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Helmholtz-Zentrum hereon

Hydro

speira

Muehlhan

Cathodic protection of aluminium alloys in seawater

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Background and objectives

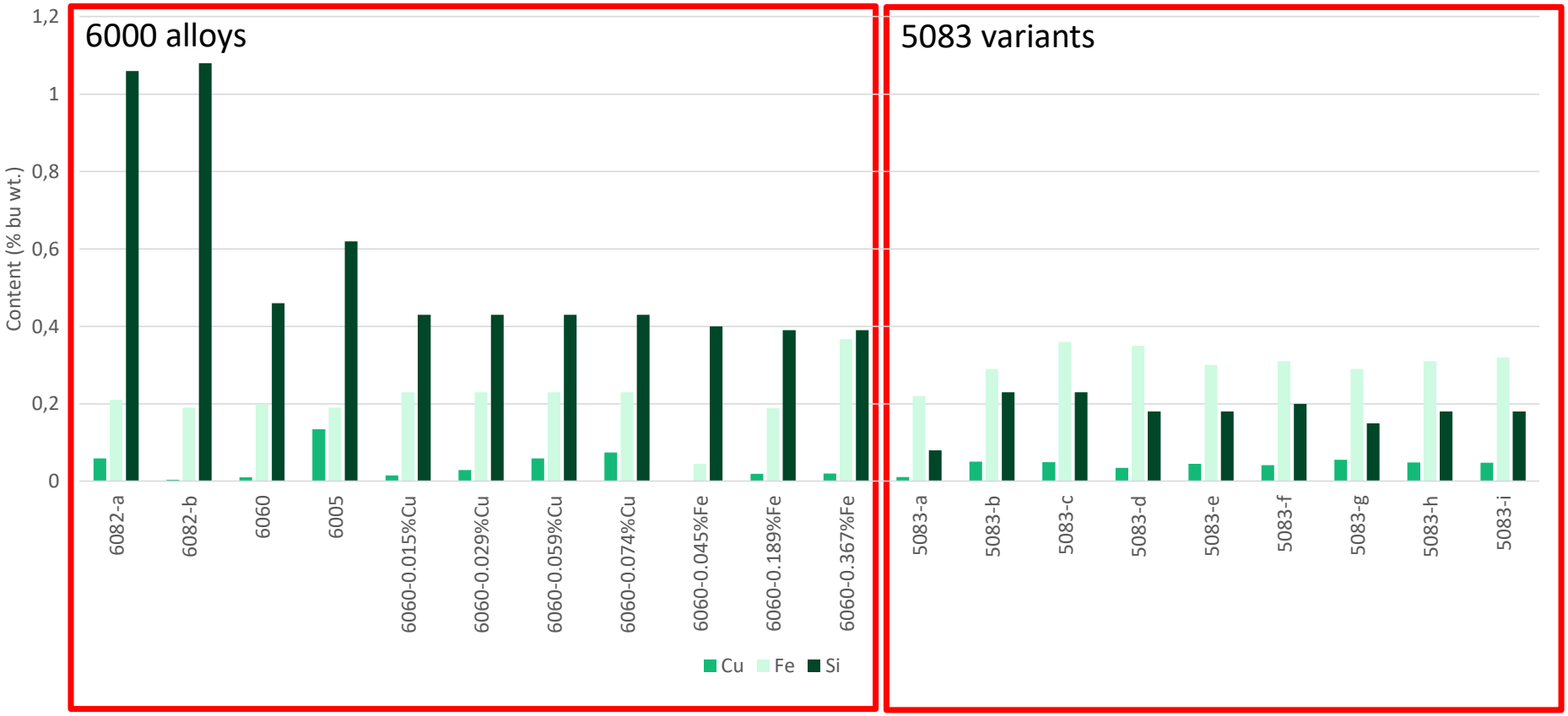
Background:

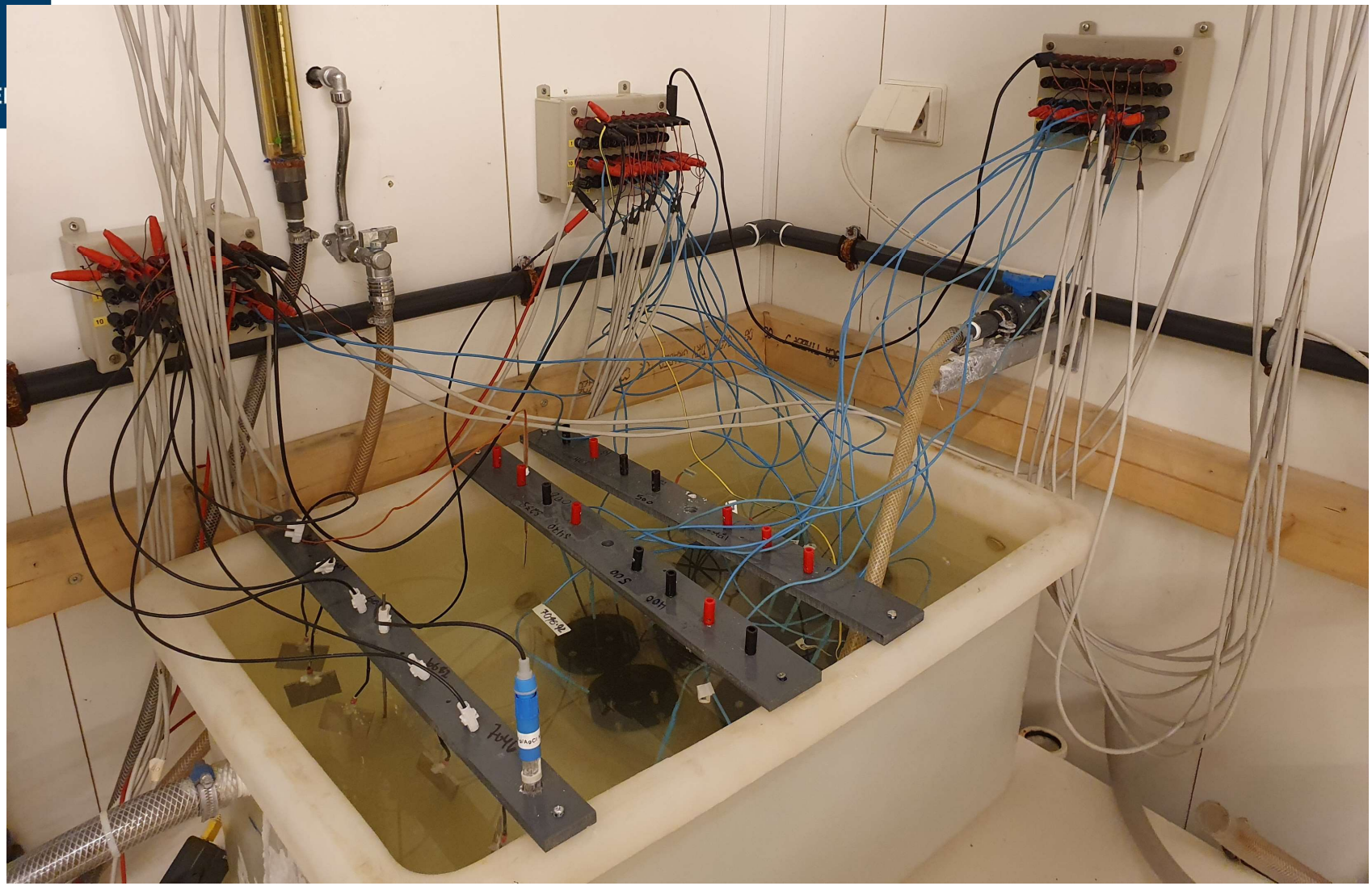
- DNV RP-B-401 recommends to use 10 mA/m² for designing CP of aluminium
- Based on experiences with thermally sprayed aluminium
- Testing has shown that cathodic current density of aluminium wrought alloys depends on alloy composition

Objectives:

- Investigate cathodic current density on various aluminium alloys
- Explain the effect of alloying elements on the cathodic current density

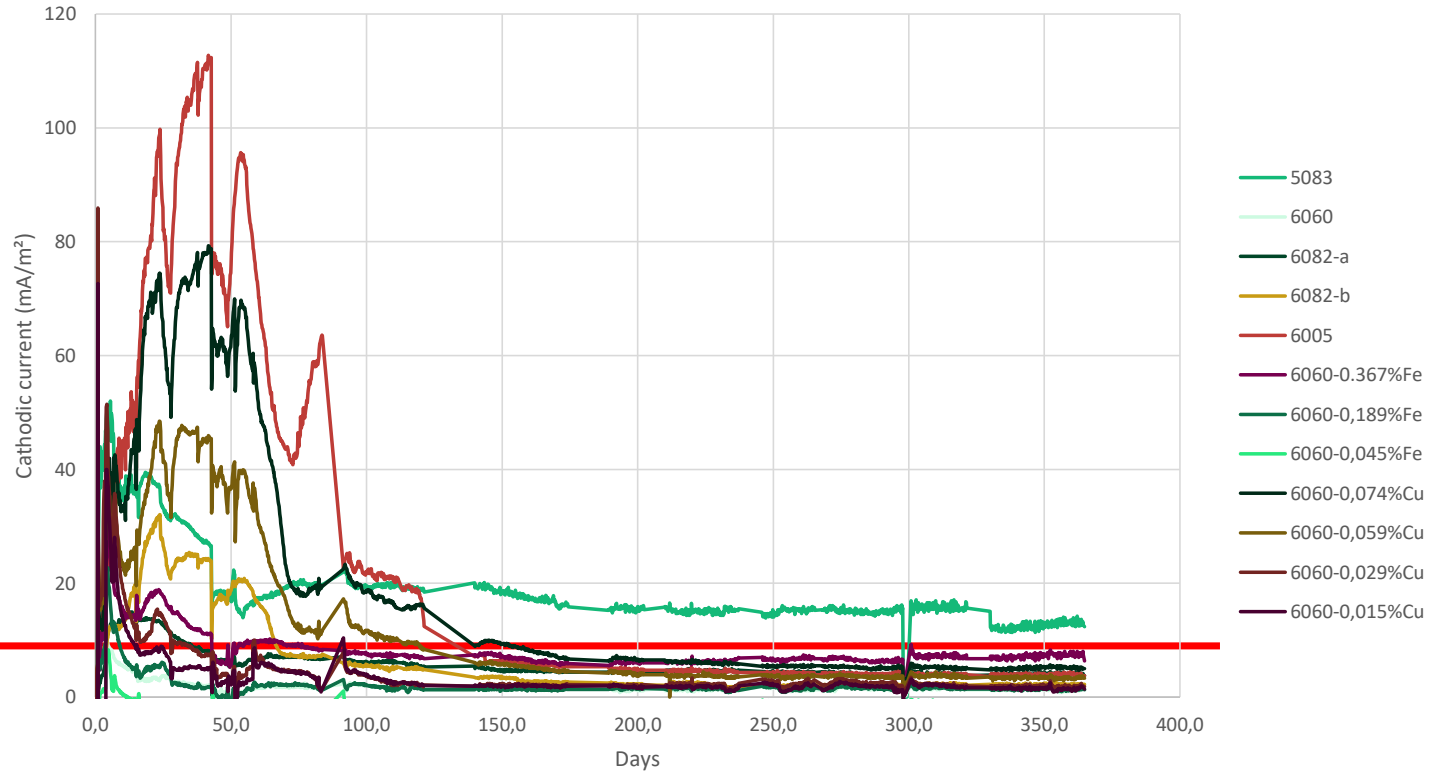
Alloys in the test





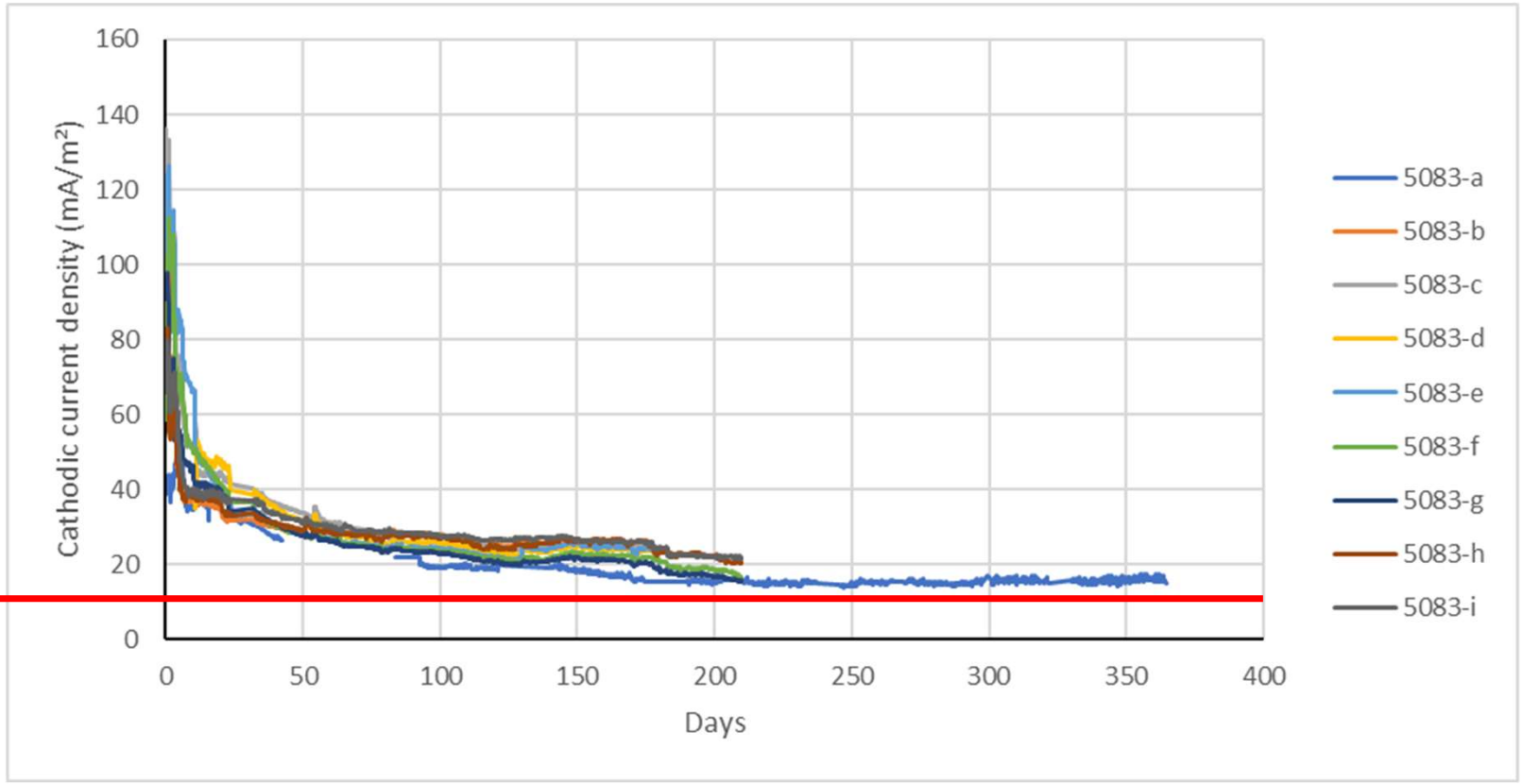
Current density for CP of 6000 alloys in seawater

DNV RP-B401

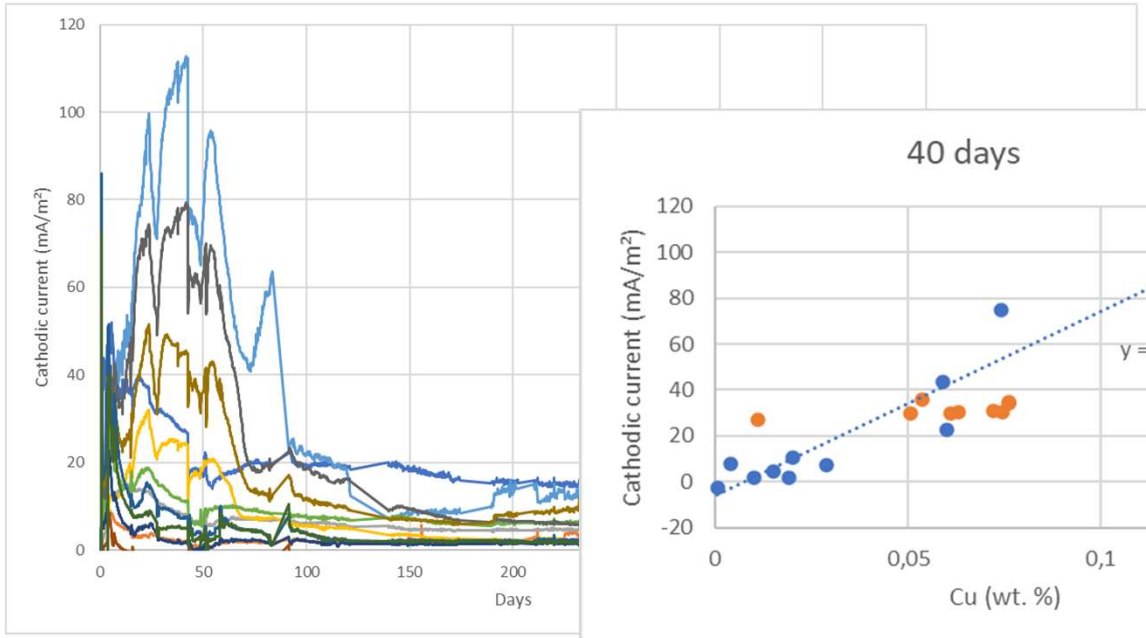


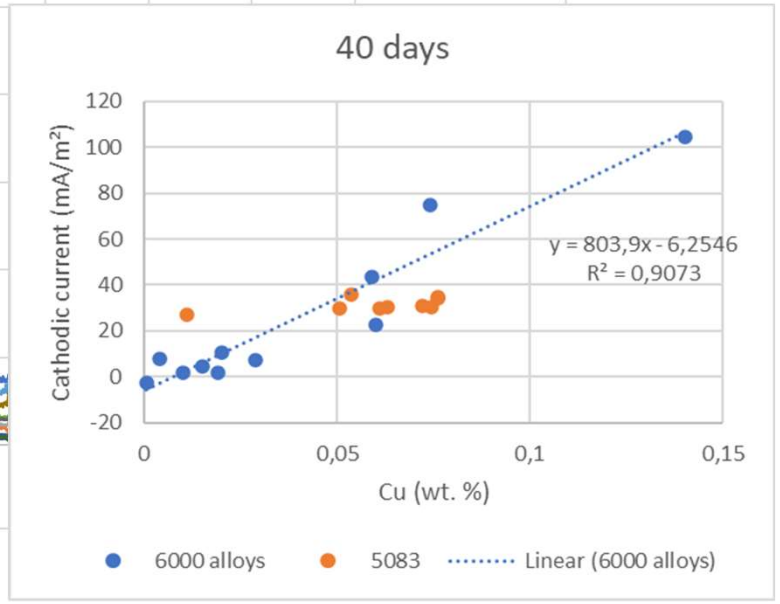
Current density for CP of 5083 alloys in seawater

DNV RP-B401

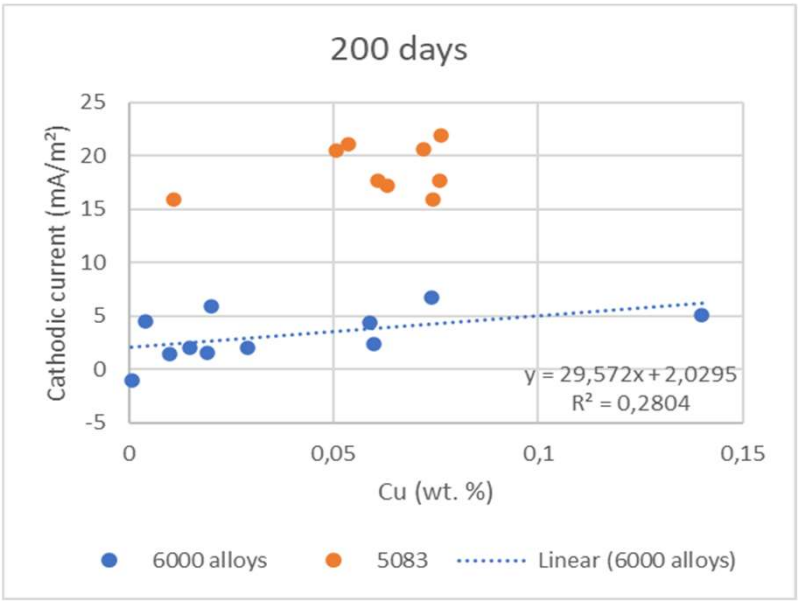


Effect of Cu on the cathodic current



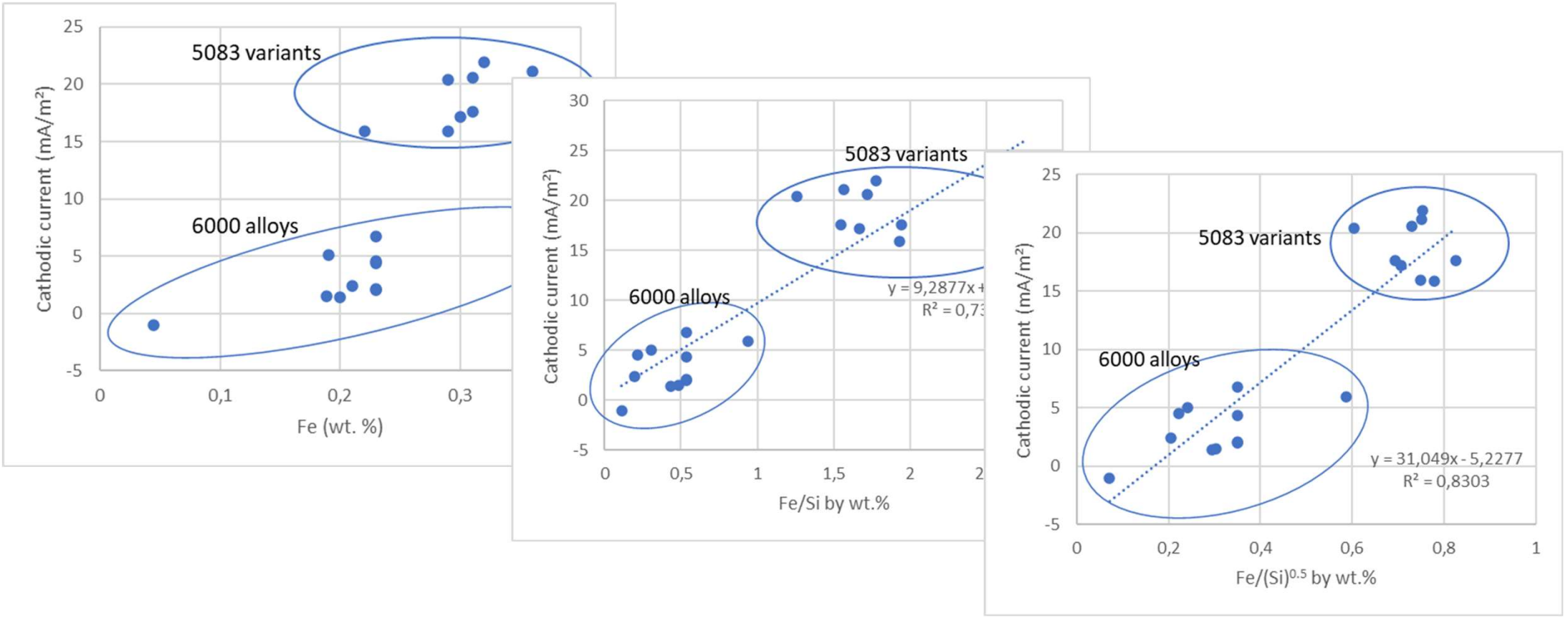


Elevated cathodic current for 6000 alloy samples with > 0,05 % Cu



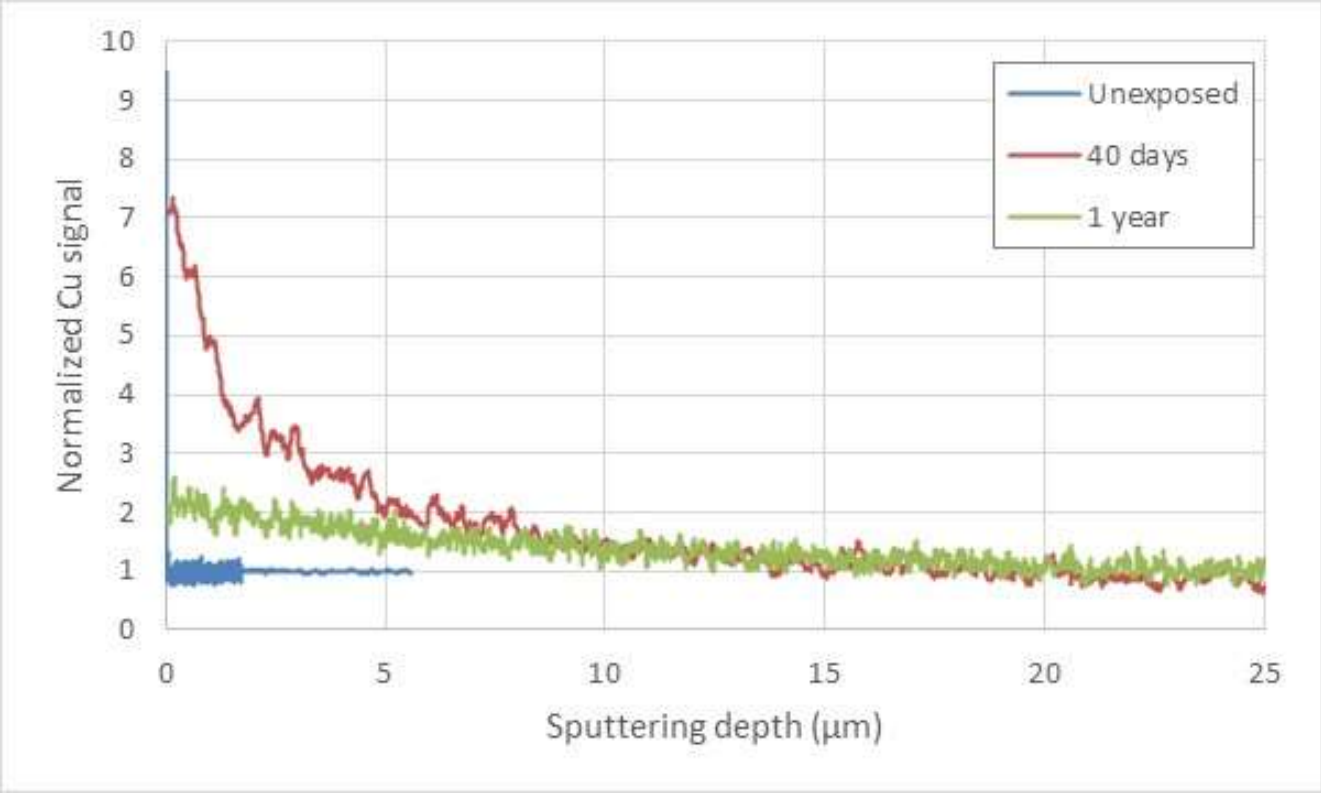
Effect mainly disappeared after 200 days

Effect of Fe and Si on cathodic current

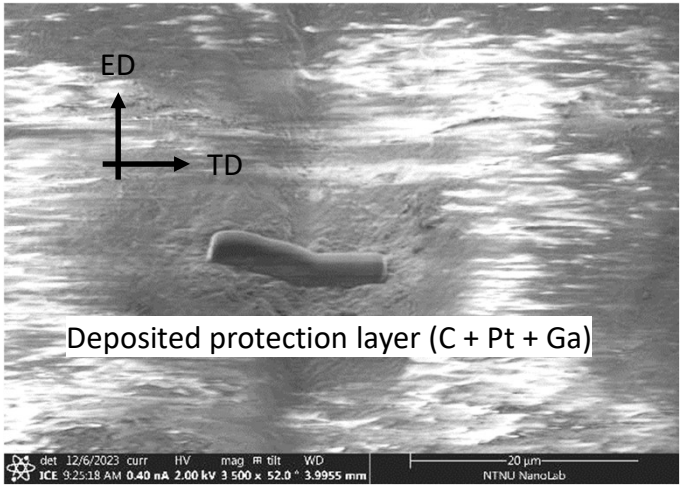


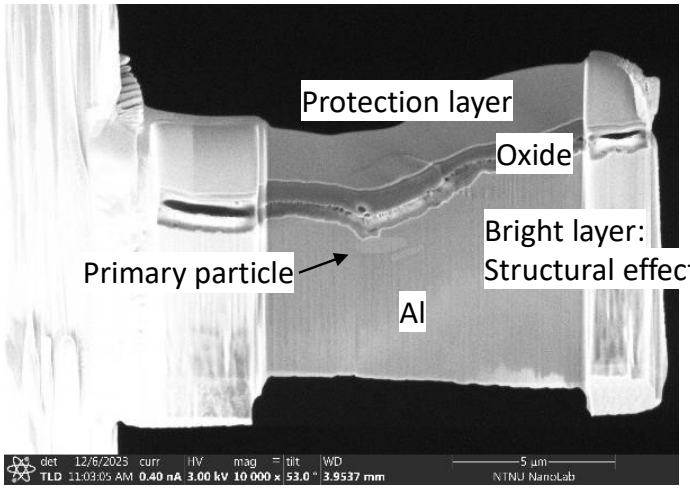
Increased cathodic current due to Cu enrichment in the surface

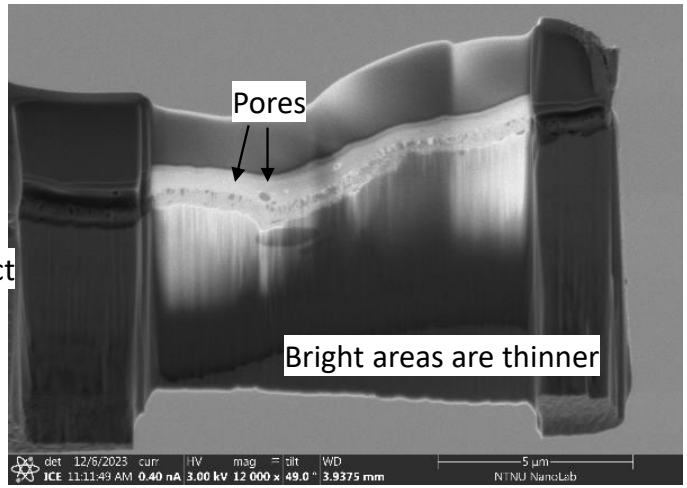
GDOES of 6005 alloy with 0.14 % Cu



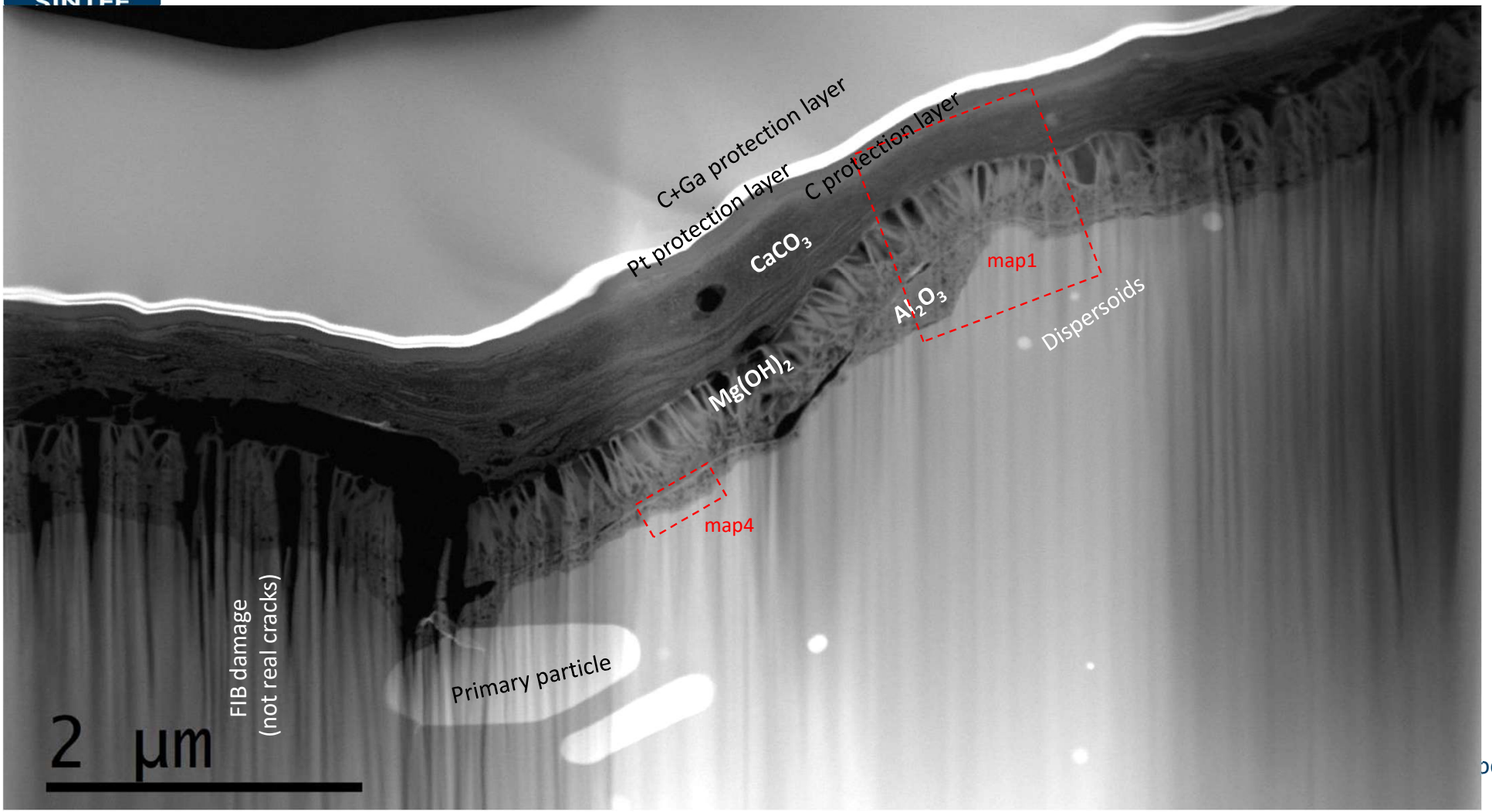
Sample preparation



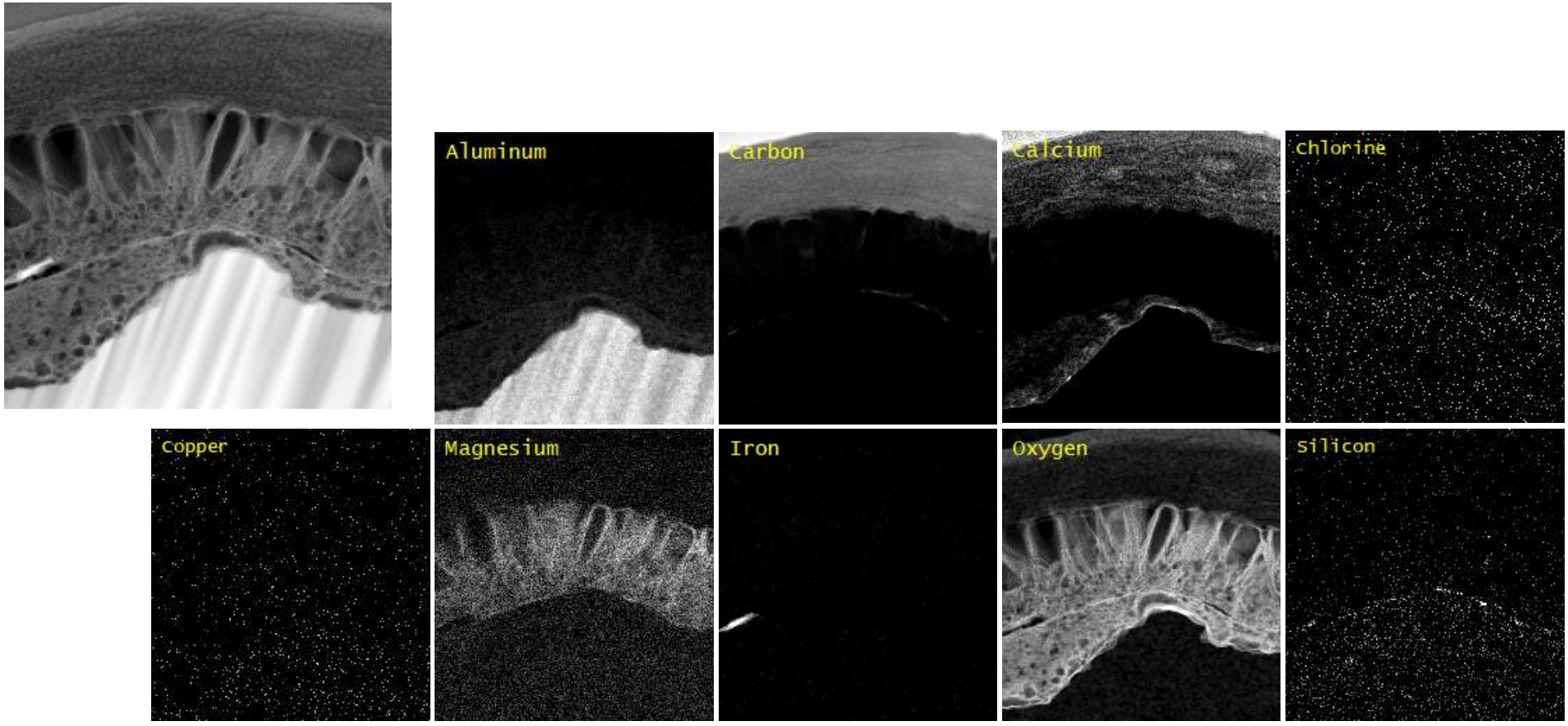




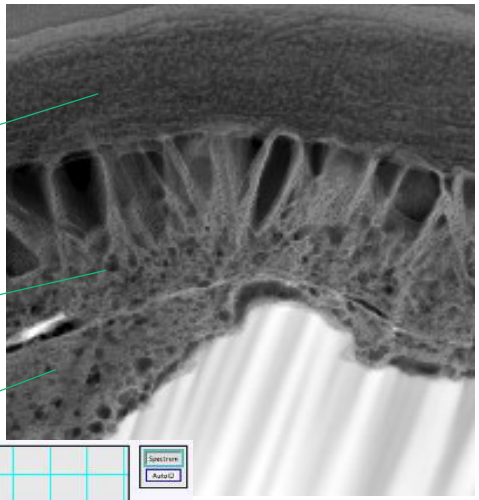
Overview STEM image



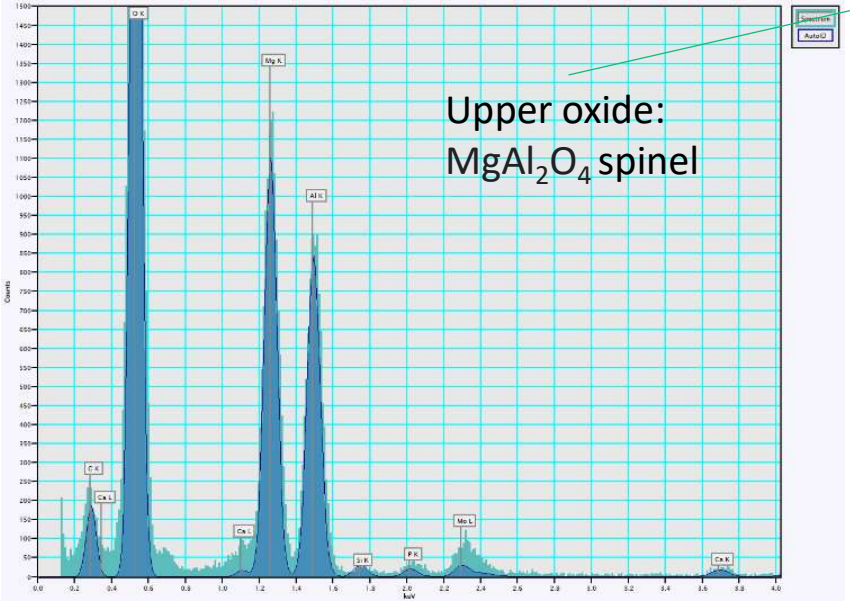
Chemical map 1



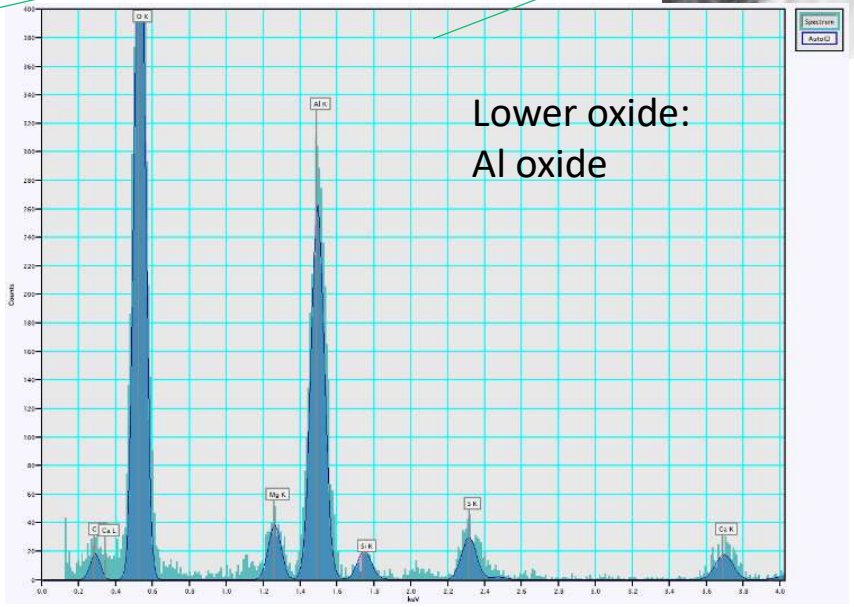
Chemical map 1 – EDS spectra



$CaCO_3$

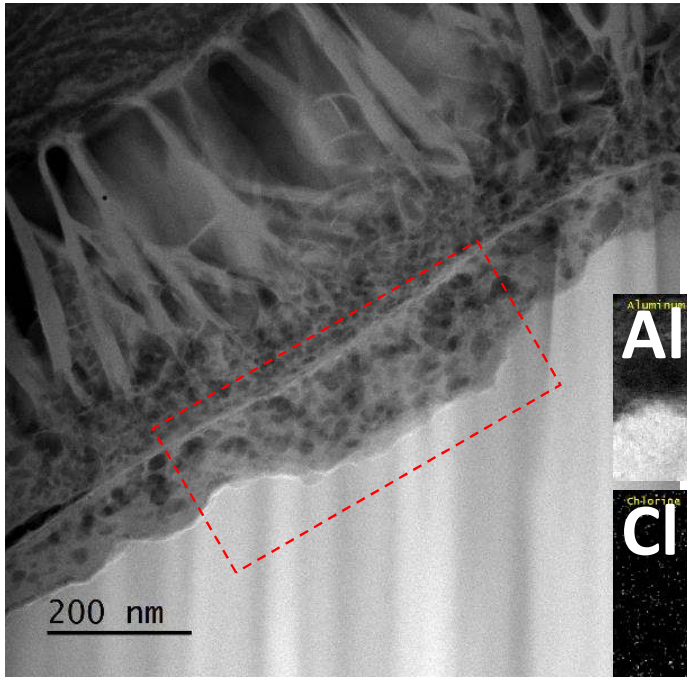


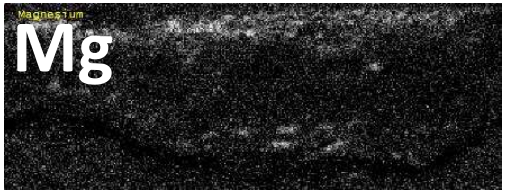
Upper oxide:
$MgAl_2O_4$ spinel

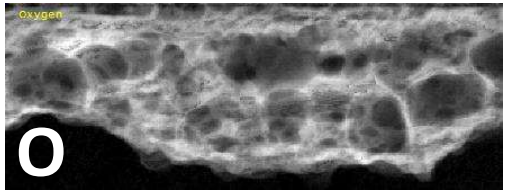


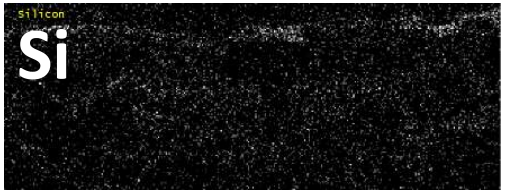
Lower oxide:
Al oxide

Chemical map 4

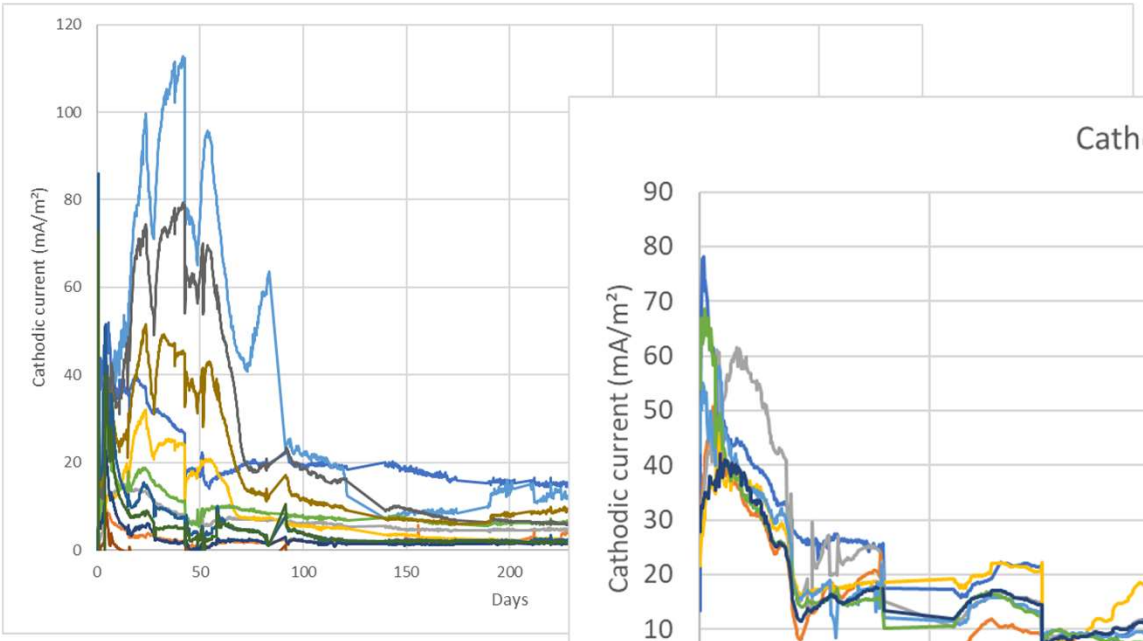


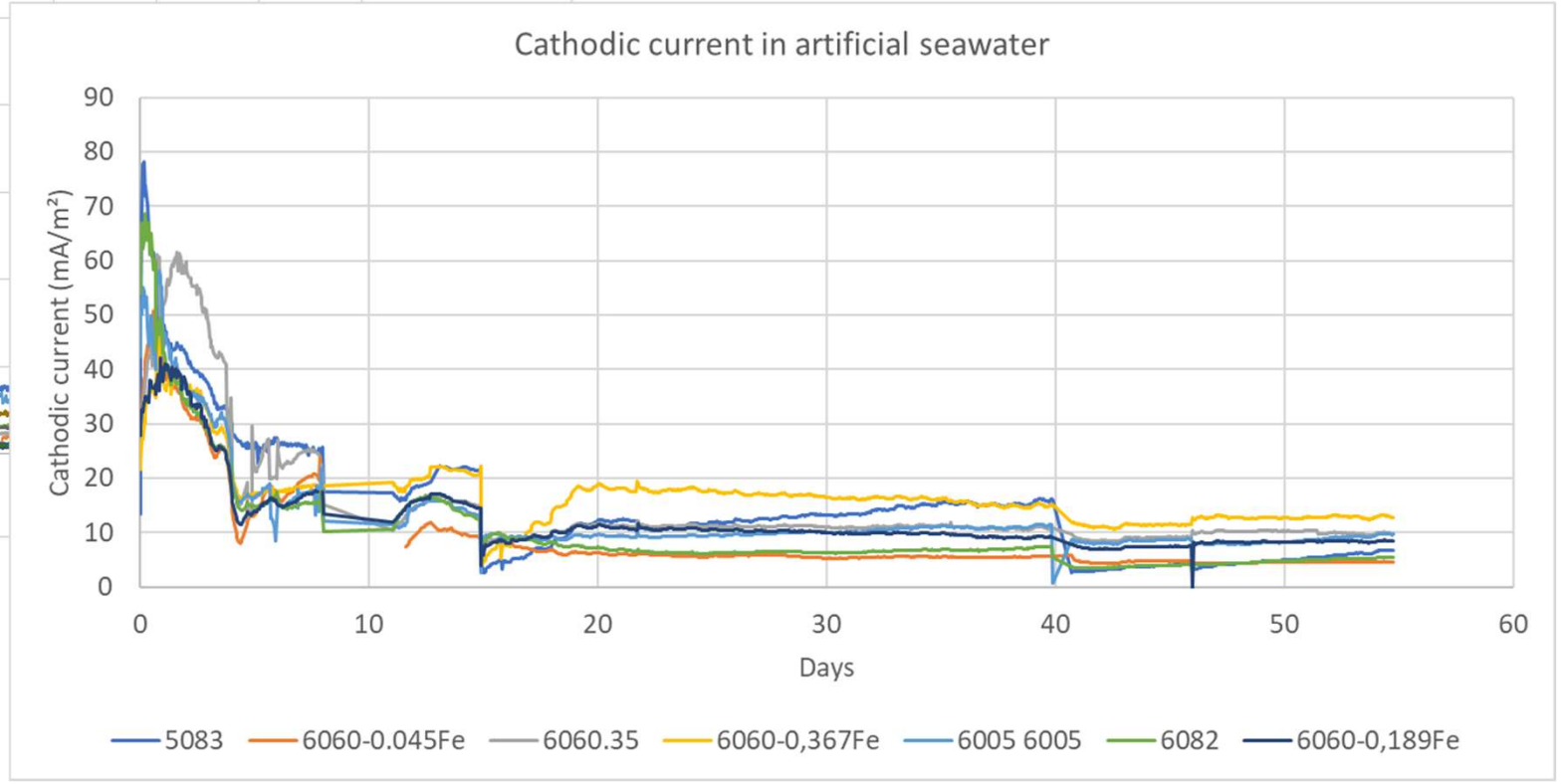




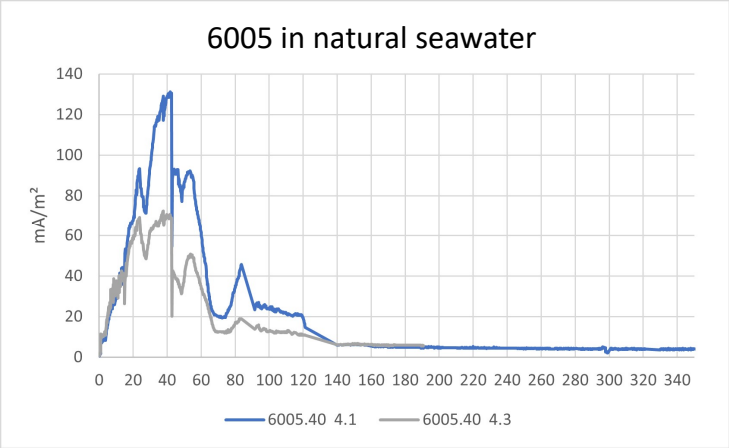


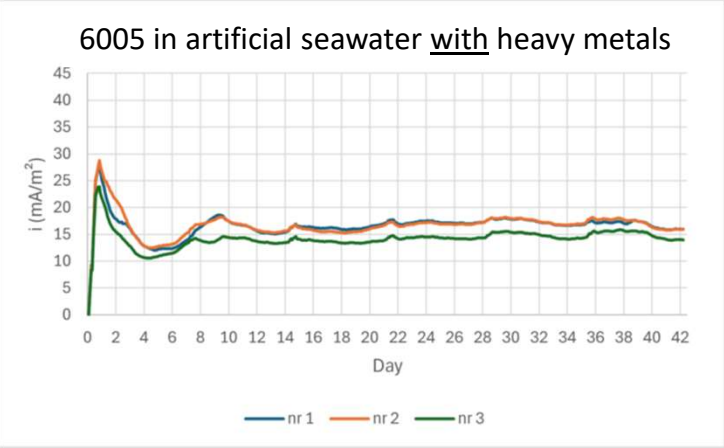
Cathodic current in artificial seawater

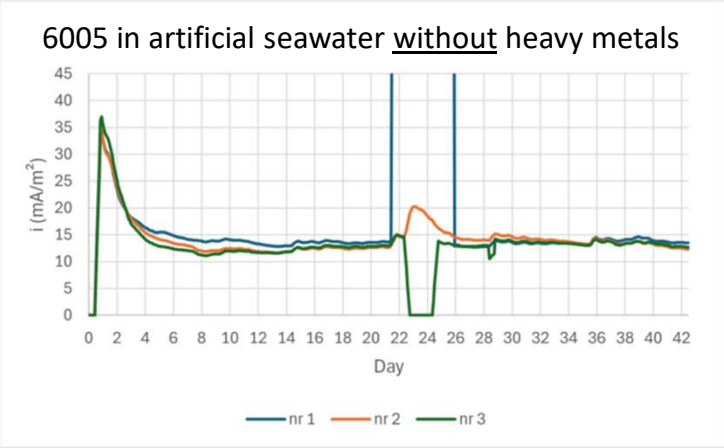




Mechanism for Cu enrichment



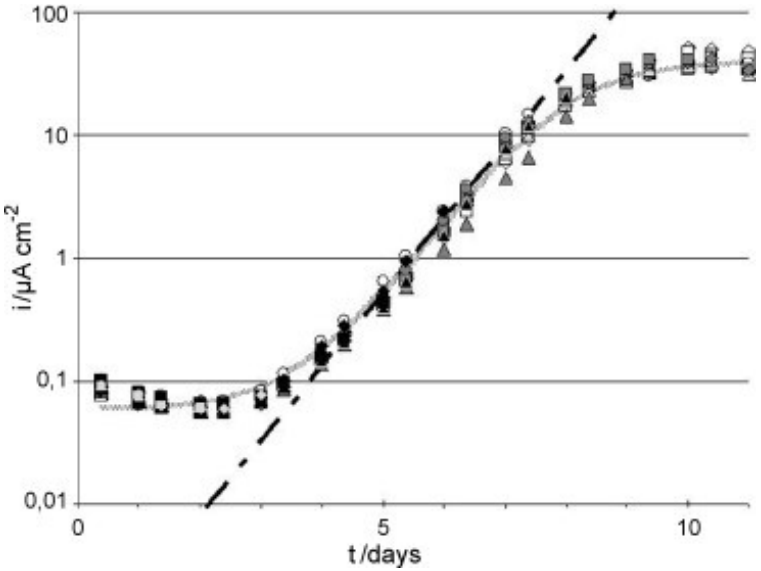




- The cathodic current peak after about 40 days does not appear in artificial seawater
- Cu^{2+} concentration in the seawater does not affect the current – no deposition of Cu from the seawater
- Cannot find Cu enrichment by GDOES or TEM

Mechanism for Cu enrichment

- In seawater, a biofilm is formed on the Al surface, catalysing the oxygen reduction reaction



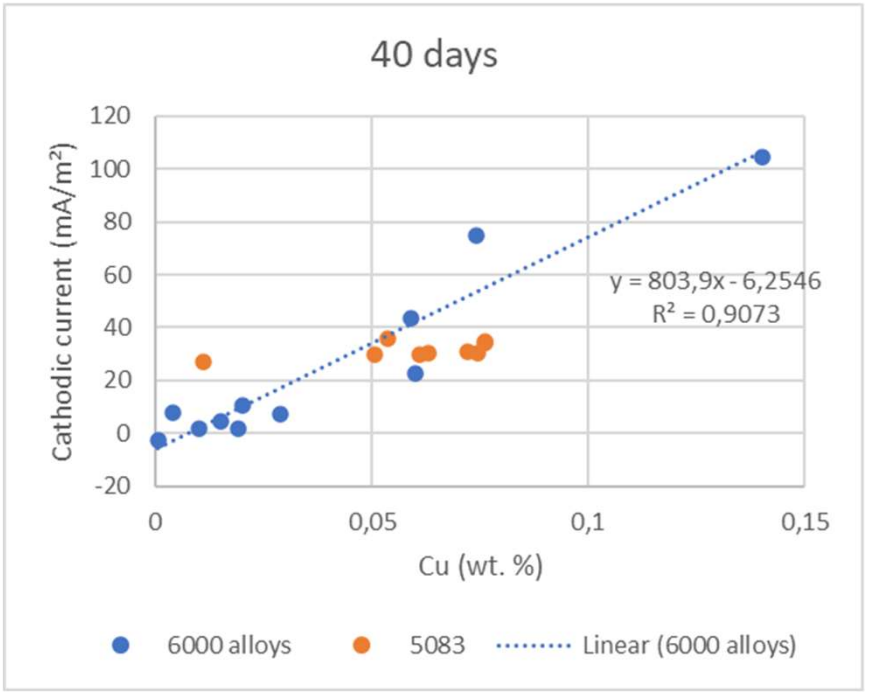
Evolution of cathodic current on stainless steel polarised at −200 mV Ag/AgCl in natural seawater at T = 12–13 °C.
Faimali et al. 2008
https://doi.org/10.1016/j.electacta.2008.02.115

Mechanism for Cu enrichment

- The biofilm increases the cathodic current density on alloys with more than 0.05 % Cu
- The cathodic reaction causes the pH at the surface to increase
- When surface pH exceeds 9, alkaline corrosion of aluminium will start:

$$Al + H_2O + OH^- = AlO_2^- + 1{,}5\ H_2$$

- Cu in the alloy will not corrode, since it is cathodically protected, and will accumulate on the metal surface
- With time, the Cu film is buried under calcareous deposits and aluminium oxide, and the effect disappears



Conclusions

- The recommended current density for CP design of aluminium is too low for many of the alloys used in marine structures
- Current demand for cathodic protection of aluminium alloys depends on alloy composition
- Fe and Si content determines the long term cathodic current density
- A temporary current peak after about 40 days is due to Cu enrichment at the metal-oxide interface and is caused by a biofilm that catalyses the oxygen reduction reaction
- The effect is temporary because the film is buried under oxides and calcareous deposits

Acknowledgements

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