Fundamental Challenges to Materials Integrity in Biodigester Environments

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Future of Digesters to Manage Food and Farm Waste

- New York state will ban food waste from landfills in the next decade.
- In California, the state is making big investment digesters. In 2017-18 alone, $99 million is available from the California Department of Food and Agriculture (Cdfa) to industry-led projects for installation of digesters.
- In October, I-GIT organized a National Grid sponsored workshop in Syracuse to identify key challenges to biogas production in digesters.
- Digester technology will be key to economical production of renewable gas (RNG).

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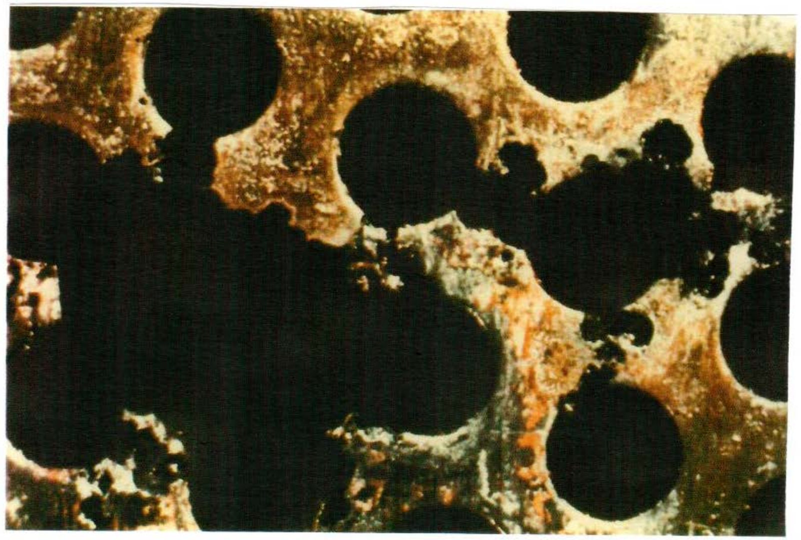
Sulphate Reducing Bacteria (SRB) Induced Corrosion of 304ss Screen and Tank Weldment

- **Biodigesters expose construction alloys to a complex organic/biological environment that can lead to corrosion and costly down time for maintenance.**

- **Most alloys are designed for Inorganic exposure and little is still known about the effect of organic compounds on corrosion.**



Source: Microbiologically Influenced Corrosion Ed: G Kobrin p202 NACE Int. 1993

Factors Contributing to Corrosion in Biodigesters: Microbial Influenced Corrosion

- **Biofilm formation creating differential aeration cells and modifying passive films and alloy surface composition**
- **Organic Acids activating iron dissolution by chelation and delaying Active-Passive Transition**
- **Ubiquitous Sulphate Reducing Bacteria (SRB) generating hydrogen sulphide which forms sulphides with elements needed for passive film formation**

Biofilm Formation

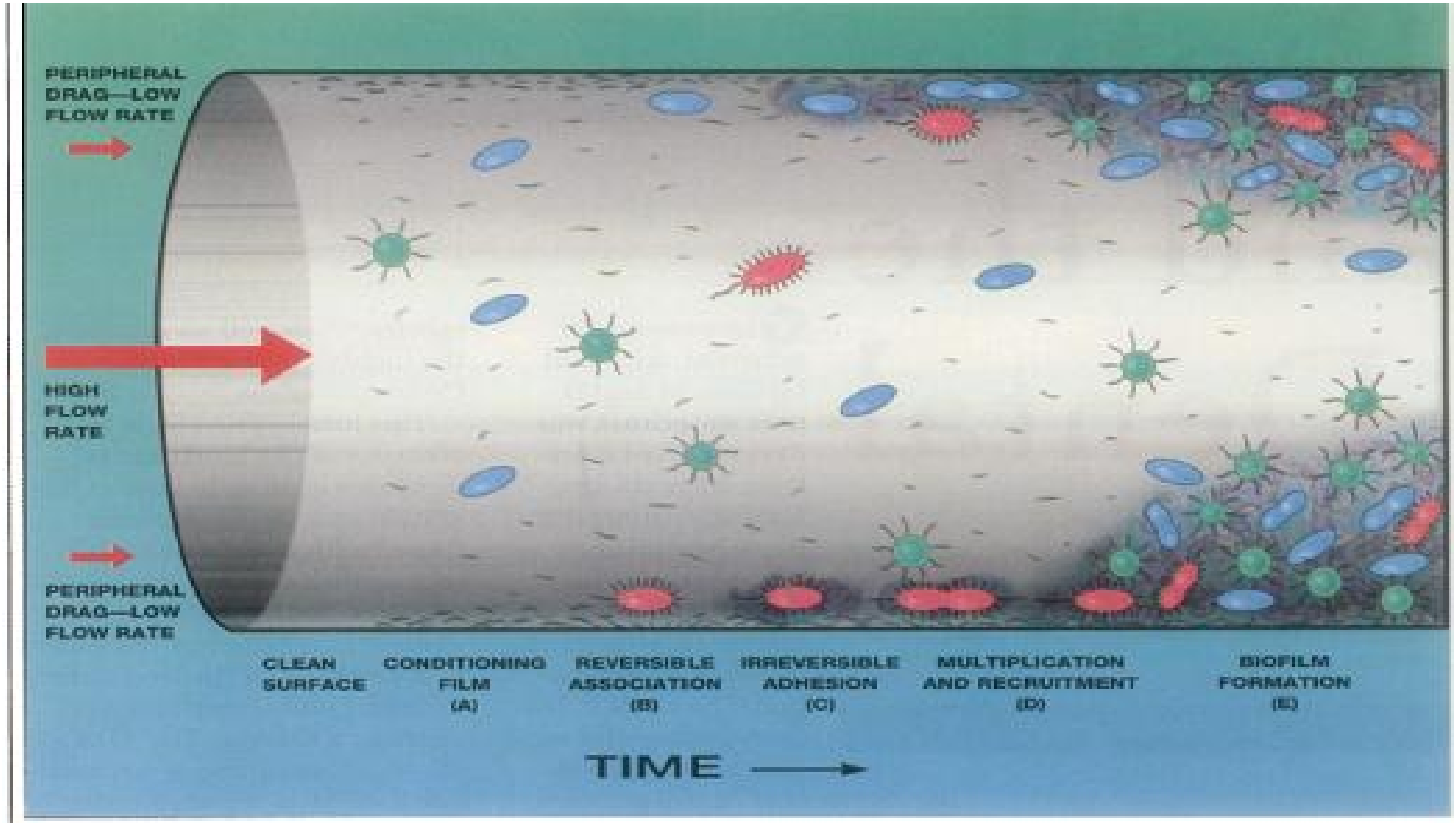
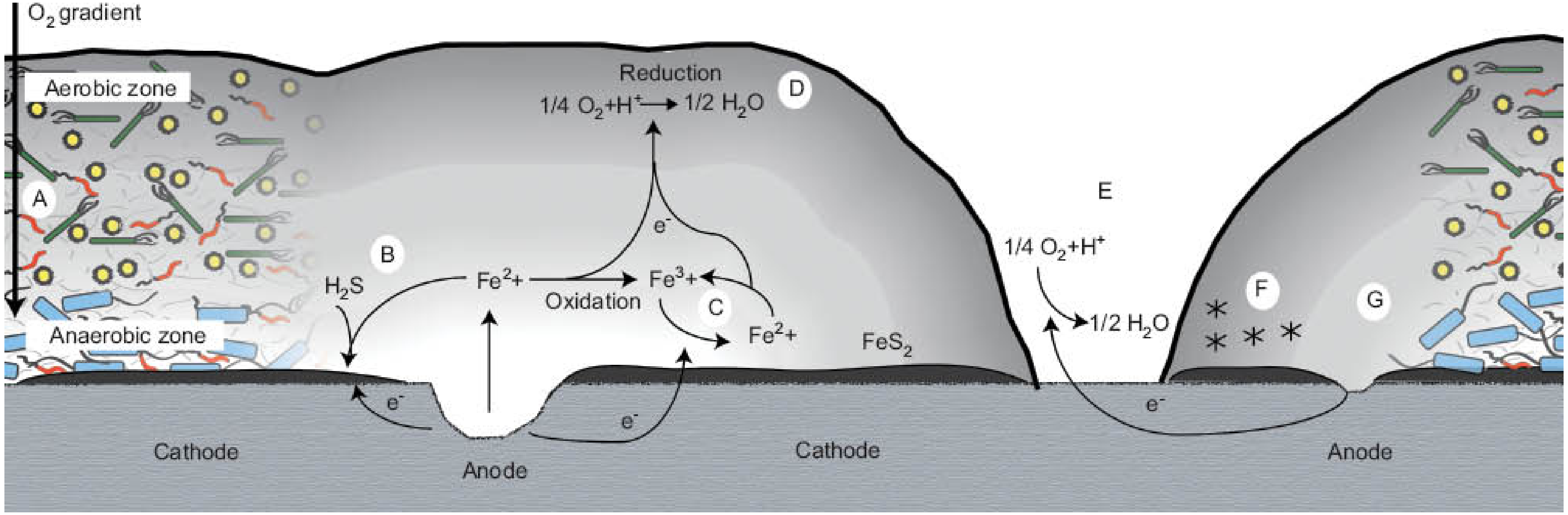


Figure 1. Biofilm formation in narrow-bore tubing. On adsorption of macromolecules from the aqueous phase and the formation of a conditioning film (A), bacteria may either associate reversibly with the surface (B) or adhere irreversibly (C). Subsequent division of adherent cells (D) and recruitment of planktonic cells from the bulk fluid phase results in biofilm formation (E).

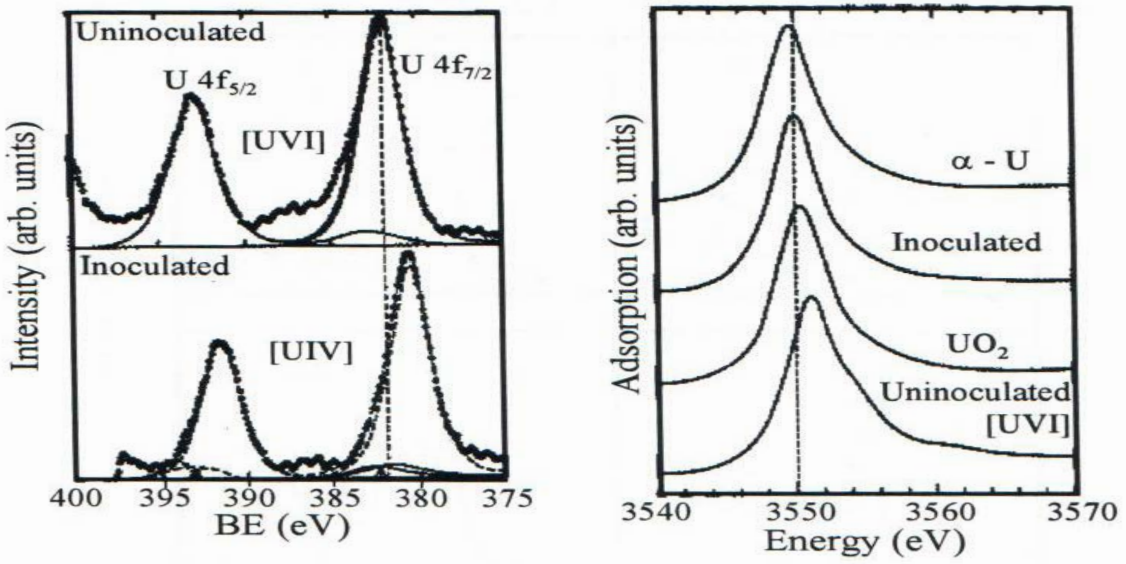
Source M. Ozcan et al J Oral Rehabilitation 30 (2003) 290

Corrosion of Substrate: Cathodic Activity at Sloughed Region of Biofilm Driving Under-film Anodic Dissolution (Differential Aeration Cell)



Source: De Gruyter Online

XPS *In Vacuo* and XANES (Synchrotron) Data



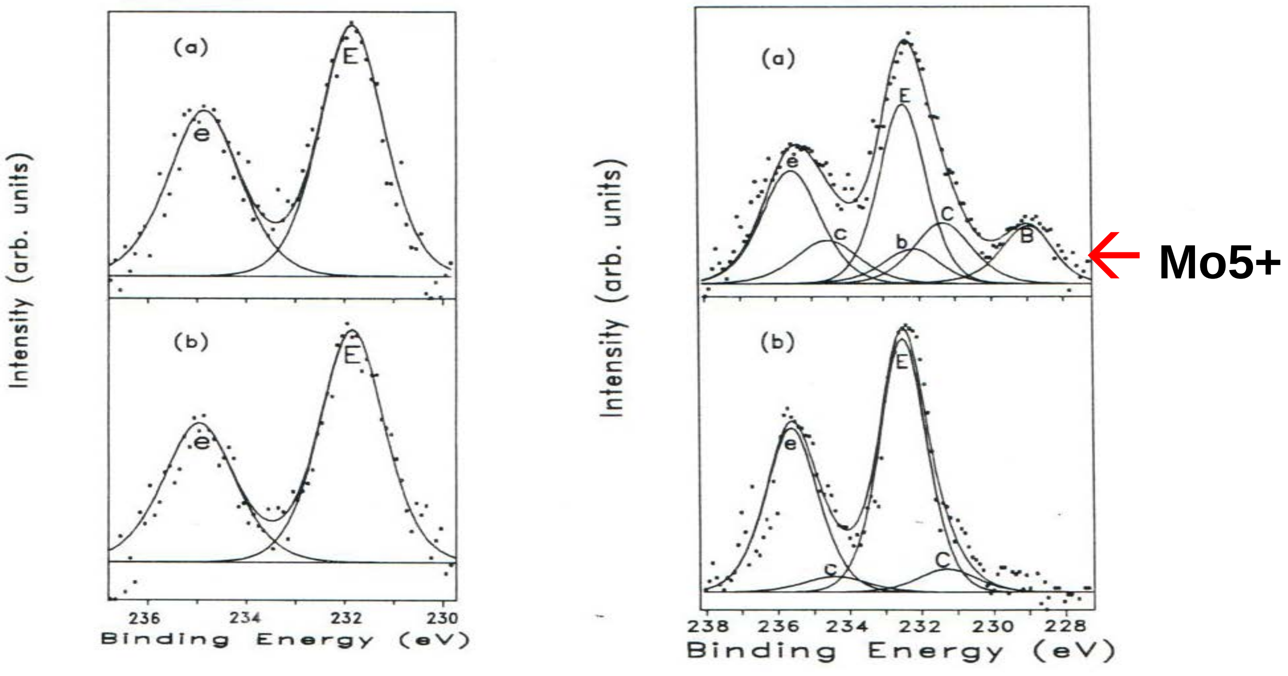
a) XPS Spectra **b)** XANES Spectra

Comparison of XPS spectra and XANES spectra for Uranium from uninoculated *clostridia sp* media and from inoculated *clostridia sp* media.[30]

- **Data show good agreement for microbe speciation studies**

Source A.J Francis et al Env. Sci. and Tech. Vol 28, 4, 636 (1994)

Biofilm Protein Component Attachment via Protein Sulphur to $MoO4^{2-}$ Adsorbed on 304 ss Surface

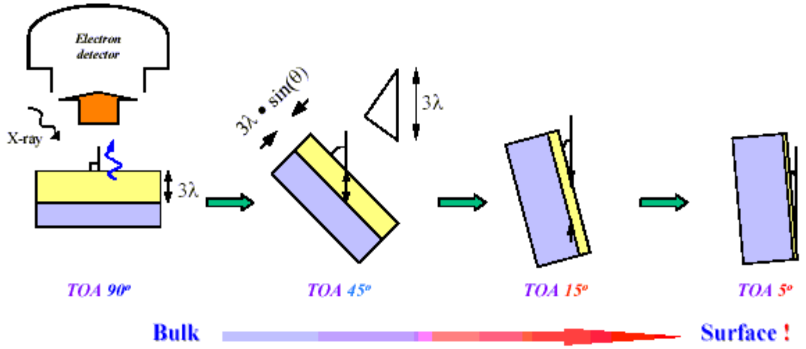


4a Before exposure to the exopolymer

4b After exposure to the exopolymer

B, b: MoO_2; C, c: Mo^{5+}; E, e: MoO_4^{2-}.

Figure 3. 4 The influence of the deaerated protein-containing exopolymer of *D. marina* on Mo3d on the surface of 304 SS following molybdate treatment. (a) take-off angle 20°; (b) take-off angle 50°.

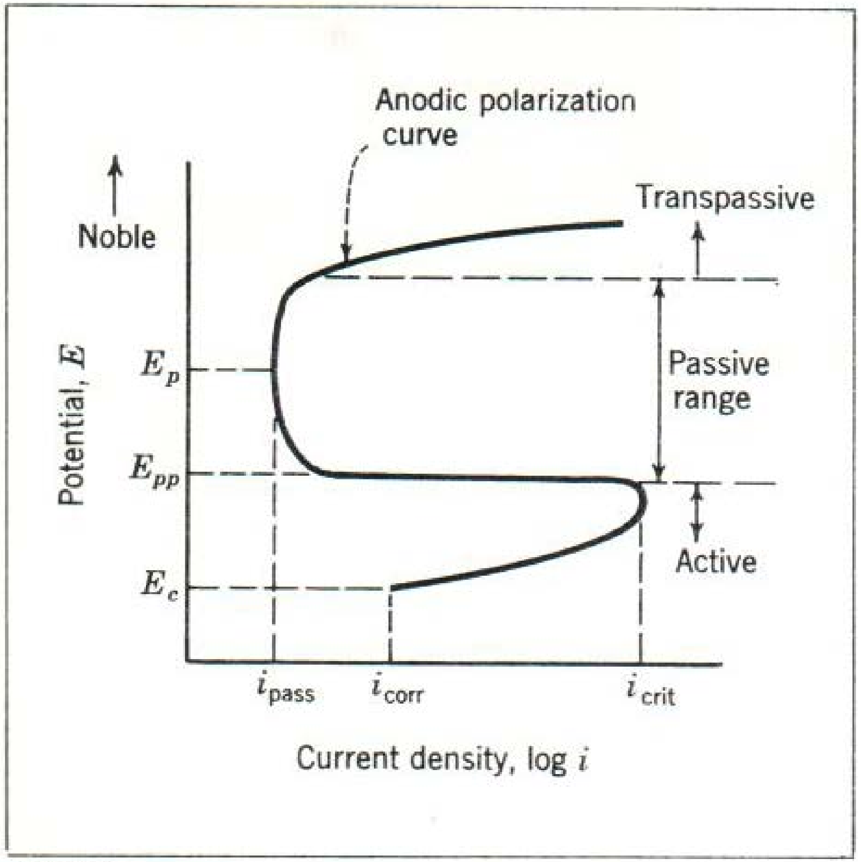


Reduction of Surface Molybdate to Mo5+ is possibly induced by the Sulphur containing residual proteins in the Exopolymer of Delaya (Pseudomonas) Marina

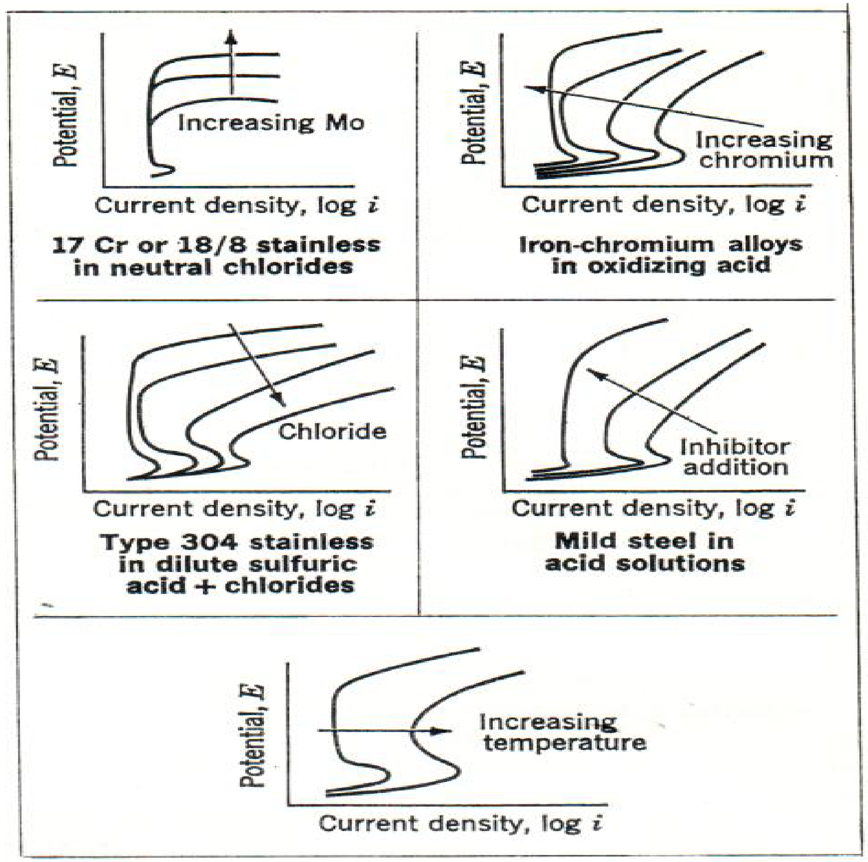
Molybdate is a powerful pitting inhibitor!

Source: G. Chen et. al. Corrosion Vol 52, No 12 (1996) p 891

Polarization analysis of Stainless Steel: Factors Affecting Corrosion characteristics in a Test Solution



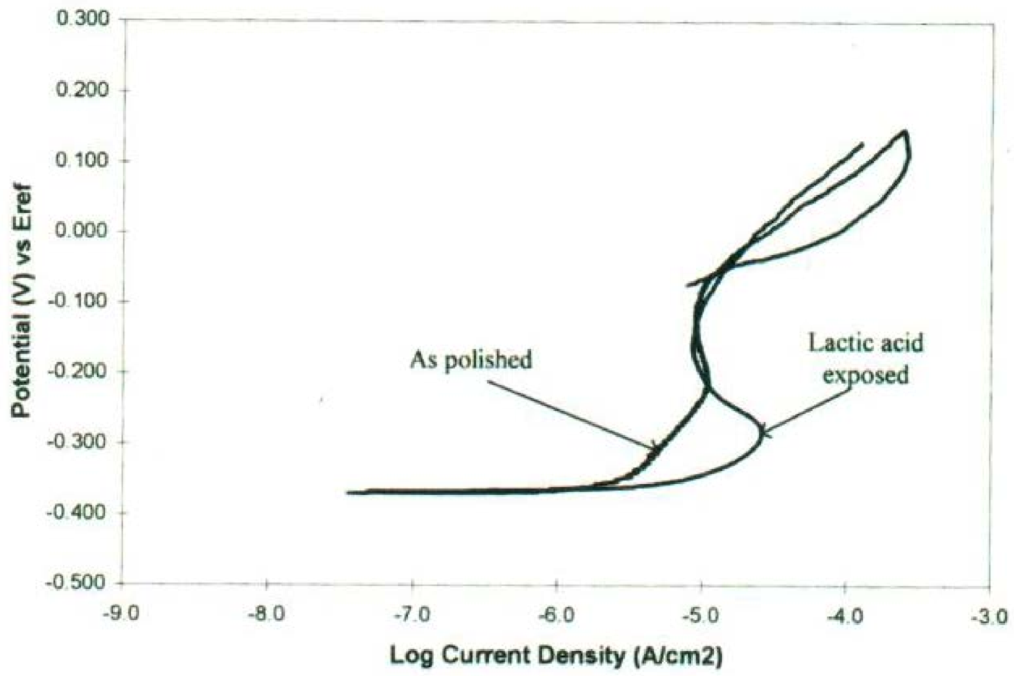
ANODIC-protection parameters from data—Fig. 6



MATERIALS and environment effect changes in the behavior of anodic polarization—Fig. 12

Example of Prior Exposure to Organic Acid Showing Anodic Activation

Potentiodynamic Polarization Plots of untreated Stainless Steel type 304 and Stainless Steel type 304 after exposure to lactic acid performed in 0.1 M HCl



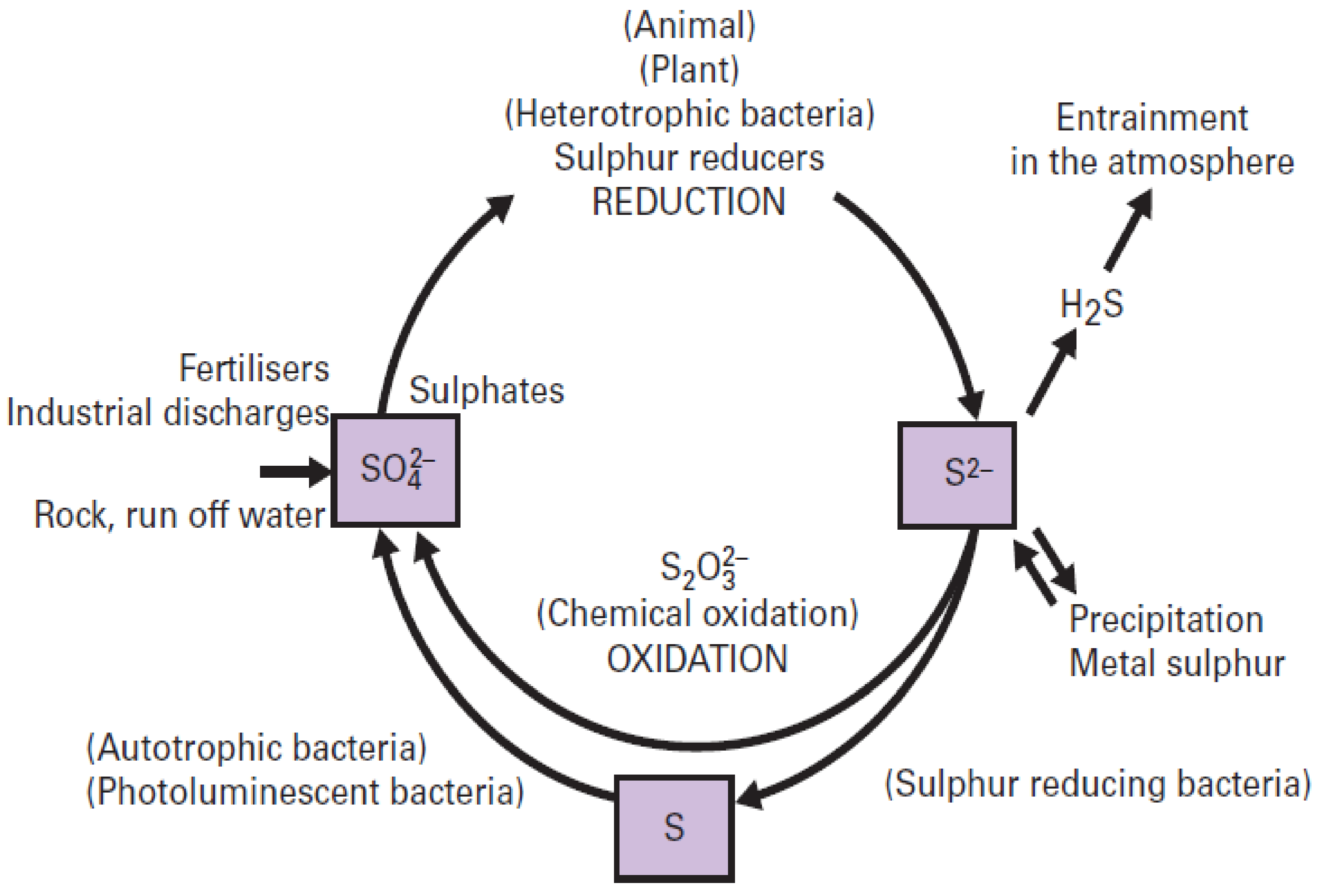
Eref is SCE, the scan rate was 1 mV/sec and there was no cathodic pretreatment of the samples.

Figure 28

Preexisting protective oxide film appears to be stripped by exposure to Lactic Acid by chelation. Similar results were found for citric and oxalic acids

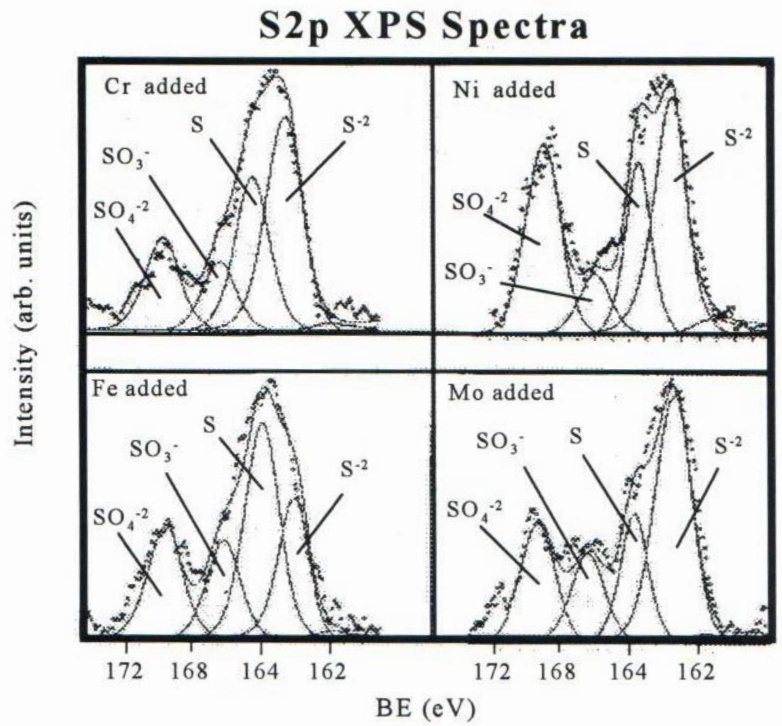
Source: Glenn French MS Thesis Stony Brook University (1998)

Mechanism for Generation of Multiple Sulphur Species



SRB Generate multiple Sulphur compounds which are corrosive. H2S most aggressive to stainless steels and degrades concrete.

XPS of SRB (Desulfovibrio sp.) Biomass Following Injection of Metal Additions in Solution (components of 317 ss)



S2p Spectra for biomass of Desulfovibrio sp. following addition of Fe^{+3}, Cr^{+3}, Ni^{+2} and Mo^{6+} additions.[31]

Corresponding Sulphides observed on 304 SS on exposure to SRB

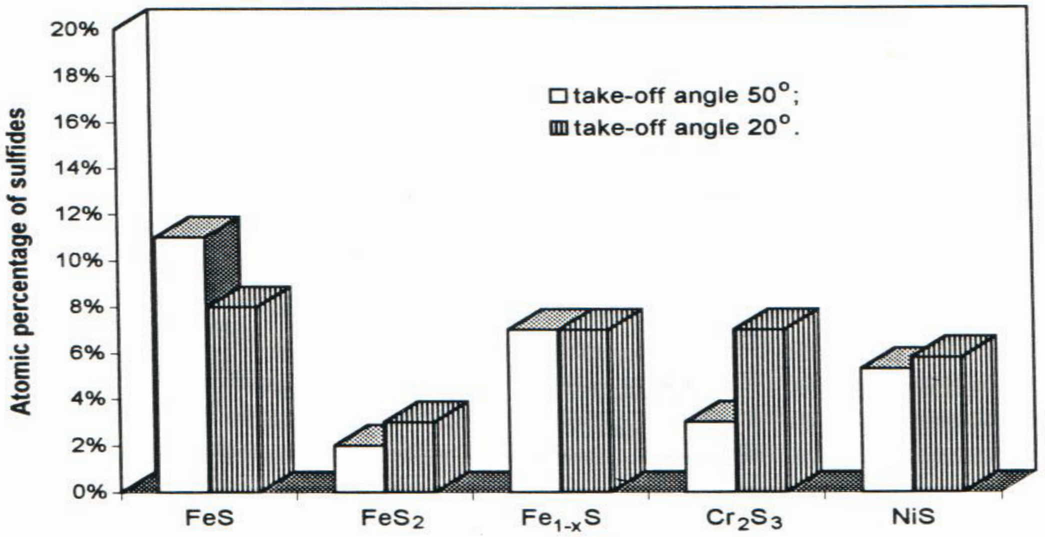


Figure 4. 6. Relative proportions of sulfides in the percentage of total metal components formed on the surfaces of 304 SS coupons during the exposure to SRB

Source: C.R.Clayton ECASIA 97 Eds I.Olefjord et al. p21 Wiley (1997)

Reactions of with Stainless Steel in Digester Environments

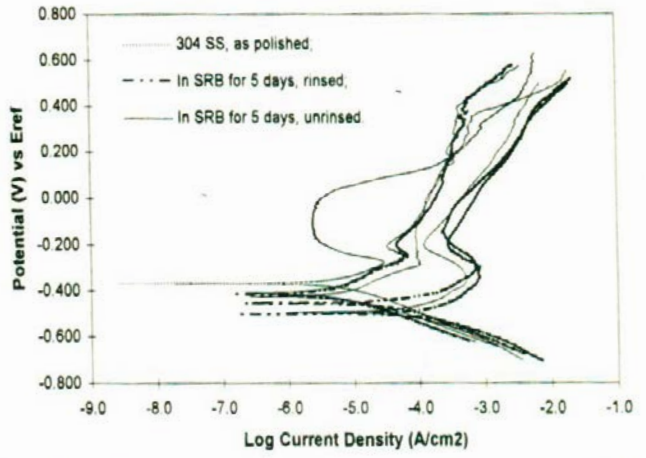


Figure 4. 1a. Potentiodynamic polarization diagrams of 304 SS in deaerated 0.1 M HCl following exposure to SRB for 5 days

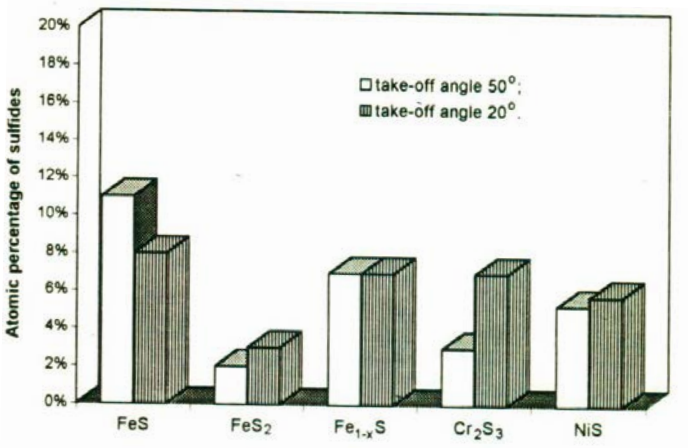


Figure 4. 6. Relative proportions of sulfides in the percentage of total metal components formed on the surfaces of 304 SS coupons during the exposure to SRB

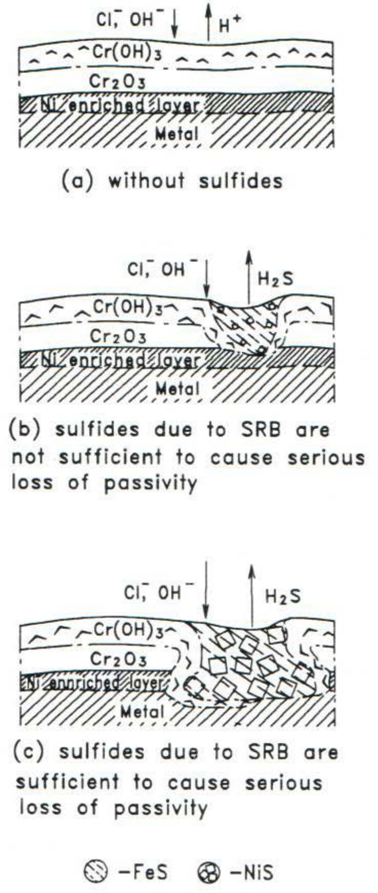


Figure 4. 20 An schematic illustration of nonuniform interaction on the surface of 304 SS resulting from prior exposure to SRB

SRB (Desulfovibrio sp.) Environment Reacts with 304ss to Inhibit Passive Formation in Test Electrolyte (deaerated 0.1 M HCl)

SRB Influence on 317 ss Corrosion Resistance

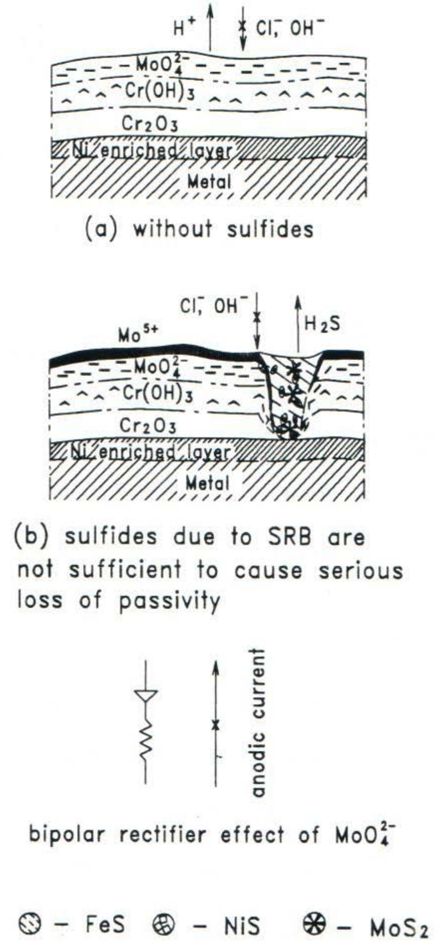


Figure 5. 15 An schematic illustration of the uniform interaction resulting from the exposure of 317L SS to SRB, and the protection effect of the biofilm.

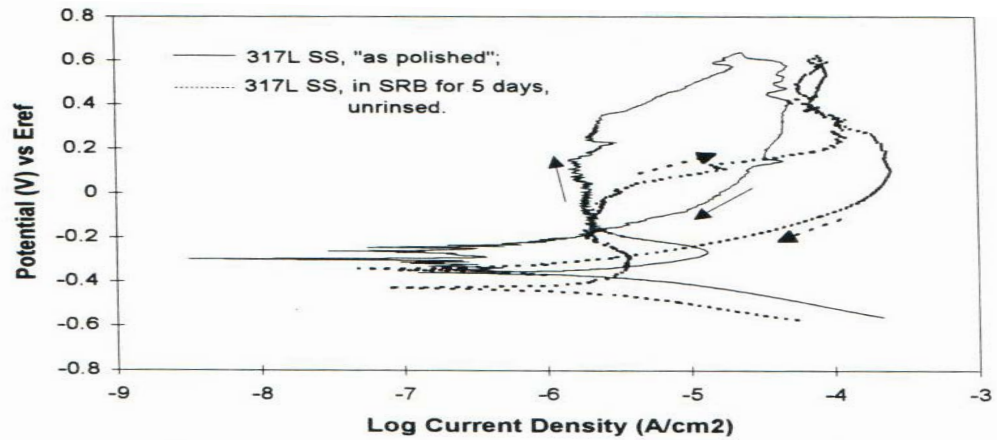


Figure 5. 1a Potentiodynamic polarization diagrams of 317L SS in deaerated 0.1 M HCl following exposure to SRB for 5 days, unrinsed prior to the test

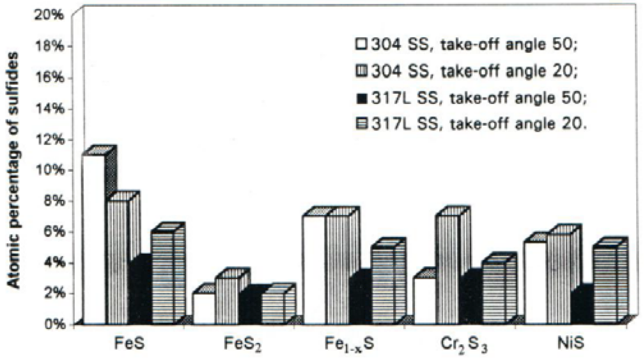
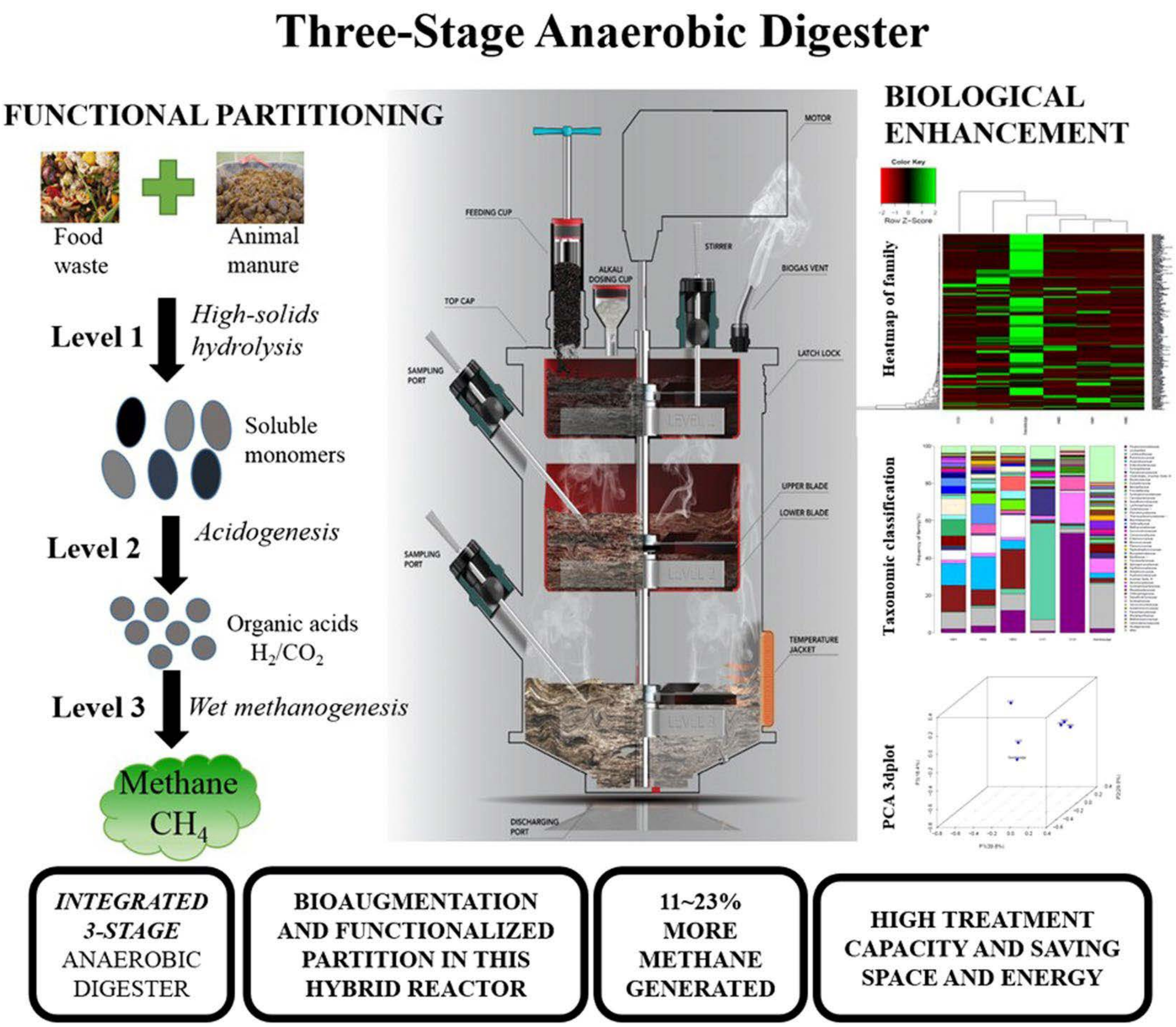


Figure 5. 6 Relative proportions of sulfides in the percentage of total metal components formed on the surfaces of 304 and 317L SS coupons during the exposure to SRB



Three-Stage Anaerobic Digester
FUNCTIONAL PARTITIONING
Food waste
Animal manure
Level 1
High-solids hydrolysis
Soluble monomers
Level 2
Acidogenesis
Organic acids
H_2/CO_2
Level 3
Wet methanogenesis
Methane
CH_4
MOTOR
FEEDING CUP
STIRRER
ALKALI DOSING CUP
BIOGAS VENT
TOP CAP
LATCH LOCK
SAMPLING PORT
UPPER BLADE
LOWER BLADE
SAMPLING PORT
TEMPERATURE JACKET
DISCHARGING PORT
BIOLOGICAL ENHANCEMENT
Color Key
Row Z-Score
Heatmap of family
Taxonomic classification
PCA 3dplot
INTEGRATED 3-STAGE ANAEROBIC DIGESTER
BIOAUGMENTATION AND FUNCTIONALIZED PARTITION IN THIS HYBRID REACTOR
11~23% MORE METHANE GENERATED
HIGH TREATMENT CAPACITY AND SAVING SPACE AND ENERGY

Concluding Remarks

- Fundamental understanding of organic corrosion mechanisms can improve materials selection and corrosion prevention strategies for digester equipment.
- The understanding can lead to better corrosion resistant design of digesters.
- Collaboration between Materials Scientists and Chemical Engineers will be crucial for a successful outcome.

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