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Optimization of Dissolved Hydrogen in Primary Water to Mitigate PWSCC in Ni-Based RCS Components

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MRP/PWROG Briefing to NRC RES

MRP Chemical Mitigation of PWSCC: Background and Objectives

- PWR primary water chemistry is known to have a limited effect on the initiation of PWSCC in Alloy 600.
- However, it must be assumed that cracks (some below NDE-limit) have already initiated in many thick-walled components.
- Thus the need for reliable data on crack growth rate (CGR) effects.
  - ***Can advantage be taken of moving to higher hydrogen levels to mitigate PWSCC (and extend inspection intervals)?***
- Strong theoretical basis, supported in particular by extensive test data from the NR program, to recommend moving to higher hydrogen levels in PWR primary water to obtain some mitigation of PWSCC for Ni-base alloys used in thick-wall components.
- Goal is to develop data to optimize the primary water chemistry guidelines to achieve some PWSCC mitigation. The potential mitigation benefit is enormous because it would apply to almost all of the RCS.

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PWSCC Mitigation by Elevated H_2

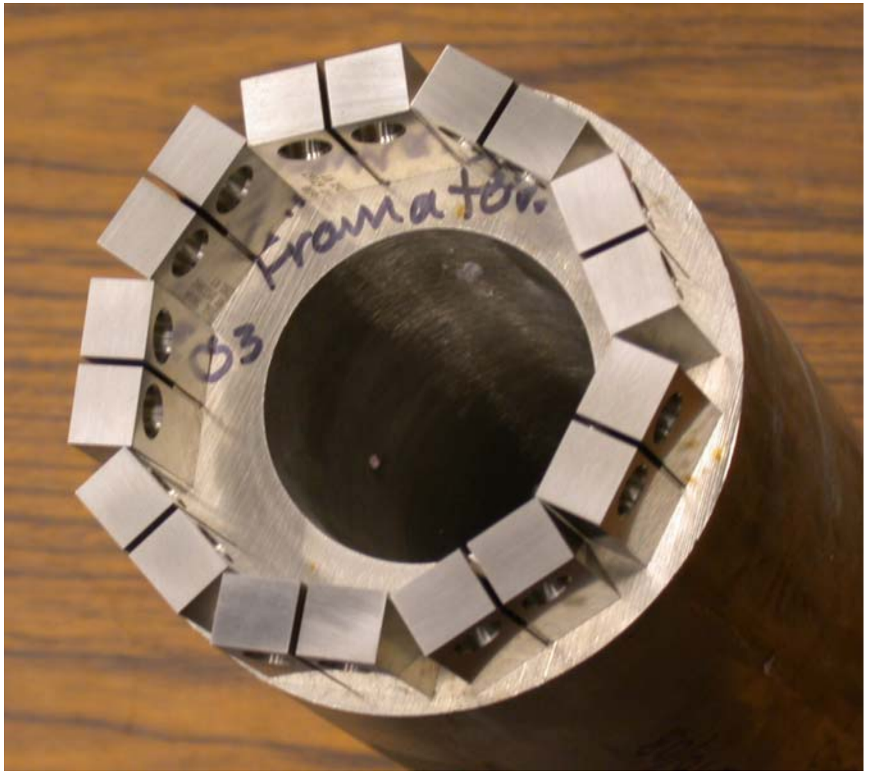
- MRP test program at (GE-GRC) has now been running for over 2 years. Need for very long duration tests has resulted in a limited number of data.
- Results to date on elevated hydrogen are encouraging but not conclusive. Testing to continue at least until 2008.
- The April 2006 meeting of the MRP Expert Panel on PWSCC was devoted mainly to consideration of chemical mitigation where Naval Reactors data on this subject was made available.
- This presentation will focus on the prospects for PWSCC mitigation by means of optimizing H_2 levels in primary water.

Experimental Strategy

- Crack growth rate measurements techniques with thorough transition from fatigue to SCC.
- Use susceptible heat of A600, ~120,000 hrs testing (CRDM heat 93510 from Framatome).
- Two 0.5T CT specimens tested in series.
- Moderate stress intensity factor, K = 25 ksi√in
- Test in 325C water with a range of Zn, B/Li & H2
- Use B/Li-equilibrated demineralizer to maintain high water purity and good H_2 control.
- Use ZrO_2 / Cu_2O and Pt reference electrodes.

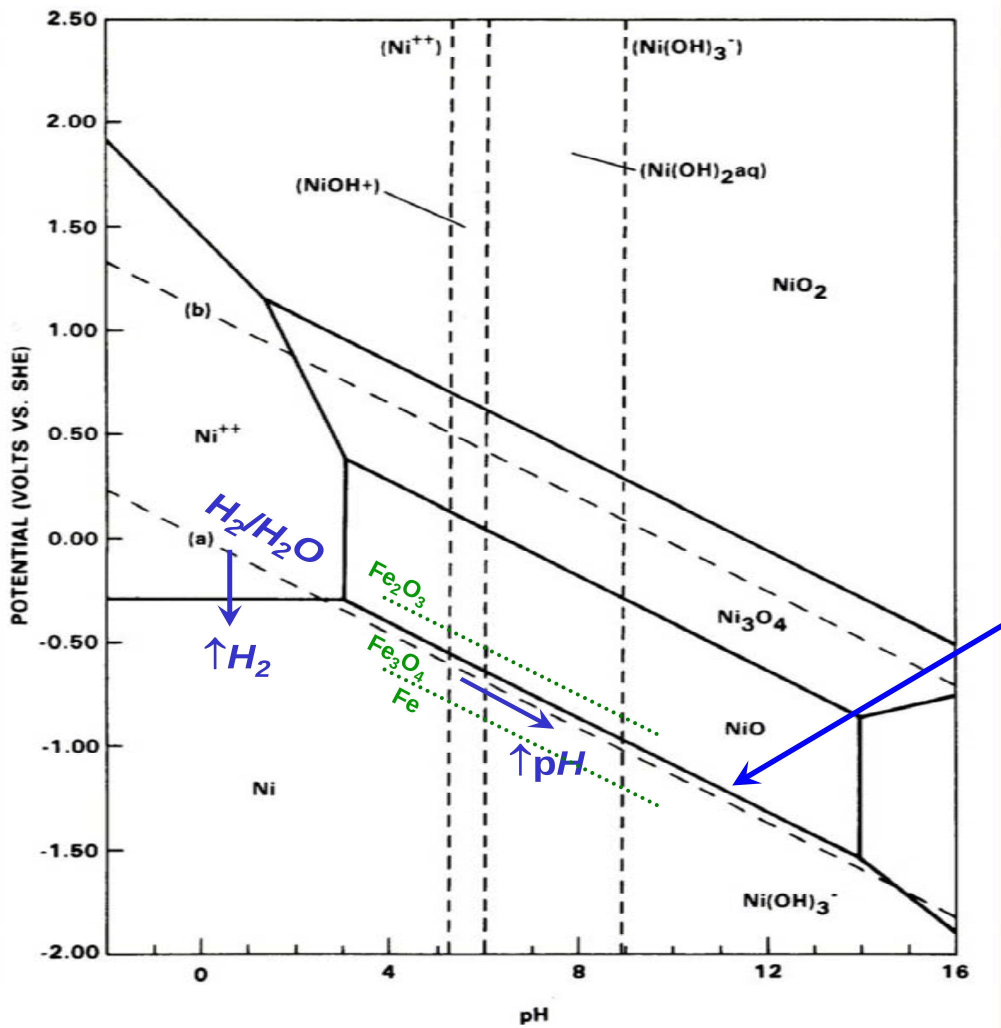
Alloy 600 CRDM Housing

Heat 93510 received from Framatome



Considered various orientations; used orientation at right, which is the C-L orientation

Ni Alloy Crack Growth Rate vs H_2



Proximity of Ni/NiO and H_2/H_2O is very important for Ni alloys

Proximity depends on H_2 & temperature but not on pH

Low H_2 unwise because of radiolysis in core

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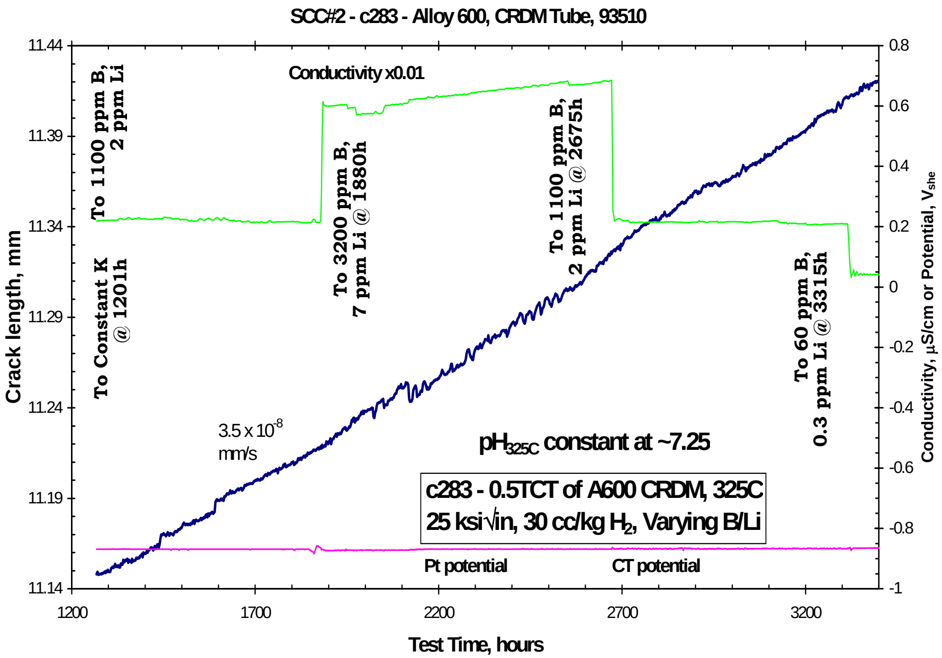
B/Li Effects at Constant pH

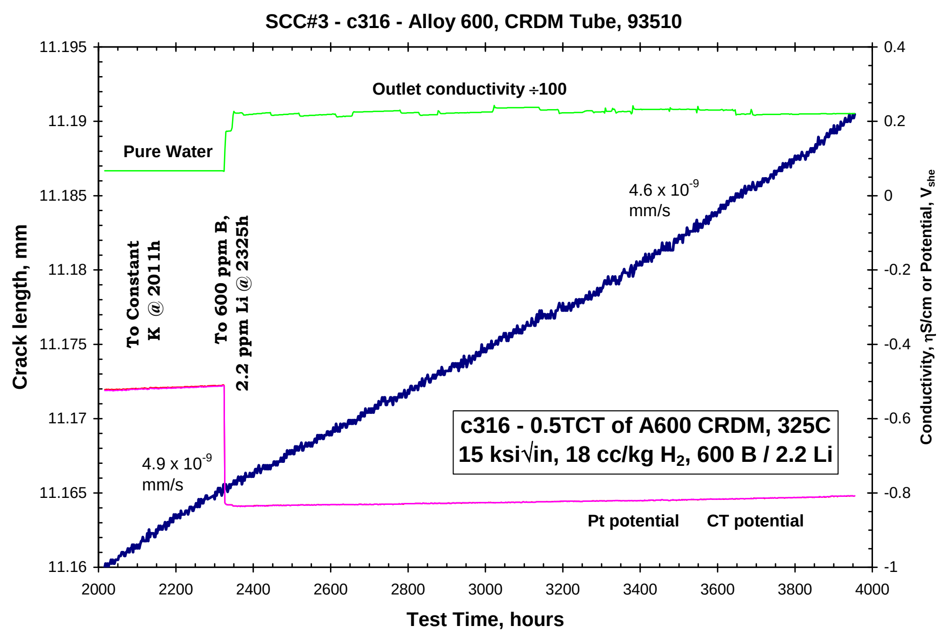
B = 1100 → 3200 → 1100 → 60 ***pH_{300C} = 6.9***

Li = 2 → 7 → 2 → 0.3 ***pH_{325C} = 7.25***



Pure water → 600B / 2.2Li

pH_{325C} = 5.86 → 7.53



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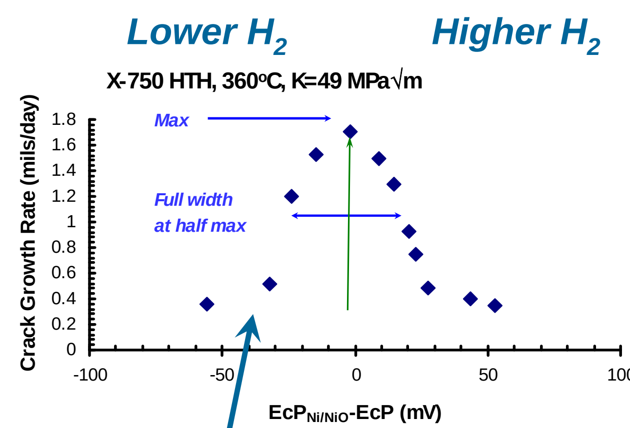
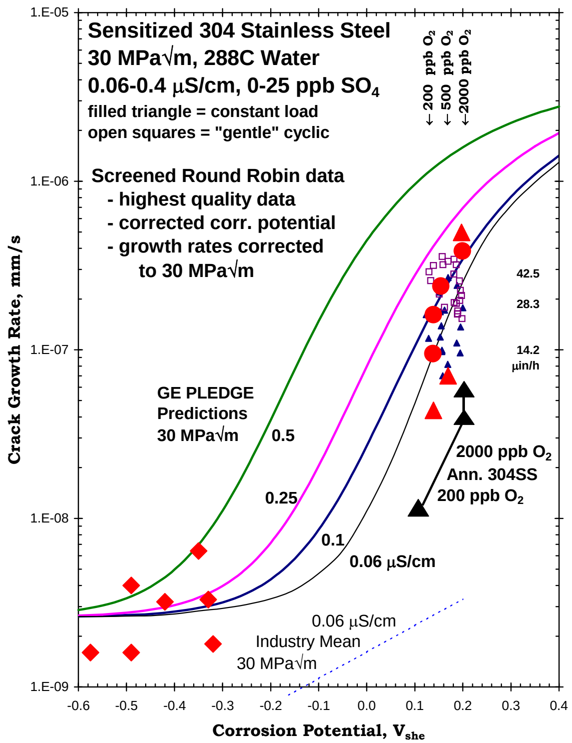
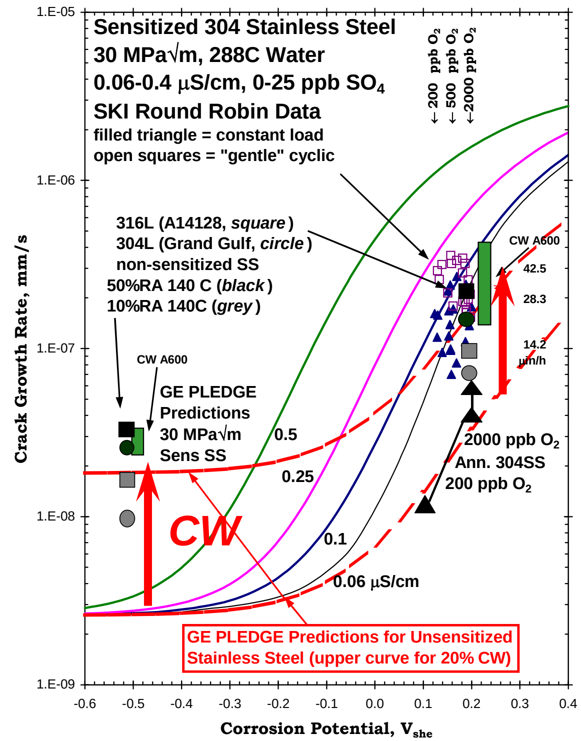
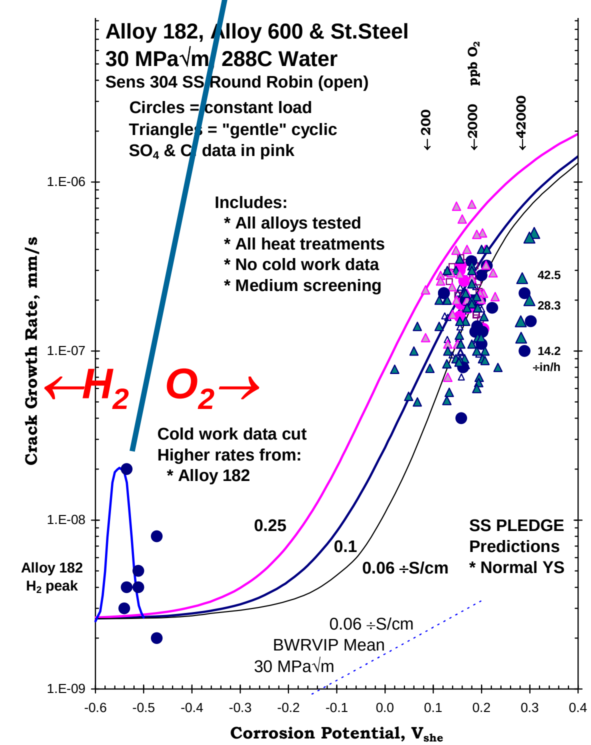
Effect of Corrosion Potential & Cold Work of SS & Ni Alloys



↑Yield strength ↑growth rate at low potential

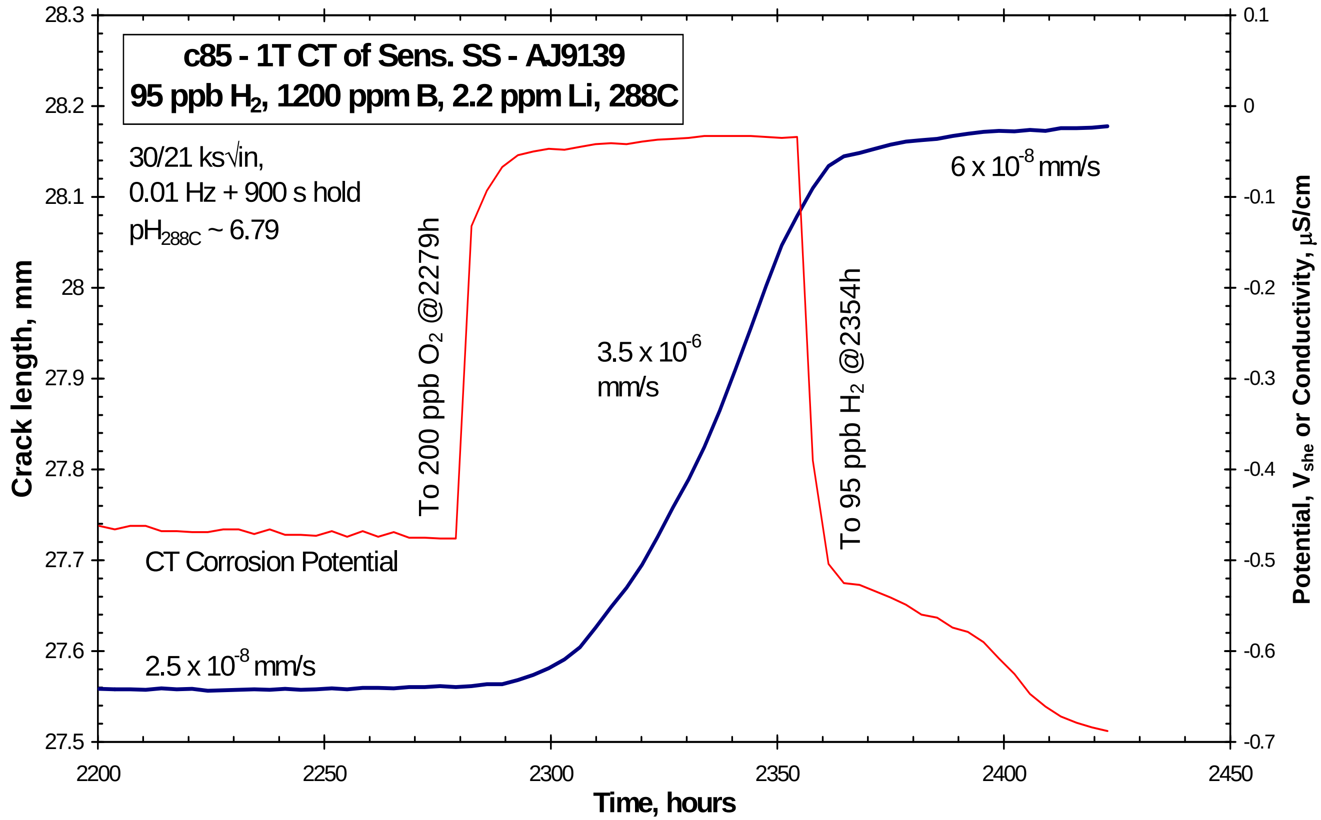






Sensitized SS ***Cold worked SS/600*** ***Ni alloys***

Very High Growth Rate in B/Li + O_2

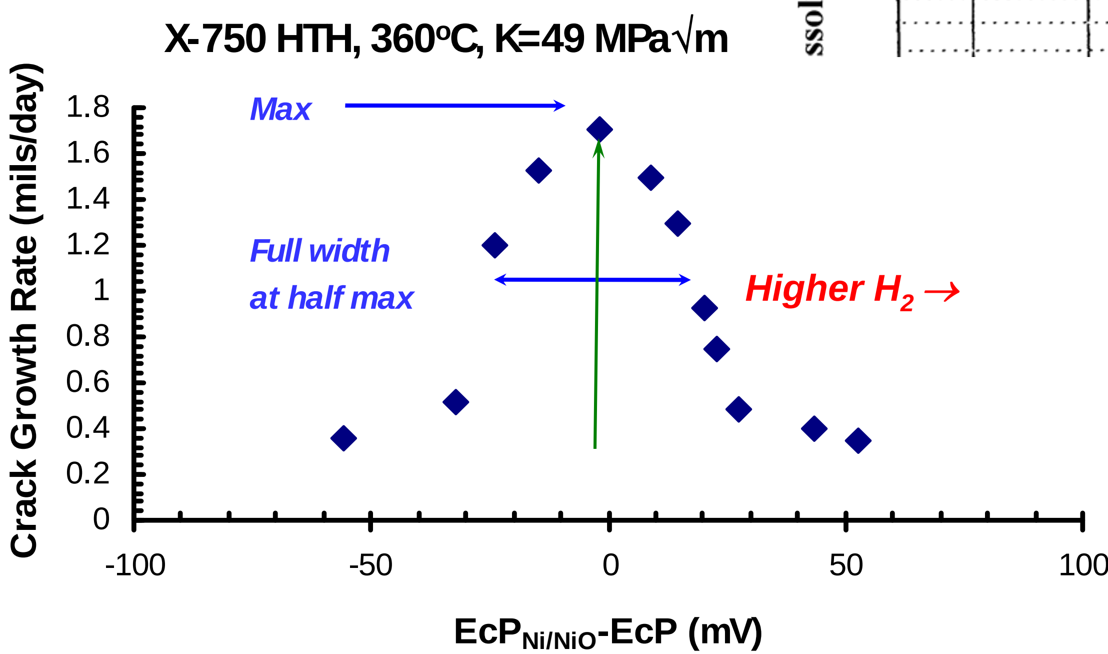


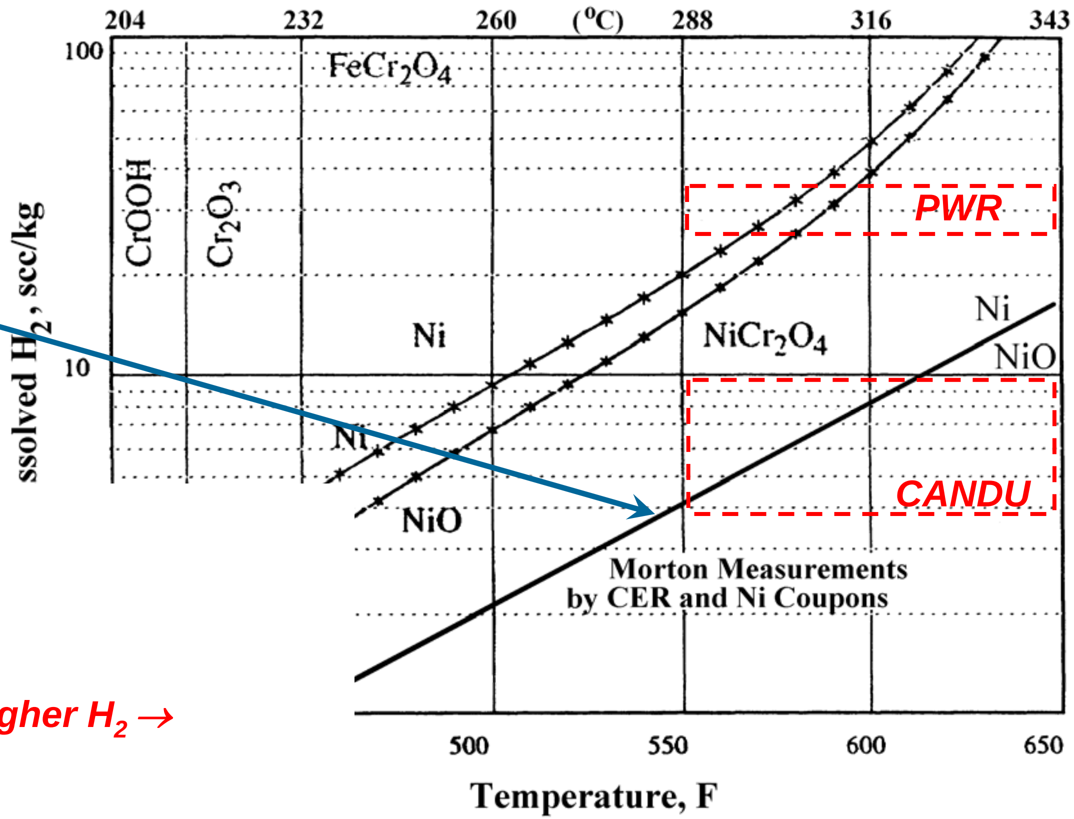
Thus, high growth rates occur as oxidants shift the crack chemistry – and can overwhelm B/Li buffering

CGR Peak at Ni/NiO Phase Boundary

A 3-8X peak in growth rate occurs at Ni/NiO boundary

$fH_2 = f(\text{Temp})$





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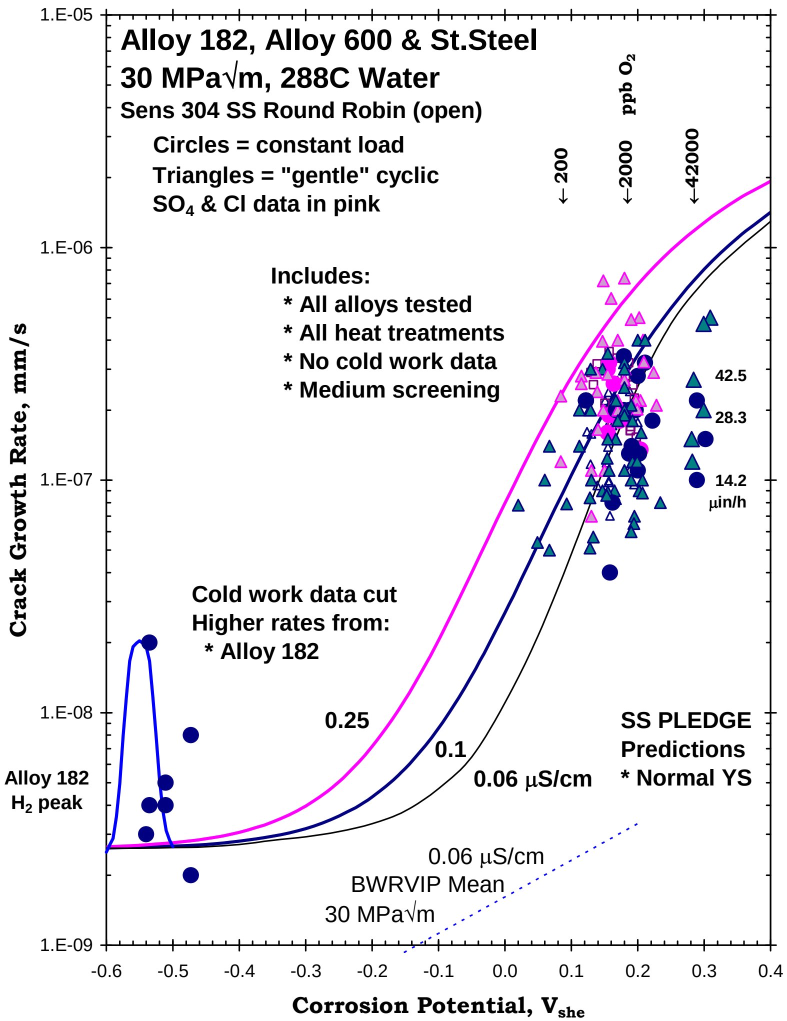
Role of H_2 and B/Li/pH Water Chemistry



Connection between BWR & PWR leverages data & understanding.

Extensive PWR data – applicable because B/Li/pH is not important in deaerated water.

There is a ~8X peak vs. H_2 for Alloy 82/182 weld metal that is relevant to BWRs.

Thermal activation also important.

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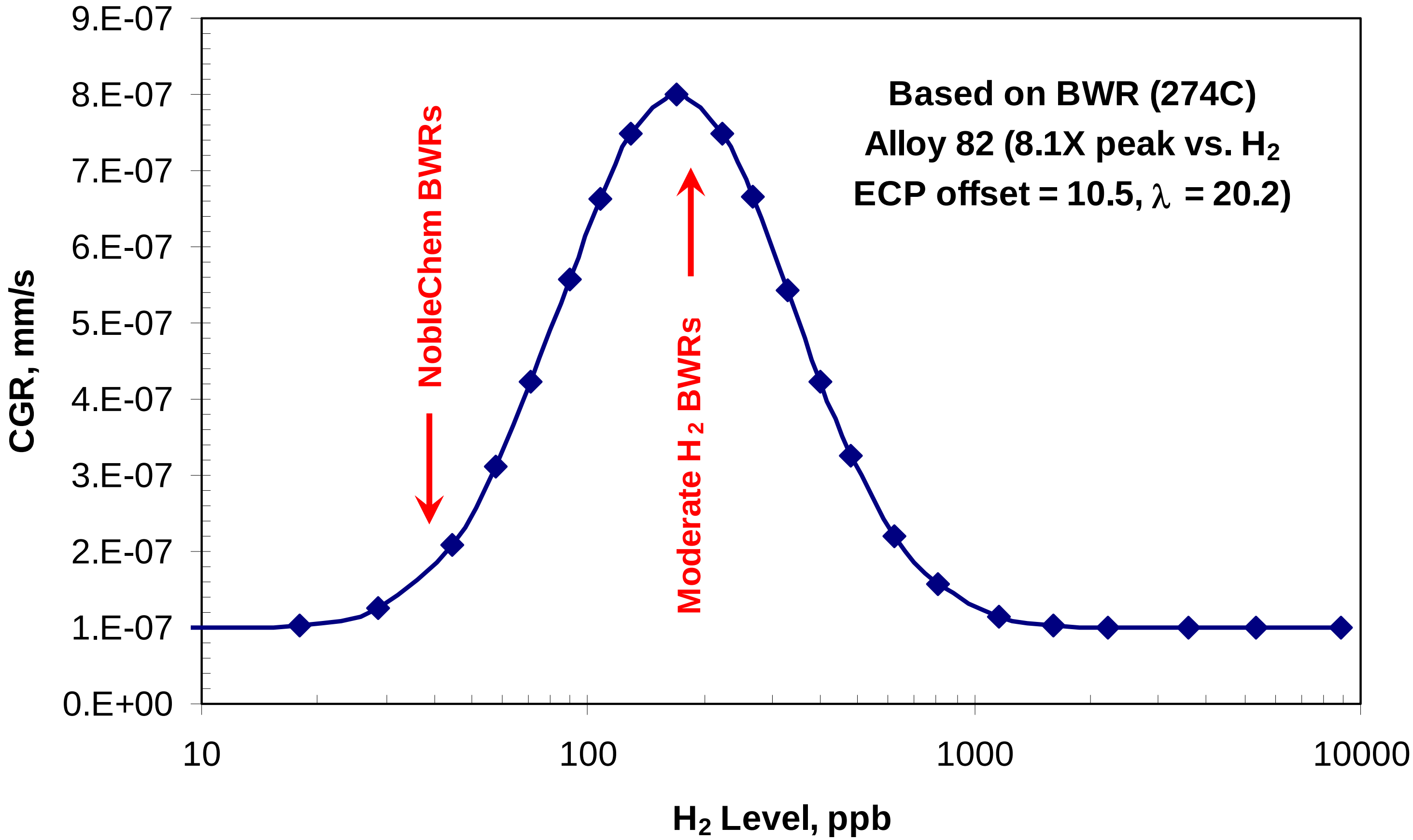
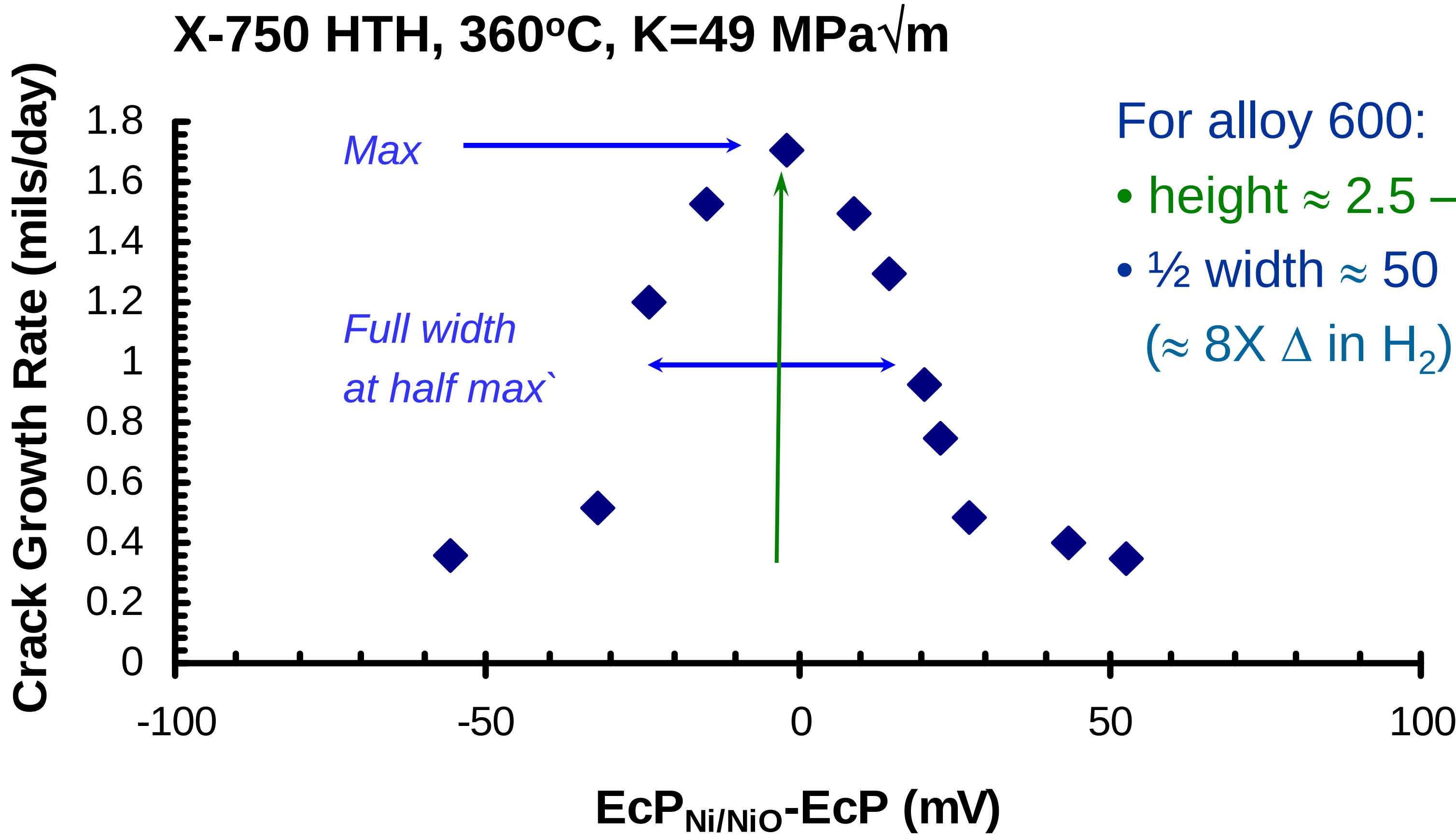
Role of H_2 Also Relevant to BWRs



Peak growth rate occurs at much lower H_2 at 274C of BWR materials

Ni Alloy Crack Growth Rate vs. H_2

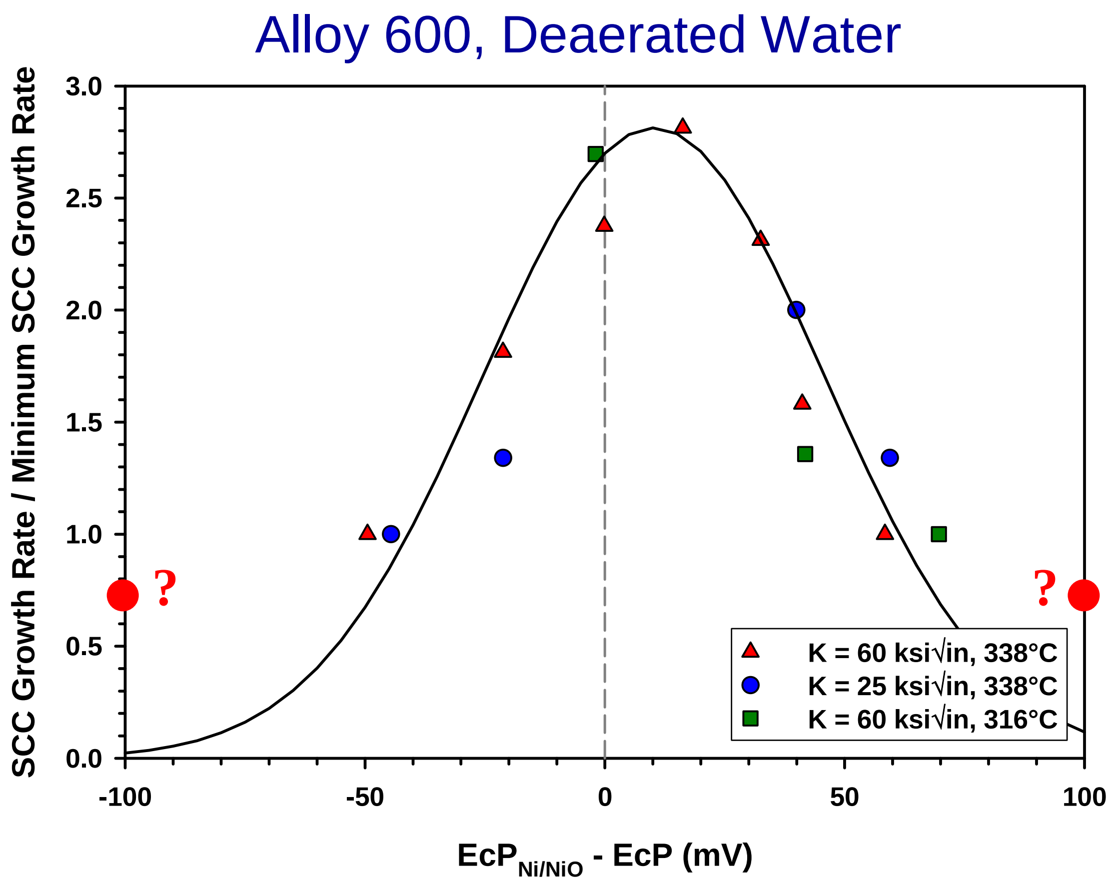


For alloy 600:

- height ≈ 2.5 – 3X
- ½ width ≈ 50 mV
  (≈ 8X Δ in H_2)

KAPL data: consistent benefit of ↑H_2 288 – 360 °C

Ni Alloy Crack Growth Rate vs. H_2



"Background" CGR at low or high H_2 is likely a bit lower – this could markedly increase the peak height

KAPL data: consistent benefit of ↑H_2 vs. temperature & K

Hard to conclude that the peak is not actually at Ni/NiO

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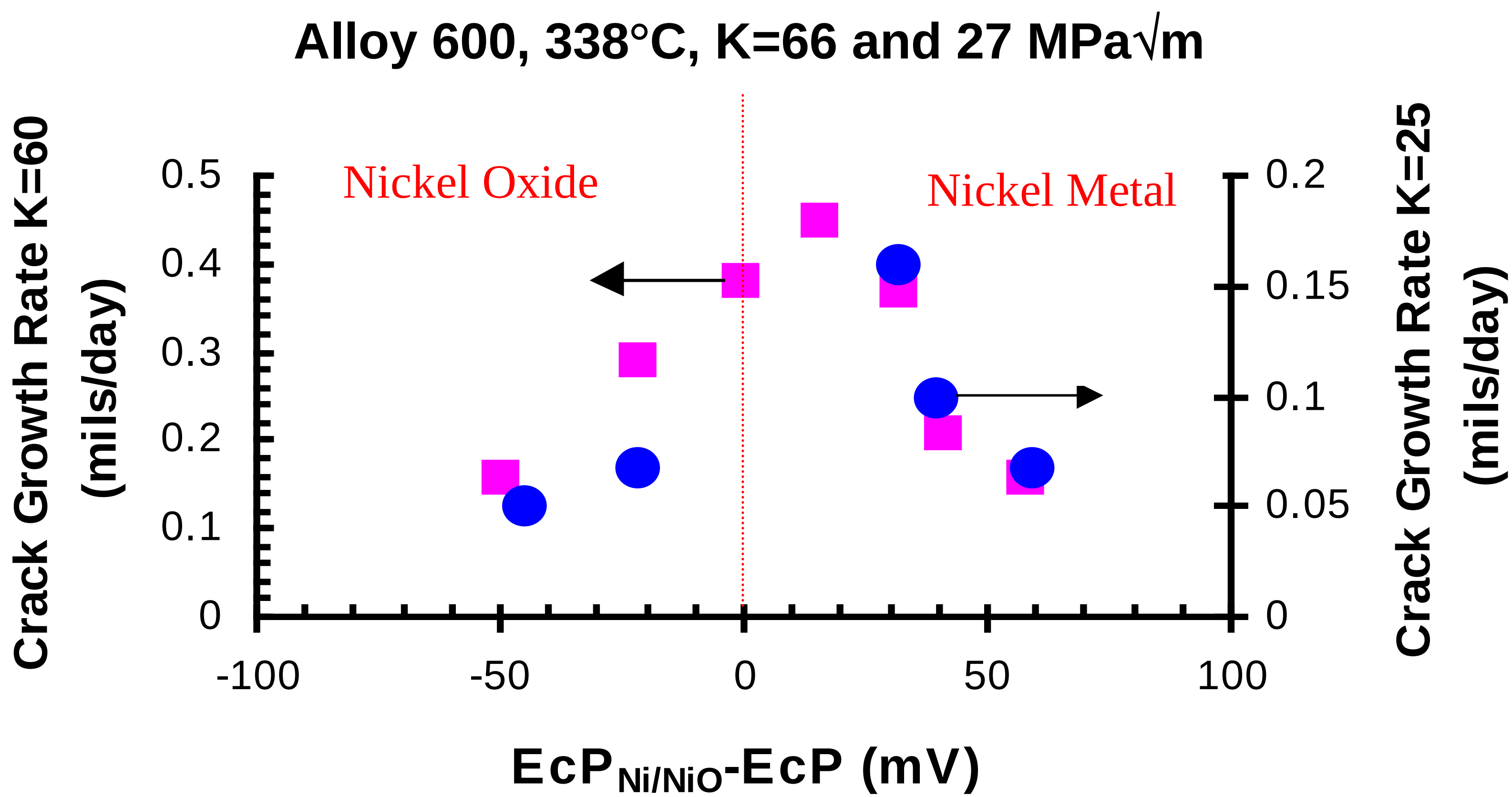
Ni Alloy Crack Growth Rate vs. H_2



KAPL data: CGR different, but peak vs. H_2 is similar for different temperatures and K

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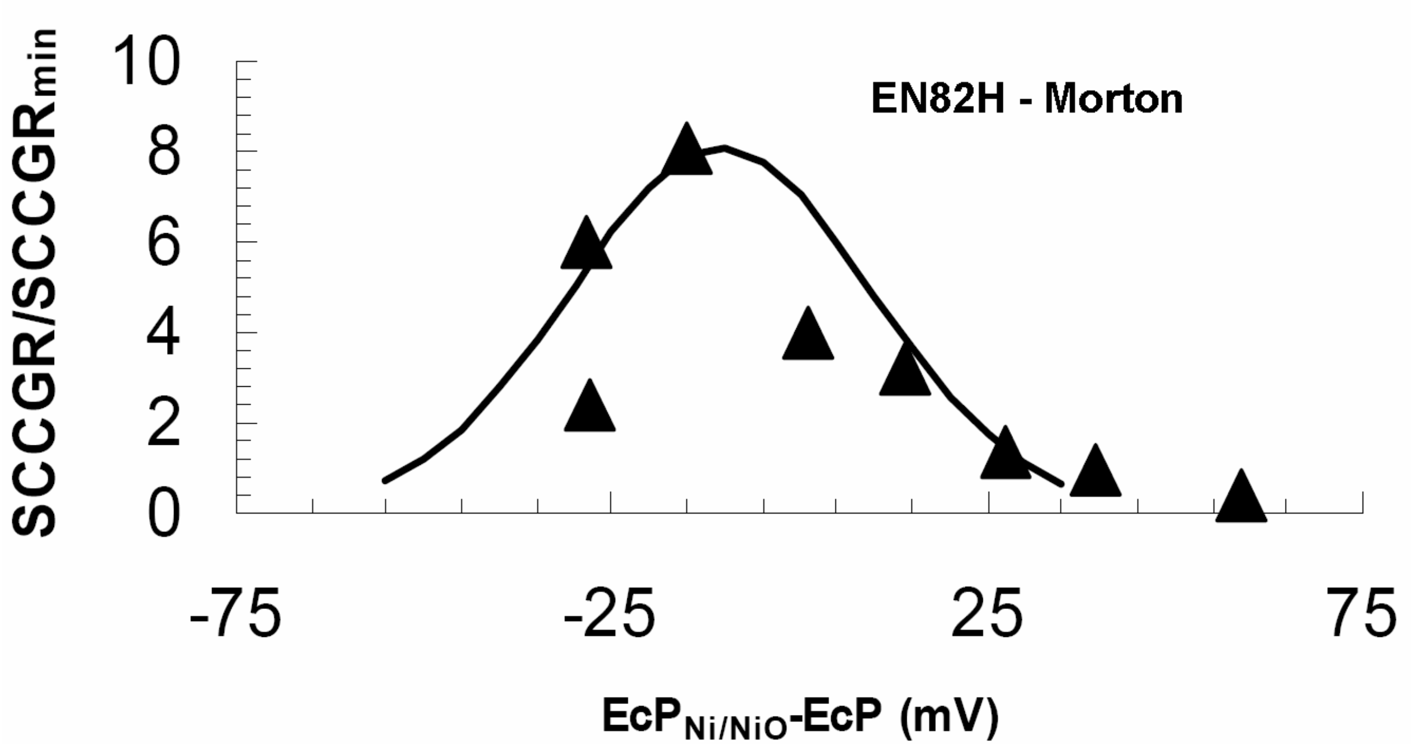
Alloy 82 Weld Metal Crack Growth Rate vs. H_2



Hard to conclude that the peak is not actually at Ni/NiO

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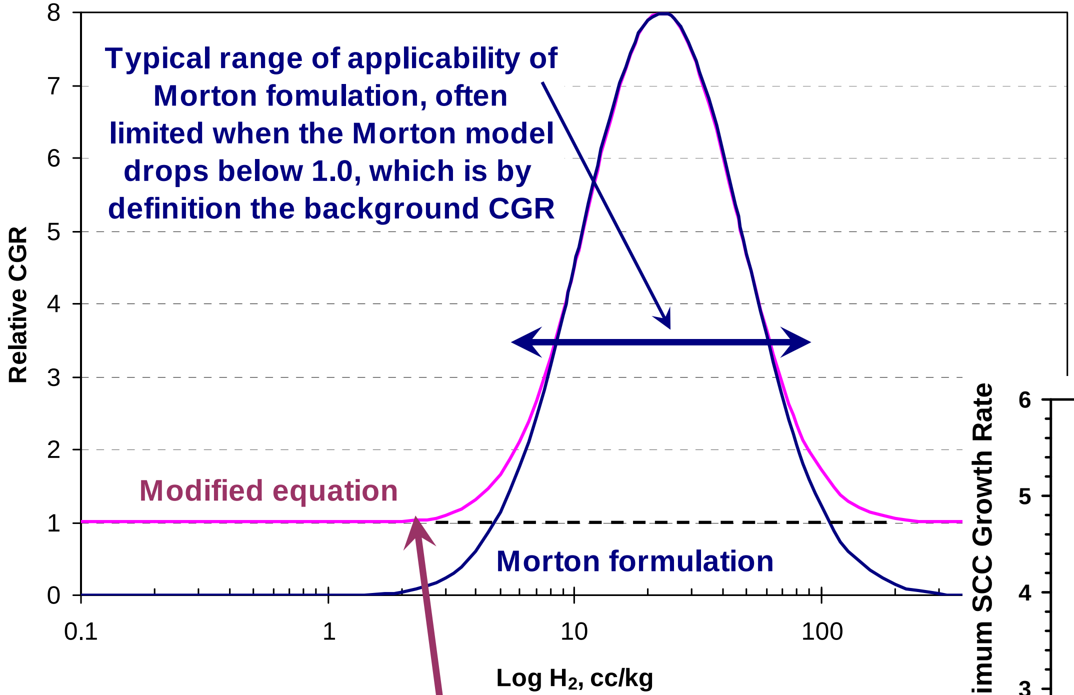
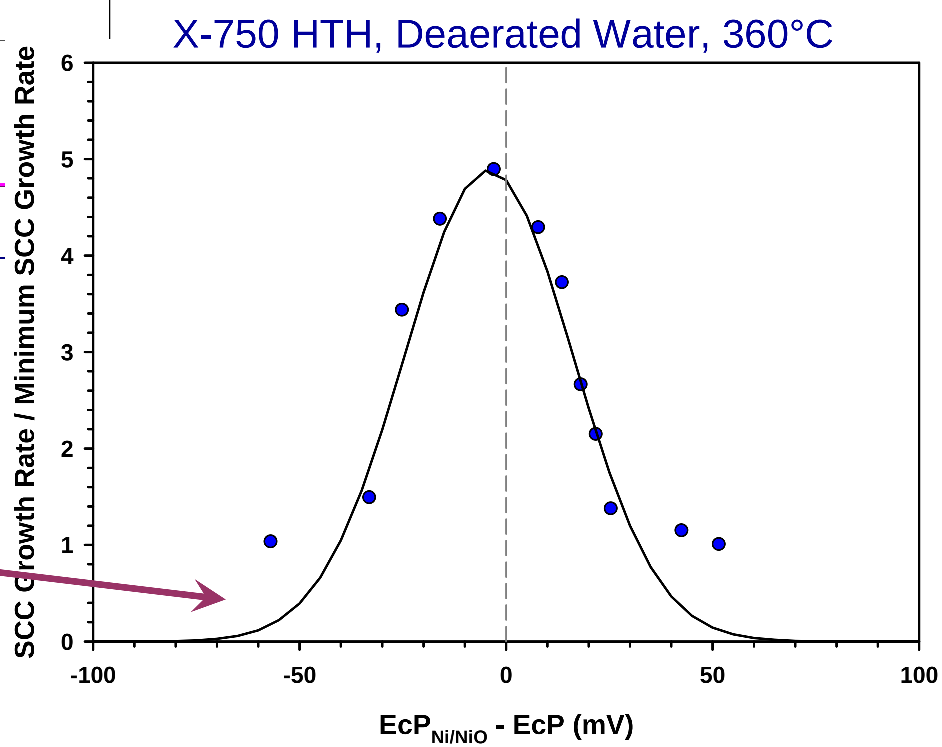
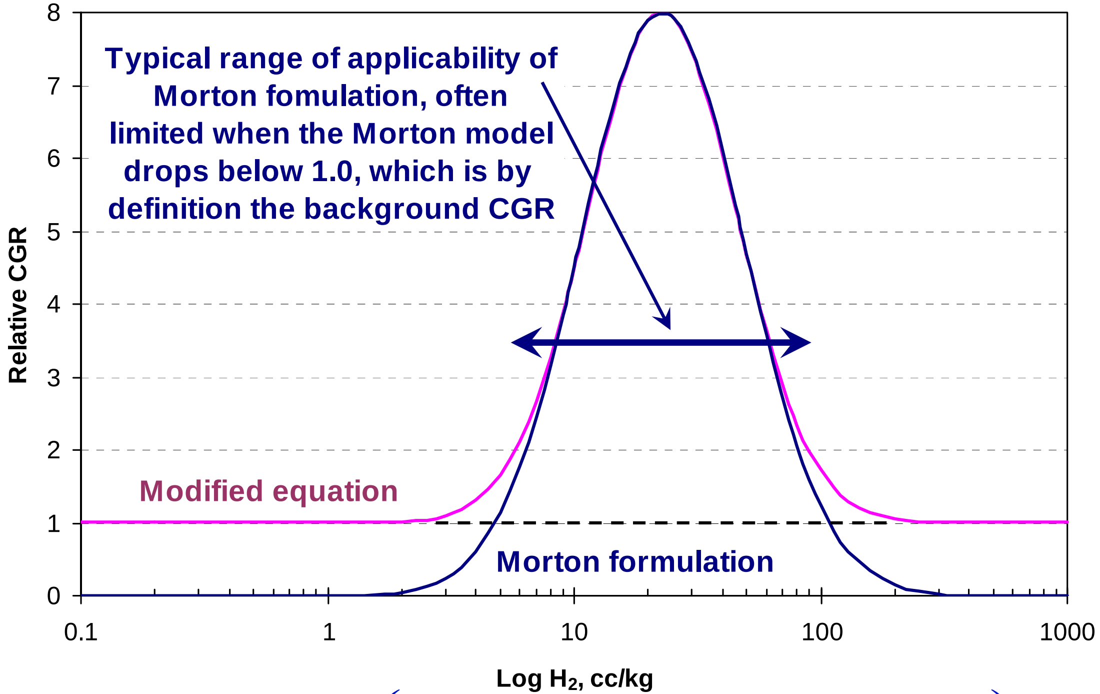
Modeling H_2 Effects on CGR



KAPL model modified to →1 rather than →0 and fit data better



Modeling H_2 Effects on CGR



$$V_P = (P-1)\exp\left(-0.5\left[\frac{\Delta ECP + ECP_{OS}}{\lambda + (0.46)^{1/P}}\right]^2\right) + 1$$

ECP_{os} = offset of CGR peak from Ni/NiO phase boundary (see Morton)

Ni/NiO Phase Boundary

$= 10^{(0.0111*T(°C) - 2.59)}$ cc/kg H_2

V_P = velocity vs. peak (e.g., 1-8)

P = height of peak (e.g., 3-8X)

λ = width of peak (see Morton)

= 20.2 (A82) or 35.6 (A600)

ΔECP = H_2 value vs. peak H_2

=29.58 (T+273.3)/298.2 * log (H_2/$H_{2\text{-Peak}}$)

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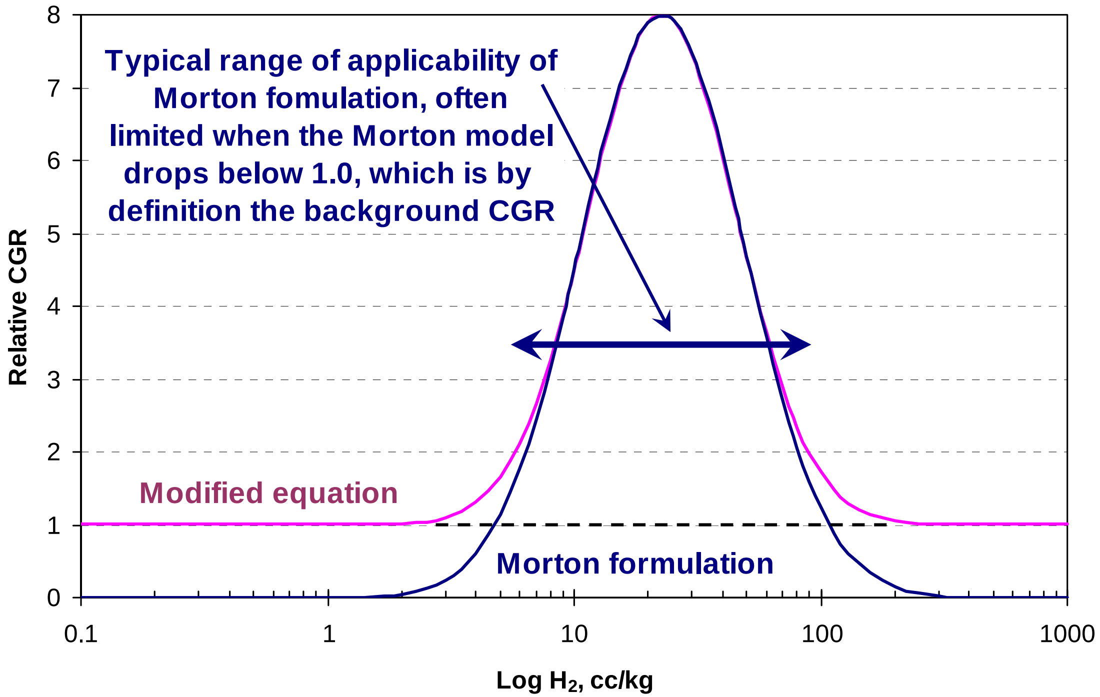
Modeling H_2 Effects on CGR



Morton Formulation

$$V_P = P \exp\left(-0.5\left[\frac{\Delta ECP + ECP_{OS}}{\lambda}\right]^2\right)$$

Morton parameters from

Attanasio & Morton, Proc. 11th Int. Conf. on Environmental Degradation of Materials, 2003.)

Test Material and Condition	$\frac{SCCGR_{max}}{SCCGR_{min}}$	ΔEcP_o	λ	Range of Applicability†
EN82H, 338°C	8.09	10.5	20.2	- 52 mV < ΔEcP < 31 mV
Alloy 600, 338°C	2.81	-10.2	35.6	- 41 mV < ΔEcP < 61 mV
Alloy X-750 HTH, 360°C	4.89	4.2	20.4	- 41 mV < ΔEcP < 32 mV
Alloy X-750 AH, 338°C	7.19	30.8	40.0	- 110 mV < ΔEcP < 49 mV

† *The SCCGR effect of dissolved H_2 seems to have an appreciable influence in a narrow range of EcP near the Ni/NiO phase transition.*

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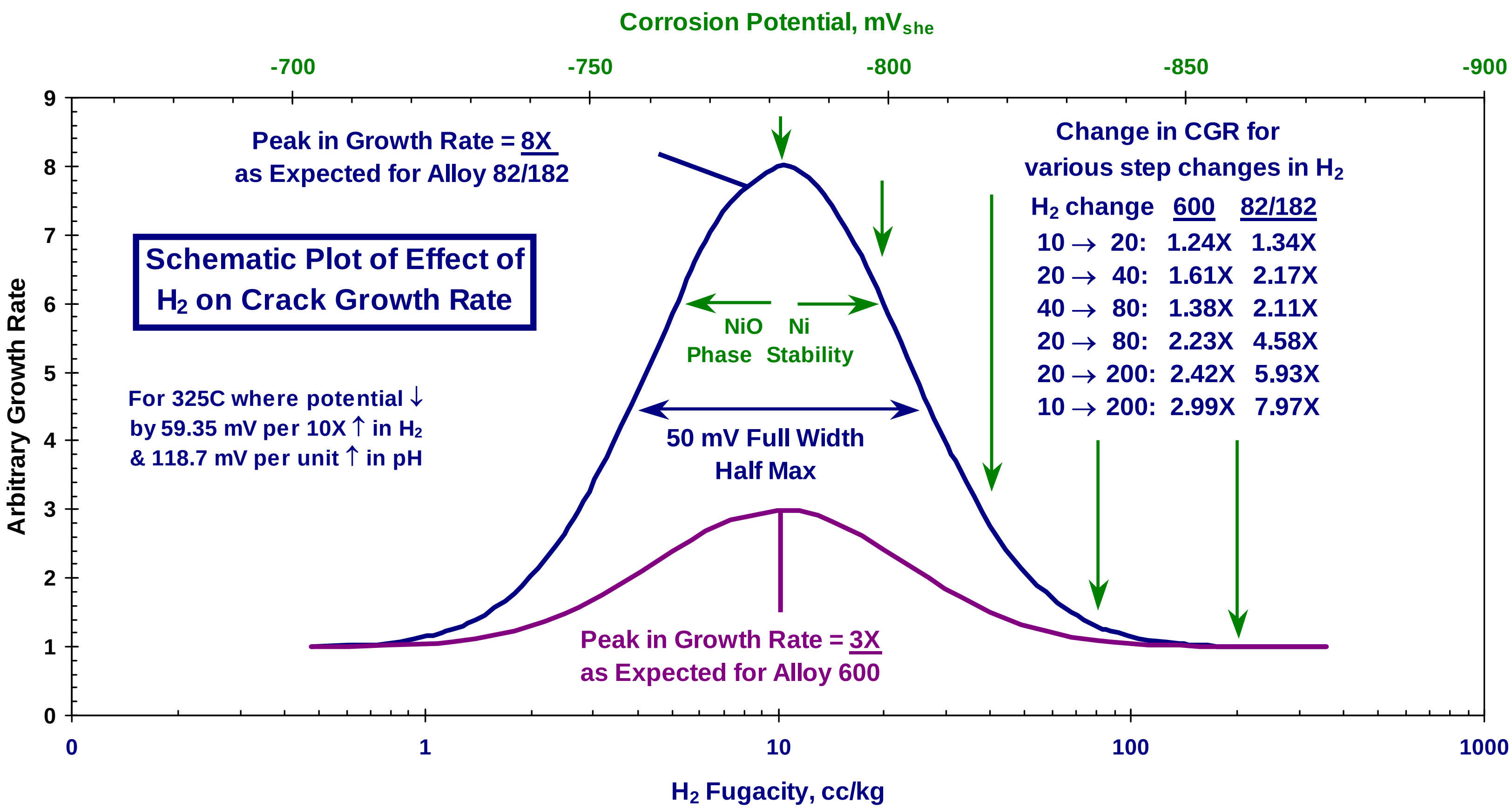
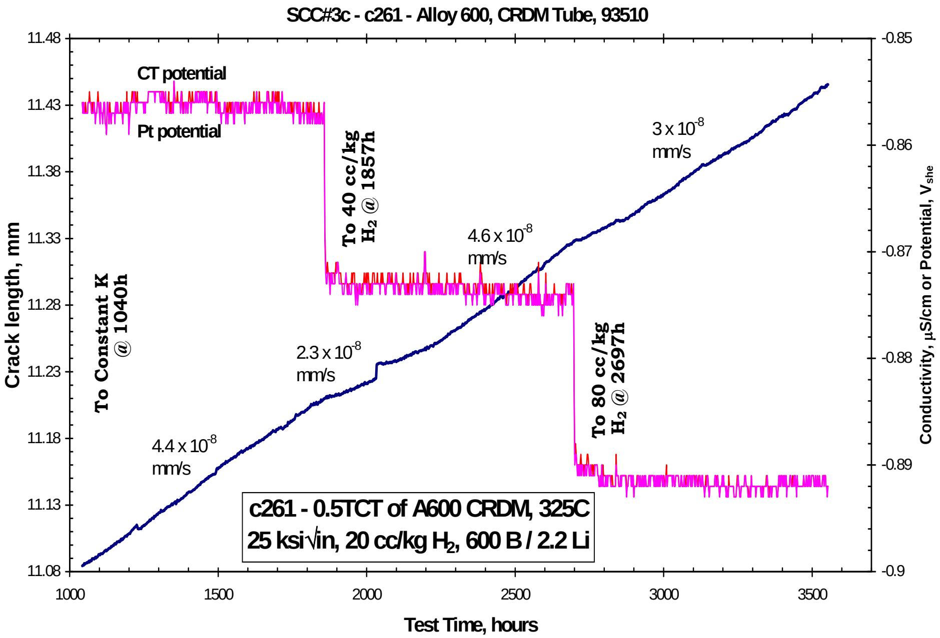
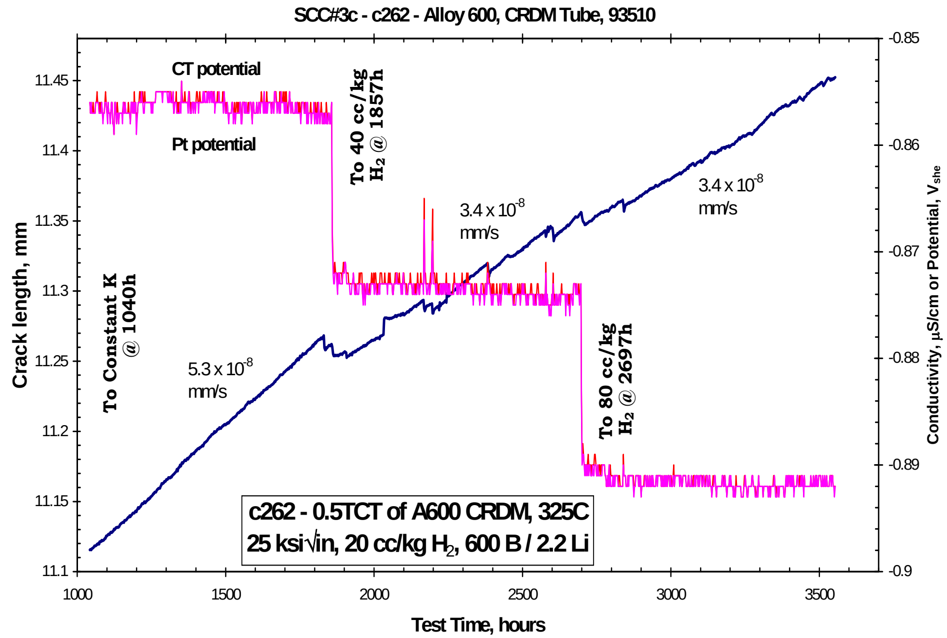
Alloy 600 Crack Growth Rate vs. H_2



Schematic of change in growth rate vs. H_2
for Alloy 600 & Alloys 82/182

H_2 Effects on SCC Growth Rates



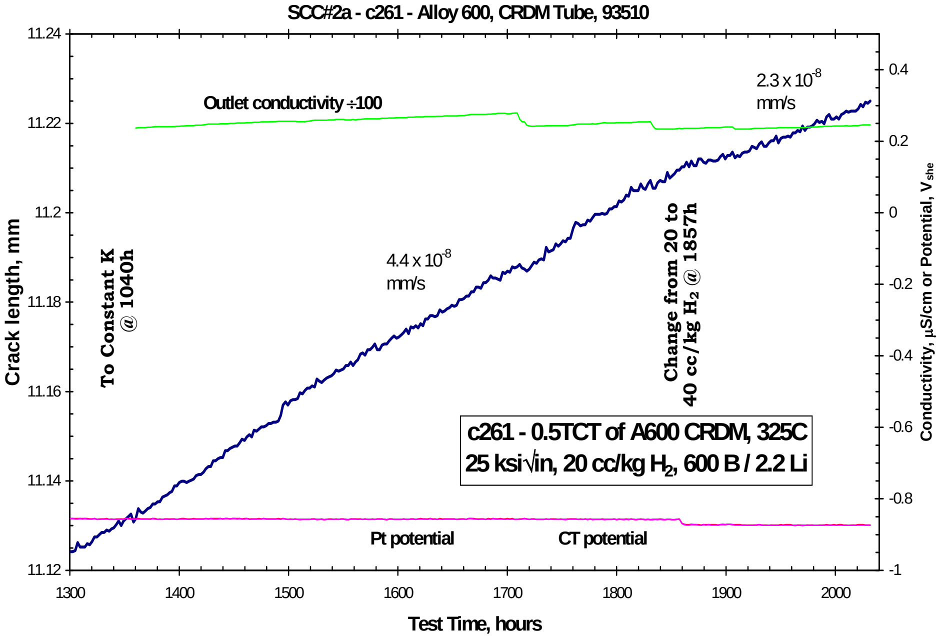


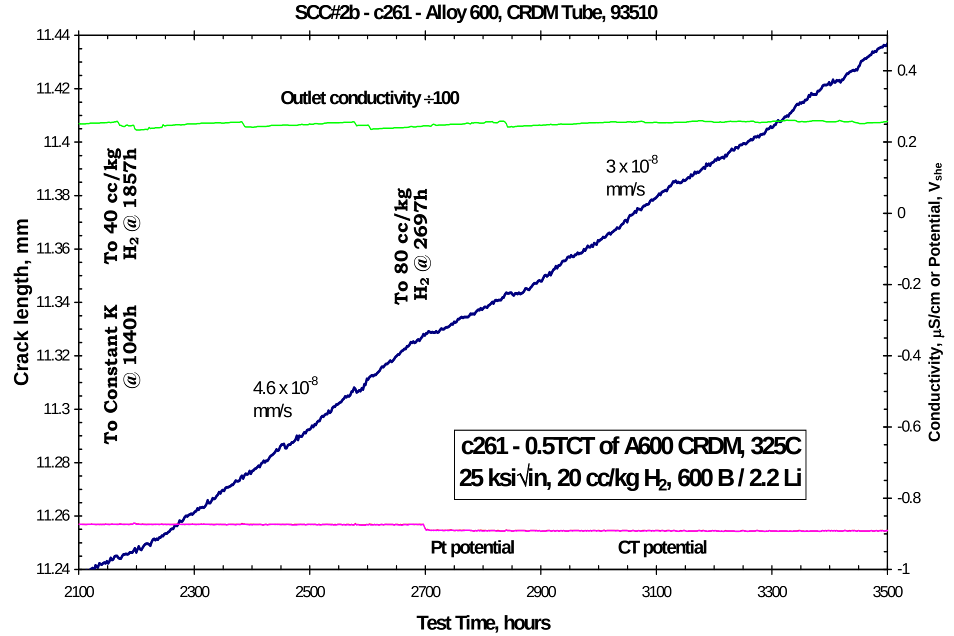
Thermodynamic response in ECP to changes in H_2

2X change in H_2 = 17.9 mV at 325C

Alloy 600 CRDM, 325C, 600 B / 2.2 Li, 20 cc/kg H_2

H_2 Effects on SCC Growth Rates

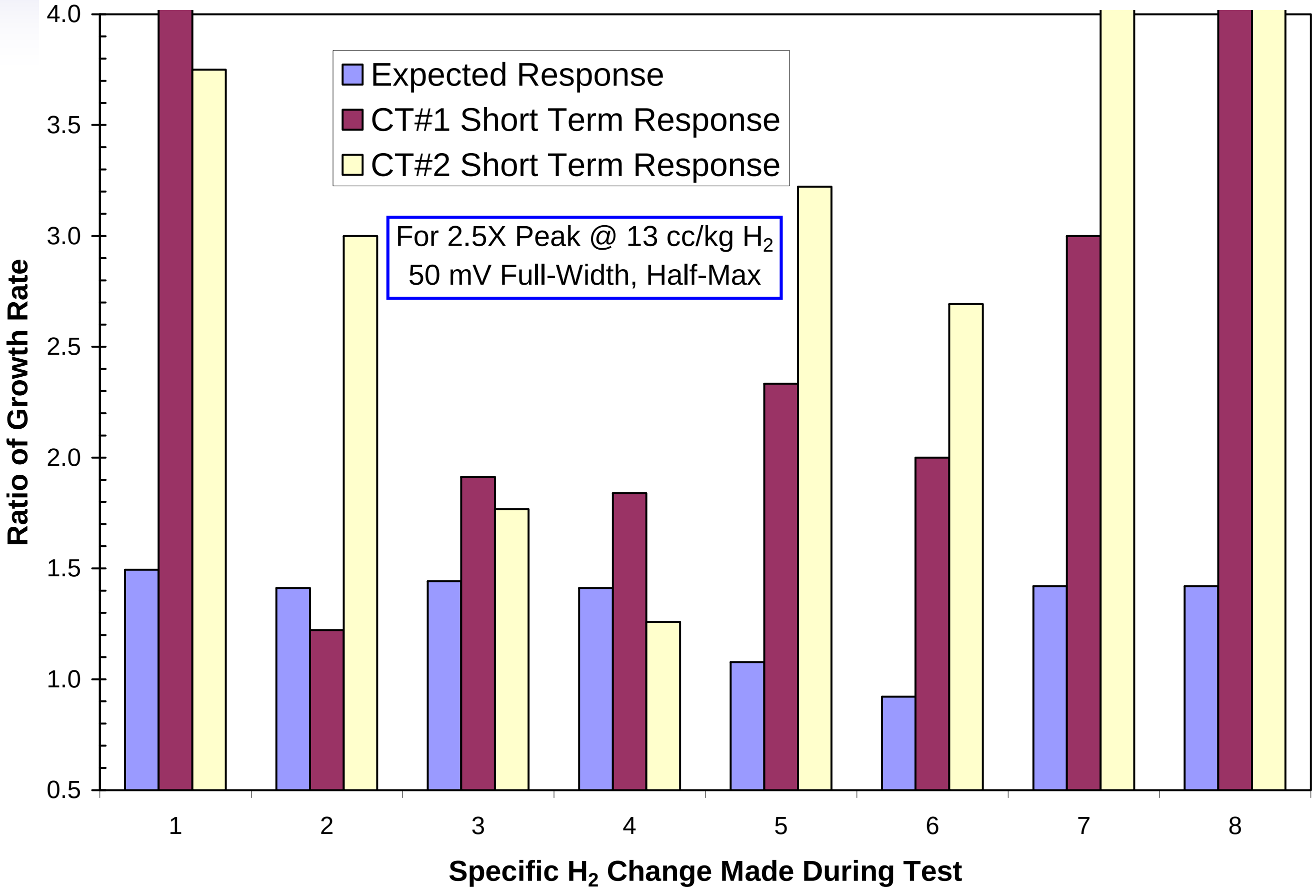




Response immediately after H_2 change, but then ↑ in CGR

Alloy 600 CRDM, 325C, 600 B / 2.2 Li, 20 cc/kg H_2

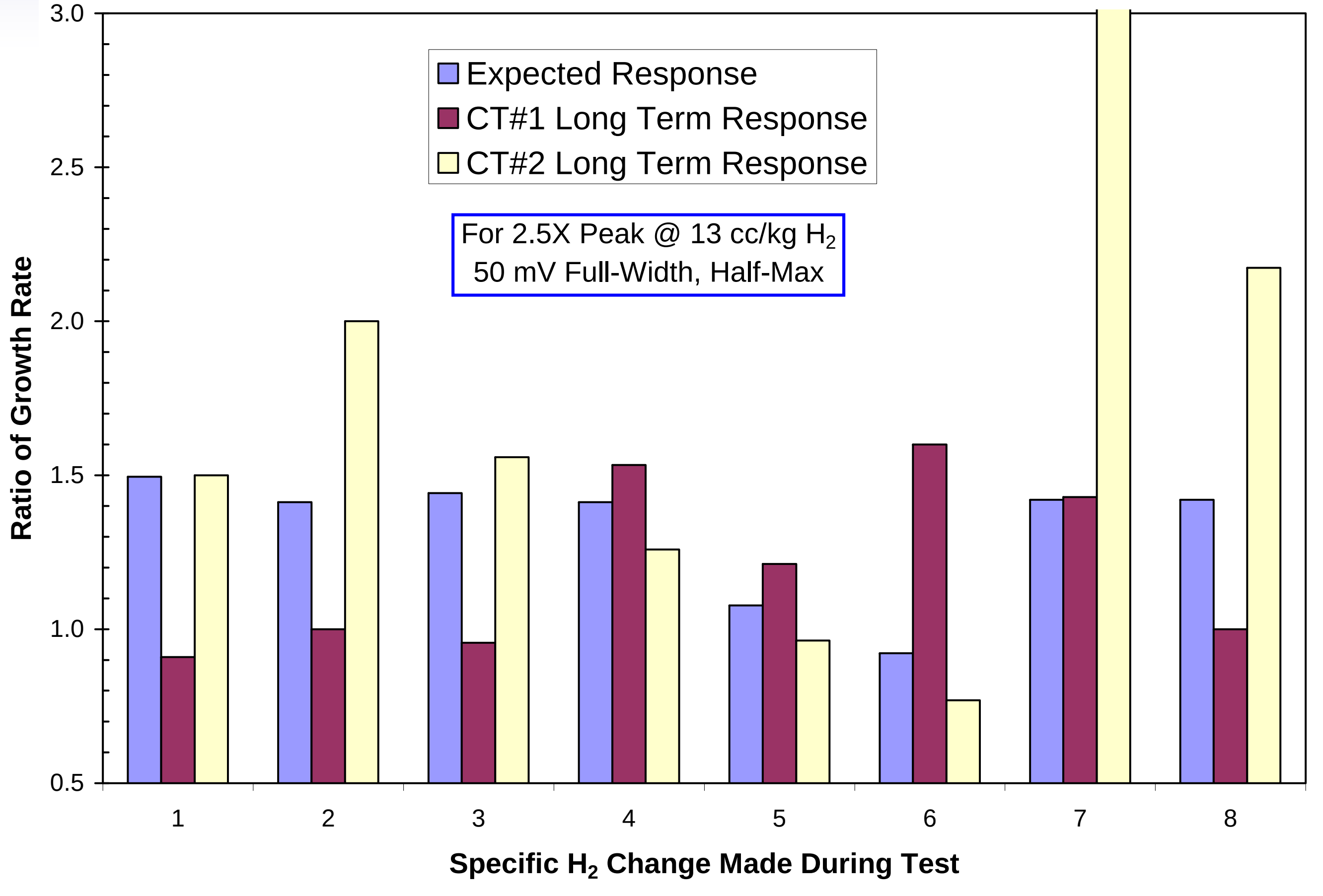
H_2 Effects – Short Term



Stronger short term effect is likely related to dcpd "shorting" when moving farther into Ni-metal stability as H_2 ↑

Expected & short-term observations of ratio in crack growth rate for specific changes in H_2, e.g., 20 to 40 cc/kg

H_2 Effects – Long Term



Long-term effect is more representative of actual effect of H_2

Expected & long-term observations of ratio in crack growth rate for specific changes in H_2 – average overall agreement is 10%

H_2 Effects on SCC Growth Rates (35 cc/kg reference)

Alloy 600 | Alloy 82/182

Baseline= 35 cc/kg	Alloy 600 (3X Peak Height, λ = 35.6, ECP_{OS} = 0)				Alloy 182/82 (8X Peak Height, λ = 20.2, ECP_{OS} = 0)			
Temp, °C	290 °C	310 °C	325 °C	343 °C	290 °C	310 °C	325 °C	343 °C
H_2 at Ni/NiO	4.3 cc/kg	7.1 cc/kg	10.4 cc/kg	16.5 cc/kg	4.3 cc/kg	7.1 cc/kg	10.4 cc/kg	16.5 cc/kg
35 → 100	1.30	1.53	1.69	1.76	1.14	1.62	2.52	3.94
35 → 80	1.27	1.44	1.55	1.56	1.14	1.59	2.36	3.22
35 → 50	1.14	1.20	1.22	1.19	1.10	1.37	1.63	1.66
35 → 10	0.54	0.58	0.68	0.91	0.24	0.23	0.33	0.76
35 → 3	0.47	0.69	1.02	1.67	0.16	0.37	1.04	3.63
35 → 1	0.72	1.21	1.74	2.41	0.54	1.37	2.55	4.84
50 → 100	1.14	1.27	1.39	1.47	1.03	1.18	1.54	2.37
50 → 80	1.11	1.20	1.27	1.31	1.03	1.16	1.45	1.93

Predicted effects for specific changes in H_2 at various temperatures

Based on CGR peak at Ni/NiO phase boundary with peak height and width as specified by Morton et al.

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H_2 Effects on SCC Growth Rates (30 cc/kg reference)

Alloy 600 / Alloy 82/182

Baseline= 30 cc/kg	Alloy 600 (3X Peak Height, λ = 35.6, ECP_{OS} = 0)				Alloy 182/82 (8X Peak Height, λ = 20.2, ECP_{OS} = 0)			
Temp, °C	290 °C	310 °C	325 °C	343 °C	290 °C	310 °C	325 °C	343 °C
H_2 at Ni/NiO	4.3 cc/kg	7.1 cc/kg	10.4 cc/kg	16.5 cc/kg	4.3 cc/kg	7.1 cc/kg	10.4 cc/kg	16.5 cc/kg
30 → 100	1.40	1.66	1.84	1.87	1.25	1.97	3.17	4.71
30 → 80	1.36	1.57	1.68	1.66	1.24	1.94	2.97	3.84
30 → 50	1.22	1.31	1.33	1.27	1.21	1.67	2.05	1.99
30 → 10	0.58	0.63	0.74	0.97	0.27	0.27	0.41	0.91
30 → 3	0.50	0.75	1.10	1.77	0.17	0.44	1.31	4.34
30 → 1	0.77	1.31	1.88	2.56	0.59	1.67	3.20	5.79
50 → 100	1.14	1.27	1.39	1.47	1.03	1.18	1.54	2.37
50 → 80	1.11	1.20	1.27	1.31	1.03	1.16	1.45	1.93

Predicted effects for specific changes in H_2 at various temperatures
Based on CGR peak at Ni/NiO phase boundary with peak height and width as specified by Morton et al.

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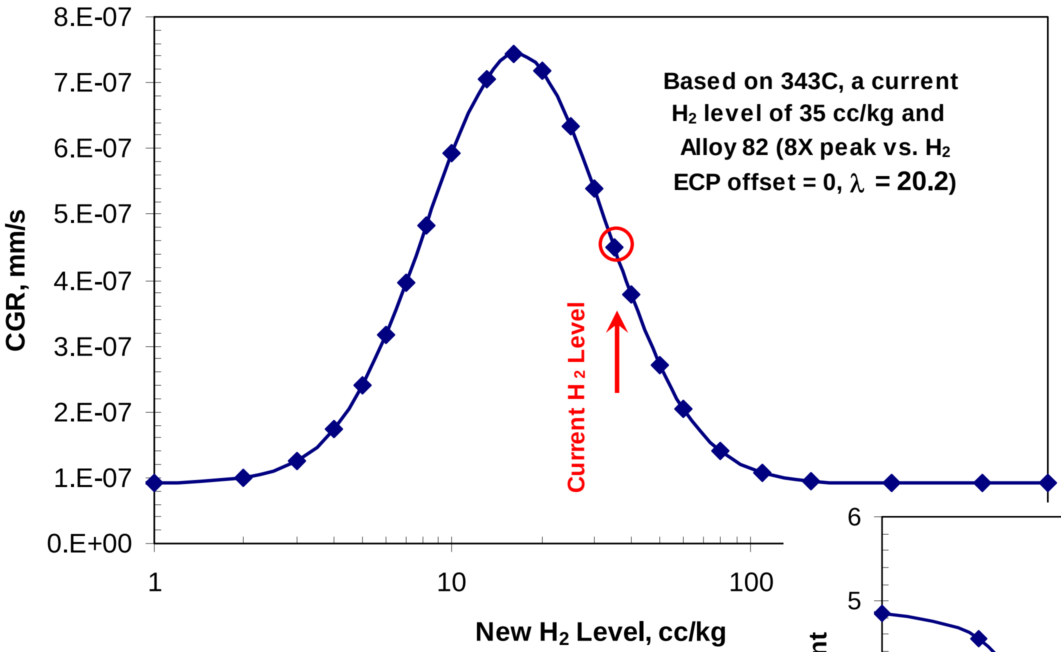
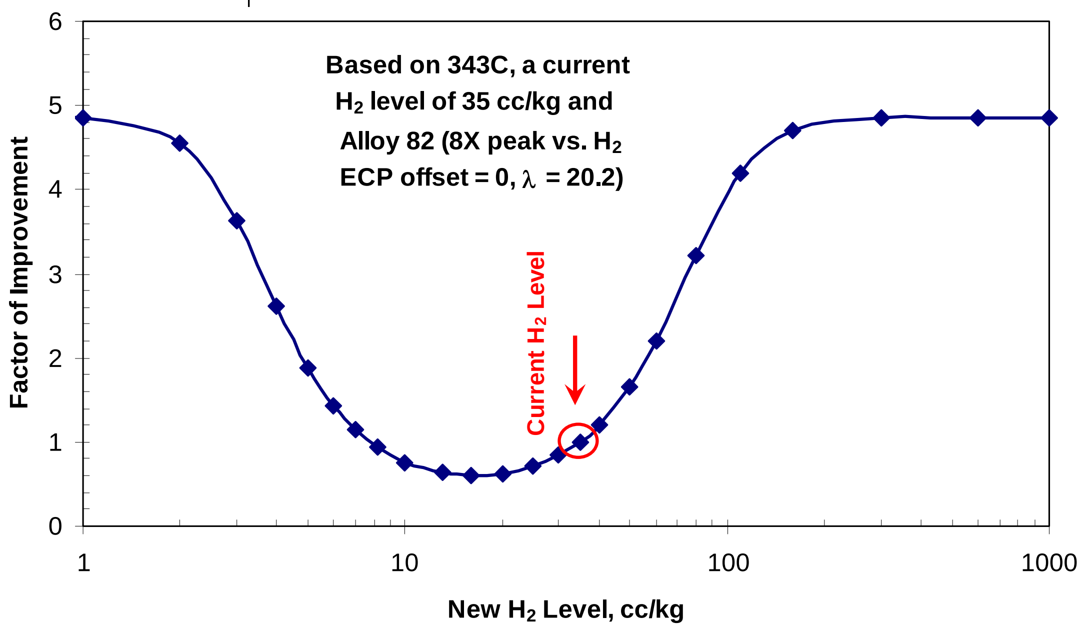
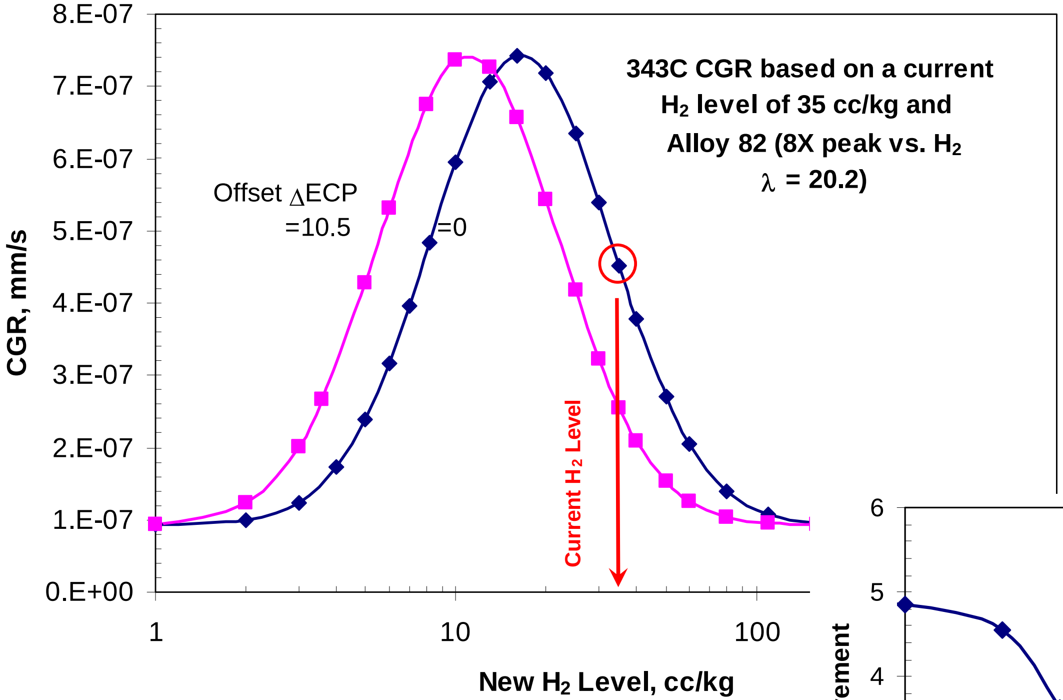
H_2 Effects on SCC Growth Rates



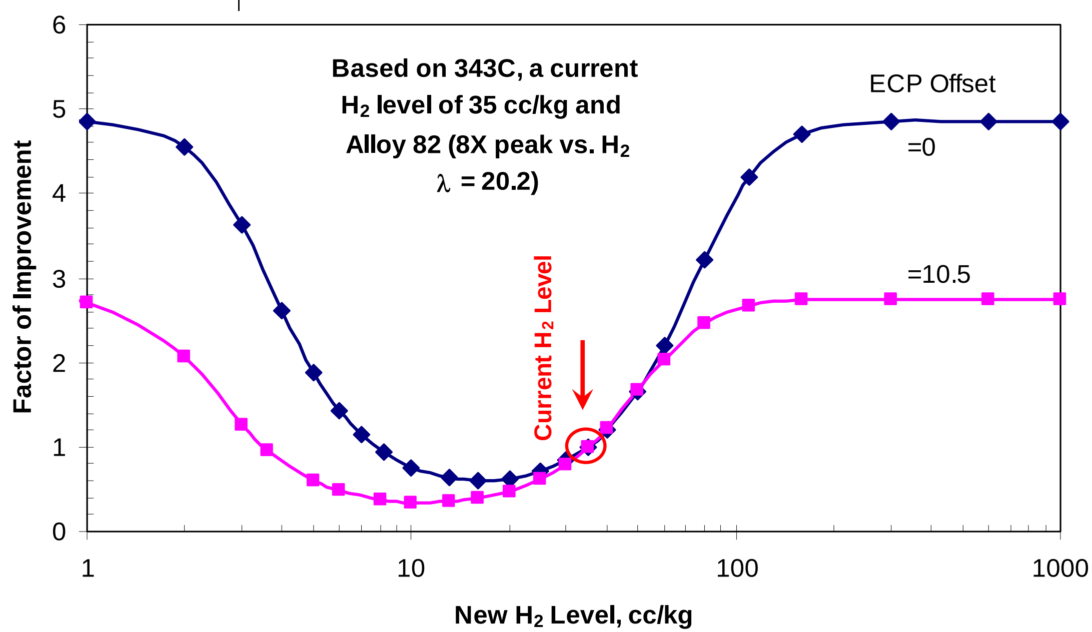
Growth Rate and Factor-of-Improvement at 343C



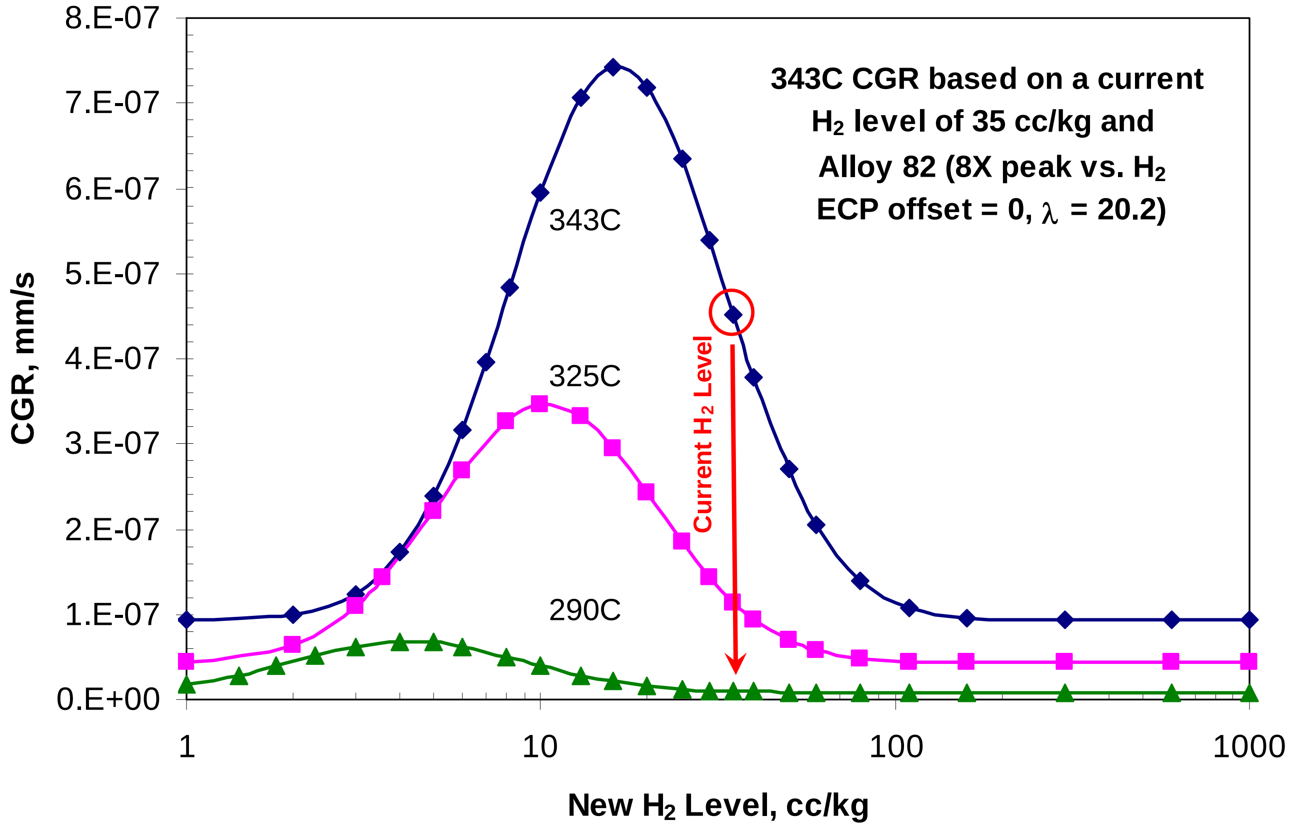
Effect of H_2 or ECP Offset on CG Rate



ECP offset from Ni/NiO not justified: Alloy 82 = +10 mV and Alloy 600 = -10 mV



H_2 Effects on SCC Growth Rates



If decreasing from 35 cc/kg H_2 the same growth rate (no benefit) occurs at:

343 °C = 7.7 cc/kg H_2

325 °C = 3.1 cc/kg H_2

310 °C = 1.4 cc/kg H_2

290 °C = 0.5 cc/kg H_2

Current operating H_2 is above peak, so large reduction in H_2 is needed to get benefit – concern for radiolysis below ~2 – 4 cc/kg H_2

Conclusions on Modeling H_2 Effects

Summary and Interpretation of H_2 Theory & Modeling:

- Thermodynamic ECP response for SS & Ni Alloy vs. H_2
  - true even for H_2 < 0.1 cc/kg (9 ppb) in pure water or B/Li.
- H_2 effect appears to apply ~identically independent of temperature, stress intensity factor, B/Li, or heat.
- H_2 peak height (peak-to-background) is ~3X for Alloy 600 and ~6 – 8 for 182/82 weld metals & Alloy X750.
  The "background" growth rate may be lower, so peak is higher
- Deviations (offsets) from Ni/NiO are probably noise/scatter:
  the offset for Alloy 600 = -10 mV;   Alloy 82 = +10 mV.
- H_2 peak width (e.g., FWHM) seems to vary, but more data are needed
- Factor-of-improvement analyses are complex because they must account for temperature, historical H_2, new H_2, material, etc.

Conclusions on Measuring H_2 Effects

Summary and Interpretation of H_2 Results:

- Observed thermodynamic response to ECP for changes in H_2
- Short term CGR response may be related to changes in Ni/NiO and Ni-Fe-Cr/spinel oxide stabilities on dcpd
- Effects of H_2 on CGR of alloy 600 agrees with KAPL data:
  - peak to background is only ~2.5 – 3X
  - peak at 325C is ~10.4 cc/kg H_2
  - width of peak at half-max is ~50 mV = 7X change in H_2
  - a peak height of 5 – 8X is observed for X750 or 82/182
- Mitigation benefit for a given component depends in rather complex manner on alloy, temperature & current vs. target H_2
- Future work will include Alloy 182 (larger effect of H_2)

MRP Current Position on Desirability of Raising H_2

- Strong theoretical basis, supported in particular by extensive test data from the NR program, to recommend moving to higher hydrogen levels in PWR primary water so as to obtain some mitigation of PWSCC for Ni-base alloys used in thick-wall components.
- Such a change is expected always to have a positive effect in slowing down crack growth, no matter what exact material or operating temperature is involved. Some mitigation benefit already being accrued with the current trend of moving to higher H_2.
- Quantifying the predicted benefit of such a change for any particular component, however, is complex.
- Overall, the benefit of hydrogen optimization will always be greater at higher temperatures (e.g., in the pressurizer) and for higher-strength alloys (e.g., weld metals or Alloy X750, rather than Alloy 600).
- Parallel effort on plant safety/operability evaluation for increased hydrogen is under way; assessment of effect on fuel integrity of higher hydrogen is planned (next 3 slides)

H_2 Optimization: Prioritized List of Issues

Issue	Rank
Elevated hydrogen during operation	
Will elevated H_2 levels during operation affect the performance of PWR Zr-based alloys? (crud, subnucleate boiling, fuel, etc.)	High
Will elevated H_2 levels during operation result in explosive gas mixtures in containment during a LOCA and other licensing/safety issues?	High
Can the plant maintain ≥ 50 cc/kg dissolved H_2 with the existing VCT and all plant systems?	Medium
Will the increase in total dissolved gases cause operational problems (gas pocket formation)?	Medium
Will the increase in total dissolved H_2 on the primary side affect conditions on the secondary side?	Medium
What are the possible consequences of elevated H_2 under off-normal conditions (make-up additions, letdown loss, etc.) that would be counter-productive?	Medium
Will elevated hydrogen levels have an effect on plants using Zn addition?	Medium
Reduced hydrogen during operation	
What margin will be required to ensure radiolytic oxygen production does not occur?	High
Under what conditions will low H_2 have no benefit or a negative benefit?	High
Hydrogen effects during plant shutdown	
LTCP? Is stored hydrogen important? How quickly can H_2 be removed prior to shutdown?	Medium

- All safety items were given the highest priority ranking
- Other lower priority issues will be addressed in the final report

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FRP: Concerns with Elevated Coolant DH

1. Possible H_2 pickup increase in Zr-based alloys
   - Hydride rims (layers with [H]>~1000 ppm) at the outer zone of the cladding wall thickness could increase corrosion
   - 18% volume expansion of Zr upon conversion to the hydride contributes to in-reactor growth, dimensional stability
   - Zr-hydrides, $ZrH_{1.6}$, may further decrease ductility, fracture toughness of the metal
2. Elevated DH affects Fe, Ni solubility
   - Anticipate that Fe solubility increases and Ni solubility decreases. What happens to crud composition and morphology?
     - Enhanced corrosion under deposits? AOA?
3. Possible Ni metal precipitation on cladding, grids, and thimble tubes during startup
   - Possible pathway for H_2 entry from DH into Zr components

FRP: Recommendations for Implementing Elevated Coolant Hydrogen

Task 1: Perform out-reactor testing of M5 and ZIRLO to screen for sensitivity of corrosion and H_2 pickup at elevated DH. Tests should include post-transition corrosion oxides, high DH, Zr-4, -2 controls.

Task 2: Assess the impact of DH on corrosion product species in the coolant and on startup and shutdown procedures.

Task 3: In-reactor loop tests may be considered and can be used as a second screening. But it is nearly impossible to simulate commercial PWR system corrosion & crud deposition in loop tests.

Task 4: Pending favorable screening, begin demonstration in commercial plants using a cautious approach of increasing DH in steps of ~10 cc/kg and following with fuel surveillance. First implementation should be in low or medium duty plants. High duty plants can follow.

Effect of Reduced Hydrogen on PWSCC

- Ongoing MRP test program focuses on increasing H_2 fugacity to obtain lower CGRs, but growth rates are also predicted to decrease at much lower H_2 levels, except for components operating at the lowest temperatures in the primary circuit.
- Low H_2 approach to optimizing H_2 levels is being investigated in Japan and emerging results should be followed closely.
- Radiolysis is a possible concern here, since the increase in CGR that would result from a significant elevation of ECP is much larger than benefit from adjusting H_2.

Reduced Hydrogen to Mitigate PWSCC

- To reduce crack growth rates to a level comparable to that of 50 cc/kg, hydrogen would have to be reduced to approximately 2.5 cc/kg H_2 at 325°C, which does not provide an adequate operating margin
- Current data indicate that >1-5 cc/kg H_2 is required to suppress radiolysis and avoid oxidizing conditions
- Japan Atomic Power Company (JAPC) has developed a multi-year plan to investigate operation as low as 5 cc/kg H_2
- Possible Issues:
  - Effect on corrosion product transport and deposition
  - Effect on crack growth rates