Influence of electroplated coatings on Hydrogen Embrittlement of low-alloy steel for subsea applications. Electrochemical and Mechanical analysis.

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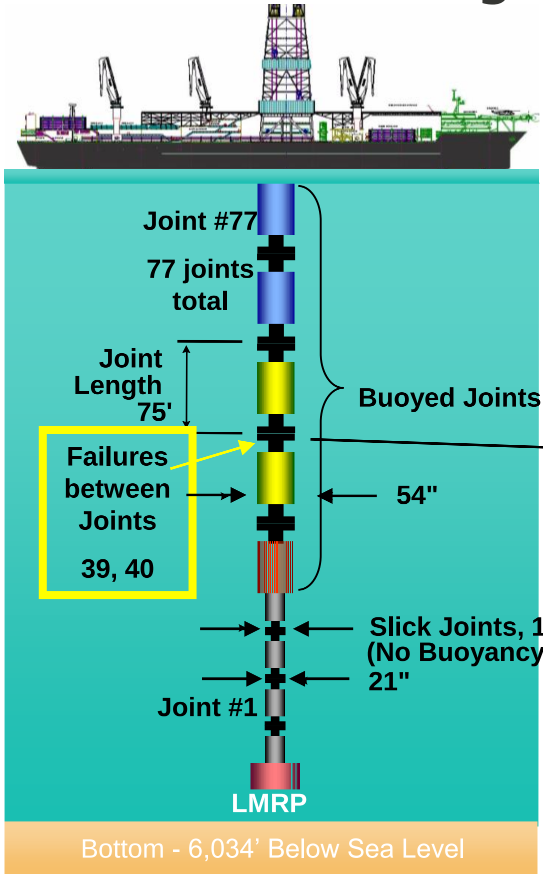
OUTLINE

- **Failures:** Introducing **four** hydrogen embrittlement case studies
- **Theory:** How hydrogen embrittlement happens and how it affects operations
- **Experimental: H**ydrogen embrittlement affecting bolts when using different coatings
- **Final Remarks**

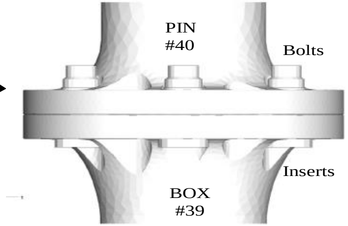
Offshore Industry Failures

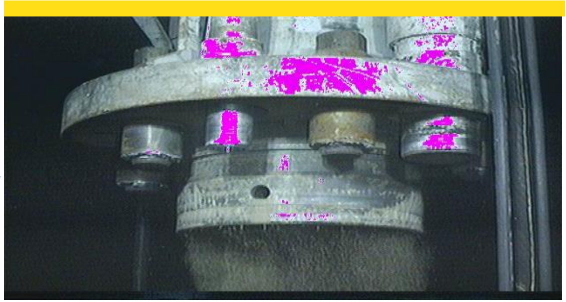
- Hydrogen Embrittlement failures are catastrophic in nature
- Hydrogen embrittlement failures in drilling equipment lead to significant safety and environmental risks
- Failures have significant economic consequences
- Failures occur mostly in a subsea environment

Failure 1: Drilling Riser Connection (2003)

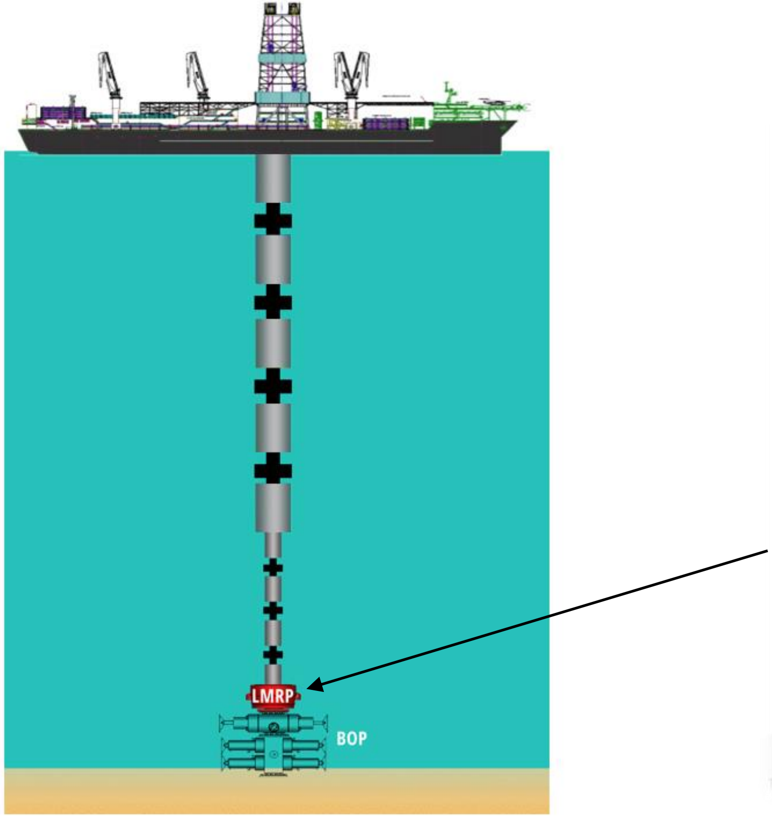


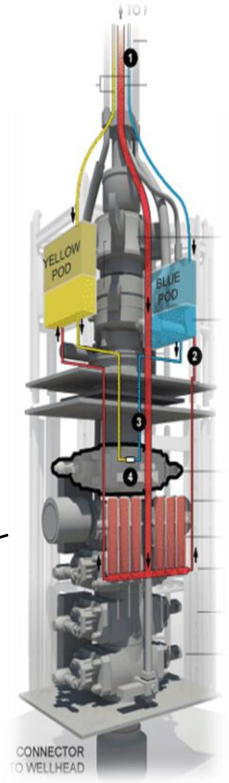
Riser parted at 3,200 ft below sea level between joints 39 & 40



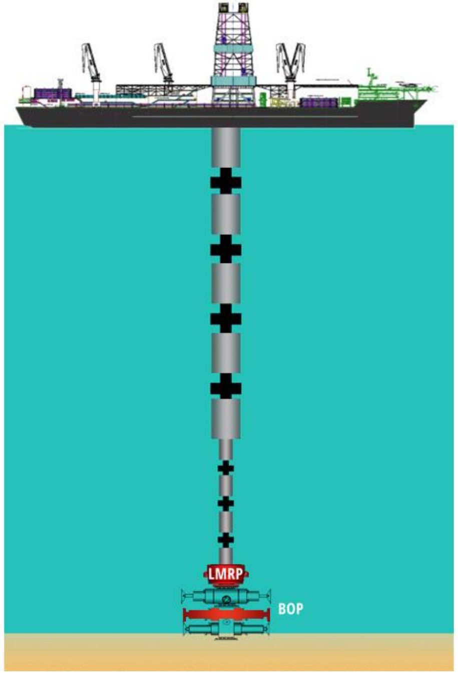


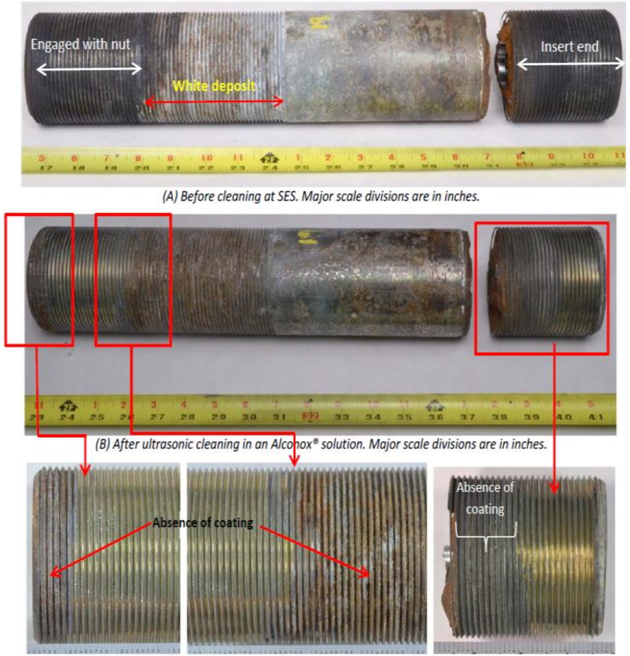
Failure 2: Lower Marine Riser Package (2012)





Failure 3: Blow Out Preventer (BOP) Flange Bolt Failure (2014)





(A) Before cleaning at SES. Major scale divisions are in inches.

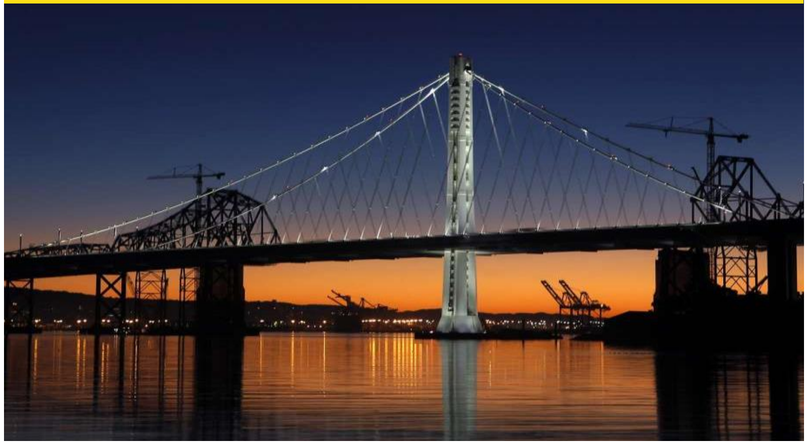
(B) After ultrasonic cleaning in an Alconox® solution. Major scale divisions are in inches.

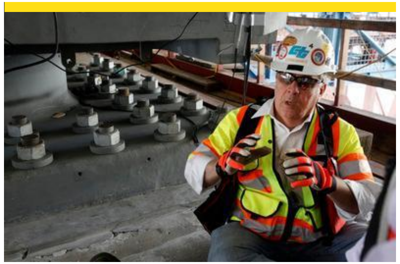
(C) Close-up view of Stud #19 showing difference in coating coloration. Scale divisions are 0.1 inch.

- Flange bolting plated with zinc is missing where cracking occurs in stud threads
- High hardness in excess of HRC 34
- Arrows point at areas with consumed sacrificial coating

Figure 4: Hydraulic connector flange/fasteners showing failures and first engaged threads

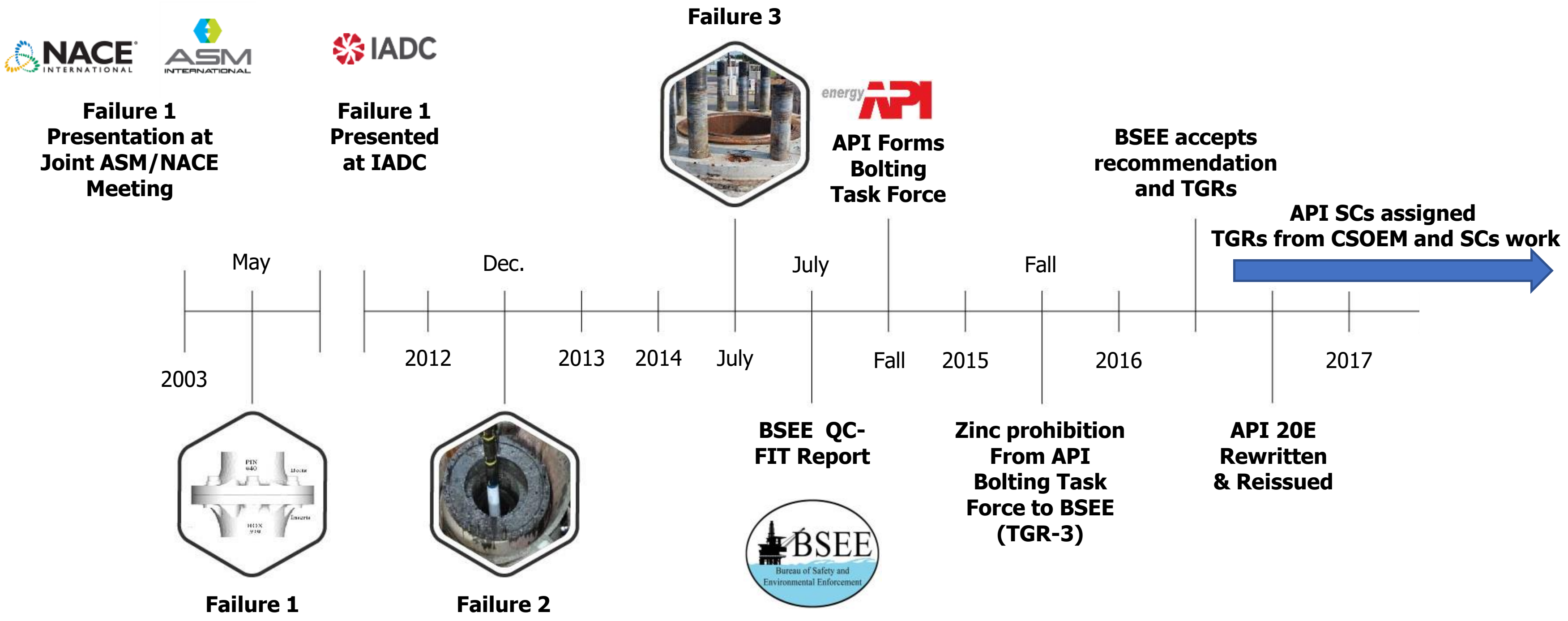
Failure 4: Bay Bridge Failure



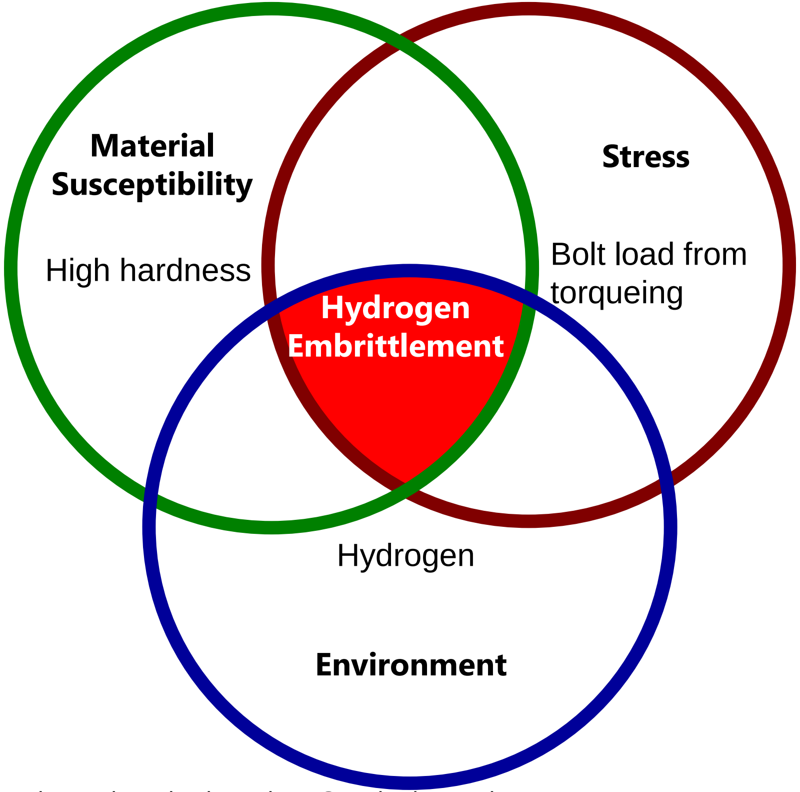


- San Francisco Bay Area Bridge Failure
- High strength bolting
  - (ASTM A490 39 HRC Maximum)
- Hot Dip Galvanized Zinc
- Bridge closed for repairs
- Long and costly repairs
- Offshore and on land

Efforts to address Hydrogen Embrittlement on bolting

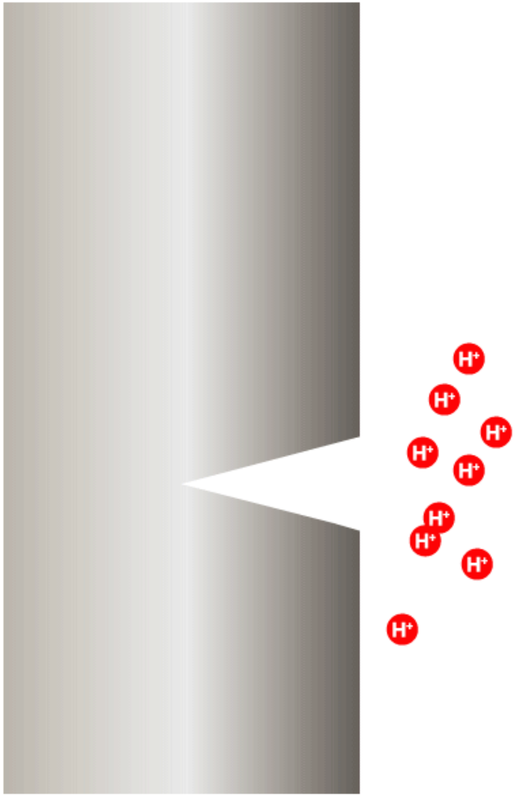


What is Hydrogen Embrittlement?



- Hydrogen embrittlement is the mortal enemy of fasteners.
- It causes metals to become brittle and fracture easily.
- Caused by tensile stress, material susceptibility to hydrogen, and corrosive environments.

Hydrogen Embrittlement in Action



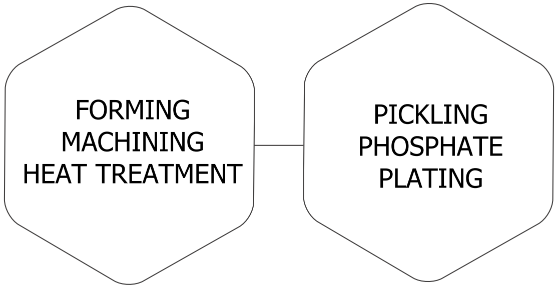
$2H^+ + 2e^-$ → H_2 (hydrogen gas)

$2H^+ + 2e^-$ → $2H^+$ (atomic hydrogen)

- Positively-charged hydrogen breaks out of water molecules and is attracted to metal
- Hydrogen atoms enter the metal through high-stress areas
- Hydrogen interacts with iron atoms to weaken and embrittle the metal

How Hydrogen Embrittlement Happens in Fasteners

Manufacturing Process



API 20 E
ASTM B994 SC18 CLASS1
ASTM F519

In Service Environment

Evaluation of Hydrogen embrittlement in bolting

ASTM F519: No failure after 200 hours at 75% NTS. It evaluates IHE

ASTM 1940: Specifically related to fasteners. It evaluates IHE

ASTM 2660: Effect of residual hydrogen in the steel as a result of processing. It evaluates mainly EHE

ASTM 1624: Tests in air to investigate IHE. Tests in 3.5% NaCl and cathodic polarization to investigate EHE.

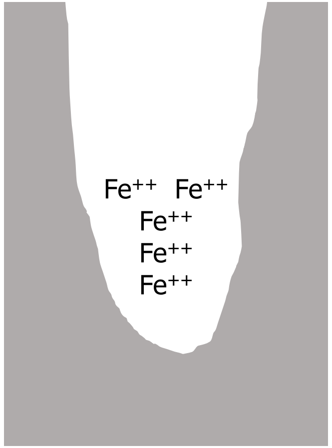
Electrochemical Approach to Hydrogen Embrittlement

- Every material possesses a **Potential** and delivers a **Current**
- **Potential** = Corrosion energy
  The higher the potential, the more resistant to corrosion.
- **Current** = How reactive a material is to its environment
  The higher the current, the more hydrogen will be produced.
- **The Protection Potential** = the potential value (-0.85 V vs Ag/AgCl) where no electrons are exchanged between a material and its environment due to corrosion reactions
  Potential Values equal or more negative produce hydrogen.

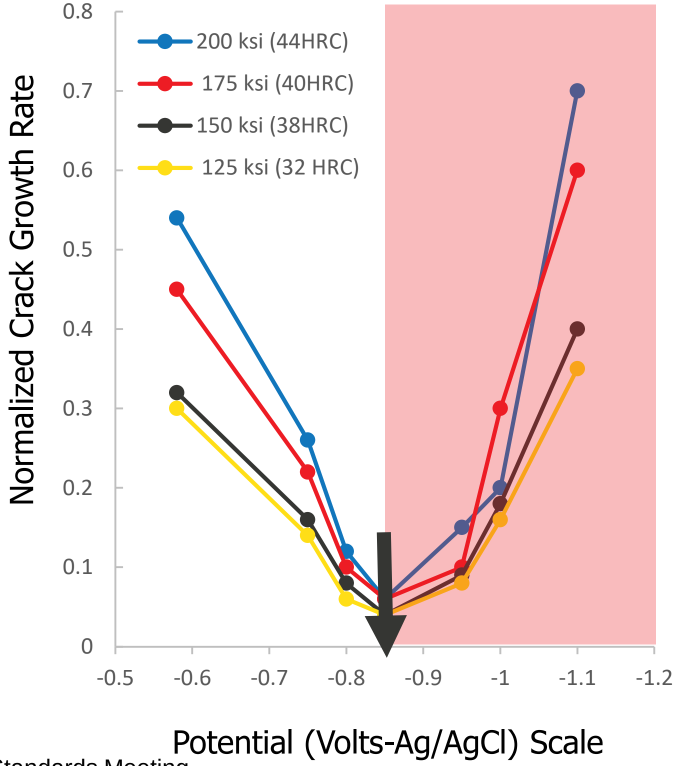
The Protection Potential

Anodic Reaction
$Fe = Fe^{++} + 2e^-$

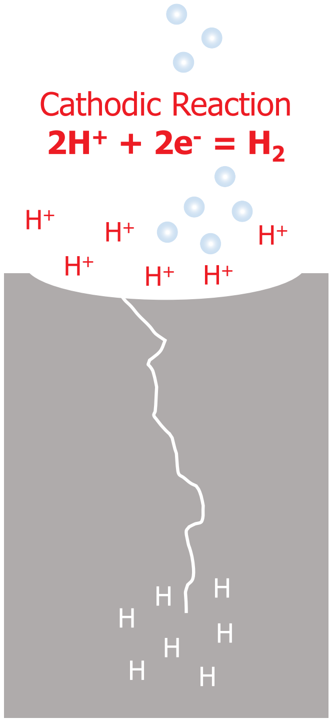
Seawater Corrosion



Anodic Stress Corrosion Cracking



Cathodic Reaction
$2H^+ + 2e^- = H_2$

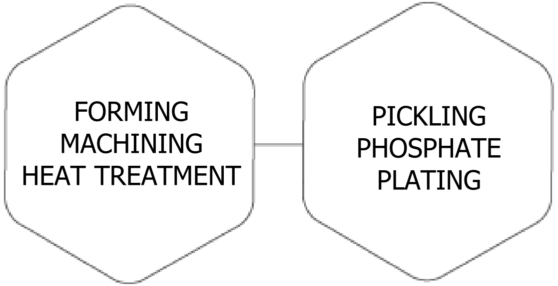


Seawater Hydrolysis

Hydrogen Embrittlement

Galvanic Coupling

Manufacturing Process



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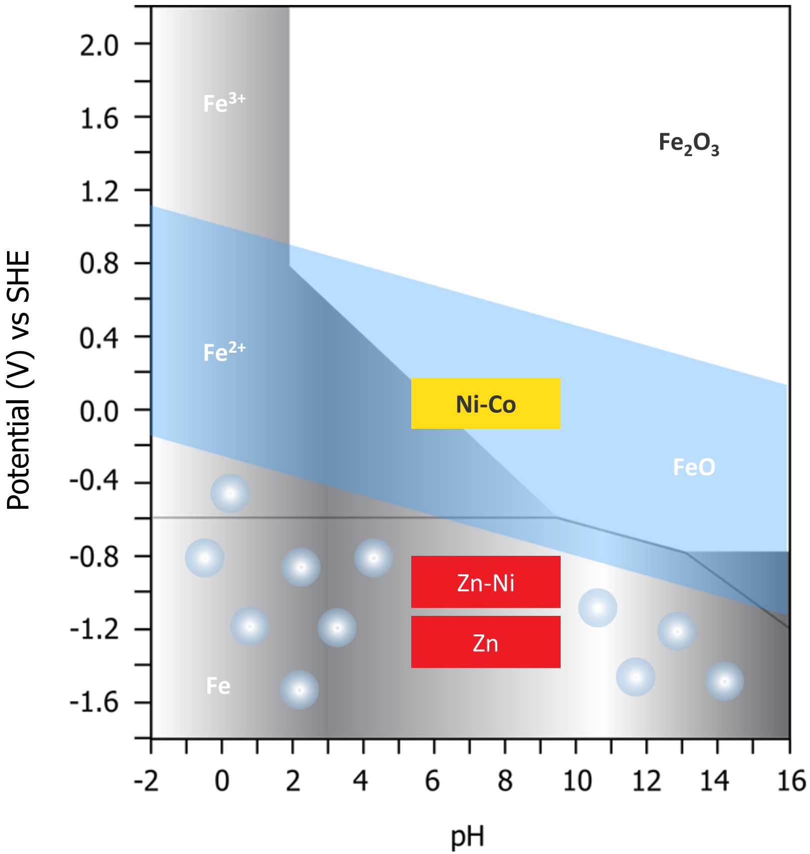
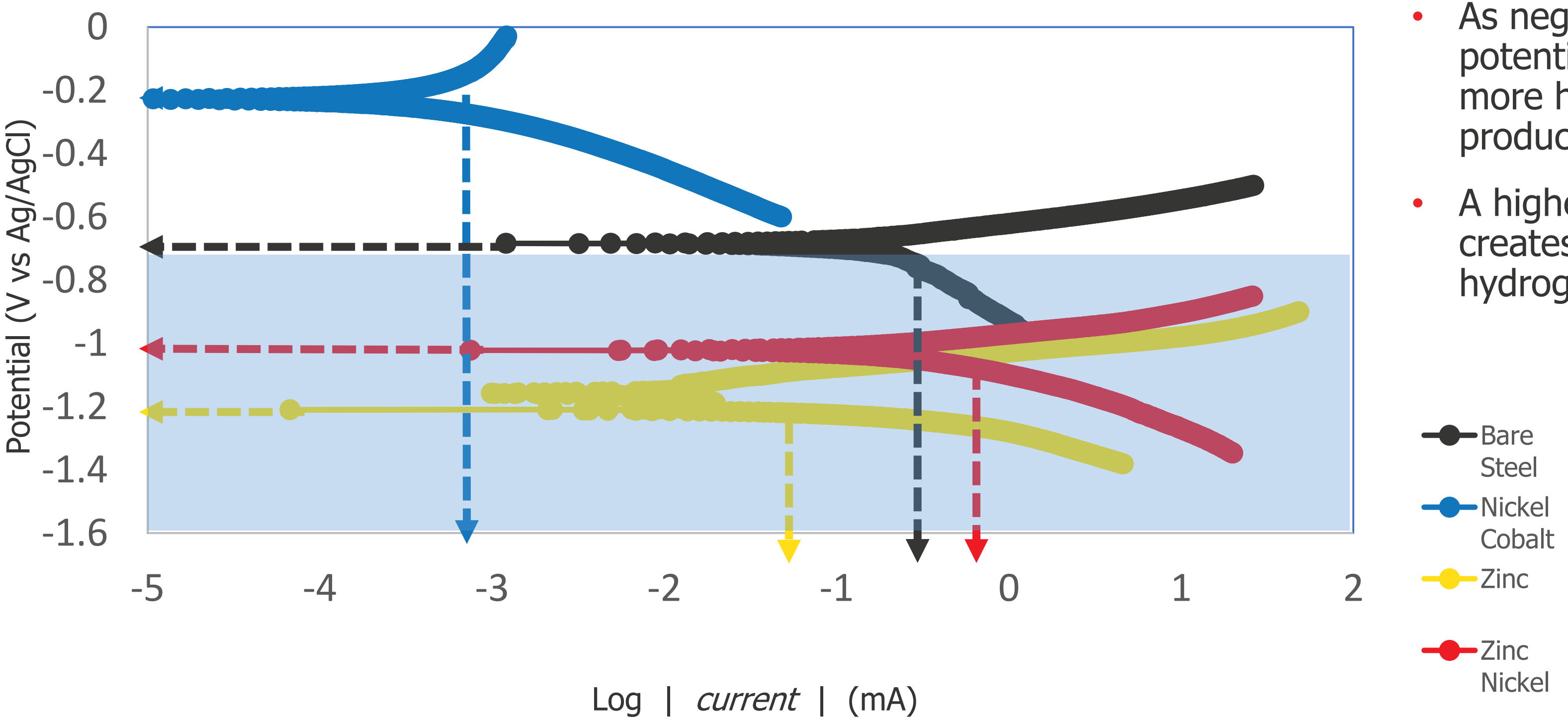
Thermodynamics of Hydrogen Production



- More negative potential increases the risk of hydrogen embrittlement.
- Below the water stability region, hydrogen is produced
- Nickel-Cobalt will not cause hydrogen embrittlement. Zinc does.
- Zinc will produce hydrogen gas and atomic hydrogen.

Water Stability Region

Electrochemical Performance of Different Metallic Coatings



- As negative potentials decrease more hydrogen is produced
- A higher current creates more hydrogen discharge

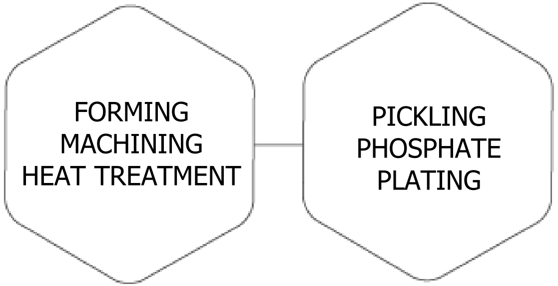
Summary of electrochemical performance

	Potential	Current	Corrosion resistance	Hydrogen production
Zinc	↓	↑	↓	↑
Zinc-Nickel	↓	↑	↓	↑
Nickel-Cobalt	↑	↓	↑	↓

- Zinc and Zinc-Nickel have a very low potential and delivers a very high current, so it is very reactive and its cathodic current will produce hydrogen.
- Nickel-Cobalt has a high potential and delivers a very low current, so it reacts very slowly and is resistant to corrosion.

Cathodic Overprotection

Manufacturing Process



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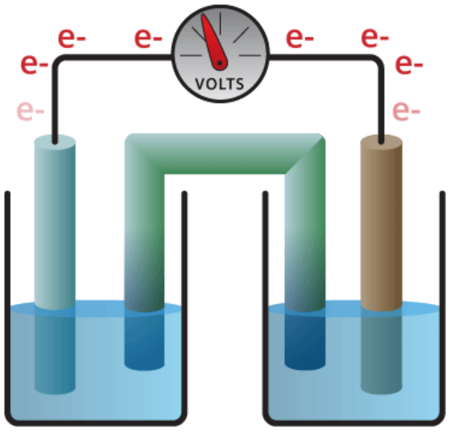
Cathodic protection (overprotection)

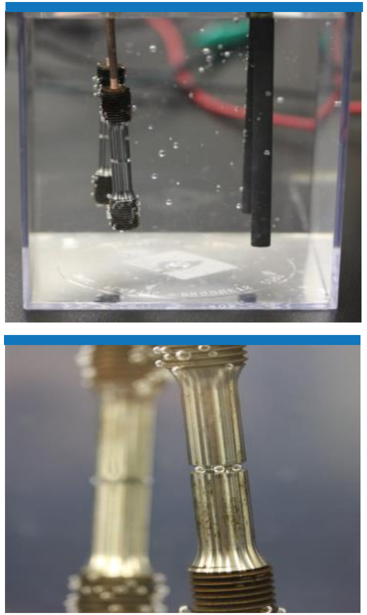


Anode Cathode

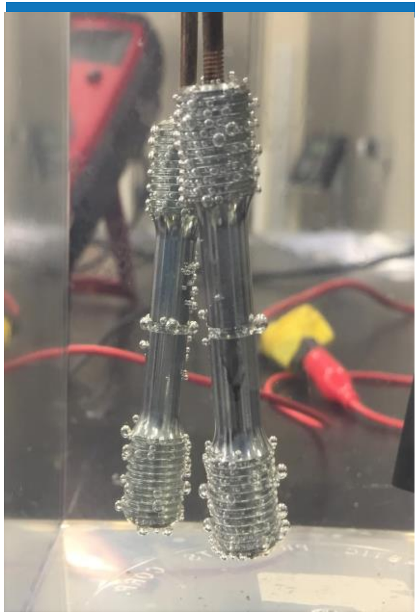
Cathodic overprotection to -1.2 V vs Ag/AgCl

- Cathodic Protection charges metals with current to prevent corrosion.
- Too much current accelerates hydrogen production, putting fasteners at risk of hydrogen embrittlement. This is easy to do by accident due to the design of cathodic protection.
- Coatings must protect fasteners from accidental cathodic overprotection.
- Cathodic charging was used for hydrogen production tests, hydrogen permeation tests, and the effect of cathodic protection on the mechanical strength of coupons.

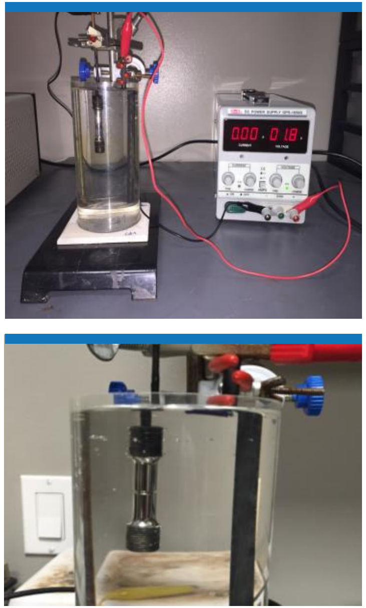
Nickel-Cobalt:
Hydrogen Embrittlement Test for Cathodic Protection



Bare Steel



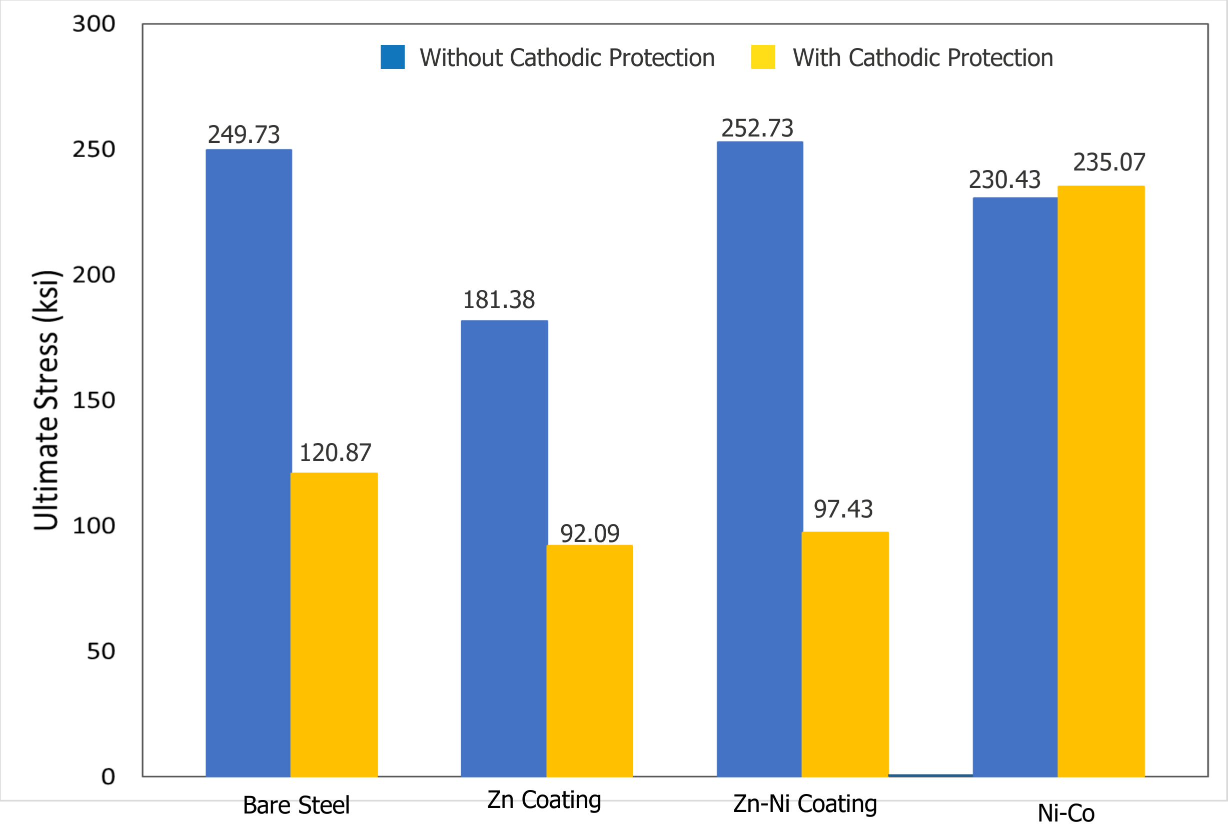
Zinc coating



Nickel-Cobalt

- Notched tensile samples (49 HRC) were subject to cathodic overprotection of -1.0 V vs Ag/AgCl in 3.5%wt NaCl.
- Tensile tests to break the samples were performed after 30 days of polarization.

Tensile Tests with Cathodic Protection

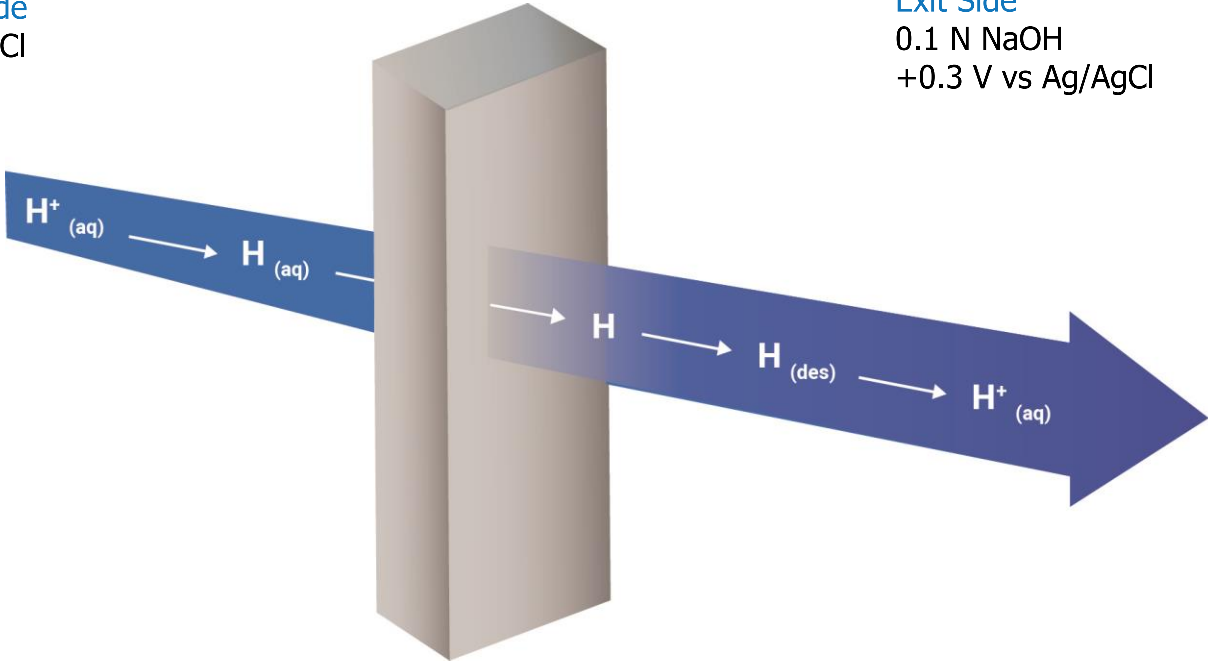


- Nickel-Cobalt plating has a minimal effect on a fastener's mechanical performance.
- Cathodic overprotection has no effect on mechanical performance with Nickel-Cobalt plating.
- Nickel-Cobalt protects fasteners under stress from hydrogen.

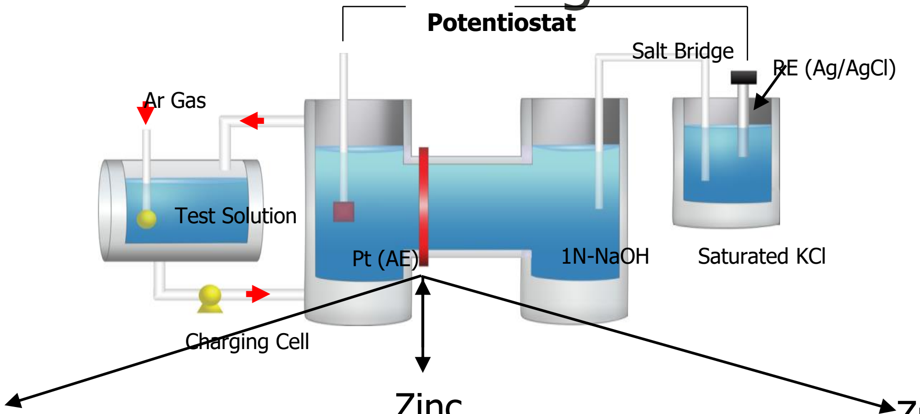
Permeation: How Hydrogen Penetrates Steel

Charging Side
3.5% wt NaCl
1.0 mA/cm^2

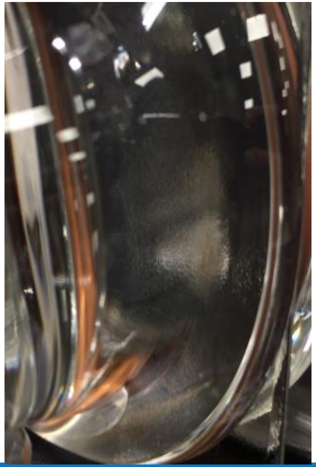
Exit Side
0.1 N NaOH
+0.3 V vs Ag/AgCl



Hydrogen Permeation Cell Testing



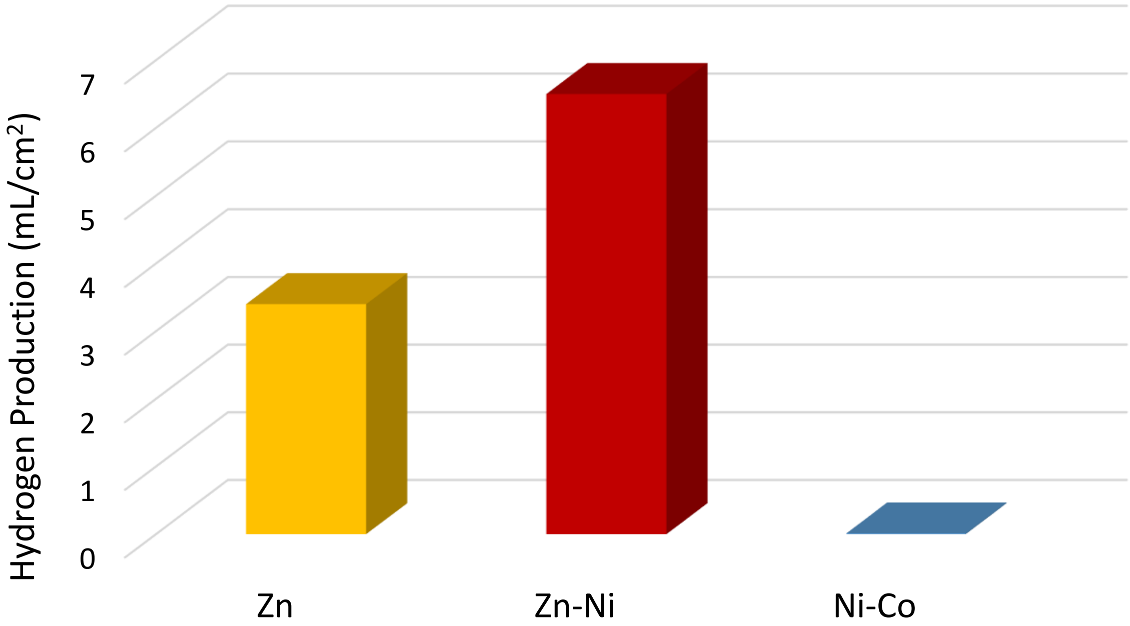
Ni-Co



Zinc

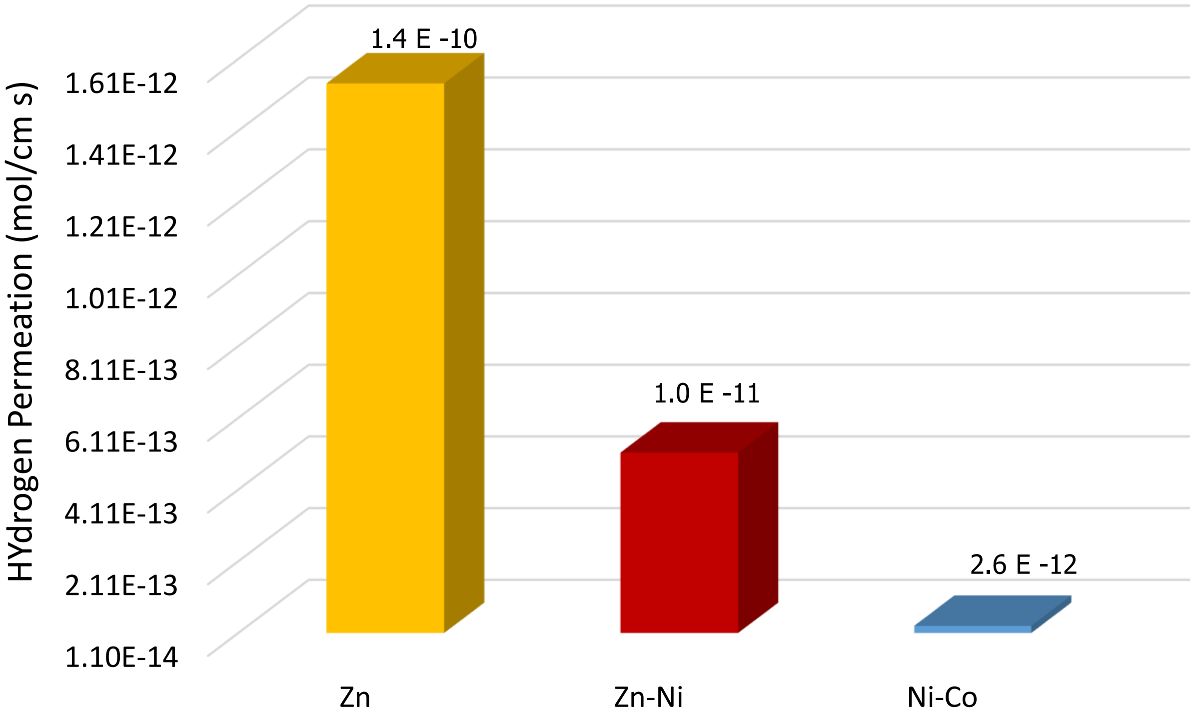
Zn-Ni

Hydrogen Production on different coatings



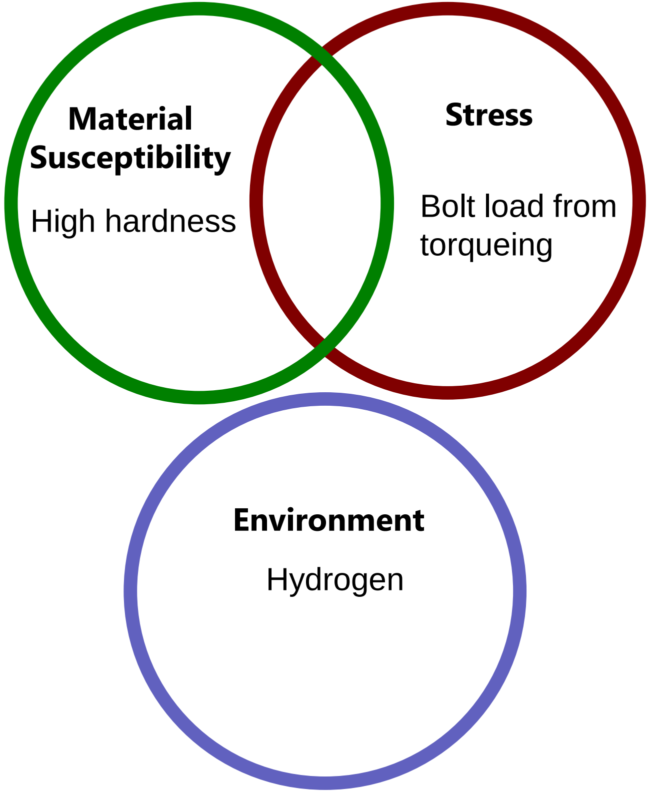
- 1 mA/cm^2 was applied during 12 hours in a 3.5wt% NaCl acidified to pH=3
- Hydrogen was collected and quantified
- Nickel-Cobalt produced the least amount of hydrogen compared to the other coatings.

Hydrogen Permeation Cell Testing: Results ASTM G148



- Zn showed the highest hydrogen permeation
- Ni-Co exhibited the lowest hydrogen permeation, one order of magnitude less than Zn-Ni and two orders of magnitude of Zn
- Despite the high hydrogen production on the Zn-Ni, Zn had a higher permeation.

Final Remarks



- Materials selection plays a crucial role regarding hydrogen embrittlement susceptibility.
- Nickel-Cobalt will not produce hydrogen even with high cathodic overprotection, Zn and Zn-Ni will do.
- Eliminating one of the elements from the catastrophic Venn diagram, may eliminate the risk of hydrogen embrittlement.
- Nickel-Cobalt protects from external sources of hydrogen in the field.

Thank you all

Any questions?

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