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Intergranular corrosion on Hastelloy

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Merck & Co., Inc., Rahway, NJ, USA

P2SAC May 2026

Biography

Tao Chen

Senior Scientist

Environmental & Process Safety Engineering (EPSE)

Educational Background:

- B.S. - Chemical Engineering, Rutgers University (2010)
  - Minor in Mathematics
- M.S and PhD
- Chemical Engineering, Stevens Institute of Technology (2017)

Professional Background:

- 2017-2019 Research Eng – Controlamatics Inc
  - Ultracapacitor synthesis research
- 2019-2022 Contractor at Bristol-Myer Squibb
- 2022 – Present Senior Scientist

Merck & Co., Inc., Rahway, NJ, USA

Technical Expertise

- Calorimetry
  DSC/ARSST/CRC/D-ARC/Easymax
- Corrosion/MoC
- Dust Explosivity
- Electrostatic/Condutivity

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Problem – Is it supposed to be this color?

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Problem statement

Corrosion was observed in one of our processes when outsourced at a CMO.

What happened?

Should it happen?

How did it happen?

Why did it happen?

Hastelloy (Alloy) C-22 vs 2M HCl (aq) in Acetonitrile

Cr: 1847ppm
Mn: 28ppm
Fe: 151ppm
V: <20ppm
W: 29ppm
Co: 27ppm
Ni: 6092ppm
Mo: 502ppm

Indications:
- Discoloration of the solution
- Elevated metals
- Roughening of the coupon

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Why is corrosion important?

Safety
- Integrity of an equipment ensures that mechanical properties are at specification
- Localized corrosion can cause equipment to fail prematurely and catastrophically

Capital investment/replacement
- Equipment is expensive

Quality of the product
- Product contamination leads to quality impacts
- Metal (Ni) contamination can cause catalyst deactivation or even trigger unwanted side reactions

Time loss
- Corrosion investigation leads to down time
- QN and Root Cause analysis
- Any safety implications

Fundamentals

Metal corrosion is a redox reaction

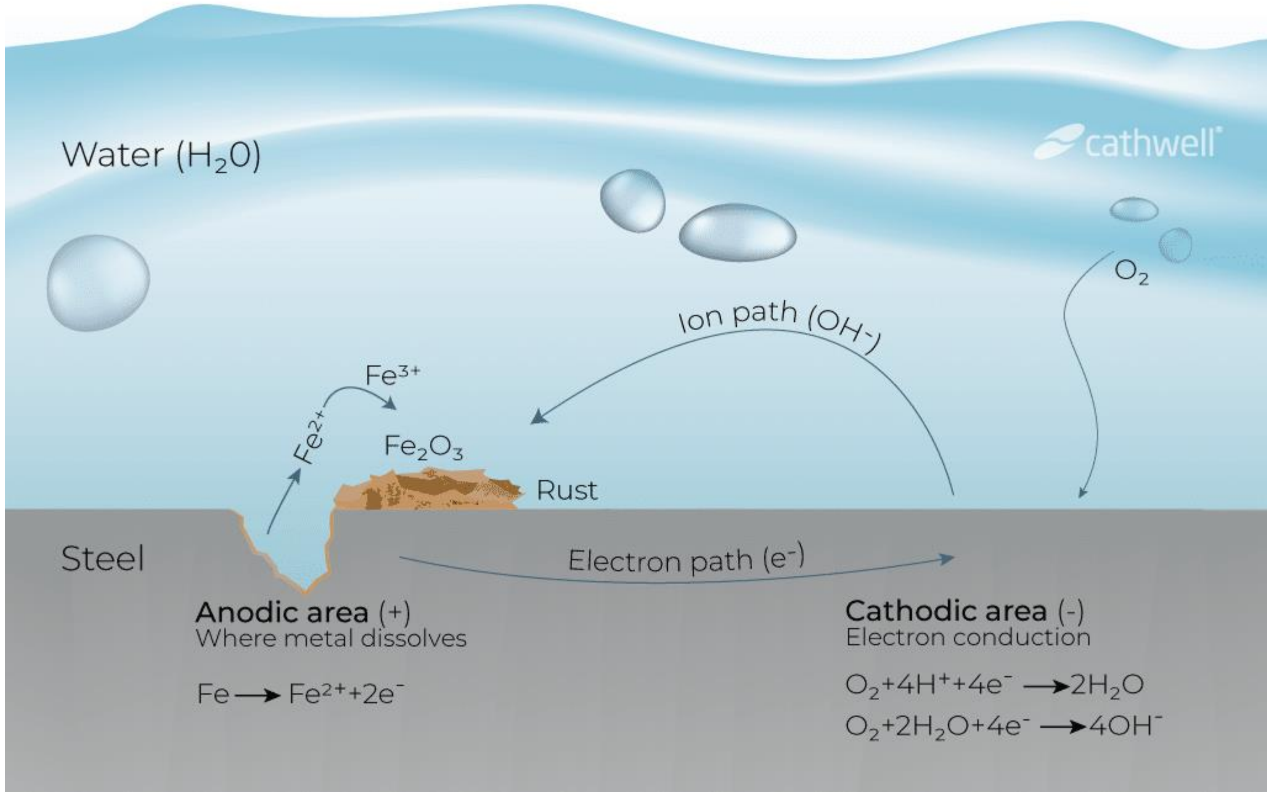
Anode: $M^0 \rightarrow M^{+n} + n\,e^-$

Cathode (most common):

$$H_2O + ½\,O_2 + 2\,e^- \rightarrow 2\,OH^-$$

$$2H^+ + 2\,e^- \rightarrow H_2$$

$$M^{+n} + e^- \rightarrow M^{+(n-1)}$$



https://cathwell.com/what-is-corrosion/

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Types of metal corrosion

Types of Corrosion

General corrosion

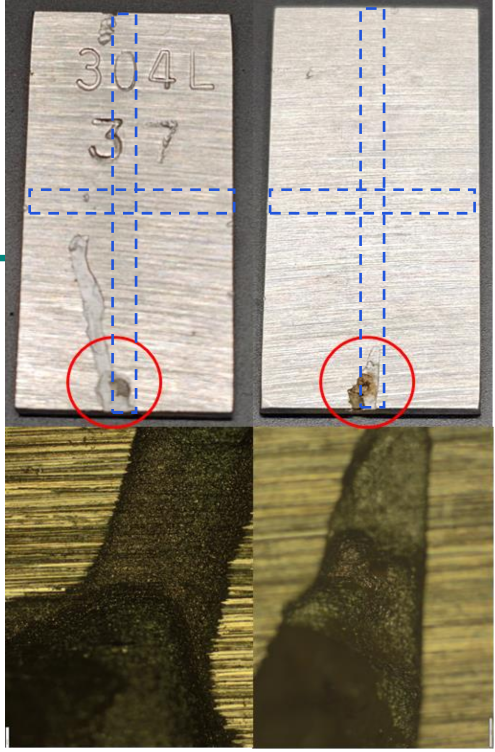
- Generally acceptable within a certain threshold
- Acceptable at <5-20 mpy

Localized corrosion

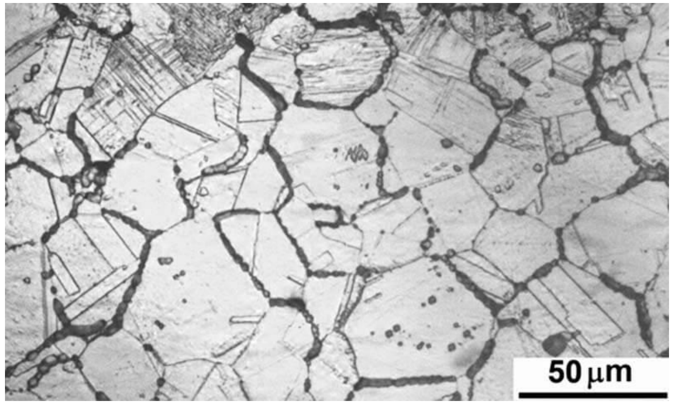
- Pitting
- Crevice attack
- Intergranular corrosion
- Stress Cracking

Galvanic Corrosion

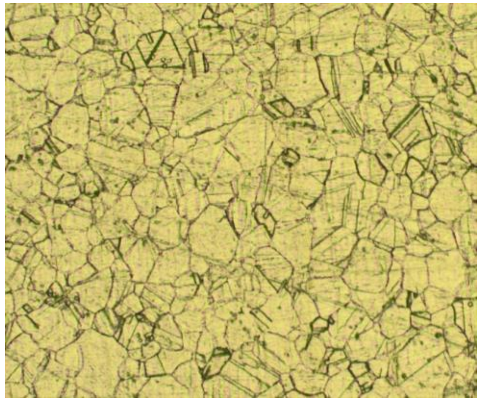
H2 Enbrittlement



Crevice attack under Teflon (blue dotted lines)
304L-SS in 6wt% of $FeCl_3$ + 1 wt% HCl , RT
Merck & Co., Inc., Rahway, NJ, USA



Intergranular corrosion on SS
https://casting-china.org/intergranular-corrosion/



Intergranular corrosion on HC-22
Merck & Co., Inc., Rahway, NJ, USA

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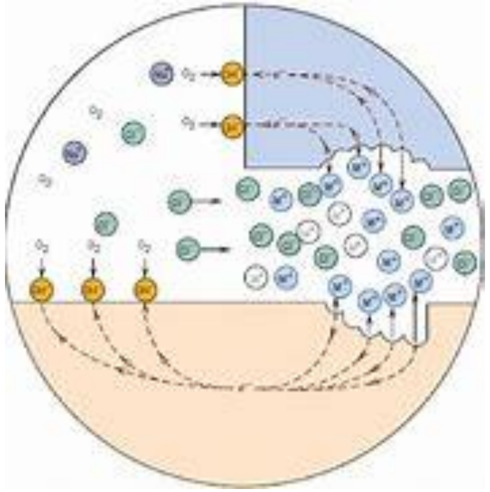
Crevice Corrosion

Typically associated with restricted access to an area of metal: Poorly sealing gaskets, poor welds, surface deposits and lap joints are common causes.

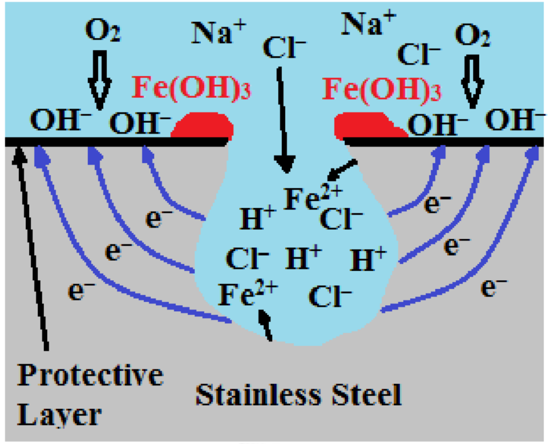
Caused by local potential differences, either from oxygen depletion or corrosion product accumulation.

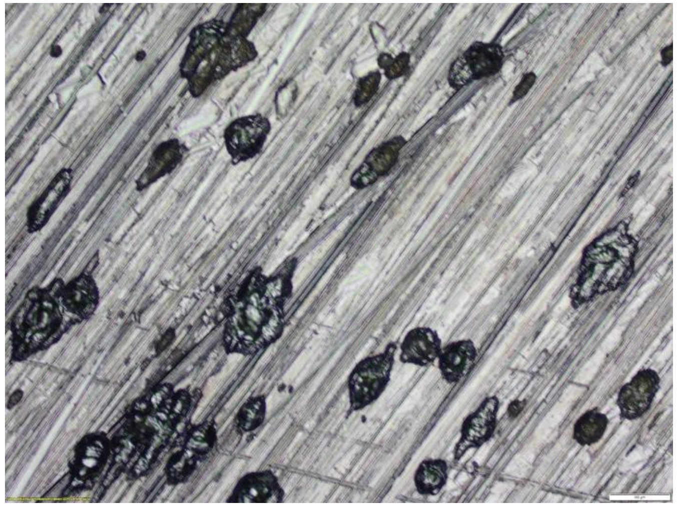
Can be mitigated by proper design: eliminate stagnant areas, proper welding techniques, using sealants.



Pitting -

- Occurs in metals with a protective film
- Localized breakdown of the passive film allows corrosion in the defect
- Corrosion products accumulate and acidify the hole – increasing the local corrosivity.
- Pits can act as drills, rapidly penetrating the metal. This effect is amplified by the area effect (small anode, large cathode).
- Countermeasures include "passivation", adding oxidizing inhibitors, deaerating the solution, increased flow





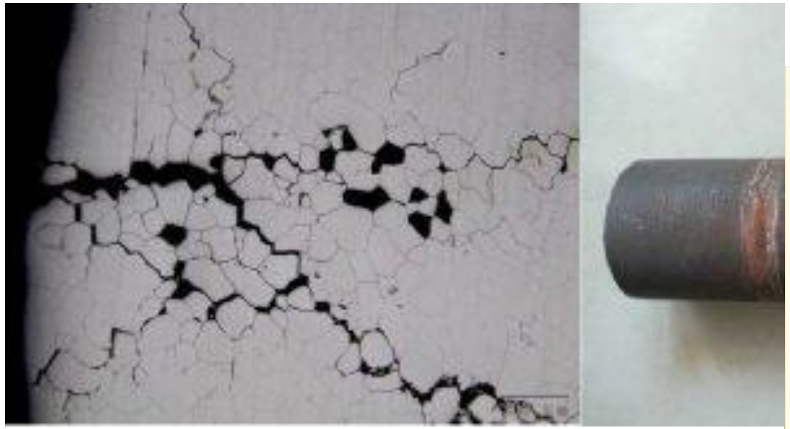
These forms of corrosion can cause catastrophic failure!

Intergranular Corrosion

Selective corrosion of grain boundaries.

Reason the "L" types of stainless were developed

Issue with welding, heat-treatment



Environmental Cracking

A combination of tensile stress, with a locally corrosive environment. Cracking initiates at a local defect, and additional corrosion + the stress causes the cracks to propagate

Environment specific:

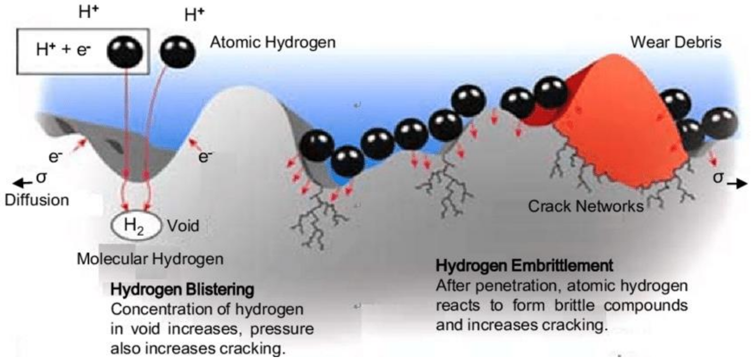
316L + Cl-

Cu + NH3

Steel+ S-2

Hydrogen Embrittlement

Diffusion of atomic hydrogen into the metal matrix, and formation of elemental hydrogen in the metal – causing high stress.
Titanium and Tantalum are very susceptible.



Experimental Methods

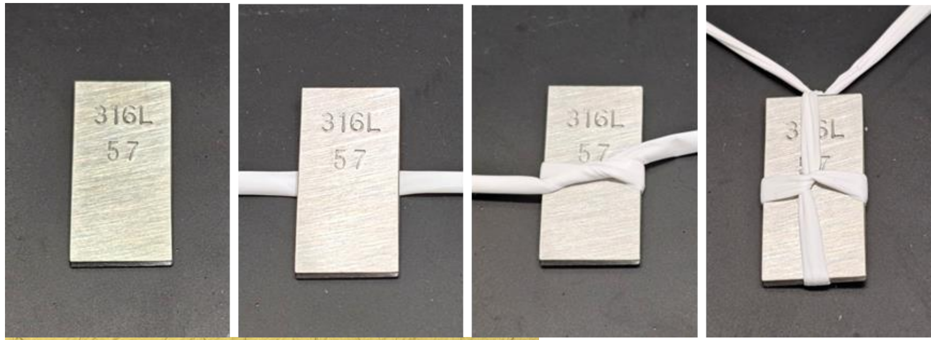
Coupons

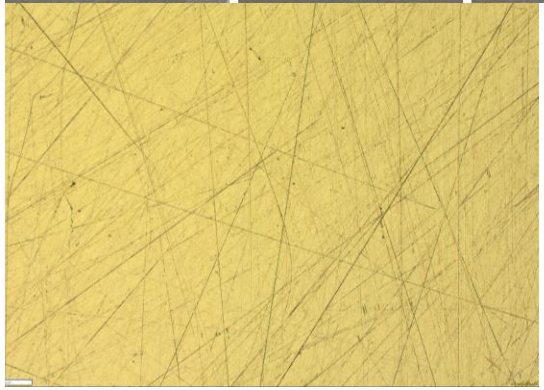
- 1” x ½” (thickness 1/16”) coupons
- Unground side has double disc finish
- Ground (one sided) using 600 grit SiC paper to a mirror polish
- Sonicated, rinsed, dried
- Coupons are tied with Teflon
- Weight recorded before and after experiment

Immersion Corrosion Test

- Coupon immersed in reaction solution for without stirring for set duration at setpoint temperature
- End of experiment, coupon is rinsed, sonicated, and dried

More details here:
Vickery, OPRD, 2025, 29 (11)
https://pubs.acs.org/doi/full/10.1021/acs.oprd.5c00329





Typical Metal Micrograph, 5x

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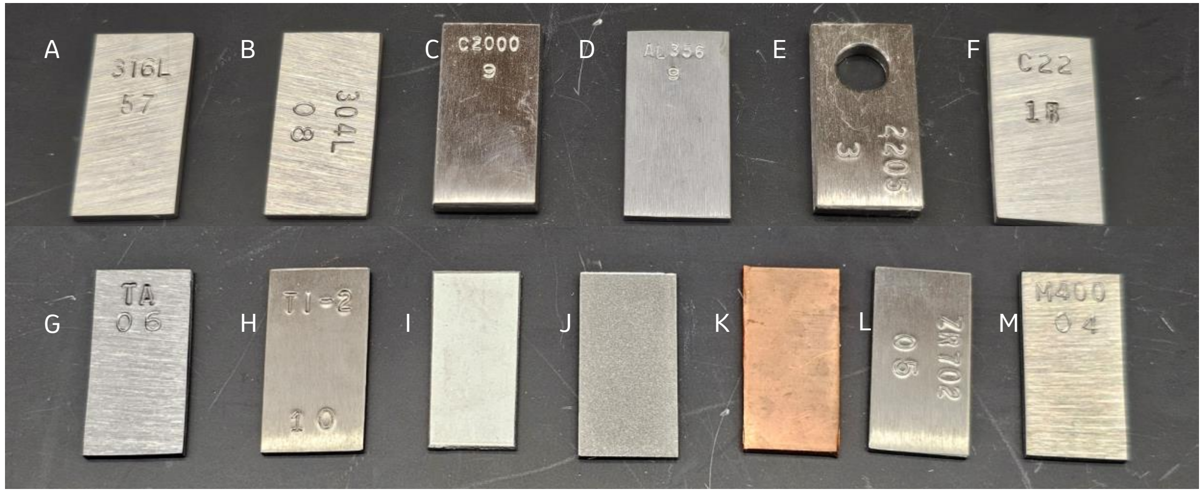
Typical MoC in the pharmaceutical space

Generally a mix of **SS, HC, and Glas-lined** vessels



Vickery, OPRD, 2025, 29 (11)
https://pubs.acs.org/doi/full/10.1021/acs.oprd.5c00329

Representative samples of metallic coupons for
A) 316L-SS
B) 304L-SS
C) Hastelloy C-2000
D) Aluminum 356
E) Duplex 2205-SS
F) Hastelloy C22/C276
G) Tantalum
H) Titanium Gr 3
I) Ultimet 6B(Cobalt alloy)
J) Stellite 21 (Cobalt alloy)
K) Copper
L) Zirconium 702
M) Monel 400

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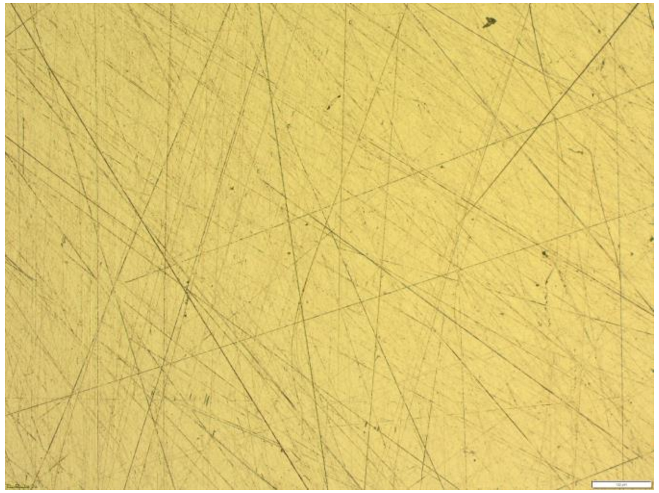
Control Experiments

HC-22, 50 °C, 7 days, unstirred, Air, Teflon tied (simulate localized conditions)

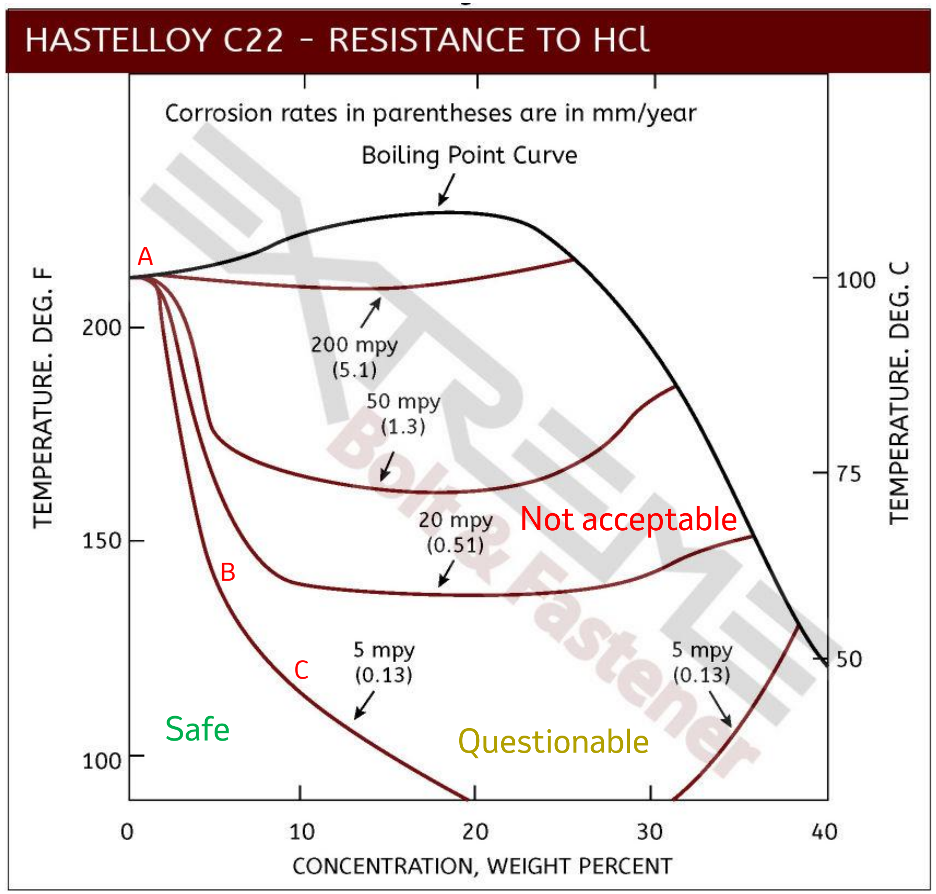
Pure MeCN, 5x
No corrosion observed on coupon
Solution did not discolor



2M HCl in H2O, 5x
No corrosion

HC-22 did not corrode in 2M HCl or Pure MeCN at 50C (as expected)

HC-22 corrosion in HCl



https://www.extreme-bolt.com/hastelloy-c22-fasteners.html#data

- At 25C, HC-22 is resistant to HCl (aq) up to 20wt%
- Corrosion rate < 5 mpy (Safe)
    - 1 wt% at 100C (Point A)
    - 5 wt% at 60 C (Point B)
    - 10wt% at 45-50C (Point C)

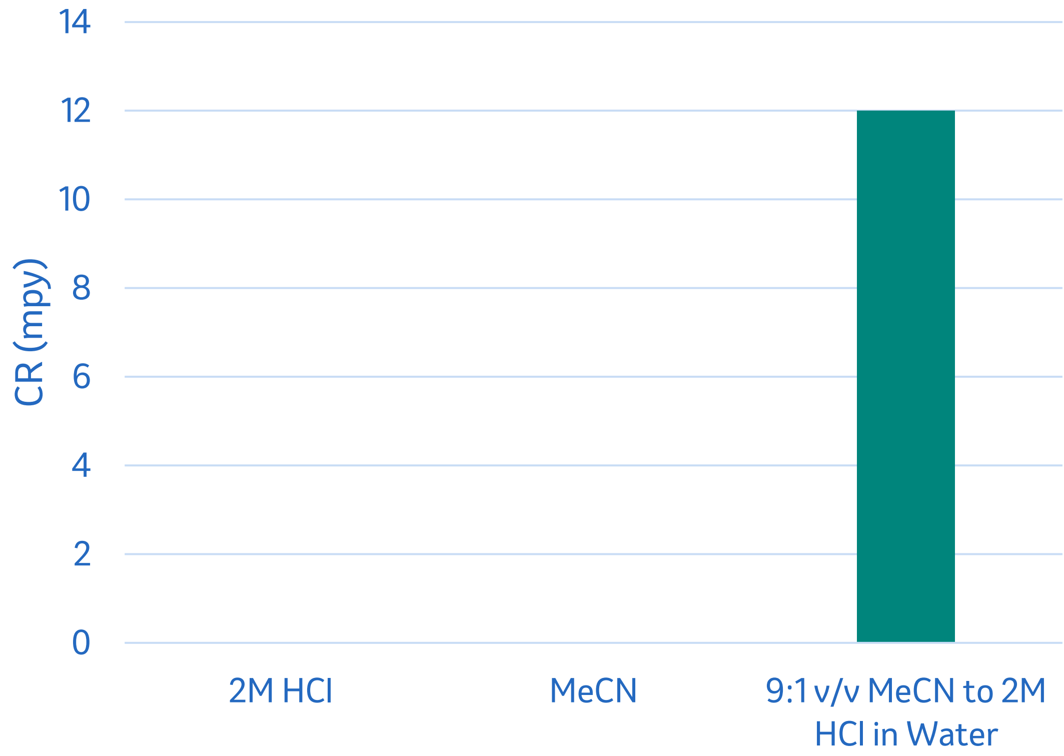
- Safe region = Excellent Corrosion Resistance
    - Low/acceptable corrosion rate
    - Low metal loss
    - Low risk and Low safety implication
    - Tolerable wear and tear

Every company has acceptable corrosion tolerance

Corrosion rate calculated based on mass loss over time
1 mpy (mils/year) = 0.001 in/year

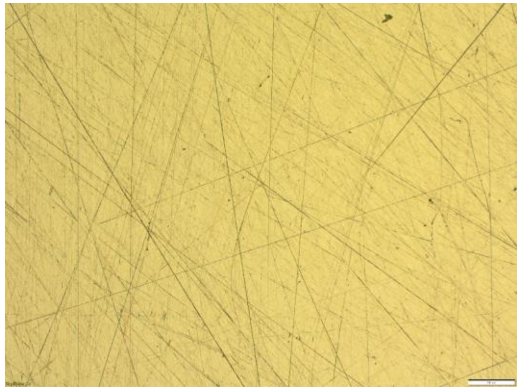
Experimental:
HC-22, 50C, 7 days, unstirred, Air
Single sampling

Effect of mixing MeCN and HCl in water

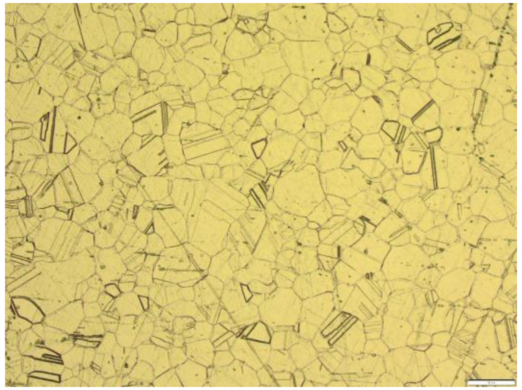


- HC-22 not corroded in 2M HCl or Pure MeCN at 50C
- Mixing the 2 “non/low-corroding” reagents at specific ratio caused the HC-22 to corrode
- There is an **<u>amplification</u>** corrosivity effect
- CR alone isn’t quantifying the severity of the corrosion

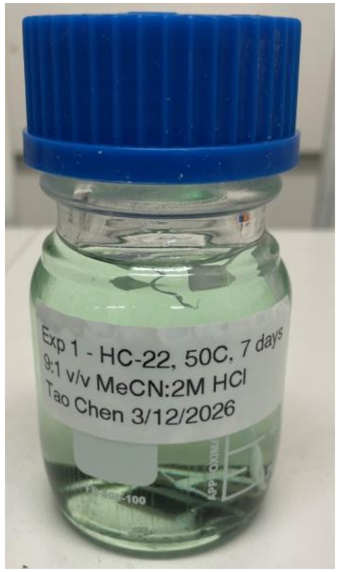
Pure MeCN, 5x
No corrosion



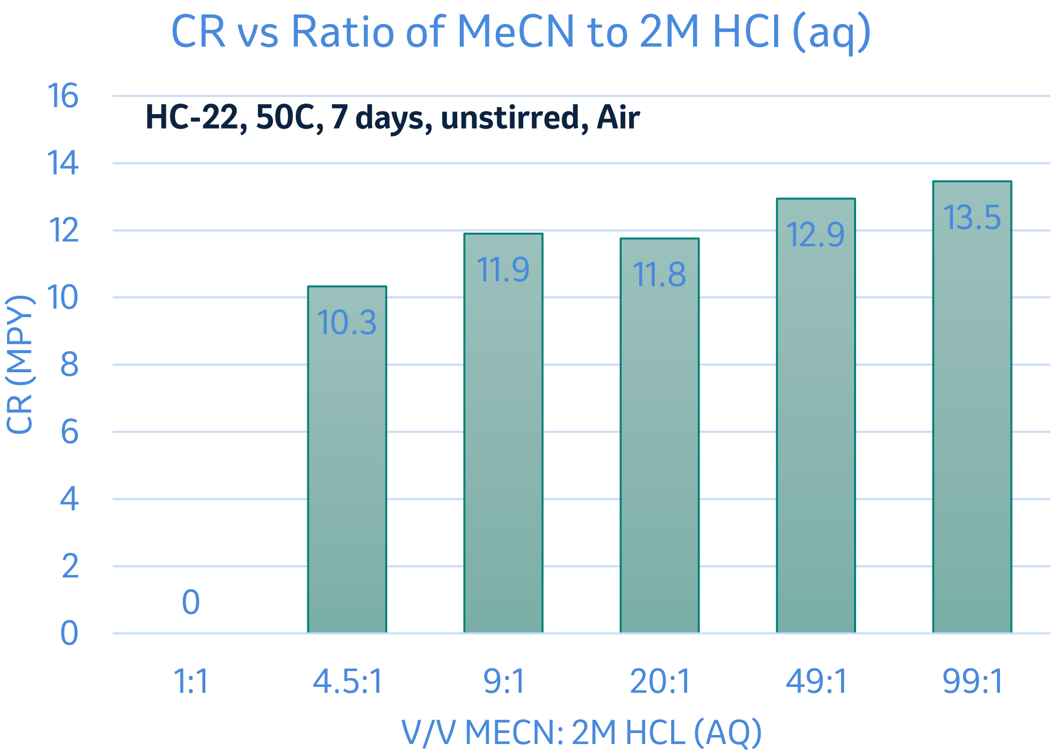
2M HCl in H2O, 5x
No corrosion



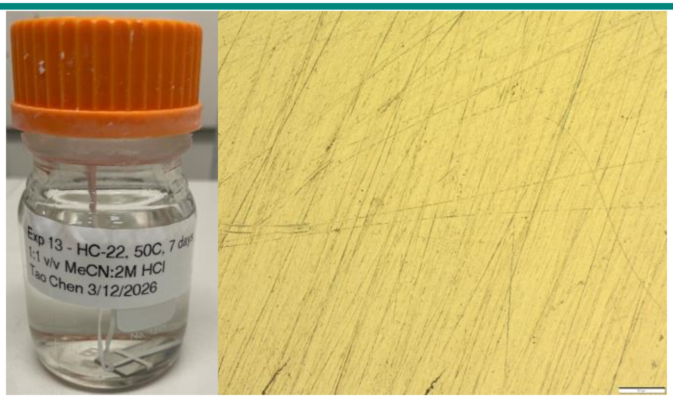
9:1 v/v MeCN to 2M HCl in Water,
Or 0.9 wt% HCl in Water+MeCN
10x, Intergranular corrosion



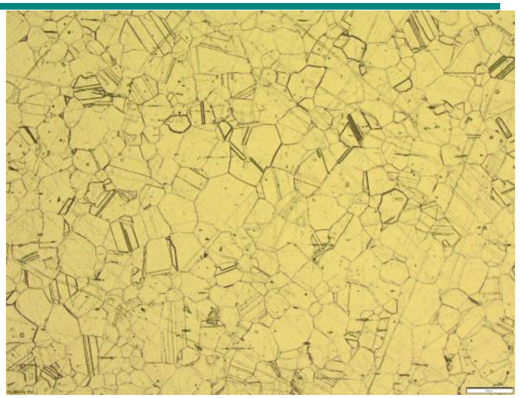
Effect of varying concentration



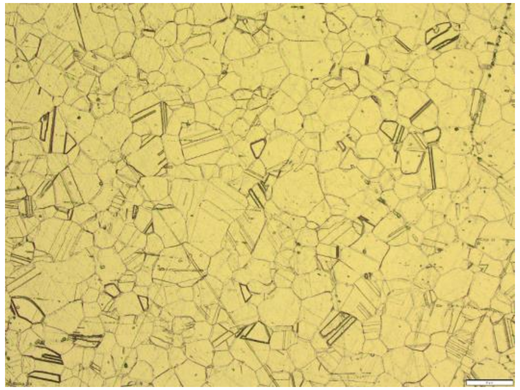
- Intergranular corrosion observed when mixed at **4.5:1 to 99:1** v/v of MeCN to 2M HCl in water at 50C
- HC-22 in > 20:1 MeCN:2M HCl in water shows severe intergranular corrosion (see photos)



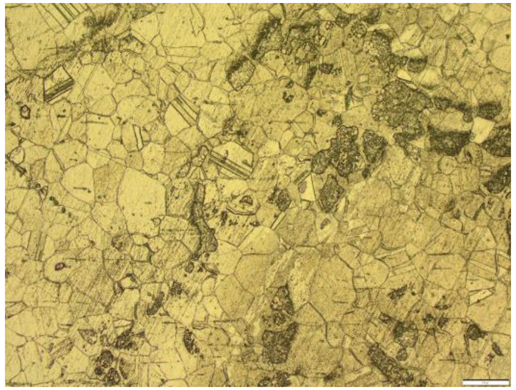
1:1 v/v, 10x ; No corrosion



4.5:1 v/, 10x; Intergranular



9:1 v/v, 10x; Intergranular



20:1 v/v, 10x; Intergranular
Most severely attacked

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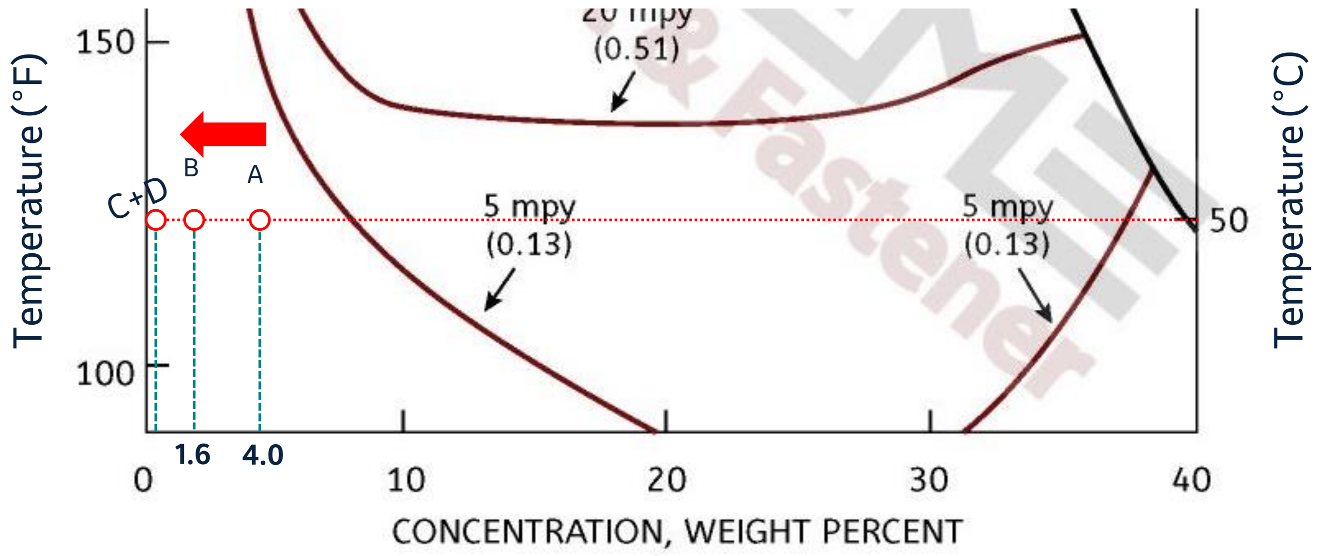
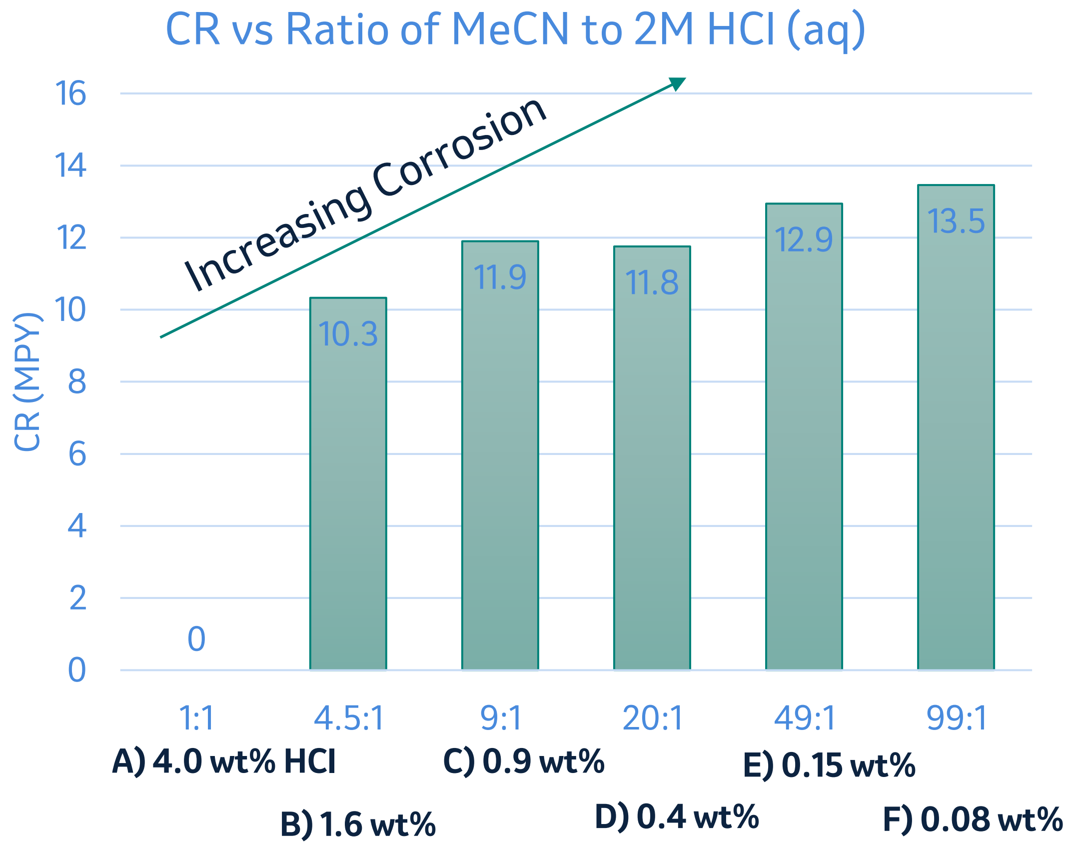
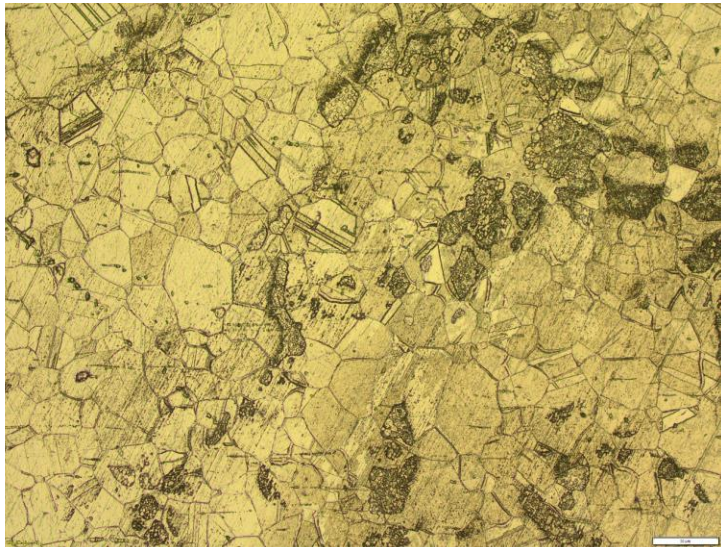
What should have been non-corrosive…



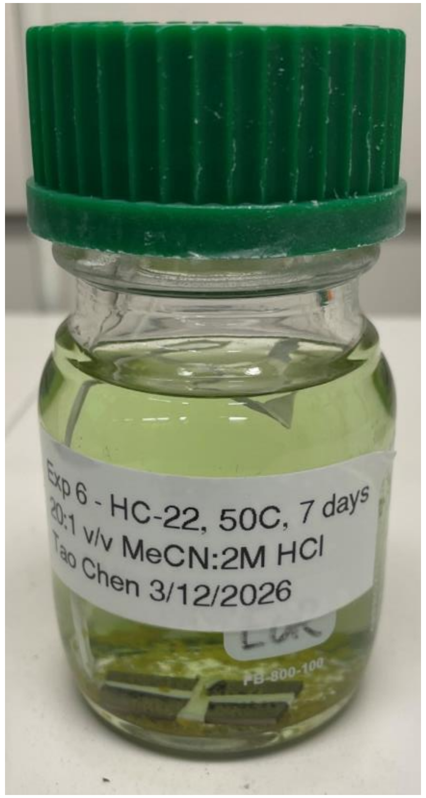


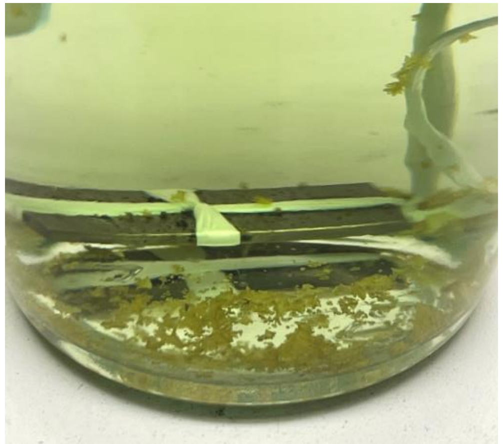
- Corrosivity of HCl increases with reduction in 2M HCl (aq) vs MeCN
- HC-22 most severely attacked at 20:1 v/v MeCN/2M HCl (aq)

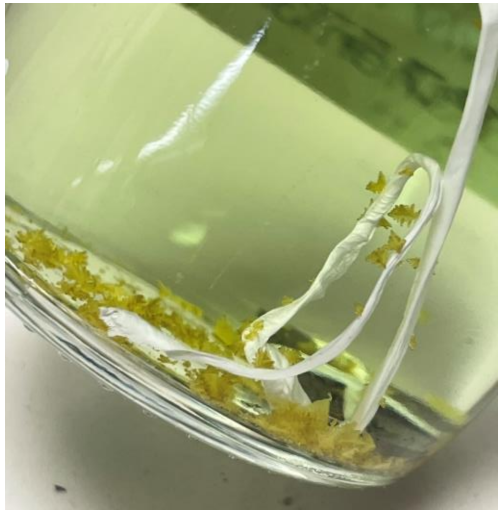
Crystal Growth at low water



20:1 v/v, 10x; Intergranular
Most severely attacked

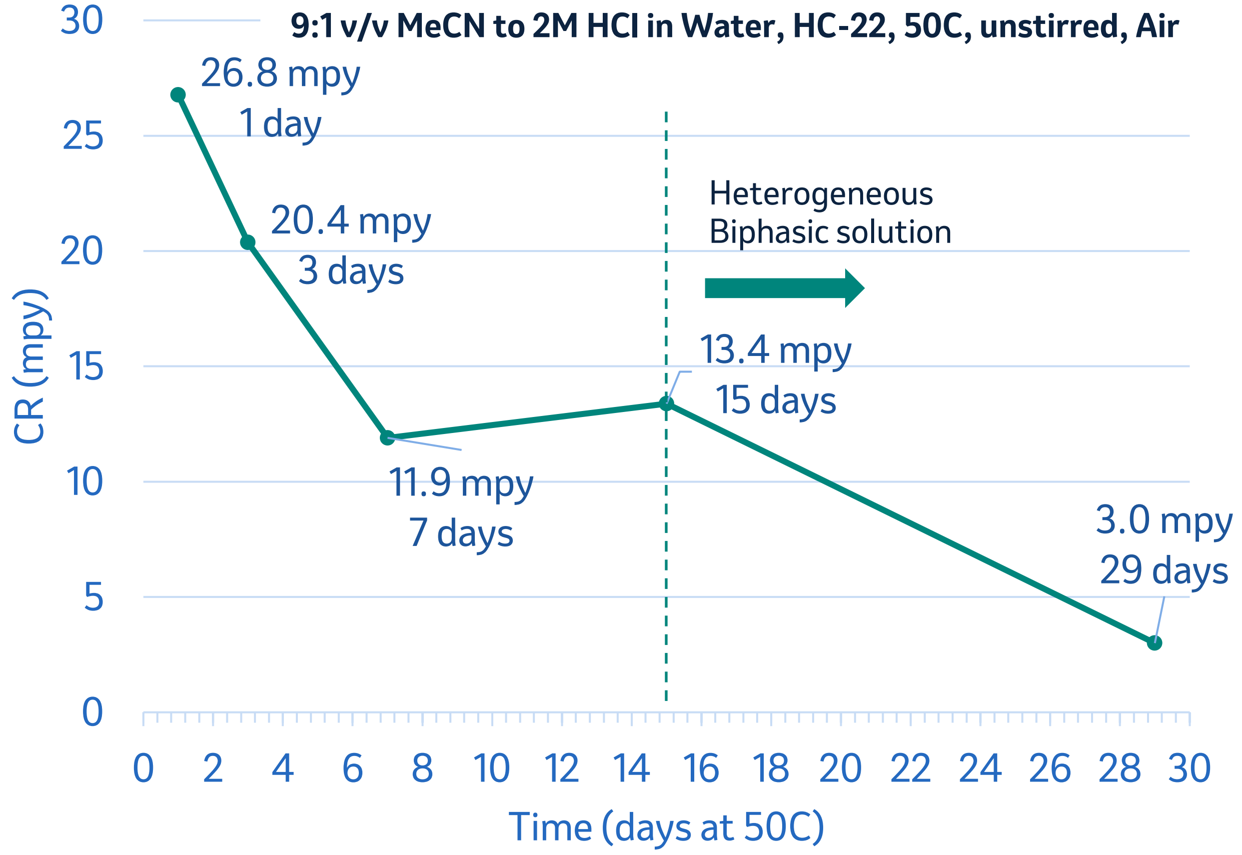


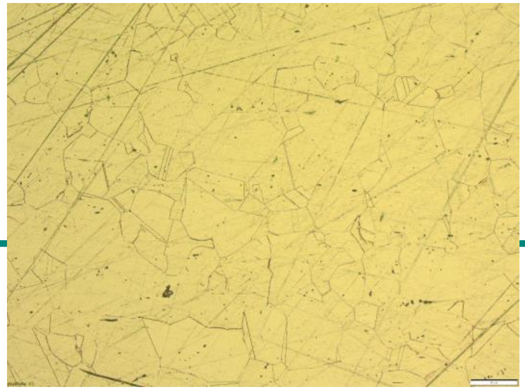




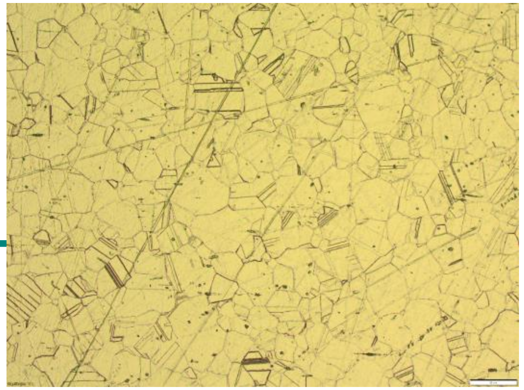
- At low water (20:1 or greater), the formation of apparent crystals is observed
- Suspected to be a corrosion product that is insoluble in MeCN

Corrosion vs Time

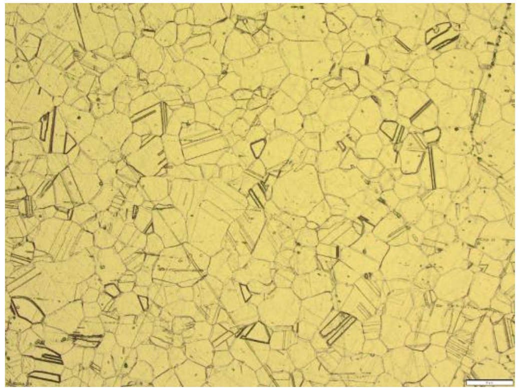




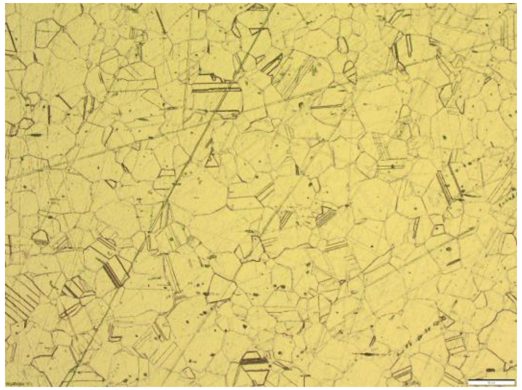
1 day, 10x; Intergranular



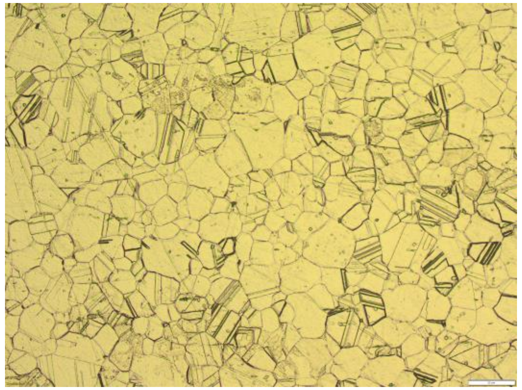
3 days, 10x; Intergranular



7 days, 10x; Intergranular



15 days, 10x; Intergranular



29 days, 10x; Intergranular

- Corrosion rate high after 1 days
- Signs of intergranular corrosion appears even after 1 day and worsens oven time

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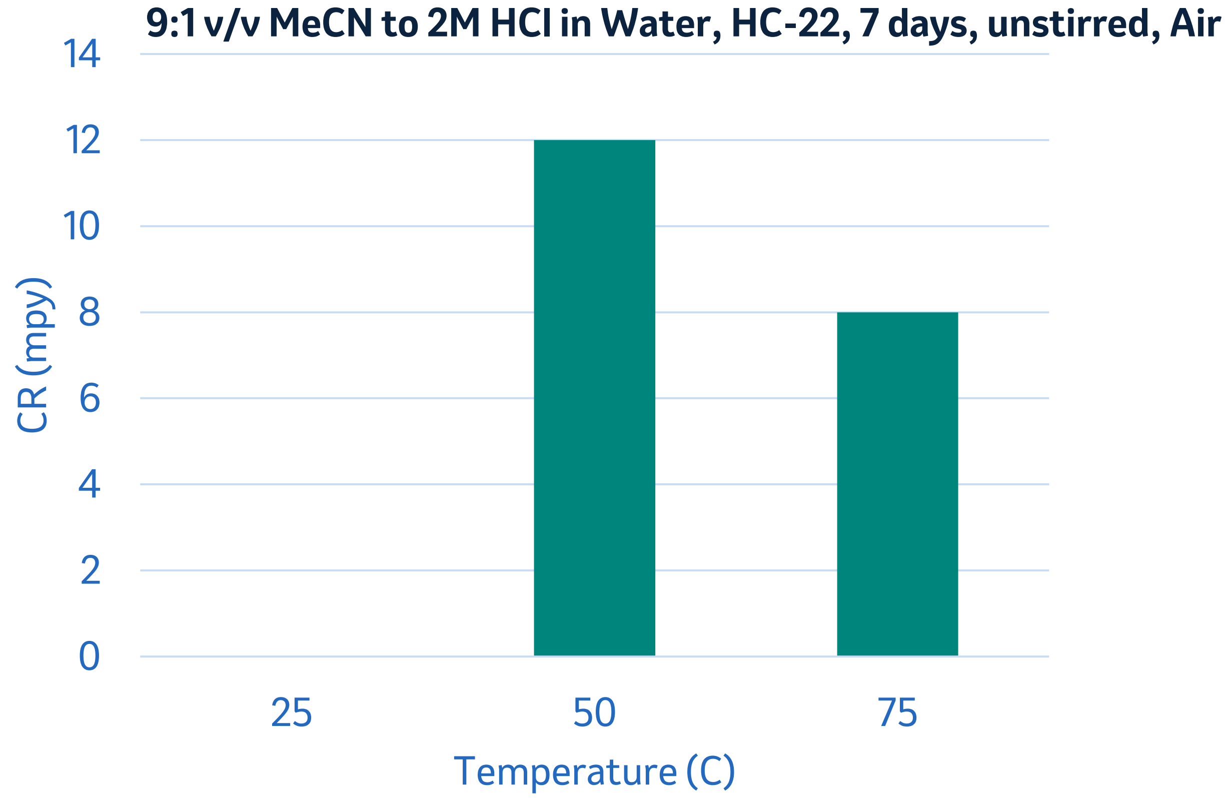
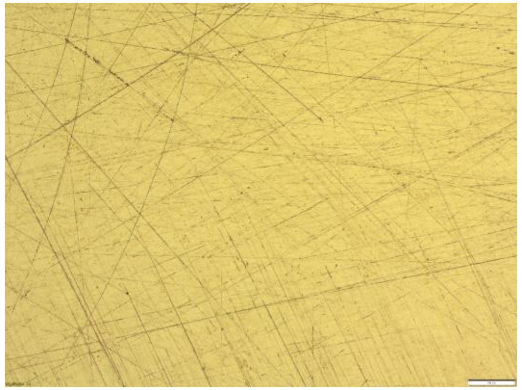
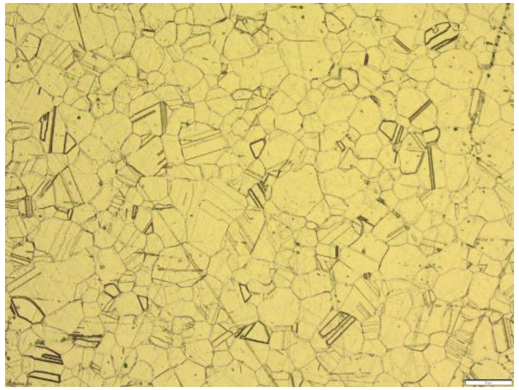
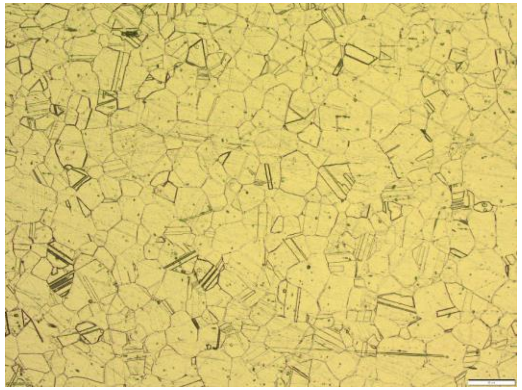
CR vs Temp

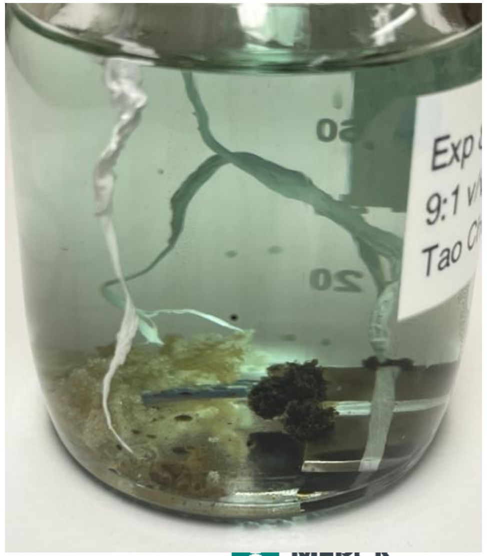


- No corrosion observed at 25C
- Higher corrosion rate observed at 50C vs 75C
- Solution partitioning effect at 50C whereas crystal growth (dendrites?) observed at 75C
- Its possible Cl ions trapped in the crystals leading to slower CR at 75C

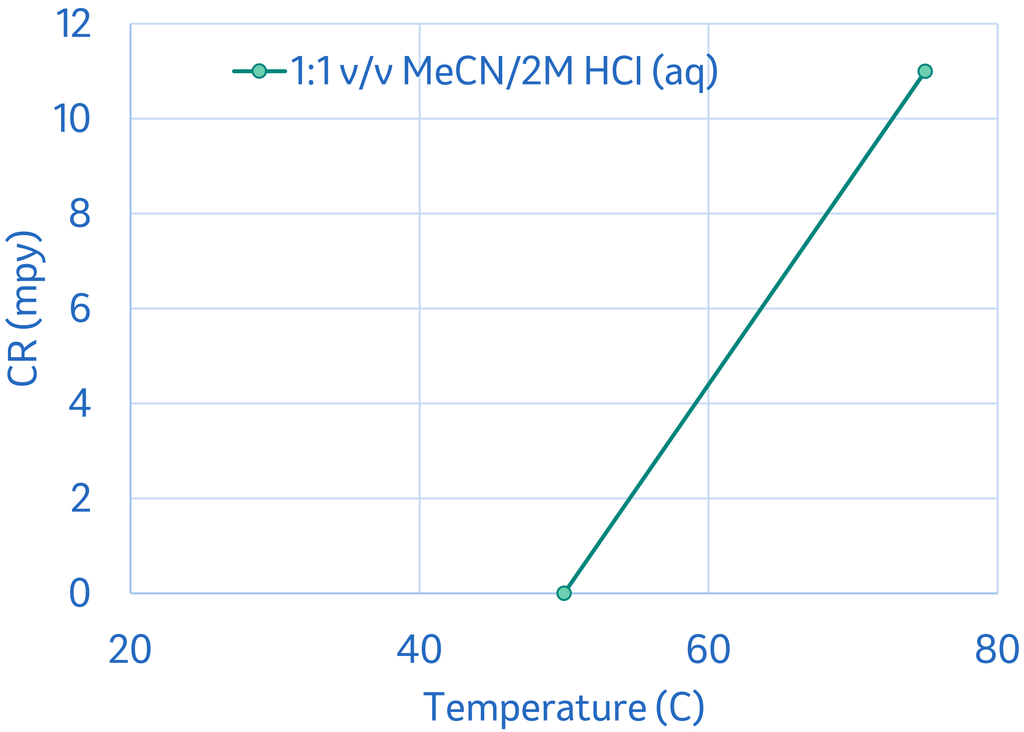

25C, 5x; No corrosion


50C, 10x; Intergranular


75C, 10x; Intergranular
Crystal growth

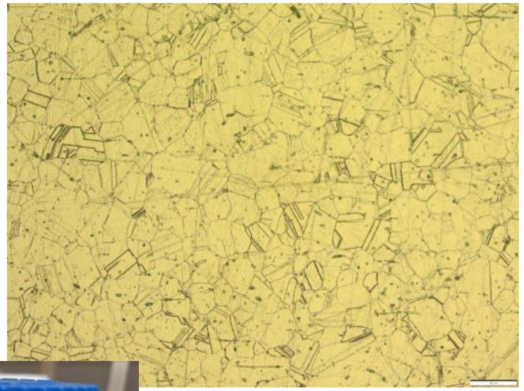


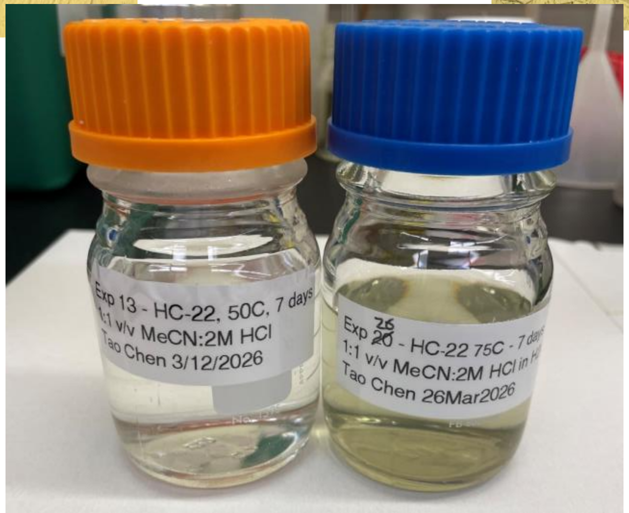
Corrosivity vs Temp



1:1 v/v @50C, 10x ; No corrosion

1:1 v/v @75C, 10x ; Intergranular



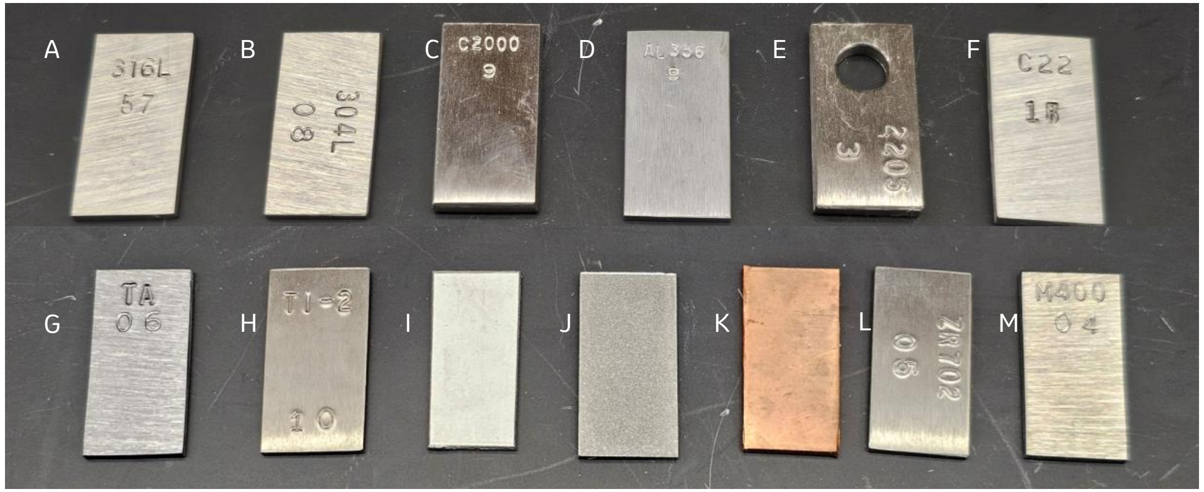


- Increase in temperature increased the corrosivity of the system vs HC-22
- The increase in corrosion rate and corrosivity is expected (to some extent) for corrosive systems for increase in temperature
- However, intergranular corrosion was not expected.
- Mechanistically, the HCl is attacking the metallic grains differently than that in a pure aqueous HCl system

What about other metals or alloys?

Is this corrosion effect specific to Hastelloy?

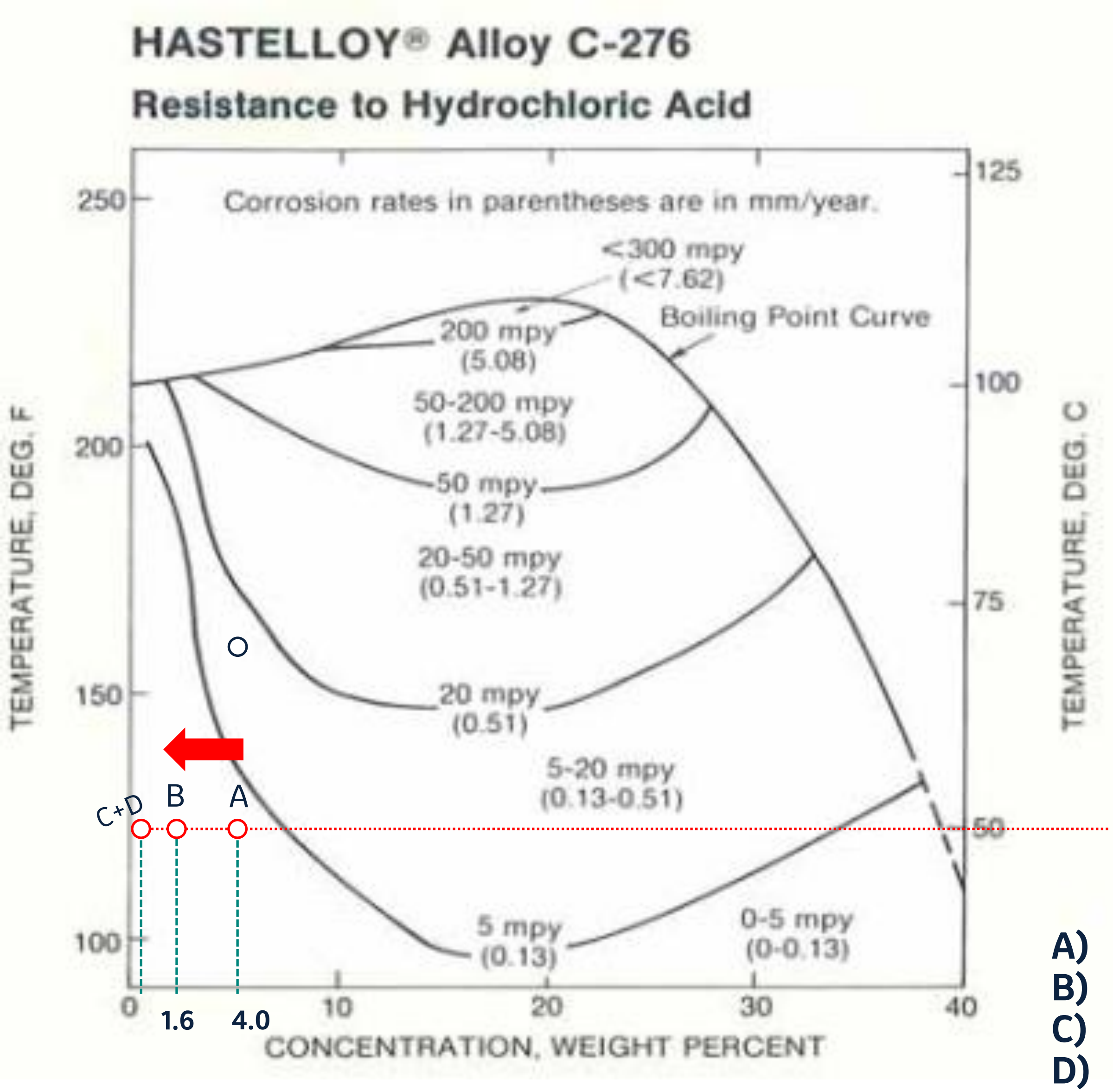
What about C-276?



Vickery, OPRD, 2025, 29 (11)
https://pubs.acs.org/doi/full/10.1021/acs.oprd.5c00329

Representative samples of metallic coupons for
A) 316L-SS
B) 304L-SS
C) Hastelloy C-2000
D) Aluminum 356
E) Duplex 2205-SS
F) Hastelloy C22/C276
G) Tantalum
H) Titanium Gr 3
I) Ultimet 6B(Cobalt alloy)
J) Stellite 21 (Cobalt alloy)
K) Copper
L) Zirconium 702
M) Monel 400

Hastelloy C-276



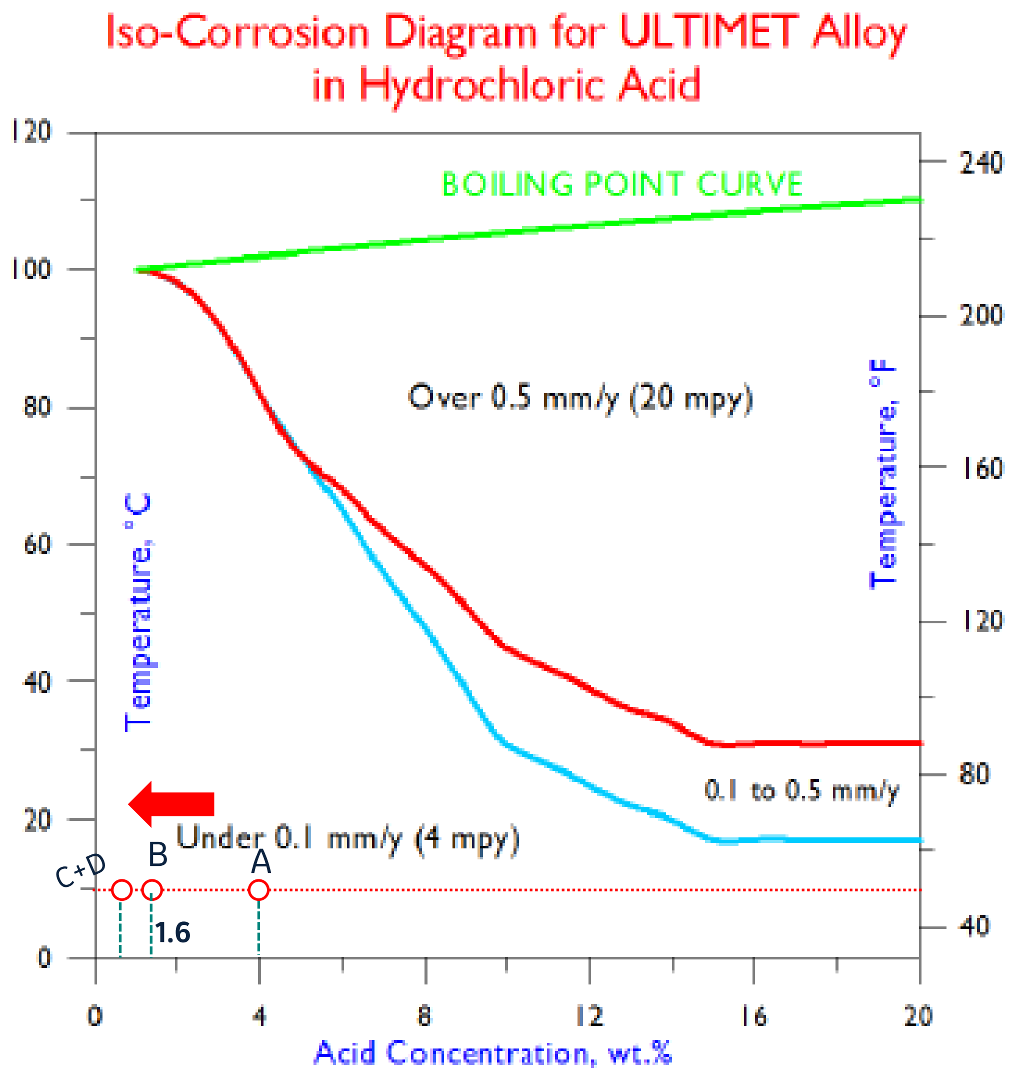
C-22 provides better corrosion resistance to pitting and crevice corrosions.

C276 is generally known for having better corrosion resistance than C-22 in reducing environment such as HCl.

And our Pilot Plants and CMO have a combination of C-22 and C-276 equipment and piping.

A) **4.0 wt% HCl**
B) **1.6 wt% HCl**
C) **0.9 wt% HCl**
D) **0.4 wt% HCl**

Ultimet 6B



Resistance to Pitting and Crevice Corrosion

ULTIMET® alloy exhibits very high resistance to chloride-induced pitting and crevice attack, forms of corrosion to which the austenitic stainless steels are particularly prone.

To assess the pitting resistance of ULTIMET® alloy relative to other corrosion-resistant materials, it has been subjected to tests in Green Death (11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$). Experiments wereperformed at various temperatures (in increments of 5°C) to determine the lowest temperature at which pitting occurs in a 24 h test period (the so-called Critical Pitting Temperature for Green Death). The results were as follows:

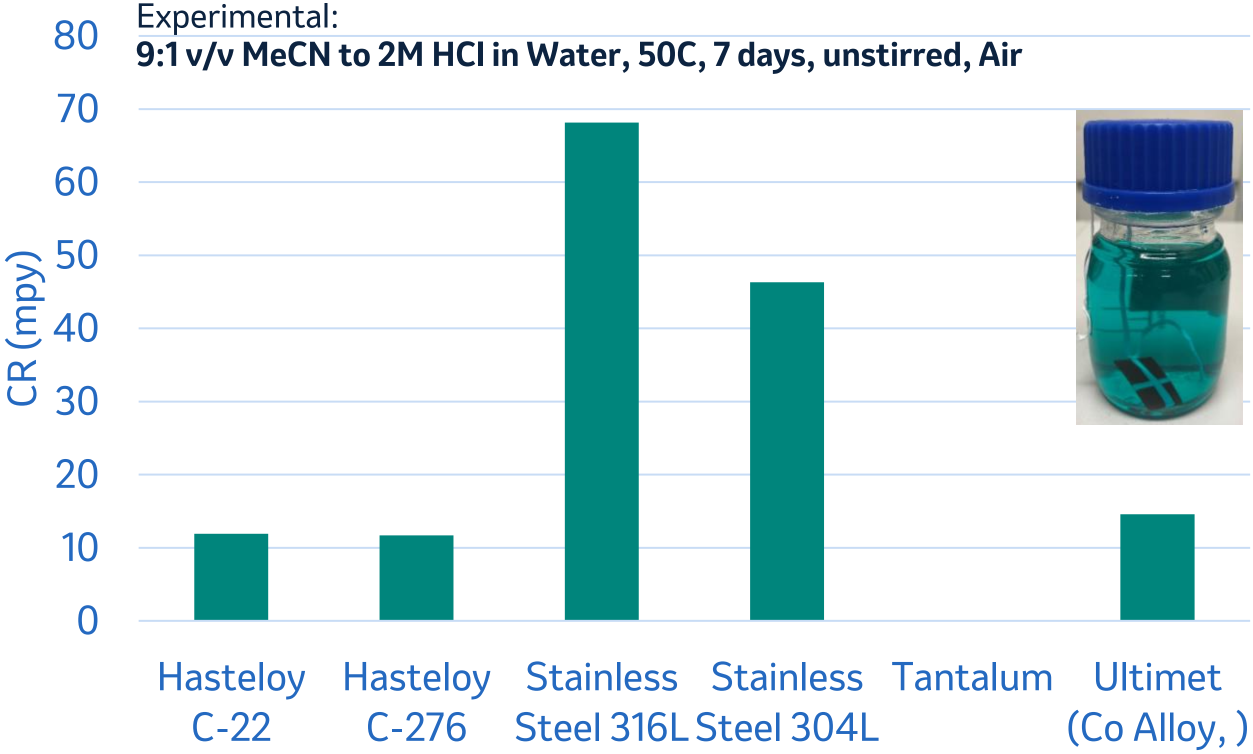
Alloy	Critical Pitting Temperature	
-	°F	°C
ULTIMET®	**248**	**120**
C-22®	248	120
C-276	230	110
625	167	75
6B	113	45
316L	77	25

https://haynesintl.com/en/alloys/alloy-portfolio/corrosion-resistant-alloys/ultimet/#principal-features

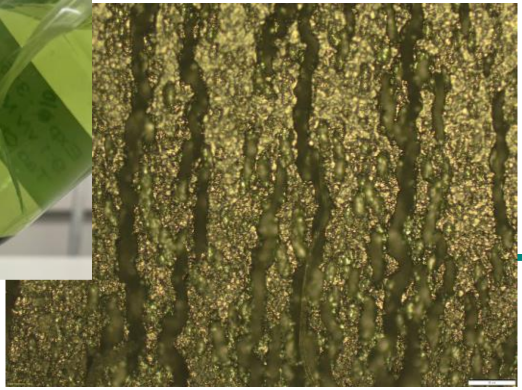
Excellent resistance to corrosion vs HCl comparable to C-22 and C-276

A) **4.0 wt% HCl**
B) **1.6 wt% HCl**
C) **0.9 wt% HCl**
D) **0.4 wt% HCl**

CR vs Metal Alloys

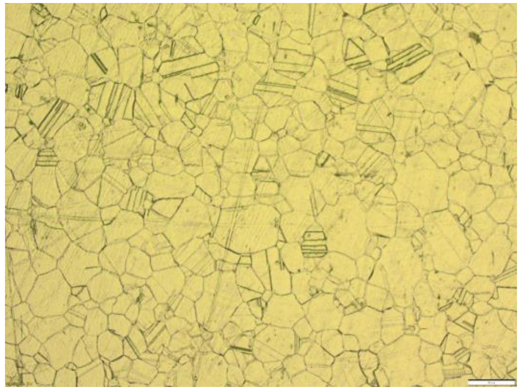


- SS aggressively attacked compared to Hastelloy
- Similar corrosion behavior on HC-276 vs HC-22
- Ultimet (Cobalt alloy) also experienced intergranular corrosion
- Tantalum highly resistant to this aggressive corrosivity

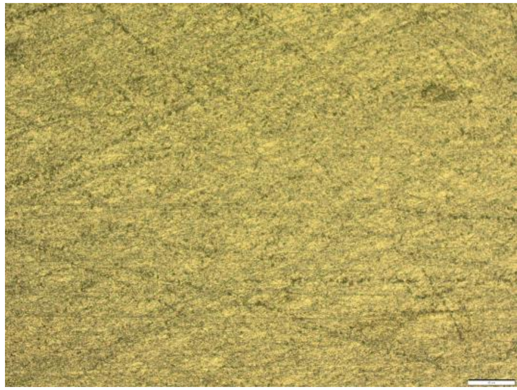


316L; Intergranular & Cracking

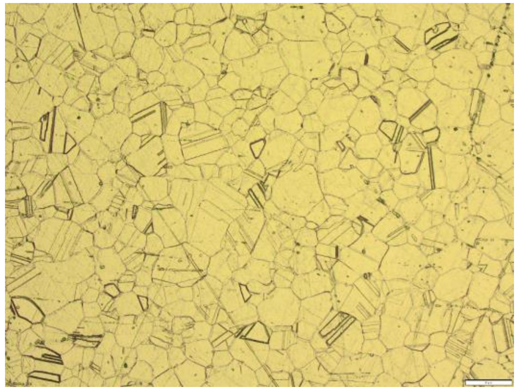
304L; Intergranular



HC-276, 10x; Intergranular



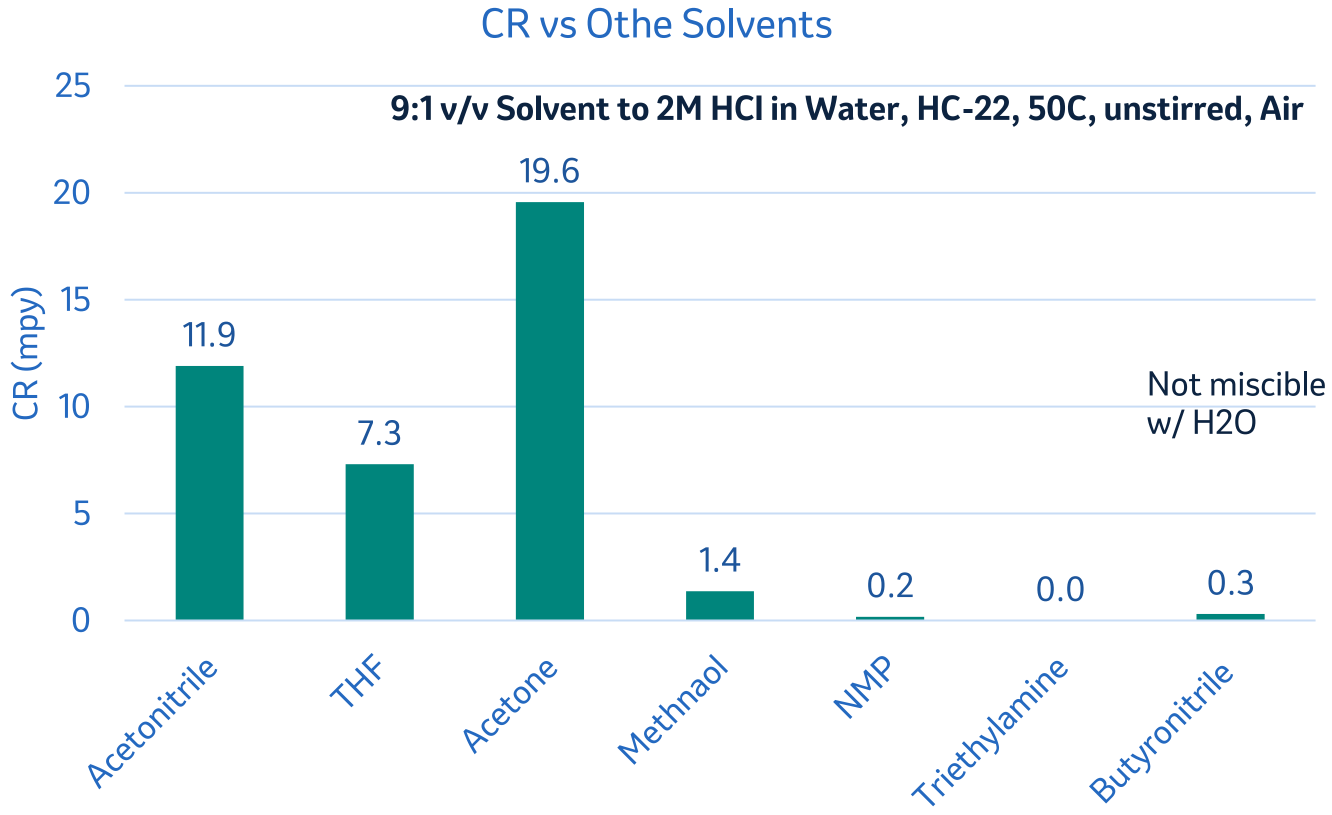
Tantalum, No corrosion



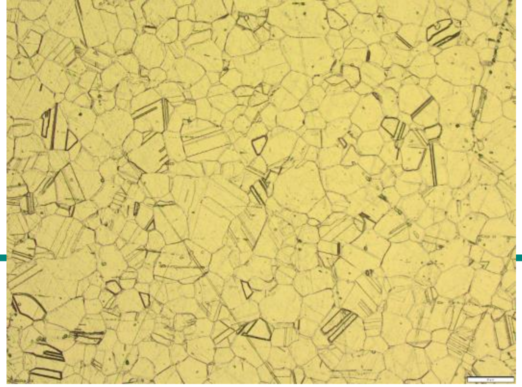
HC-22, 10x; Intergranular

Ultimet 6B, 10x; Intergranular

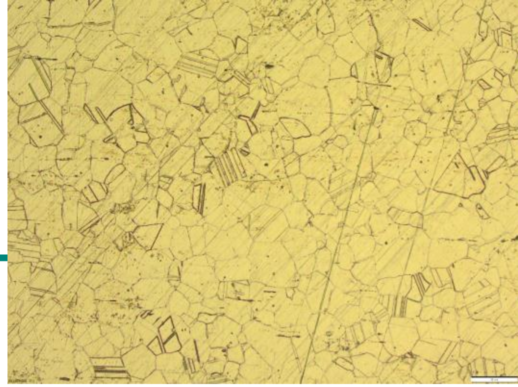
Is this unique to Acetonitrile?



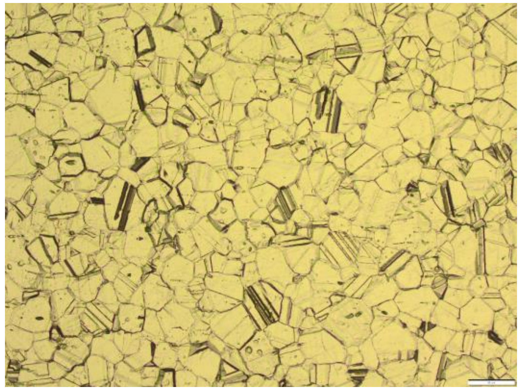
- Aggressive corrosion on HC-22 not unique to MeCN.
- Similar corrosion behaviors observed when mixing THF or Acetone with 2M HCl in water.
- No corrosion observed when mixing Methanol, NMP or TEA with 2M HCl in Water



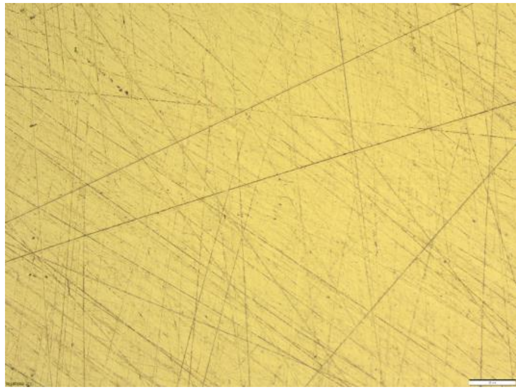
MeCN, 10x; **Intergranular**



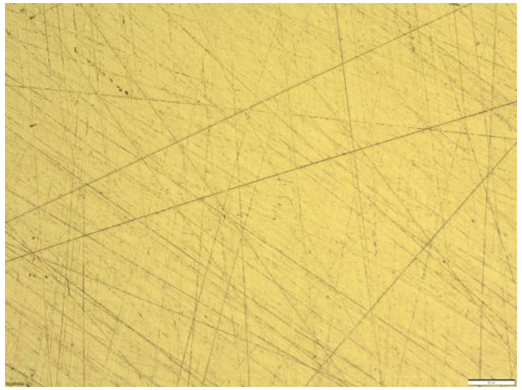
THF, 10x; **Intergranular**



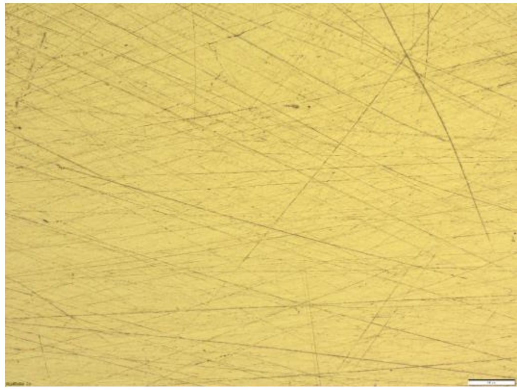
Acetone, 10x; **Intergranular**



Methanol, 10x; No Corrosion

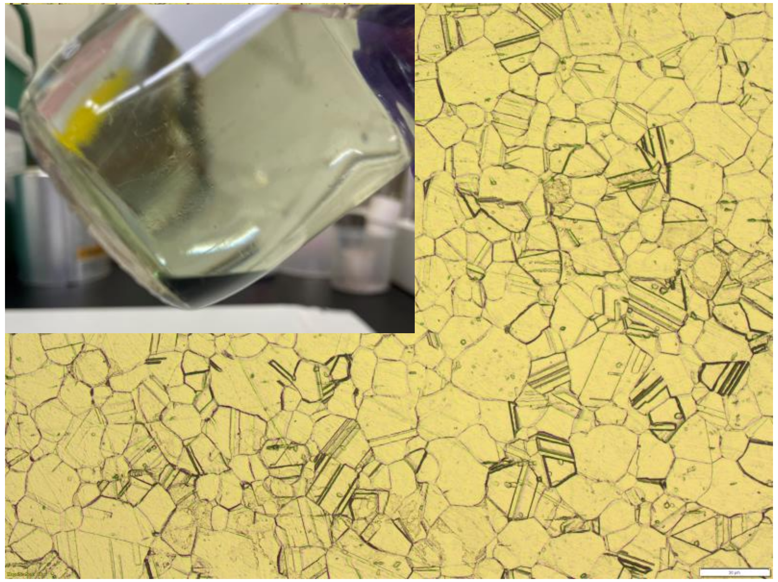


NMP, 10x; No Corrosion



TEA, 5x; No Corrosion

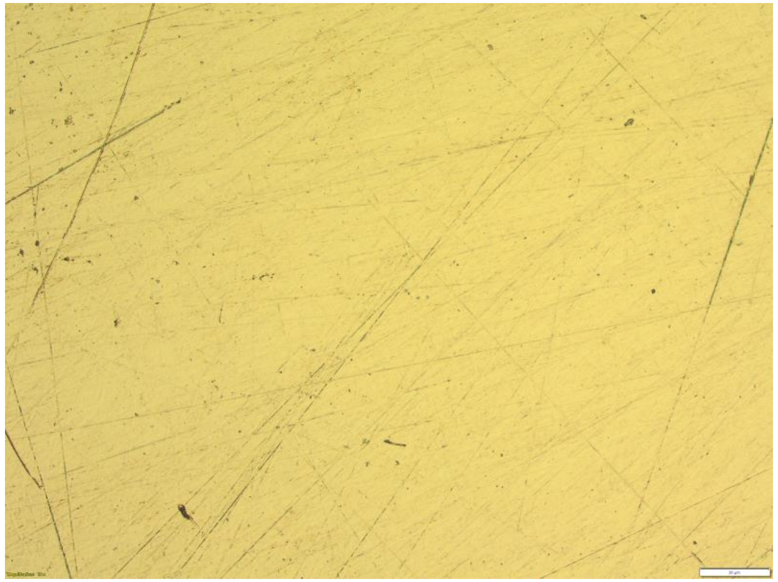
Some Good News



9:1 v/v MeCN to 2M HCl (aq)
29 Days at 50C
HC-22, Intergranular

Same Solution

Removing green aqueous layer



9:1 v/v MeCN to 2M HCl (aq)
7 Days at 50C
HC-22, No corrosion

Summary

- When combined in a specific ratio, MeCN/HCl(aq) is aggressively corrosive to Hastelloy C-22
  - Corrosivity and severity changes with ratio of MeCN/HCl (aq)
  - Corrosivity increases with increase in temperature
- Corrosion products can form bi-phasic layer as well as corrosion precipitates (crystals)
- The corrosivity of this solution is not limited to C-22 but extends to many alloys
  - SS, HC-276, Co-based alloy (Ultimet) with the exception of Tantalum (thankfully)
- Corrosivity of this combination is not limited to Acetonitrile. THF and Acetone show similar corrosive behavior on HC-22.
- "General" corrosion rate doesn't quantify the severity of the corrosion
- Mechanistic understanding on this phenomenon is under investigation

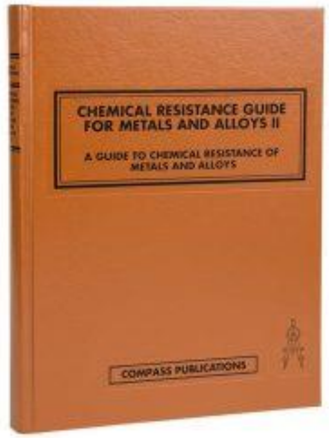
How to detect and prevent corrosion?

https://www.compasspublications.com/books/

Literature surveys and publications

If the data is unavailable, test it!

If the system seems suspicious for corrosion, test it!

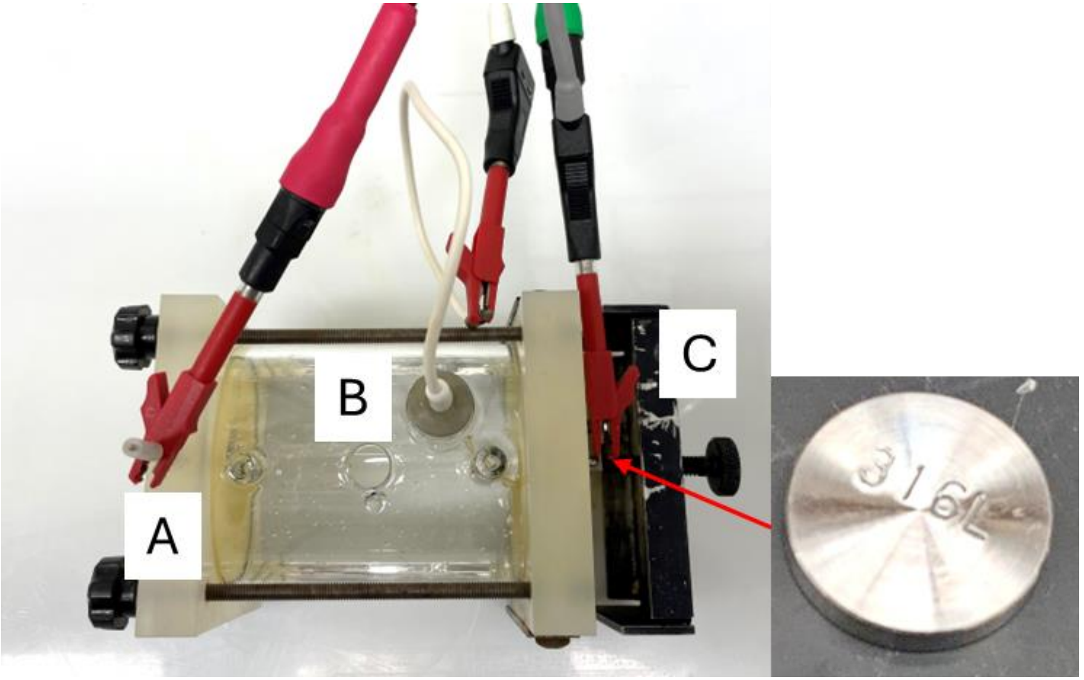


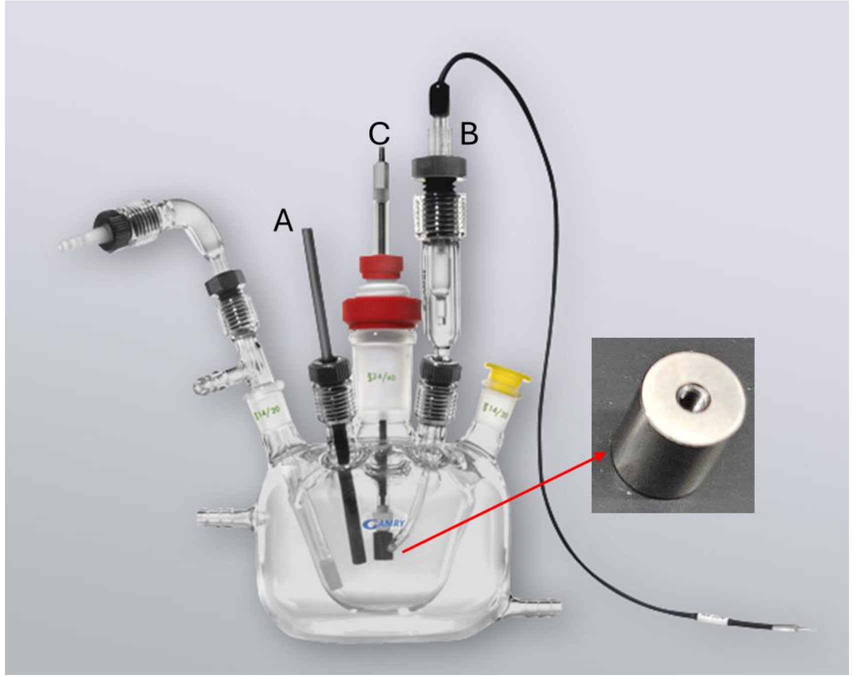
Some testing (even if its rudimentary) is better than no testing

Preventative measures include **elimination**, **substitution**, & **process modification!**

Future Work

- Temperature controlled electrochemical corrosion study
- Other halogenating reagents and solvent combinations
- HCl in MeCN (dry)





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Thank you