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# "Corrosion Inhibition: Separating Fact from Fiction"

Dr Robert Lindsay, University of Manchester



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#### About the Presenter

#### **Dr Robert Lindsay, University of Manchester**

Rob is a Reader in Corrosion Science and Engineering at the University of Manchester. Prior to taking up this position in 2005 he had appointments at a number of other research institutions, including the Fritz-Haber-Institut (Berlin), Cambridge University, and the CSIC Institute of Materials in Barcelona. He has 30+ years of research experience, with more than 80 published articles. Rob's research activity focuses on mechanistic understanding of interface properties of relevance to corrosion. He combines electrochemical measurements with surface sensitive probes, such as X-ray photoelectron spectroscopy, to develop structure-performance relationships to enable more complete understanding of corrosion related phenomena.

Qualifications: BSc in Chemistry, University of Bristol (1986-89) PhD in Surface Science, University of Liverpool (1989-93)



#### About the Topic

"Corrosion Inhibition: Separating Fact from Fiction"



#### About the Topic

For more than a century, surface-active organic species have been employed to control the corrosion of metals/alloys. Given suitable selection, such corrosion inhibitors have proven to be highly effective, preventing significant degradation of metallic substrates even in highly aggressive environments. Nevertheless, there are still considerable gaps in fundamental knowledge of corrosion inhibitor functionality, severely restricting further innovation. For example, corrosion inhibition in acidic solutions is widely reported to be the result of the adsorption of a monolayer of surface-actives. This description, however, can be considered to be largely a cartoon, as there is a significant lack of supporting experimental evidence. Many key details remain uncertain, including the surface chemistry of the inhibited substrate, the structure of the adsorbed layer, and even its surface coverage. Such information is key input for researchers attempting to predict corrosion inhibitor functionality through atomic scale interfacial modelling, and so identify next generation chemistries. In this presentation, following an introduction to corrosion inhibition in acidic solutions, I will discuss effort to reveal details of corrosion inhibitor-substrate interactions through detailed interface characterisation. For example, I will discuss recent X-ray photoelectron spectroscopy (XPS) results, indicating that the chemistry of the inhibited interface is dependent on both inhibitor concentration and acid identity. In addition, I will present data demonstrating that surface adsorption is not always sufficient for achieving the target corrosion inhibition efficiency, i.e., it will be shown that a surface-active can be bound to the surface, but not lead to sufficient reduction in corrosion rate. Moreover, I will use XPS data to argue that the widely adopted approach of determining the standard Gibbs energy of adsorption of a corrosion inhibitor from measured inhibitor efficiencies is flawed, and so should not be relied upon as a tool for corrosion inhibitor selection.

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Q&A

Presentation – "Corrosion Inhibition: Separating Fact from Fiction"

Q1. Quite often efficiency and availability of inhibitor is mixed up. Any guidance on this misinterpretation?

A1. Efficiency is a figure of merit describing how well a corrosion inhibitor works at a particular concentration. Availability quantifies how much of the time (%) a corrosion inhibitor is dosed in an engineering scenario. There is a useful paper by Bill Hedges (ex-bp) on the topic: 'The Corrosion Availability Model', B. Hedges, NACE-00034, CORROSION, 2000.

Q2. When testing OMID in HCI, is it under static conditions or dynamic? Any difference in CMC expected

A2. We usually test under static conditions. I did not expect that flow to impact on CMC.

Q3. Any chance of elemental sulphur deposition with H2SO4? What's the best technique to characterise associated elemental sulphur if any?

A3. In the S 2p spectrum, we do see low intensity signal that we attribute to surface sulphides. We suggest that this feature may be due to solution/substrate minority components, or reduction of sulphate. I favour the former currently, as reduction of sulphate seems less likely.

Q4. Is it possible to study and measure the CI film thickness by XPS?

A4. Yes, it is possible, but we typically focus on surface coverage rather than 'thickness', as the data usually suggest sub-monolayer coverages in acidic solutions. The approach for calculations of coverage and 'thickness' are essentially the same.

Q5. For sulphuric acid, does the inhibitor help build up the iron sulphate layer and does the inhibitor bond with the sulphate layer or the underlying metal in gaps in the sulphate layer?

A5. We believe that the iron sulphate surface layer is there in both the presence and absence of the inhibitor. As regards where the corrosion inhibitor bonds, we suggest that is absorbed onto a continuous layer of iron sulphate but cannot confirm this with the current data.

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Q6. What are your thoughts on corrosion inhibitor persistence? particularly as it relates to the dangerous vs non-dangerous corrosion inhibitors?

A6. Going forwards, enhancing inhibitor persistency should be a significant. It will impact positively on costs, corrosion management and sustainability.

Q7. So future research will focus potentially on tailoring CI to particular environment more precisely?

A7. Hopefully, with enhanced mechanistic understanding, we can work towards this goal.

Q8. Did you consider the effect of temperature in this adsorption process? Do you see it as an influential parameter?

A8. We did not examine the impact of temperature in the studies I presented in there talk, although it is an important parameter. We are currently examining the role of temperature for corrosion inhibition in sweet (CO2-saturated) solution.

Q9. How was CMC determined?

A9. We employed surface tensiometry to determine CMC with a Kruss Drop Shape Analyser, utilising the pendant drop method.

Q10. I'm just wondering if any interface characterization studies has been done in the alkali conditions?

A10. Largely, we have concentrated on acidic solutions, and some work at near neutral pH's. We have not really explored performance under alkaline conditions, as yet.

Q11. How about in turbulent flow conditions, have you assessed those?

A11. We have not examined turbulent flow conditions to date. It should be pointed out that such flow conditions are very unlikely to strip molecules from the surface, as is suggested in some literature; other researchers have undertaken careful work to demonstrate this point.

Q12. What about Machine learning applications/adoption?

A12. Machine learning is potentially a promising area for enhancing corrosion inhibitor selection, and worthy of further pursuit. As regards using output of the characterisation work presented in this talk, however, it will be difficult to use such data as input for machine learning, as it is far from a high throughput approach; data analysis/interpretation can take a significant amount of time.

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Q13. Does your N2 Purging process really give clean enough surfaces? are you intending to remove the passivation layer(s)? Surely it is very difficult to ensure "clean metal."

A13. I think I may have not been clear in my talk on this point. We do not prepare clean carbon-steel surfaces for insertion into solution; they are simply polished in air and display a thin oxide surface layer (as determined from XPS). The film-free (clean) surface found in the inhibited acid occurs naturally, i.e., the immersion/corrosion related processes remove the oxide layer, and a 'clean' inhibited surface is favoured in the presence of the inhibitors.

Slides of technical papers for Aberdeen branch events, along with their respective Q&A's can be found at

https://sites.google.com/site/icorrabz/and also at: Aberdeen Branch - Institute of Corrosion (icorr.org) under Local Technical Programme. A library of event recordings may also be found at:

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# Questions and Answers – ICorr ABZ / Energy Institute Joint Technical Event, **March** 2022

#### Should you have any further questions related to this Webinar,

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who will be very pleased to assist you. Thank you.

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