Pb-Assisted Stress Corrosion Cracking Susceptibility of Alloy 22

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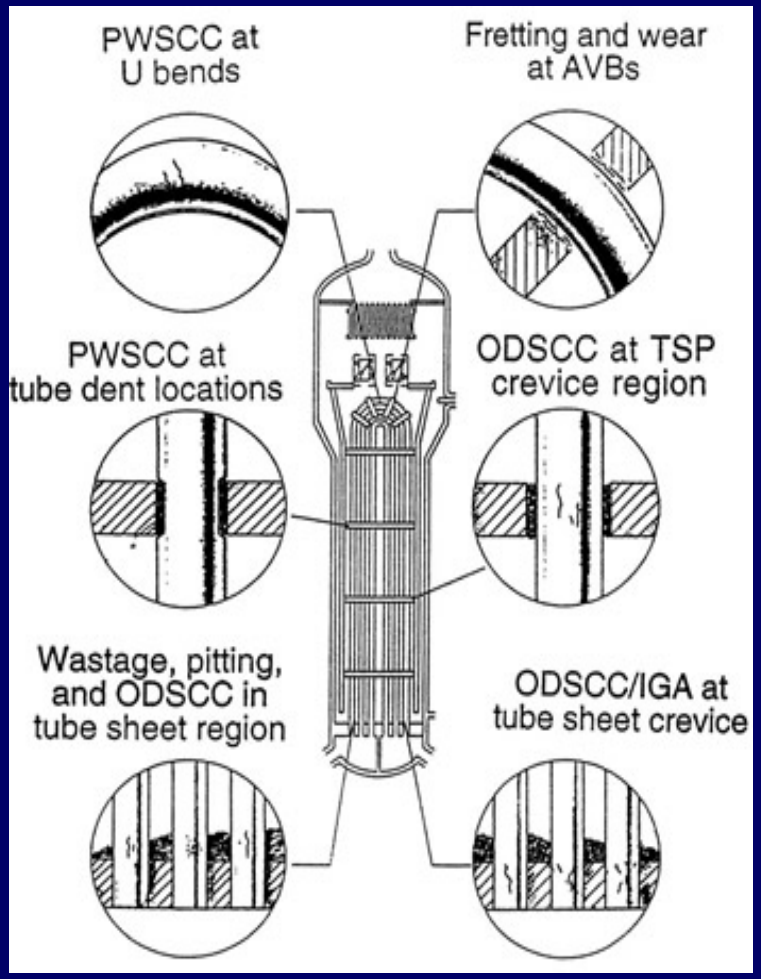
PbSCC Background:

PWR & Yucca Mountain Experiences

PbSCC Background: PWR's



- The presence of Pb as low as 0.1 ppm has been shown to cause SCC in Alloys 600/690 at elevated temps (~300°C).
- Copson & Dean first reported PbSCC for Alloy 600 in H_2O with 2.5-6 ppm Pb at pH 10 & 316ºC.
- Rocher *et al.* reported deposits of Pb on Alloy 600/690 steam generator (SG) tubing in French PWRs to be ~100-1,000 ppm.
- PbSCC of Alloys 600/690 occurs over the entire range of alkaline, neutral, & acidic pHs.
- Effects of potential and temperature on PbSCC for Alloys 600/690 have not been well developed.

PbSCC Background: Yucca Mountain

- PbSCC of MA Alloy 22 was observed by Pulvirenti et al. for single U-bend tests in 1000x J13 water with Pb-acetate additions ([Pb] ≈ 5,000 ppm) at pH 0.5 and 250 °C.
- PbSCC of Alloy 22 was not observed:
  - Estill et al. used a slow strain rate test in a concentrated $PbCl_2$ solution with [Pb] ≈ 7,500 ppm at pH ~4 and 95°C
  - Andresen et al. used compact tension specimens in Basic Saturated Water with $PbNO_3$ additions for [Pb] ≈ 1,000 ppm at 100°C
  - NRC/CNWRA experiments using single and double U-bend tests in acidified, saturated and super-saturated $PbCl_2$ and $PbNO_3$ solutions at pH 0.5, 95 °C, and $-100mV_{SCE}$.
- DOE reported Pb concentrations in J-13 well water to be 6.1 ppb which is 5-8 orders of magnitude lower than found in PWRs.

Research Objectives

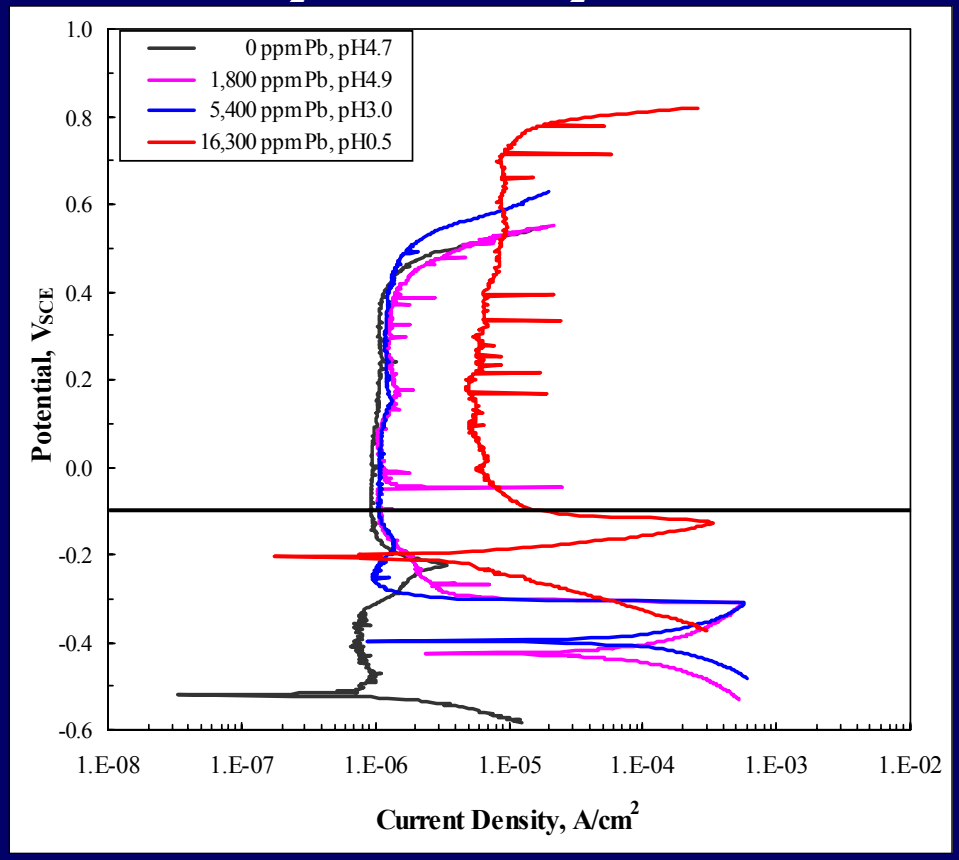
Research Objectives

- Overall research project objective:
  - As a result of PbSCC instances in PWRs and one State of Nevada test, an investigation of Alloy 22's PbSCC susceptibility in realistic Yucca Mountain environments was conducted.
- Specific objectives for the overall examination:
  - Evaluate PbSCC susceptibility of Alloy 22 as a function of:
    - » Lead concentration *(Pan et al. MRS Sym. Proc. Vol. 757, 2003)*
    - » Lead species *(This Presentation/Paper)*
    - » Applied potential *(Csontos et al., Met. Trans. 2004/JOM 2005)*
    - » Fabrication processes *(Csontos et al., Met. Trans. 2004/JOM 2005):*
      - Gas Tungsten Arc Welded (GTAW) Alloy 22
      - Solution annealed & Thermally aged MA & GTAW Alloy 22
  - Examine the chemical speciation of J-13 groundwater & NRG A pore water under realistic repository conditions containing Pb.

Anodic Polarization Behavior of MA and GTAW Alloy 22 Specimens

Effect of Pb on MA Alloy 22

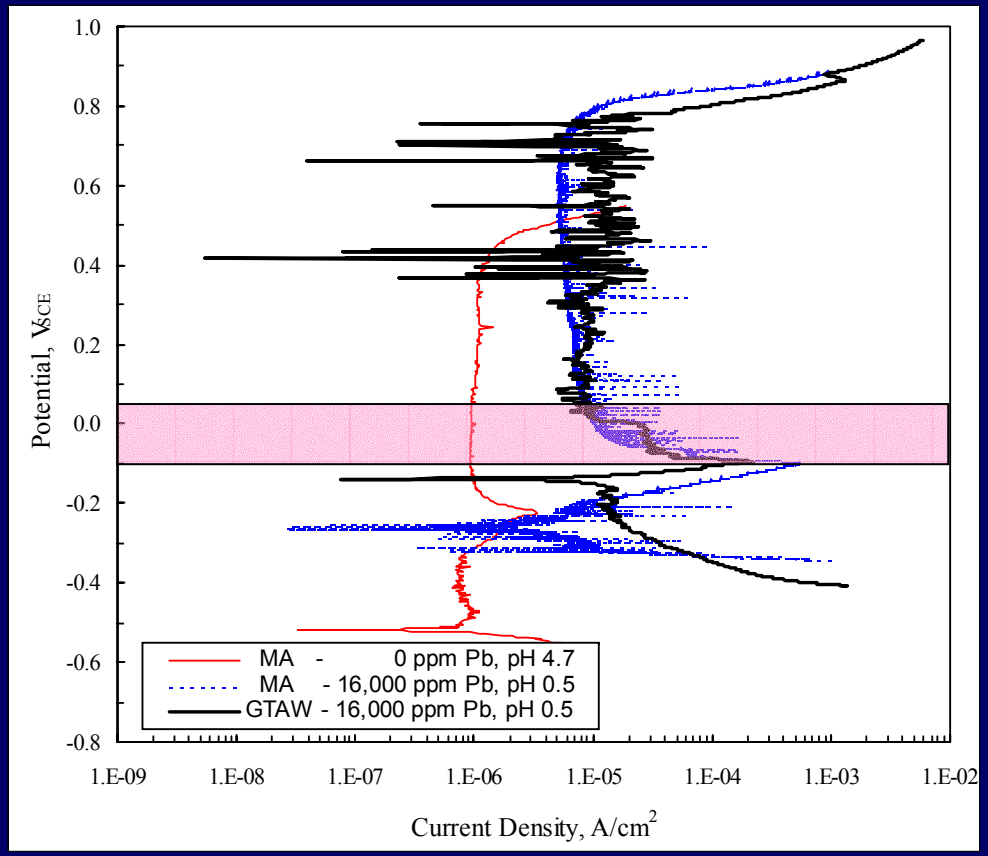
Deaerated $H_2O/HCl/PbCl_2$ solution at 95°C



- Pb Additions promote a strong anodic peak with many current spikes in the passive region
- The anodic peak was also observed using a Pt electrode
- Hence, the observed anodic peak may be coupled with Pb^{2+} oxidation
- Anodic peak potential increases with decreased solution pH
- The anodic peak & passive current density increased substantially for the supersaturated $PbCl_2$ solution (16,300 ppm Pb)

Effect of Pb on MA & GTAW Alloy 22

Deaerated $H_2O/HCl/PbCl_2$ solution at 95°C



- Pb promoted a strong anodic peak & passive current density increased by an order of magnitude for MA & GTAW
- Many large current spikes were observed, suggesting periodic events of passivity breakdown & repassivation
- The anodic peak of GTAW Alloy 22 is smaller than for the MA case
- A discontinuity appears above the anodic peak for GTAW
- Hence, applied potential may be important for PbSCC

Single & Double U-Bend Test Results for MA & GTAW Alloy 22 Plates

PbSCC Tests: MA Alloy 22

Specimen ID	Material^	Specimen Position	Test Solution			Applied Potential (mV_{SCE})	Test Duration	Test Results
			Pb (ppm)	Cl (ppm)	pH			
22–t40–SU1	MA	Apex in solution	**11,600**	**16,500**	0.51	-100	40 days (945 hours)	No SCC, shallow pits at legs
22–t40–DU1 (Inner U-Bend)	MA	Apex in solution	**11,600**	**16,500**	0.51	-100	40 days (945 hours)	No SCC, shallow pits at legs
22–t40–DU1 (Outer U-Bend)	MA	Apex in solution	**11,600**	**16,500**	0.51	-100	40 days (945 hours)	No SCC, shallow pits at legs
22–t41–SU2	MA	Legs in solution	**9,500**	**14,700**	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at apex
22–t41–DU2 (Inner U-Bend)	MA	Legs in solution	**9,500**	**14,700**	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at apex
22–t41–DU2–O (Outer U-Bend)	MA	Legs in solution	**9,500**	**14,700**	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at apex
22–t45–DU3 (Inner U-Bend)	MA	Apex in solution	**11,900**	**15,900**	0.51	-100	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t45–DU3 (Outer U-Bend)	MA	Apex in solution	**11,900**	**15,900**	0.51	-100	42 days (1,008 hours)	No SCC, shallow pits at legs

No localized corrosion was observed in 1,500-5,400 ppm $PbCl_2$ solutions at 95EC

^MA – Mill-annealed; All U-bend tests in deaerated, super-saturated $PbCl_2$ solutions at 95EC

PbSCC Tests: Effect of GTAW & Potential

Specimen ID	Material^	Specimen Position	Test Solution			Applied Potential (mV_{SCE})	Test Duration	Test Results
			Pb (ppm)	Cl (ppm)	pH			
22–t58–DU7 (Inner U-Bend)	As-welded	Apex in solution	12,000	11,700	0.55	**50**	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t58–DU7 (Outer U-Bend)	MA	Apex in solution	12,000	11,700	0.55	**50**	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t56–DU5 (Inner U-Bend)	As-welded	Apex in solution	16,000	14,000	0.50	**0**	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t56–DU5 (Outer U-Bend)	MA	Apex in solution	16,000	14,000	0.50	**0**	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t57–DU6 (Inner U-Bend)	As-welded	Apex in solution	12,000	11,700	0.55	**-50**	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t57–DU6 (Outer U-Bend)	MA	Apex in solution	12,000	11,700	0.55	**-50**	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t55–DU4 (Inner U-Bend)	As-welded	Apex in solution	16,000	14,000	0.50	**-100**	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t55–DU4 (Outer U-Bend)	MA	Apex in solution	16,000	14,000	0.50	**-100**	42 days (1,008 hours)	No SCC, shallow pits at legs

No localized corrosion was observed in 1,500-5,400 ppm $PbCl_2$ solutions at 95EC

^MA – Mill-anneal; SA – Solution-anneal 1,125EC 10min; TA – Thermal-age 870EC 30min;
All U-bend tests conducted in deaerated, super-saturated $PbCl_2$ solutions at 95EC

PbSCC Tests: Effect of Solution Anneal & Short Term Aging of MA & GTAW Alloy 22

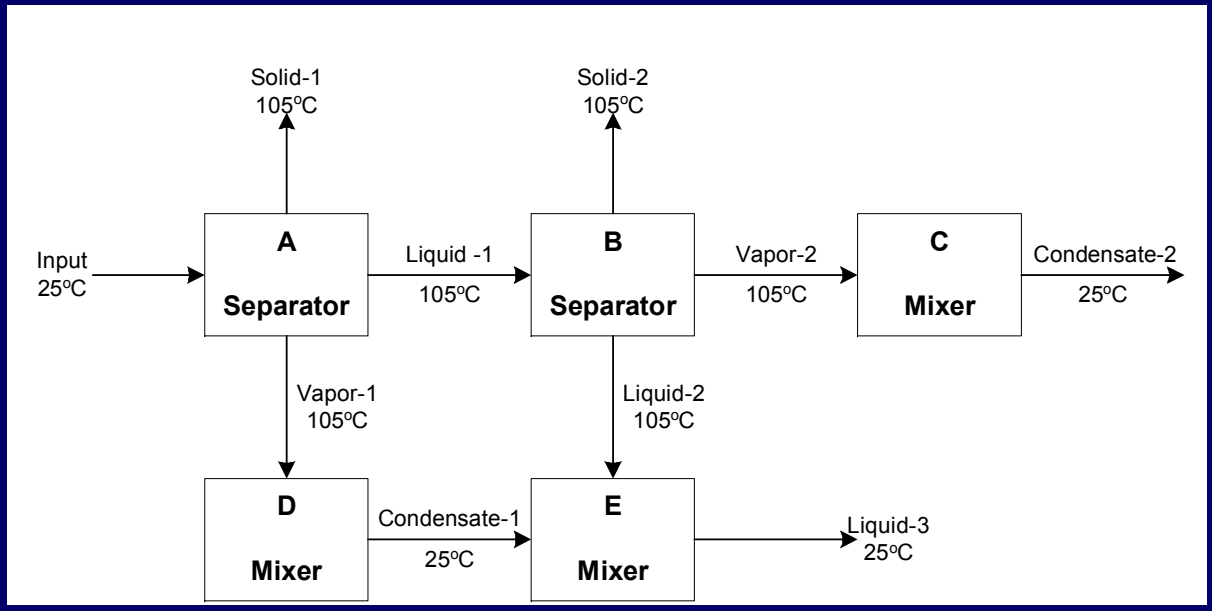
Specimen ID	Material^	Specimen Position	Test Solution			Applied Potential (mV_{SCE})	Test Duration	Test Results
			Pb (ppm)	Cl (ppm)	pH			
22–t55–DU4 (Inner U-Bend)	**As-welded**	Apex in solution	16,000	14,000	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t55–DU4 (Outer U-Bend)	**MA**	Apex in solution	16,000	14,000	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t60–DU9 (Inner U-Bend)	**Welded + SA**	Apex in solution	12,200	15,600	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t60–DU9 (Outer U-Bend)	**MA + SA**	Apex in solution	12,200	15,600	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs
22–t59–DU8 (Inner U-Bend)	**Welded + SA + TA**	Apex in solution	12,200	15,600	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs, preferential attack at apex
22–t59–DU8 (Outer U-Bend)	**MA + SA + TA**	Apex in solution	12,200	15,600	0.50	-100	42 days (1,008 hours)	No SCC, shallow pits at legs

No localized corrosion was observed in 1,500-5,400 ppm $PbCl_2$ solutions at 95EC

^MA – Mill-anneal; SA – Solution-anneal 1,125EC 10min; TA – Thermal-age 870EC 30min;
All U-bend tests conducted in deaerated, super-saturated $PbCl_2$ solutions at 95EC

Speciation Calculations of J-13 Groundwater & NRG A Pore Water with Pb Additions

Speciation Calculation Methodology



- The chemical speciation of J-13 water with Pb was examined using:
  - Environmental Simulation Program Version 6.5 by OLI Systems.
- The chemical evolution of stable and ionic Pb containing compounds in the remaining concentrated evaporative liquids was examined.
- Simulated realistic repository environments with a two-stage evaporator system that allows for evaporation and condensation.

OLI Speciation Calculations: J-13 Groundwater

- 6.08 ppb and 6.08 ppm of Pb was added to J-13 water at 25°C, evaporated at 105°C, condensed at 25°C, while under a $P(CO_2) = 1.1x10^{-3}$ and $3.3x10^{-5}$ atm
- 6.08 ppm of Pb‡ is 1000x that found in J-13 water
- The pH of the evaporative liquids rose from ~5 to ~11, while the pH of the condensate dropped to ~4
- As in PWRs, the majority of Pb is immobilized as $PbCO_3$

	Unit	J-13	J-13	J-13	J-13
$P(CO_2)$	atm	$1.1x10^{-3}$	$1.1x10^{-3}$	$3.3x10^{-5}$	$3.3x10^{-5}$
Pb Additions	ppm	$6.1x10^{-3}$	6.08	$6.1x10^{-3}$	6.08
Pb Additions	moles	$2.93x10^{-8}$	$2.93x10^{-8}$	$2.93x10^{-8}$	$2.93x10^{-8}$
$PbCO_3$	moles	$2.34x10^{-8}$	$2.93x10^{-8}$	$1.78x10^{-8}$	$2.81x10^{-8}$
% Immobilized	%	79.89%	99.98%	60.51%	95.62%

‡ ANL J-13/EJ-13 compositional analyses table for Pb in J-13 water = 6.08 ppb

OLI Speciation Calculations: J-13 Groundwater

	Unit	J-13	J-13	J-13	J-13
$P(CO_2)$	atm	$1.1x10^{-3}$	$1.1x10^{-3}$	$3.3x10^{-5}$	$3.3x10^{-5}$
Pb Additions	ppm	$6.08x10^{-3}$	6.08	$6.08x10^{-3}$	6.08
Pb^{2+}	ppm	$4.6x10^{-5}$	$4.6x10^{-5}$	$8.7x10^{-7}$	$3.7x10^{-5}$
PbO	ppm	0.11	0.10	0.09	3.87
$PbCl^{+1}$	ppm	$3.8x10^{-6}$	$3.8x10^{-6}$	$8.4x10^{-8}$	$3.6x10^{-6}$
$PbCl_2$	ppm	$2.3x10^{-6}$	$2.3x10^{-6}$	$4.2x10^{-8}$	$1.8x10^{-6}$
$PbCl_3^{-1}$	ppm	$9.4x10^{-6}$	$9.4x10^{-6}$	$1.0x10^{-7}$	$4.4x10^{-6}$
$PbCl_4^{-2}$	ppm	$9.7x10^{-5}$	$9.7x10^{-5}$	$7.6x10^{-7}$	$3.3x10^{-5}$
$PbNO_3^{+1}$	ppm	$1.2x10^{-6}$	$1.2x10^{-6}$	$2.7x10^{-8}$	$1.1x10^{-6}$
$Pb(NO_3)_2$	ppm	$1.3x10^{-7}$	$1.3x10^{-7}$	$2.5x10^{-9}$	$1.1x10^{-7}$
$Pb(NO_3)_3^{-1}$	ppm	$1.2x10^{-8}$	$1.2x10^{-8}$	$1.4x10^{-10}$	$6.1x10^{-9}$
$HPbO_2^{-1}$	ppm	4.76	4.77	15.53	679.97
PbF^{+1}	ppm	$6.0x10^{-7}$	$6.0x10^{-7}$	$3.0x10^{-8}$	$1.3x10^{-6}$
PbF_2	ppm	$9.4x10^{-8}$	$9.4x10^{-8}$	$1.0x10^{-8}$	$4.5x10^{-7}$
PbF_3^{-1}	ppm	$1.5x10^{-6}$	$1.5x10^{-6}$	$2.4x10^{-7}$	$1.0x10^{-5}$
PbF_4^{-2}	ppm	$2.5x10^{-6}$	$2.5x10^{-6}$	$7.1x10^{-7}$	$3.0x10^{-5}$
$PbOH^{+1}$	ppm	$4.3x10^{-3}$	$4.3x10^{-3}$	$6.9x10^{-4}$	$3.0x10^{-2}$

- Pb complex concentrations in evaporative liquid-1
- Majority of Pb was immobilized as $PbCO_3$ after this 1st evaporative stage
- Pb complex concentrations after the 2nd evaporative step in liquid-2 did not vary much from liquid-1
- $HPbO_2^{-1}$ is the only species present in appreciable quantities, i.e. >10 ppm

‡ ANL J-13/EJ-13 Compositional Analyses table

OLI Speciation Calculations: NRG A Pore Water

	Unit	NRG-A	NRG-A	NRG-A	NRG-A
$P(CO_2)$	atm	$1.1x10^{-3}$	$1.1x10^{-3}$	$8.5x10^{-6}$	$8.5x10^{-6}$
Pb Additions	ppm	$6.08x10^{-3}$	6.08	$6.08x10^{-3}$	6.08
Pb^{2+}	ppm	$2.4x10^{-8}$	$2.3x10^{-5}$	$2.5x10^{-8}$	$2.5x10^{-5}$
PbO	ppm	$9.3x10^{-11}$	$9.5x10^{-8}$	$2.0x10^{-10}$	$2.0x10^{-7}$
$PbCl^{+1}$	ppm	$3.3x10^{-5}$	$3.1x10^{-2}$	$3.5x10^{-5}$	$3.3x10^{-2}$
$PbCl_2$	ppm	$5.7x10^{-4}$	0.56	$6.0x10^{-4}$	0.60
$PbCl_3^{-1}$	ppm	0.05	44.85	0.05	45.91
$PbCl_4^{-2}$	ppm	5.71	5,773.44	5.72	5,784.77
$PbNO_3^{+1}$	ppm	$1.8x10^{-7}$	$1.9x10^{-4}$	$1.5x10^{-7}$	$1.5x10^{-4}$
$Pb(NO_3)_2$	ppm	$2.0x10^{-9}$	$2.2x10^{-6}$	$1.3x10^{-9}$	$1.3x10^{-6}$
$Pb(NO_3)_3^{-1}$	ppm	$2.5x10^{-11}$	$2.9x10^{-8}$	$1.1x10^{-11}$	$1.2x10^{-8}$
$HPbO_2^{-1}$	ppm	$1.5x10^{-13}$	$1.5x10^{-10}$	$3.4x10^{-13}$	$4.4x10^{-10}$
PbF^{+1}	ppm	$2.3x10^{-11}$	$2.3x10^{-8}$	$2.5x10^{-11}$	$2.9x10^{-8}$
PbF_2	ppm	$1.2x10^{-16}$	$1.2x10^{-13}$	$1.4x10^{-16}$	$1.7x10^{-13}$
PbF_3^{-1}	ppm	$7.0x10^{-20}$	$6.95x10^{-17}$	$9.1x10^{-20}$	$1.2x10^{-16}$
PbF_4^{-2}	ppm	-	$3.6x10^{-21}$	-	$7.1x10^{-21}$
$PbOH^{+1}$	ppm	$9.2x10^{-8}$	$9.3x10^{-5}$	$1.4x10^{-7}$	$1.4x10^{-4}$

- 6.08 ppb and 6.08 ppm of Pb was added to NRG A water at 25°C, evaporated at 105°C, condensed at 25°C, while under a $P(CO_2)=1.1x10^{-3}$ & $3.3x10^{-5}$ atm
- 6.08 ppm of Pb‡ is 1000x that found in J-13 water
- The pH of the evaporative liquids rose from 4.5 to ~6, while the pH of the condensate dropped to ~4
- Unlike J-13, the majority of Pb is not immobilized, but, in the form of Pb chlorides $PbCl_3^{-1}$ & $PbCl_4^{-2}$

‡ ANL J-13/EJ-13 compositional analyses table for Pb in J-13 water = 6.08 ppb

Effect of Pb Species on the PbSCC Susceptibility of MA & GTAW Alloy 22:

$Pb(NO_3)_2$ Solutions

OLI Speciation Calculations:

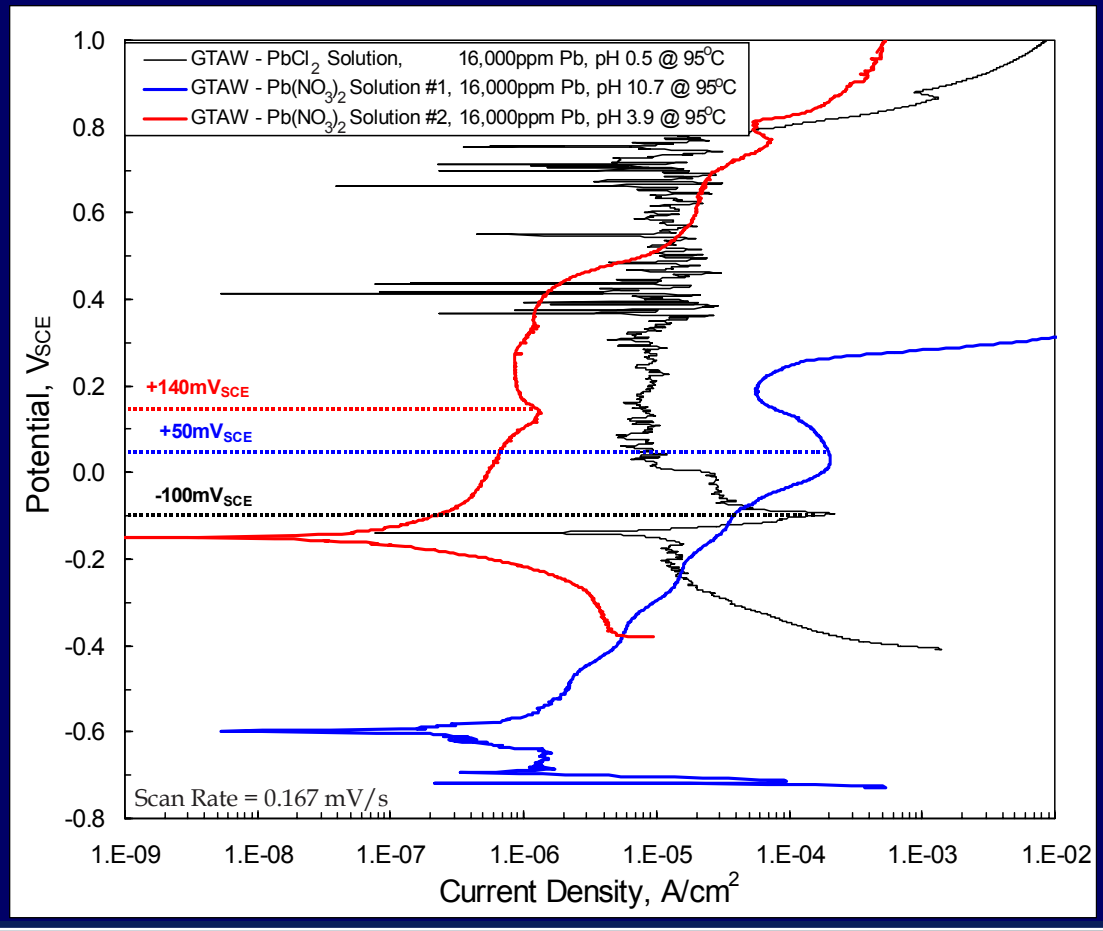
$Pb(NO_3)_2$ Solution #1: pH = 10.7 at T = 95ºC
$Pb(NO_3)_2$ Solution #2: pH = 3.9 at T = 95ºC

	Unit	$Pb(NO_3)_2$ Solution #1	$Pb(NO_3)_2$ Solution #2
Pb Additions	ppm	16,000	16,000
pH	@ 95°C	10.7	3.9
Pb^{2+}	ppm	$9.2x10^{-6}$	5,200
PbO	ppm	65	$8.7x10^{-4}$
$PbNO_3^{+1}$	ppm	$2.0x10^{-5}$	9,010
$Pb(NO_3)_2$	ppm	$6.2x10^{-6}$	1,890
$Pb(NO_3)_3^{-1}$	ppm	$3.7x10^{-8}$	6
$HPbO_2^{-1}$	ppm	873	$1.4x10^{-9}$
$PbOH^{+1}$	ppm	0.36	35

- 16,000 ppm Pb was added to deionized water as $Pb(NO_3)_2$ and allowed to evolve at temp. and pH.
- The vast majority of Pb (97.6%) in Solution #1 is immobilized as PbO.
- Solution #1 was used to evaluate the effect of $HPbO_2^{-1}$ species (J-13 data).
- The evolution of Solution #2 differs significantly from Solution #1.
- Solution #2 was used to evaluate Pb^{+2} (like the $PbCl_2$ solution), $PbNO_3^{+1}$, $Pb(NO_3)_2$, & $Pb(OH)^{+1}$ species.

Anodic Polarization Behavior of GTAW Alloy 22

$Pb(NO_3)_2$ Solution #1: pH = 10.7 at T = 95ºC
$Pb(NO_3)_2$ Solution #2: pH = 3.9 at T = 95ºC



- Deaerated $H_2O/HCl/PbCl_2$ and $H_2O/HNO_3/NaOH/PbNO_3$ solutions at 25°C and 95°C.
- Passive current densities in the $PbNO_3$ solutions generally increased with applied potential suggesting some solution effects.
- No SCC was observed through 30 days of testing constant deformation double U-bend samples in both solutions.
- No current spikes found for $PbNO_3$ solutions.

Conclusions

- Additions of 16,000ppm Pb as $PbCl_2$ were used to evaluate Pb^{2+}, $PbCl^{+}$, $PbCl_2$, $PbCl_3^{-1}$, and $PbCl_4^{-2}$ species.
- Additions of 16,000ppm Pb as $Pb(NO_3)_2$ produced two different solutions to evaluate the effect of $HPbO_2^{-1}$, Pb^{+2}, $PbNO_3^{+1}$, $Pb(NO_3)_2$, and $Pb(OH)^{+1}$ species.
- $PbCl_2$ produced a strong anodic peak and the passive current density increased by an order of magnitude.
- Current spikes were observed in the anodic polarization plots suggesting periodic events of passivity breakdown & repassivation in $PbCl_2$ which are absent at faster scan rates.
- $PbNO_3$ produced passive current densities that increased with applied potential, suggesting some solution effects.
- No current spikes were found with $PbNO_3$ solutions.

Conclusions (continued)

- PbSCC of MA and GTAW Alloy 22 was not found in supersaturated $PbCl_2$ solutions at 95°C, pH 0.5, and applied potentials in the range of -100 to 50 mV_{SCE}.
- PbSCC was not observed in 16,000 ppm $PbCl_2$ solutions at 95°C, pH 0.5, with an applied potential of -100 mV_{SCE} for the following fabrication processes:
  - MA
  - MA + Solution Anneal
  - MA + Solution Anneal + Thermal Age
  - GTAW
  - GTAW + Solution Anneal
  - GTAW + Solution Anneal + Thermal Age

Conclusions (continued)

- PbSCC of MA and GTAW Alloy 22 was not found in supersaturated $Pb(NO_3)_2$ solutions at 95°C, pH 10.7 & 3.9, & applied potentials of 50 & 140mV_{SCE}, respectively.
- Speciation calculations indicate that Pb is strongly immobilized as $PbCO_3$ in J-13 water, but, $HPbO_2^{-1}$ was present, which was evaluated with $Pb(NO_3)_2$ Solution #1.
- Speciation calculations indicate that Pb formed $PbCl_3^{-1}$ and $PbCl_4^{-2}$ for concentrated NRG A pore water, which were evaluated with the $PbCl_2$ solutions.
- In summary, MA and GTAW Alloy 22 does not appear to be susceptible to Pb-assisted stress corrosion cracking in realistic Yucca Mountain chemical environments.

Disclaimer:

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