

Corrosion protection of steels by analogues of extracellular polymeric substances (EPS) from renewable resources

D. Holuscha, C. Thyssen[#], A. Kuklinski[#], W. Sand[#], W. Fürbeth

e-mail: holuscha@dechema.de

Funded by: BMWi via AiF

Period: 01.02.2011- 31.12.2013

AIF ALLIANZ
INDUSTRIE
FORSCHUNG

Gefördert durch:

Bundesministerium
für Wirtschaft
und Technologie

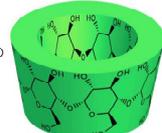
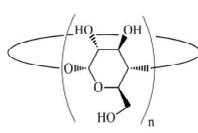
Background

Microbial biofilms and bacterial extracellular polymeric substances (EPS) can induce and speed up corrosion (microbially influenced corrosion, MIC) or even inhibit corrosion processes (microbially influenced corrosion inhibition, MICI) /1, 2, 3, 4/. Both effects are influenced by interactions of the substratum and particularly of the EPS. The chemical composition of EPS decides about the destructive or protective impact and the respective extent/5/. Comparable to classical interfacial corrosion inhibitors, specific functional groups of the EPS are crucial for EPS-surface interactions and thus facilitation of cell adhesion /6/.

Motivation and Aims

Use of EPS or EPS- analogues

- Composition of EPS is complex and their extraction is labor-intensive
- Application of pure substances rather than complex EPS mixtures

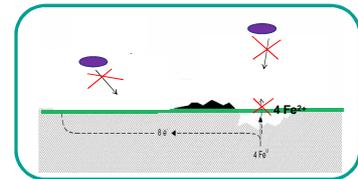


n=6 α -cyclodextrin
n=7 β -cyclodextrin
n=8 γ -cyclodextrin

Figure 1: Structure and space filling model of Cyclodextrins

Aim of this project is to use EPS-analogue substances for reducing MIC and abiotic corrosion as well as biofilm formation on metals by blocking electrochemical "active sites".

- Synthesizable
- Directed modifiable
 - ✓ Functional groups
 - ✓ Fluorescence -labelled
 - ✓ Ring size (α -, β -, γ -CD)
- non bio-degradable /7/



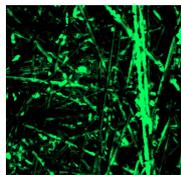
Experimental and Results

CD- Adsorbate preparation

Metal samples are covered with Cyclodextrins (CD) by dip-coating in a suspension of 10 mg * ml⁻¹ CD and 4.2 μ l * ml⁻¹ Glutarialdehyde 25% (crosslinker) for 8 hours under sterile, anaerobic and acidic conditions at 45 C.

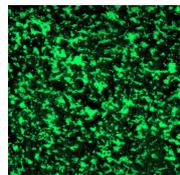
CD coatings and dissolution stability

Figure 2: FM images of 1.4301 covered by a mixture of CD C and FITC- β -CD (9.9 mg * ml⁻¹ and 0.1 mg * ml⁻¹ respectively) before (left) and after 7 days (right) of exposure in phosphate buffered solution (PBS).



polymerized
CD-coatings
(on 1.4301)

7d PBS



For visualizing the CD adsorbate the samples are stained with a fluorescence active β -CD. The high intensity of the green signal in the fluorescence-microscopical (FM) images confirms the presence of a CD adsorbate.

CD influence on pitting corrosion under abiotic conditions

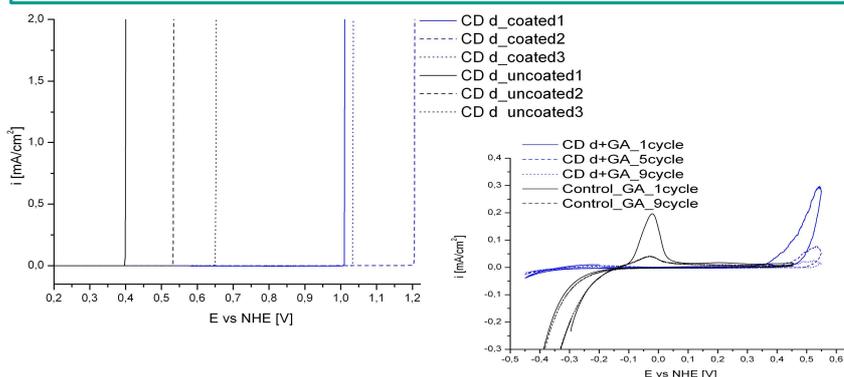


Figure 5: (A) Current density-potential curves for CD (un)coated alloyed steel (1.4301) after exposition in 1 M NaCl solution for 1 hour. Measured under aerobic conditions. Anodic sweep direction, scan rate: 0.03 mV*s⁻¹. (B) Cyclic voltammograms for CD (un)coated alloyed steel after exposition in coating solution for 8 hours. Measured under aerobic conditions. Start of polarisation at: E_{ocp} -50 mV. Anodic sweep direction, scan rate: 10 mV*s⁻¹

Corrosion tests with sulfate reducing bacteria

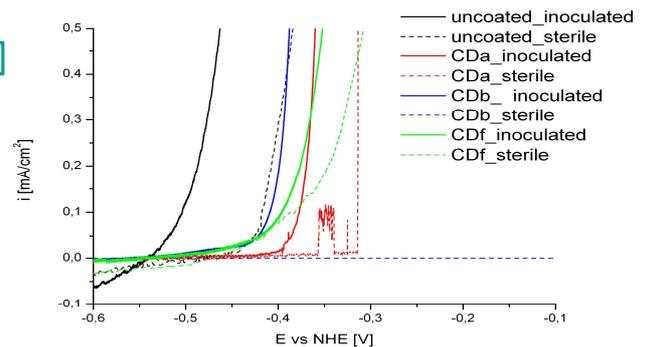


Figure 3: Current density-potential curves for St-37 after exposition in Postgate C for 3 days: SRB (*D.vulgaris*) inoculated (full lines); sterile Postgate C (dotted lines). Anodic sweep direction, scan rate 0.5 mV/s.

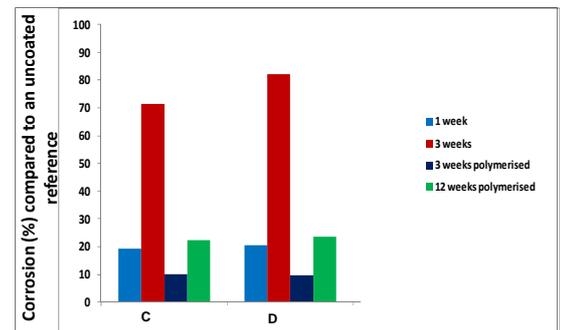


Figure 4: Weight loss of St37 coated with CD C or CD D after exposition time in SRB inoculated Postgate C (v. Rege)

Summary

- ✓ FM images show improved dissolution stability of CD coatings after polymerization
- ✓ CD impact on electrochemical corrosion reaction
 - CD layers on alloyed steel have an influence on the pitting corrosion potential and on the passivation behaviour
 - shift of "activation peak" in anodic direction for unalloyed steel after 3d exposition in sterile / inoculated Postgate C medium
- ✓ Presence of CD's induces a slightly wider passive region
- ✓ Reduction of weight loss up to 80% (3 months) for polymerised CD's

[#] Biofilm Centre, University of Duisburg-Essen

References:

- /1/ I. B. Beech, J. A. Sunner: Biocorrosion - Towards understanding interactions between biofilms and metals. Curr. Op. Biotech. 15: 181-186, (2004)
- /2/ I. B. Beech, J. A. Sunner, K. Hiraoka: Microbe-surface interactions in biofouling and biocorrosion processes. Int. Microbiol 8 (3): 157-168, (2005)
- /3/ H. A. Videla, L. K. Herrera: Understanding microbial inhibition of corrosion. A comprehensive overview. Int. Biodegrad. Biodegrad. 43(7): 896-900, (2009)
- /4/ R. Zuo: Biofilms - strategies for metal corrosion inhibition employing microorganisms. Appl. Microbiol Biotechnol 76: 1245-1253, (2007)
- /5/ G. M. Ferrari, H. J. A. Breur: Biopolymers for the corrosion protection of steel. Proc. ICC, Peking, PRC, (2005)
- /6/ R. Stadler, A. Kuklinski, W. Fürbeth, W. Sand: Schützende Biofilme - Korrosionsschutz durch Bakterien. Biospektrum 17: 2 - 5, (2011)
- /7/ Fenyvesi, E., et al. Biodegradation of cyclodextrins in soil. Chemosphere. 60, 2005, S. 1001-1008.