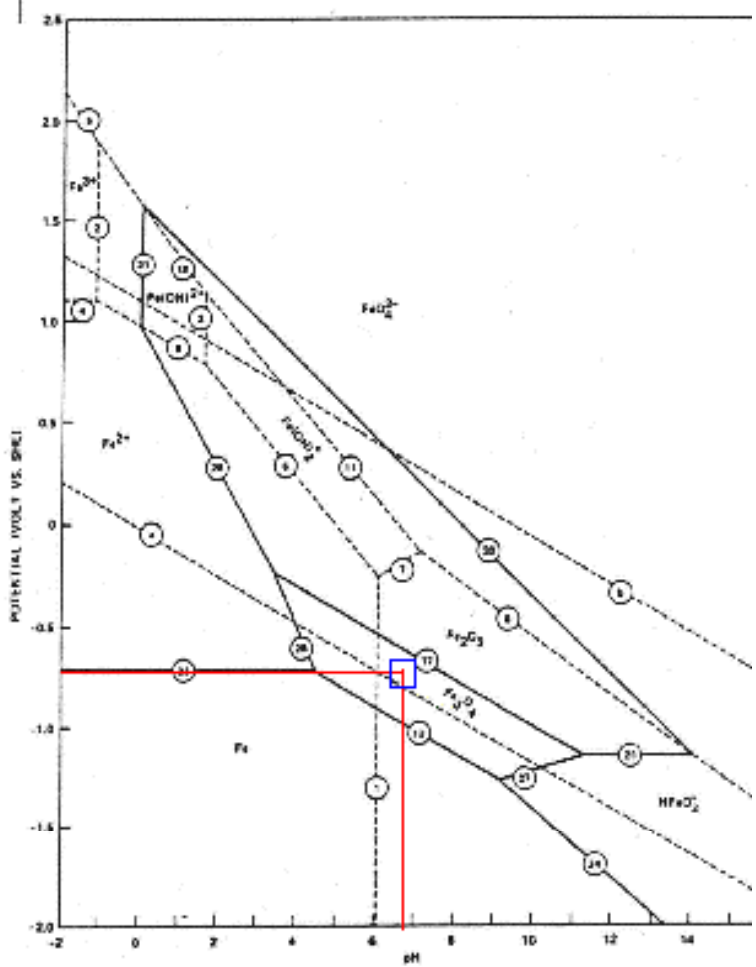


ECP vs. T for 3500-wppm-B, 2-wppm-Li solution @ T = 288/316°C P = 1800 psig



E(V) vs. PH diagram for B-O-H and Fe-O-H





Summary *(Task#4)*

1. **Established the test facilities for various tests: BA Solution, molten H-B-O, and high T & P tests in high boric acid concentrations**

2. **ECP measurements & PD tests were performed on A600, A308 and A533Gr.B materials to define the specific environmental conditions for wastage tests under Task#3**
   - **High T (100 to 316°C) and P (1,300-1,800 psi)**
   - **Ambient environment, P = 1 atm and T = 100°C, and**
   - **Molten H-B-O conditions**