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Review of disseminated concepts on galvanic corrosion

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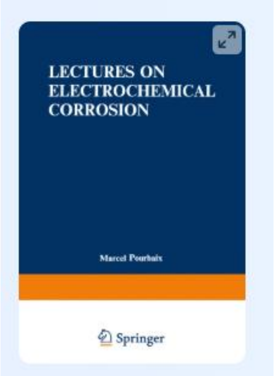
Motivation

- ✓ Definitions and concepts that are widespread, whether in corrosion science or other scientific areas, are not always absolutely accurate and comprehensive.
- ✓ A classic example and very close to our focus here in our Congress is the very definition of "Corrosion“

Corrosion is the gradual deterioration or degradation of a material, usually a metal, caused by chemical or electrochemical reactions with its environment. This process often results in the formation of oxides, hydroxides, or other compounds, **leading to structural weakness and damage of the material over time**.



LECTURES ON
ELECTROCHEMICAL
CORROSION

Marcel Pourbaix

Springer

Pilar of Delhi - Índia

The **iron pillar of Delhi** is a metal structure 7.21 m high with a 41 cm in diameter that was constructed by Chandragupta II (reigned c. 375–415 BC) and now stands in the Qutb complex at Mehrauli in Delhi, India. **It would have been expected to have turned into a pile of rust if the definition of corrosion were true.**

The presence of second-phase particles (such as unreduced iron oxides) in the iron microstructure, large amounts of phosphorus in the metal, and alternate wetting and drying under atmospheric conditions are three of the main factors in the formation of this protective film.

There is no doubt that the given definition make no sense here!

Objective

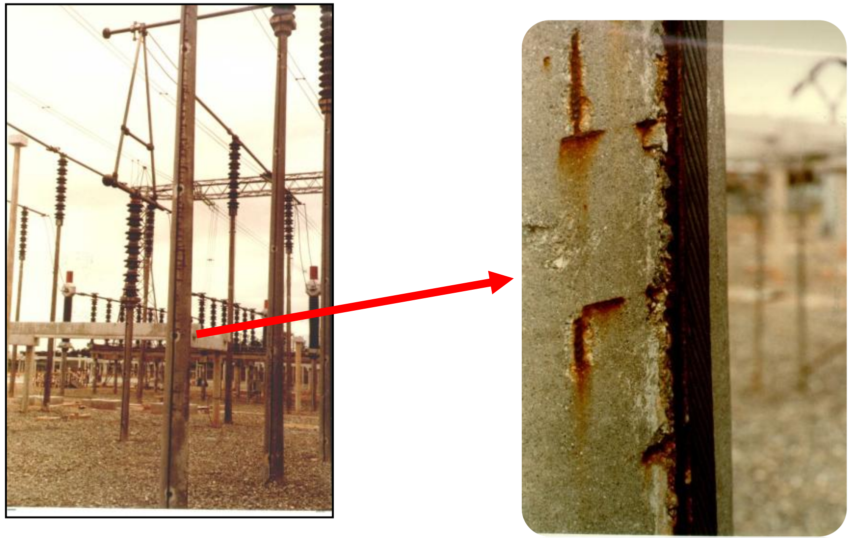
This work presents two studies of galvanic corrosion with non-conventional characteristics and how they were studied, aiming to contribute to their understanding.

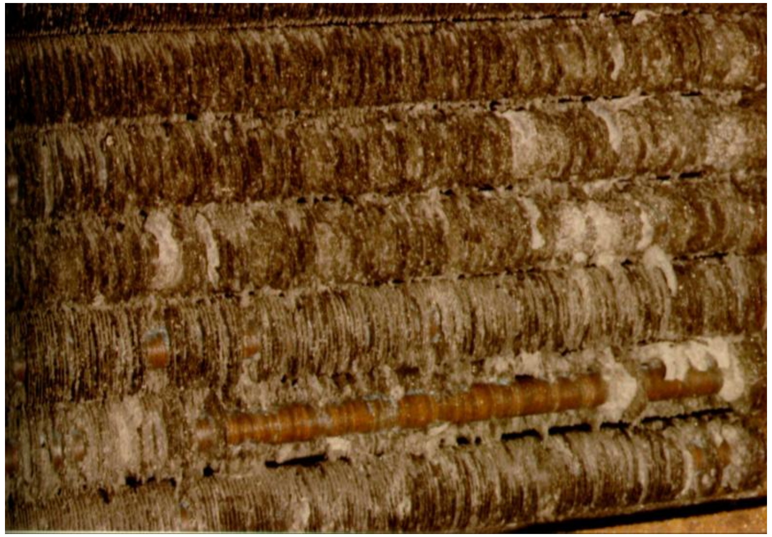
A classical galvanic corrosion was included!

Classical galvanic corrosion

✓ Galvanic corrosion, also known as bimetallic corrosion, is an electrochemical process where one metal corrodes preferentially when it's in electrical contact with a different metal in the presence of an electrolyte. This occurs because the two metals have different electrochemical potentials, creating a galvanic couple where one acts as the anode (corroding) and the other as the cathode (relatively protected).

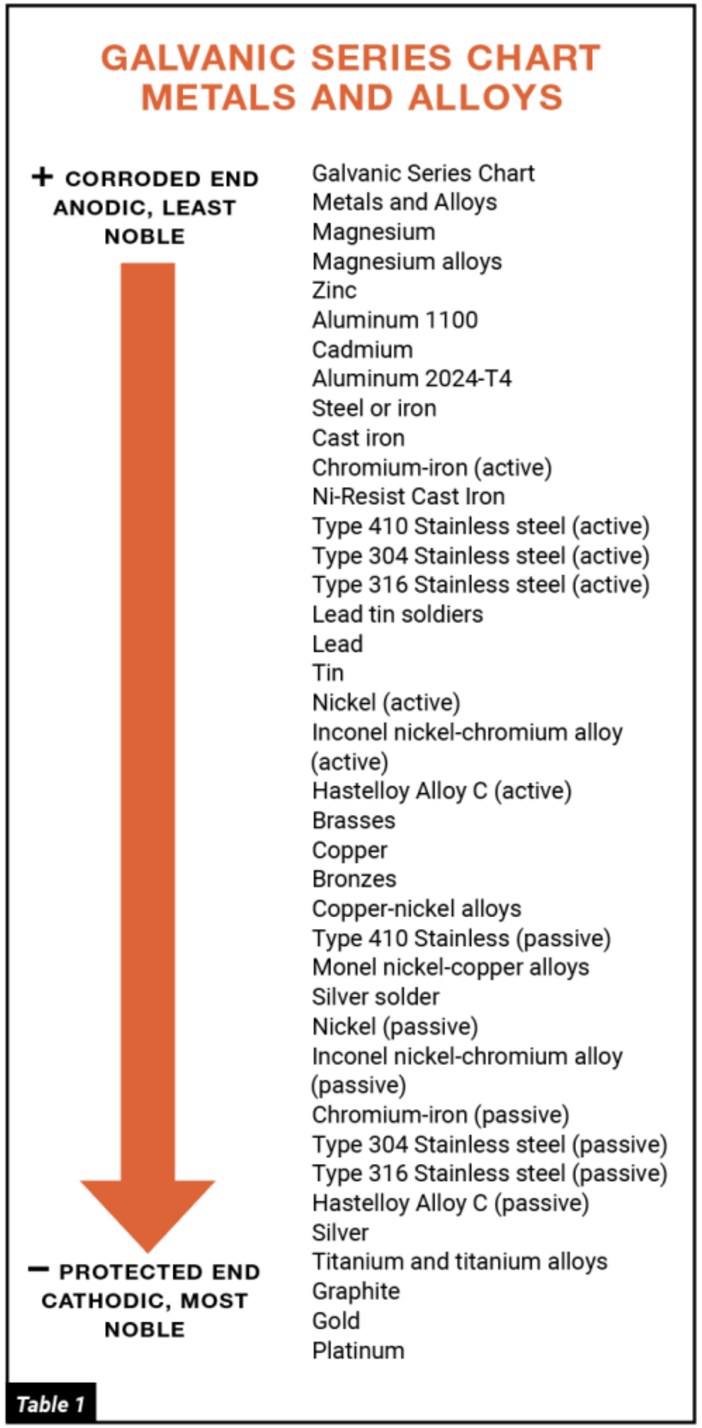
- **Anode:** the more reactive (less noble) metal acts as the anode.
- **Cathode:** the more corrosion-resistant (noble) metal acts as the cathode.





Industrial air conditioner
Local atmosphere was contaminated with hydrochloric acid fumes

Classical galvanic corrosion



GALVANIC SERIES CHART
METALS AND ALLOYS

+ CORRODED END
ANODIC, LEAST NOBLE

Galvanic Series Chart
Metals and Alloys
Magnesium
Magnesium alloys
Zinc
Aluminum 1100
Cadmium
Aluminum 2024-T4
Steel or iron
Cast iron
Chromium-iron (active)
Ni-Resist Cast Iron
Type 410 Stainless steel (active)
Type 304 Stainless steel (active)
Type 316 Stainless steel (active)
Lead tin soldiers
Lead
Tin
Nickel (active)
Inconel nickel-chromium alloy (active)
Hastelloy Alloy C (active)
Brasses
Copper
Bronzes
Copper-nickel alloys
Type 410 Stainless (passive)
Monel nickel-copper alloys
Silver solder
Nickel (passive)
Inconel nickel-chromium alloy (passive)
Chromium-iron (passive)
Type 304 Stainless steel (passive)
Type 316 Stainless steel (passive)
Hastelloy Alloy C (passive)
Silver
Titanium and titanium alloys
Graphite
Gold
Platinum

− PROTECTED END
CATHODIC, MOST NOBLE

Table 1

- Galvanic corrosion are driven by the difference in electrochemical potential between distinct metals or metallic alloys. The open circuit potential (OCP) in sea water is used for the classification of galvanic series.
  - However, in many cases where different electrolytes are used, the individual OCP are not mentioned, and the galvanic series are used as a reference.

- The passive and active state change the position of the metal or alloy.

- It is always highlighted that the conductivity of the medium, and the relative area are important point to be considered.
  - However, the real active area of the couple determined by the conductivity of the medium is not always considered.

Carbon steel/AISI 304 in H_2SO_4

- Although, the high agressiviness of concentrated H_2SO_4, carbon steel tanks are used to storage this acid.
- However, for transportation, even in slow flow rates and short distances, stainless steels are prefered.
- This practices create a galvanic coupling of carbon steel with stainless steels.

https://www.chemengonline.com/safety-sulfuric-acid-storage-tanks/

http://www.sulphuric-acid.com/techmanual/strong%20acid/sa_piping.htm

Carbon steel/AISI 304 in H_2SO_4

- Information regarding the galvanic corrosion in H_2SO_4 in the literature is restricted.
- Corrosion tests with concentrated sulfuric acid is not an easy task, as this acid is extremaly difficult to handle in laboratory and it is extremely hygroscopic, requiring a strinct control of the absorption of atmospheric humidity.
- This may explain the scarcy published literature related to the corrosion testing in H_2SO_4.
- This system is one of spectial cases of galvanic corrosion!

Test vessel used for the corrosion rate determination

Experimental arrangement for electrochemical and galvanic corrosion tests

Carbon steel/AISI 304 in H_2SO_4

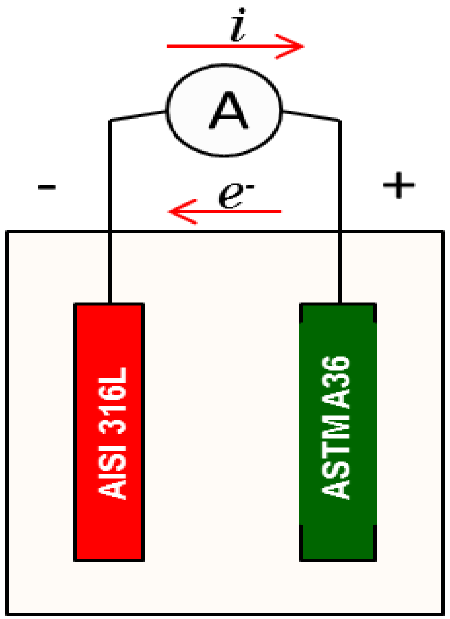
- Corrrosion rates for individual alloys and after galvanic coupling in different acid concentration and temperature were determined.

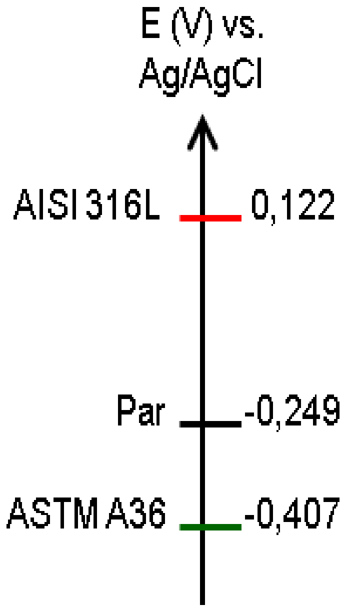
- Individual polarization curves were also obtained.

- The galvanic potentials after coupling were also determined.

- Only some results will be discussed here.

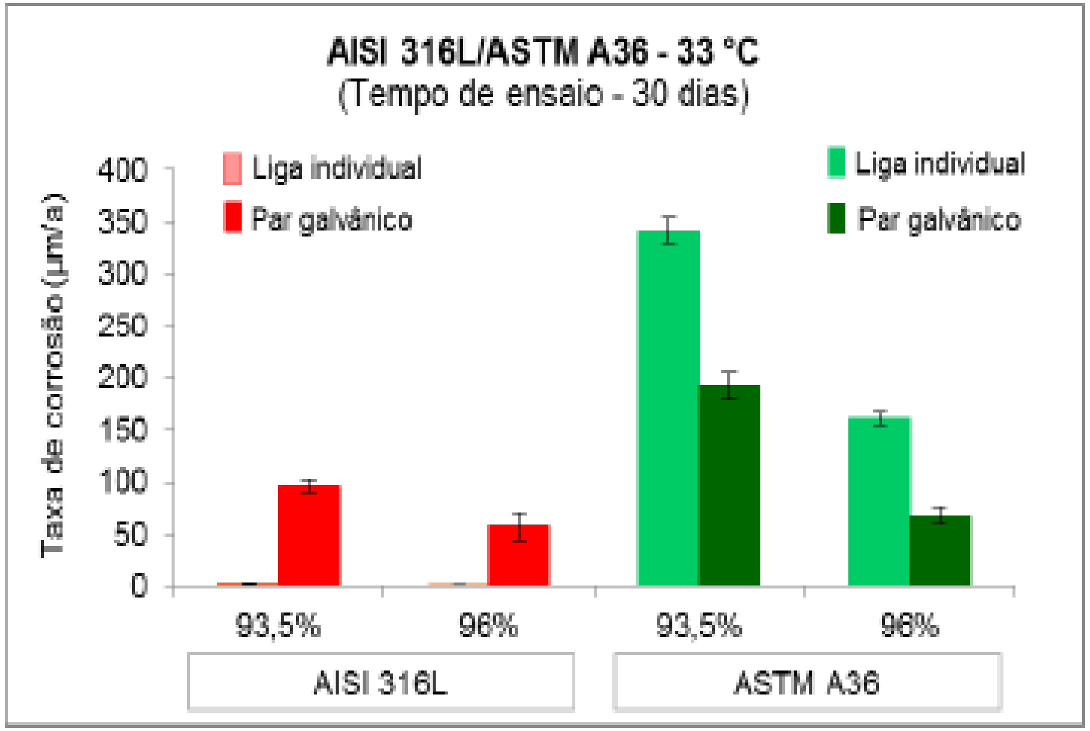
What does it happen when coupling occurs?





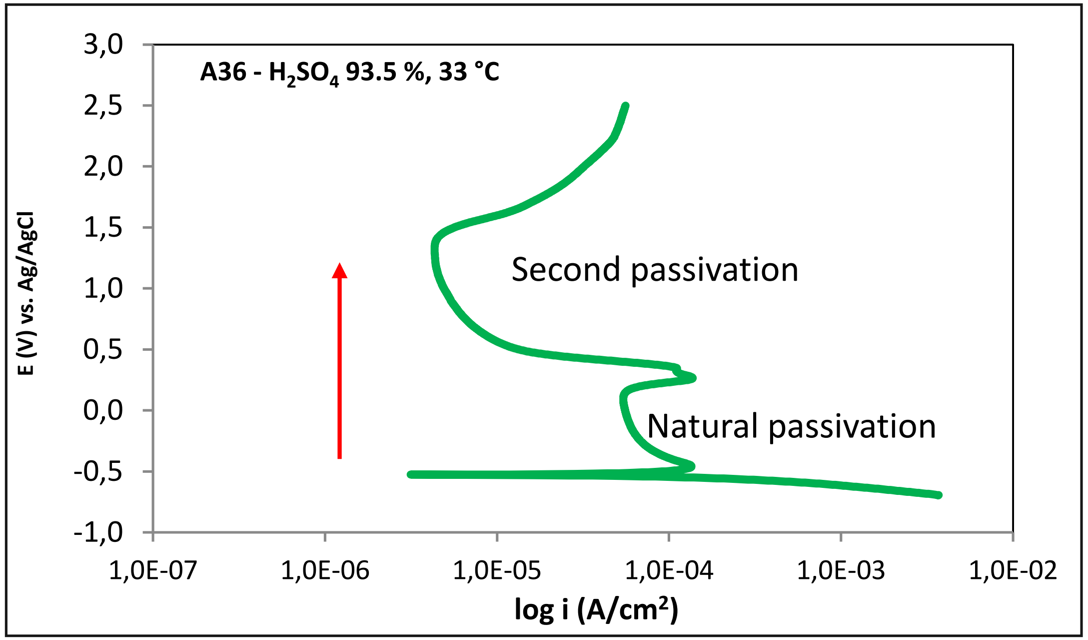
Classically....

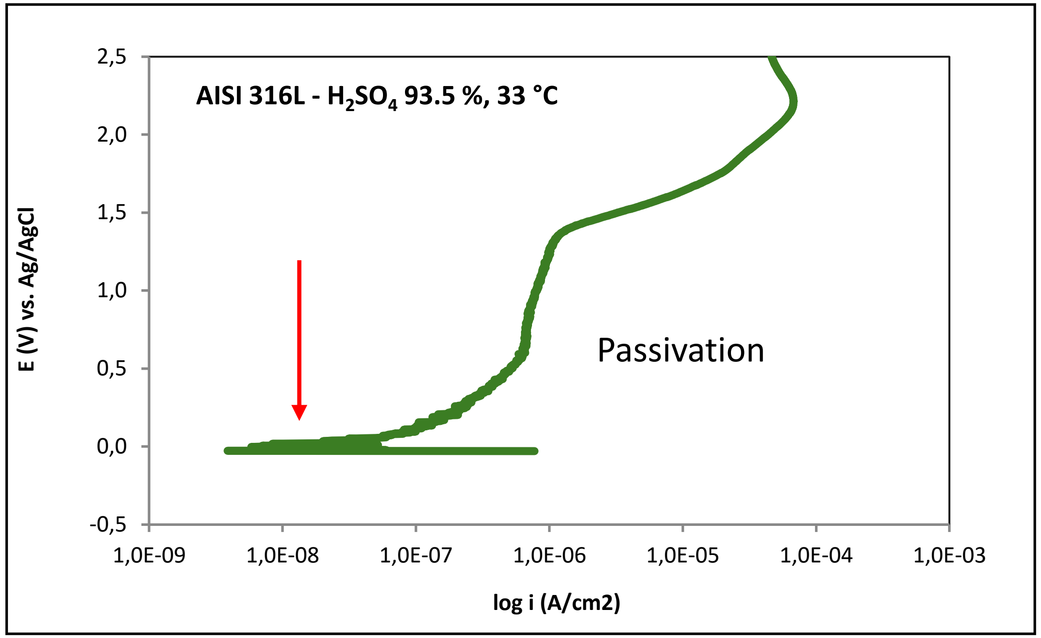
- ➢ The galvanic couple assumes a potential values between the individual OCP values.
- ➢ It is expected that the more noble alloy should be protected, and the less noble alloy corrosion will be enhanced after the galvanic coupling.



How can we explain this unexpected behaviour?

Investigation through polarization curves





- A36 natural passivation is related to $FeSO_4$ formation (sulfation): $i_{passivation}$ lies between 10^{-5} A/cm^{2} and 10^{-4} A/cm^{2}.
- A36 second passivation is relate to the formation of a mixture of iron oxide and iron sulfate (de Fe_2O_3 mixed with $Fe_2(SO_4)_3.5H_2SO_4$ e $FeSO_4.3H_2SO_4$), more effective: $i_{passivation}$ lies between 10^{-6} A/cm^{2} and 10^{-5} A/cm^{2};
- AISI 316 passivation current density lies between 10^{-7} A/cm^{2} and 10^{-6} A/cm^{2};
  - this value is lower than the values of the passivation current density of carbon steel, which, in the sulfation region, assumes values between 10^{-5} A/cm^{2} e 10^{-4} A/cm^{2}.

The unexpected results can be explained by the active/passive behaviour of A36 and AISI 316 in concentrated sulfuric acid which was possible through laboratory tests! No literature support was found at the time of the project development!

Preferential weld corrosion (PWC) in low conductivity medium

- In this case, there was a very large number of published papers available.
- The first ones referring to the description of a PWC failure identified early in 1910.
- However, the considerable studies conducted along the year leads controversies because comparisons were always made with the first failure, even in cases occurred in completely different medium.

1910

Weld metal anodic to the parent metal in sea water!!!!!!!

Similar failures were verified in O&G, in sea water injection pipes.
The solution: using more noble weld metal (Ni and Cu alloyed) to prevent galvanic corrosion.

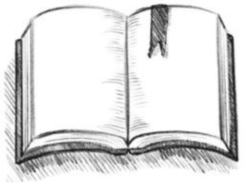
1997

Corrosion of heat affected zone of pipelines, even using steel with ~0,65 % Ni. More noble weld alloys is not a global solution!

1999

Some studies pointed out that the rule of using a cathodic (noble) weld metal to avoid preferential weld corrosion does not apply low conductivity media…… But the papers were controversial with no clear definition.

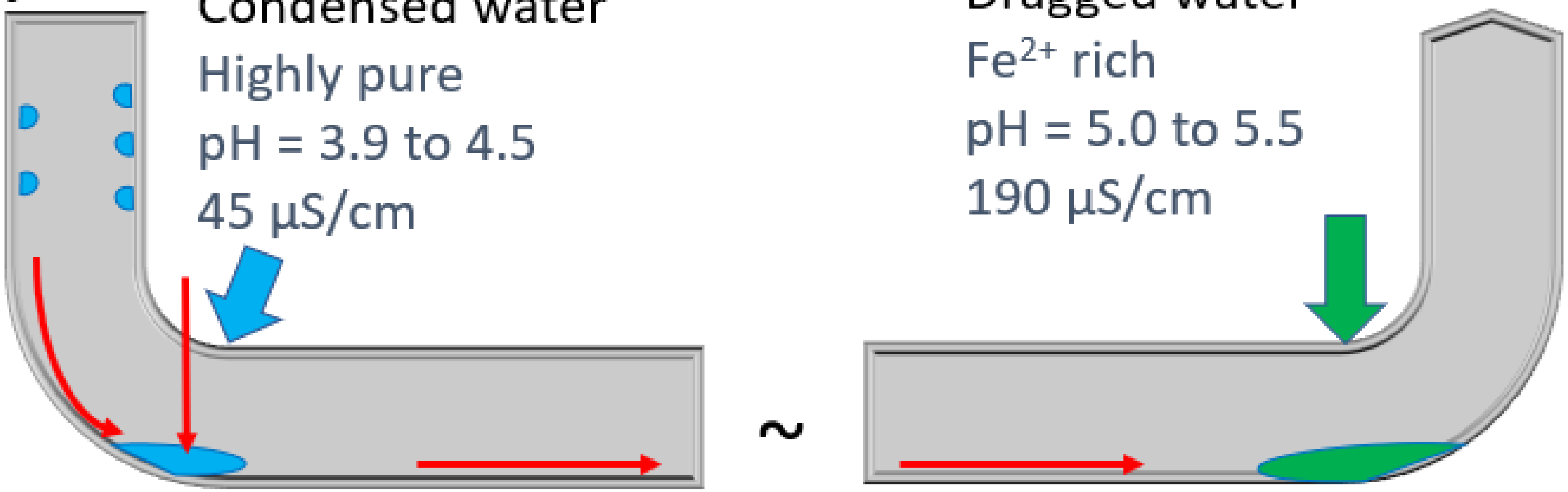
2016



McIntyre e Achour (2016) book informs that the use of more noble weld metal is not applied for low conductivity media!

Investigation of galvanic corrosion in low conductivity media

- Preferential weld corrosion was observed in gas-exportation in contact with low conductivity CO_2 condensed water



From production
After treatment

Condensed water
Highly pure
pH = 3.9 to 4.5
45 µS/cm

Dragged water
Fe^{2+} rich
pH = 5.0 to 5.5
190 µS/cm

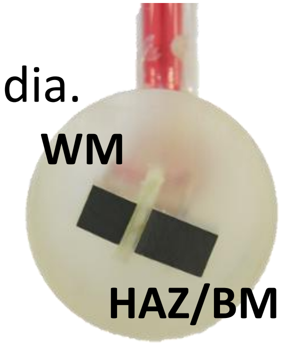
To refinery

~

Gas-transportation pipeline

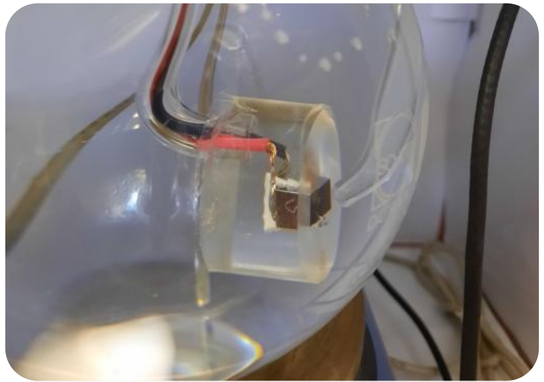
Investigation of galvanic corrosion in low conductivity media

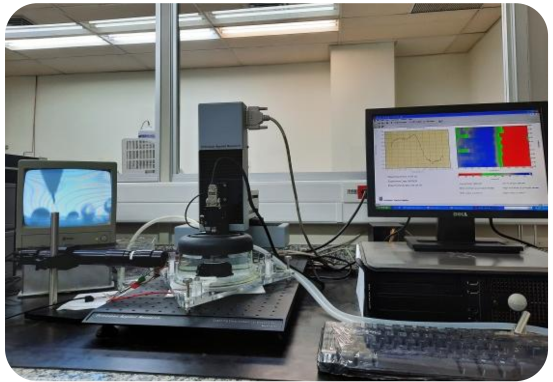
- Several preliminary tests were conducted for the selection of methodologies for low conductivity media.



- Galvanic current measurement: anodic and cathodic regions of the galvanic couple MS/MB+ZTA alternate over time. No clear indication of preferential weld attack was obtained.

- Immersion test and SVET technique using the **entire joint** were selected.





Immersion test

48 h (in low conductivity medium)

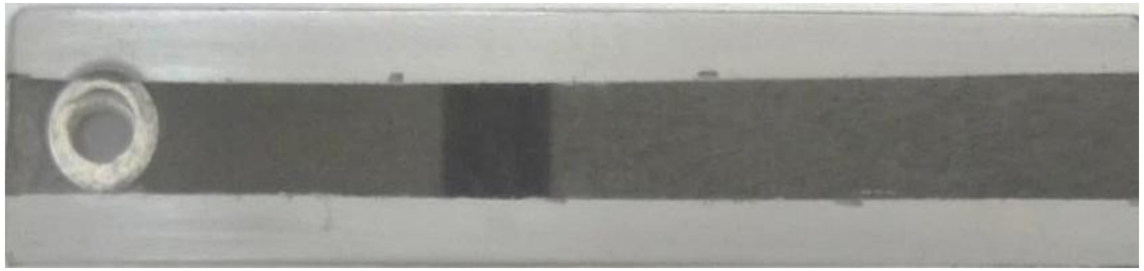
Specimens – dimensions and preparation

100 mm x 20 mm x 6 mm

Sample ready to test

470 Scotch tape to protect the surface
This area was used as a reference for
thickness-loss measurement

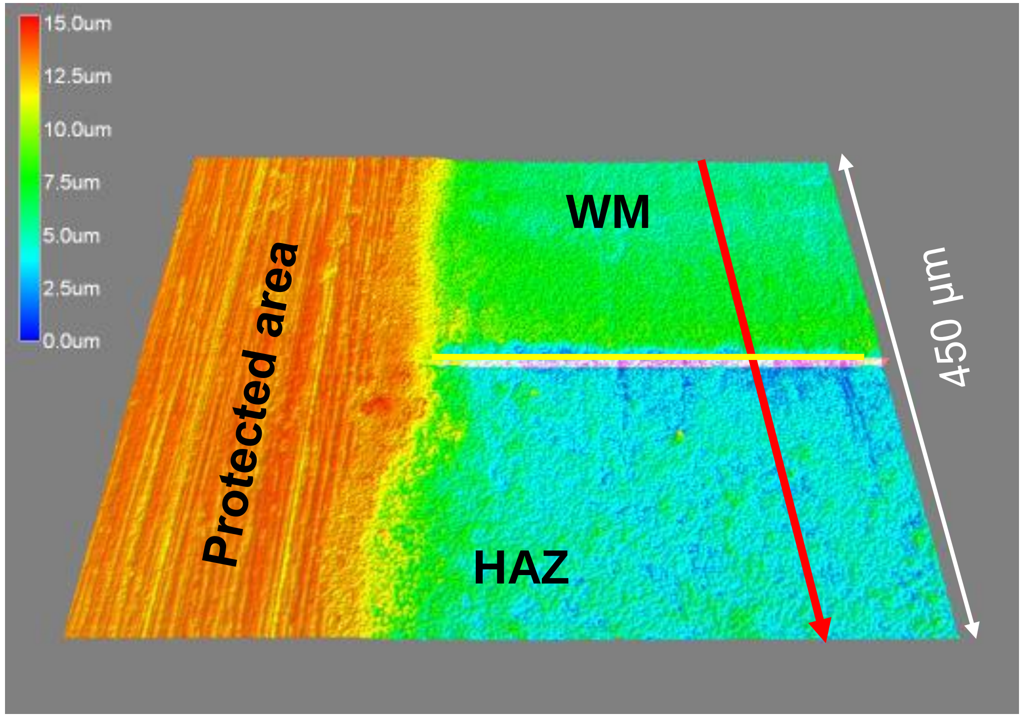
Sample after the test

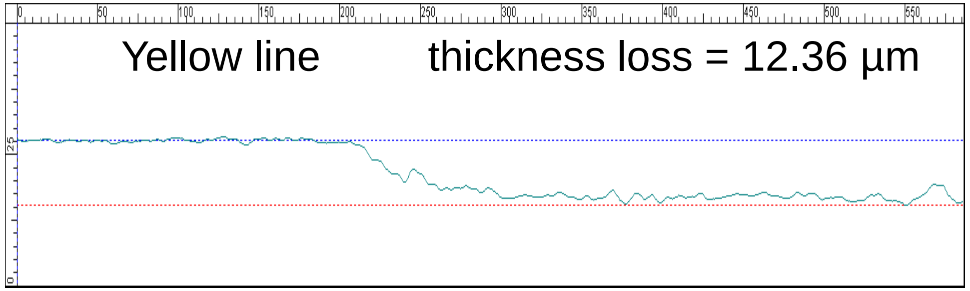


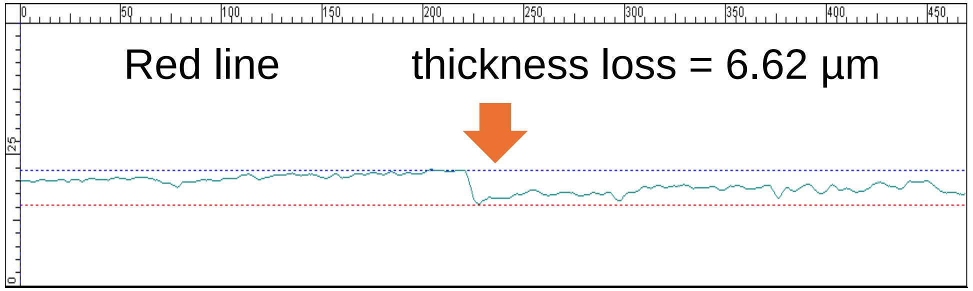
Non-corroded area
(reference)

Identification of galvanic corrosion using confocal microscope

In a low-conductivity medium, the galvanic action may be restricted to a distance as low as 100 µm.



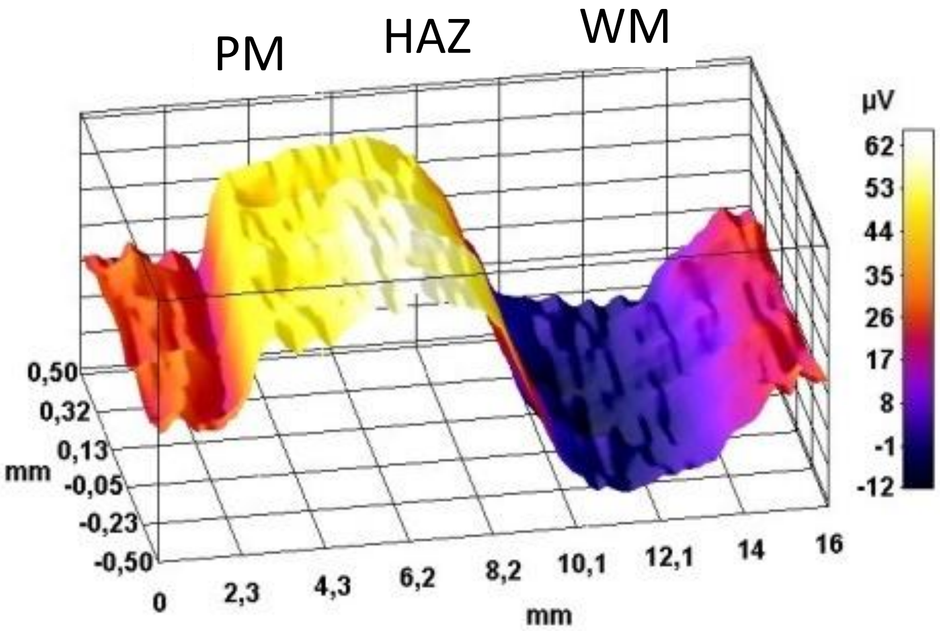

Yellow line thickness loss = 12.36 µm

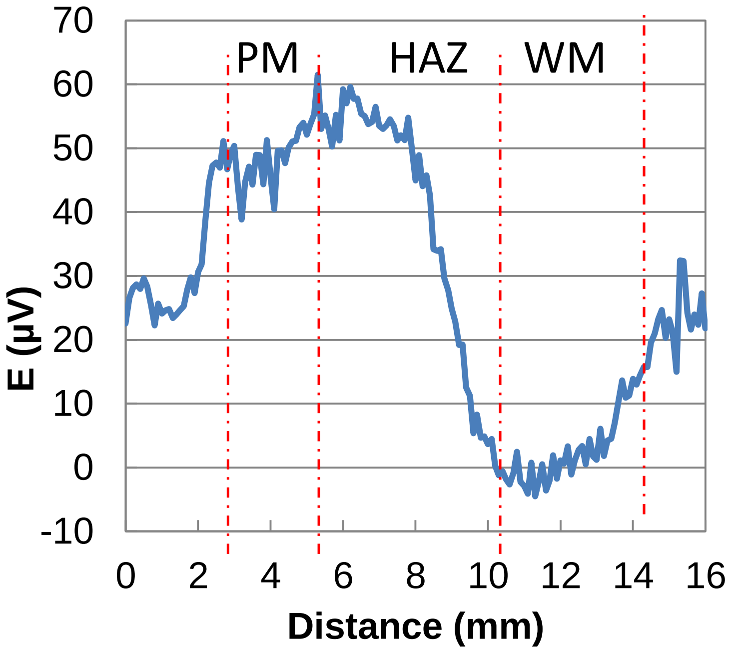

Red line thickness loss = 6.62 µm

Identification of galvanic corrosion using SVET

Low conductivity media in the study of weld preferential attack

weld metal (WM) is the cathode in the vicinity of the fused line





Conclusion

- The results obtained in this study show that the classical concept of corrosion by galvanic couples cannot be generalized.
- If the metals of the galvanic coupling are in an active state and do not show a tendency to passivate, then the classical concept applies, namely: in a galvanic couple, the more noble metal, cathodically polarized, has its corrosion rate reduced and the less noble metal, anodically polarized, has its corrosion rate increased.
  - However, if one or both metals of the galvanic coupling are in a passive state, the behavior of the couple will depend on the degree of passivation, the level of polarization imposed by the electrical connection between the metals.
- In low conductivity media, the galvanic corrosion cells established are short-range cells formed in the vicinity of the electrical contact and may not exceed 100 µm. In this cases, other techniques would be necessary to access this type of corrosion.

thank you!