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News

Fundamental Research

Physical chemistry

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Surface, interface and materials science

Electrochemistry and corrosion

**Carbon steel is a construction material that is widely used in industry, due to its excellent cost/performance ratio. Nevertheless, in certain applications, it can come into contact with an aggressive environment, such as aqueous environments that have been acidified by the presence of $CO_2$, leading to corrosion-induced deterioration. In order to gain a better**

**understanding and improve the protection of carbon steels in environments of this type, corrosion teams from IFPEN, INSA-Lyon's Mateis Laboratory and the University of Leeds' Institute of Functional Surfaces (IFS) have pooled their expertise to conduct joint research. The research is aimed at controlling the performance of the "pseudo passive" surfaces observed on these steels, developing characterization methodologies to study the protection mechanisms involved.**

## Corrosion resistance, an Achilles' heel for different usages related to the ecological transition

The transition to a low-carbon economy requires new technologies. Some of these, including CCUS (Carbon Capture Utilization and Storage) and biofuel synthesis, involve **aqueous effluents containing $CO_2$ in solution**. These environments may be a source of corrosion affecting the equipment employed, particularly if it is made of carbon steel. **Carbon steel** is associated with numerous advantages due to its low cost, availability, and recyclability, as well as its mechanical and assembly (machining, welding) properties. However, its corrosion resistance remains a weak point. Nevertheless, in certain conditions, **its surface may be protected by the formation of a "pseudo passive" layer**. A layer of iron oxide or carbonate is formed on the surface, which can potentially be reinforced by the incorporation of other metallic elements.

## Evaluation of the physicochemical conditions close to the corroding surface

In order to better characterize the aqueous environment in the corrosion zone, a specific set-up (figure 1) was developed to evaluate the local pH in the closed vicinity of a sample immersed in an aqueous medium containing $CO_2$. The set-up takes the form of a carbon steel grid.

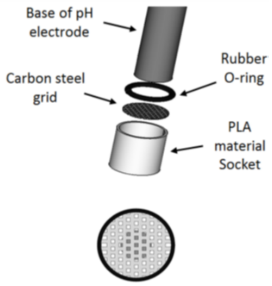

Figure 1: pH electrode diagram [1]

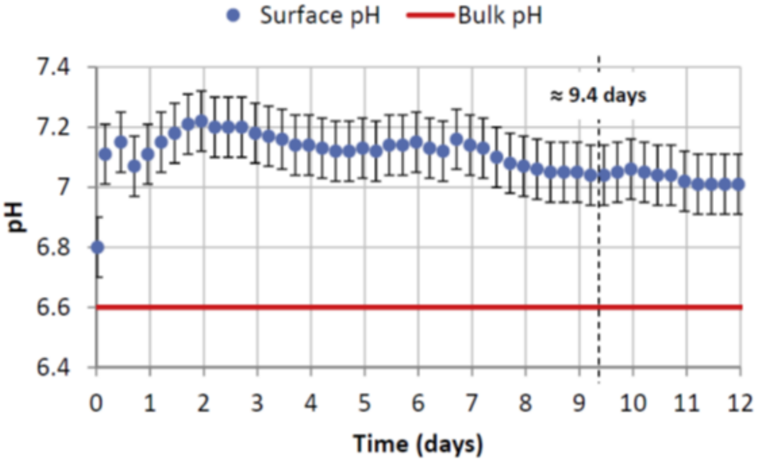

Figure 2: Surface pH measurement conducted for a pH of 6.6 measured in a full bath (a long way from the sample surface) over a test period of 12 days at 80°C at 0.54 bar of CO2 [1]

As indicated in figure 2, at the interface where corrosion takes place, the pH measured is less acidic by around 0.4 units of pH compared to the pH of the solution a long way from the interface [1]. **This local condition is favorable to the formation of a pseudo passive layer.**

## Carbon steel “pseudo passivity” protection mechanisms

Electrochemical measurements have confirmed that **the pseudo-passive state is characterized by a change in open circuit potential** and **a significant reduction in the corrosion rate**. This can be observed in figure 3 with, after 10 days, a corrosion rate that has become so low (less than 0.02 mm/year) that it enables long-term use of carbon steel.

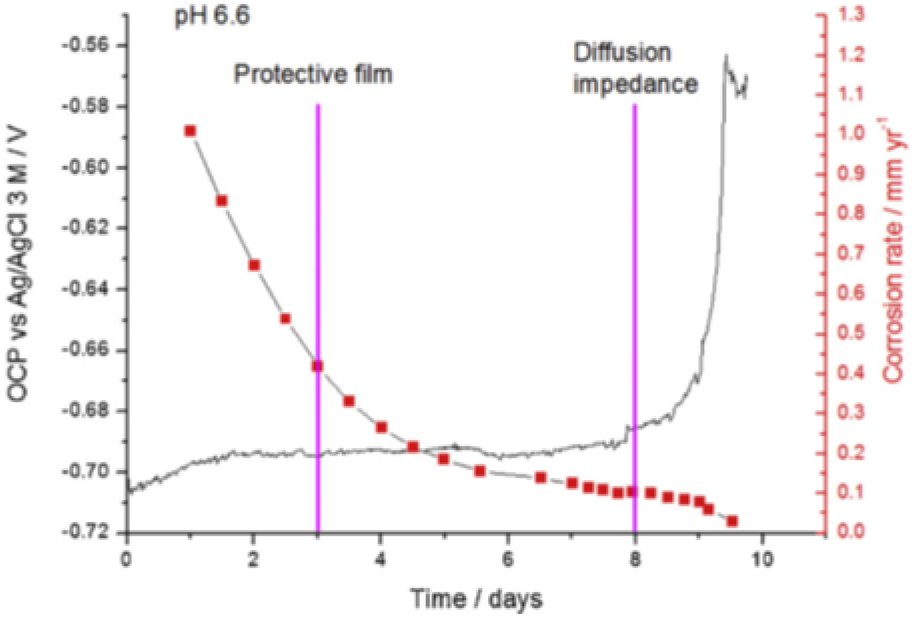

Figure 3: evolution of Open Circuit Potential and corrosion rate as a function of immersion time for a bulk bath pH of 6.6 (interfacial pH of 7) at 80°C and 0.54 bar of CO2 [2]

For a sample exposed to 80°C and a pH of 6.6, surface analyses identified traces of a magnetite phase (Fe3O4) at certain places, beneath a more dominant iron carbonate (FeCO3) film (figure 4). In addition, over the course of time, **the corrosion layer acquires a very low porosity**, resulting in the formation of a “diffusion barrier”. This is indicated in figure 3 by **a significant increase in the open circuit potential (OCP)**, which is considered to be a key corrosion protection indicator [2].

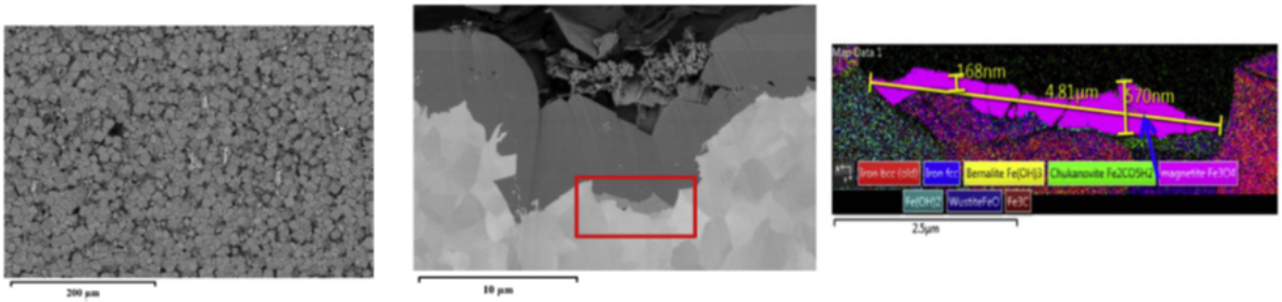

Figure 4: SEM image of the surface (left) - SEM image of a cross-section of the pseudo-passive layer (center) - EBSD map showing the presence of magnetite at the steel/pseudo-passive layer interface (right) after 12 days' immersion at a bulk-bath pH of 6.6 (interfacial pH of 7) at 80°C and 0.54 bar of CO2 [2]

[1] Electron Backscatter Diffraction

## In situ corrosion monitoring using synchrotron radiation

In situ synchrotron X-ray diffraction (SR-XRD) was also used to monitor **the evolution of corrosion products on X65 carbon steel in an aqueous environment containing $CO_2$** (following exposure to 80°C, pH 6.3–7.3). A custom-designed flow cell was built for the purpose, enabling real-time monitoring of concomitant changes in electrochemical behavior and corrosion product growth [3]. Measurements were carried out both during **natural "pseudo-passivation"** stages and under potentiodynamic polarization conditions , to investigate electrochemical mechanisms in the cathodic and anodic domains (Figure 5).

[2] i.e., varying the sample potential

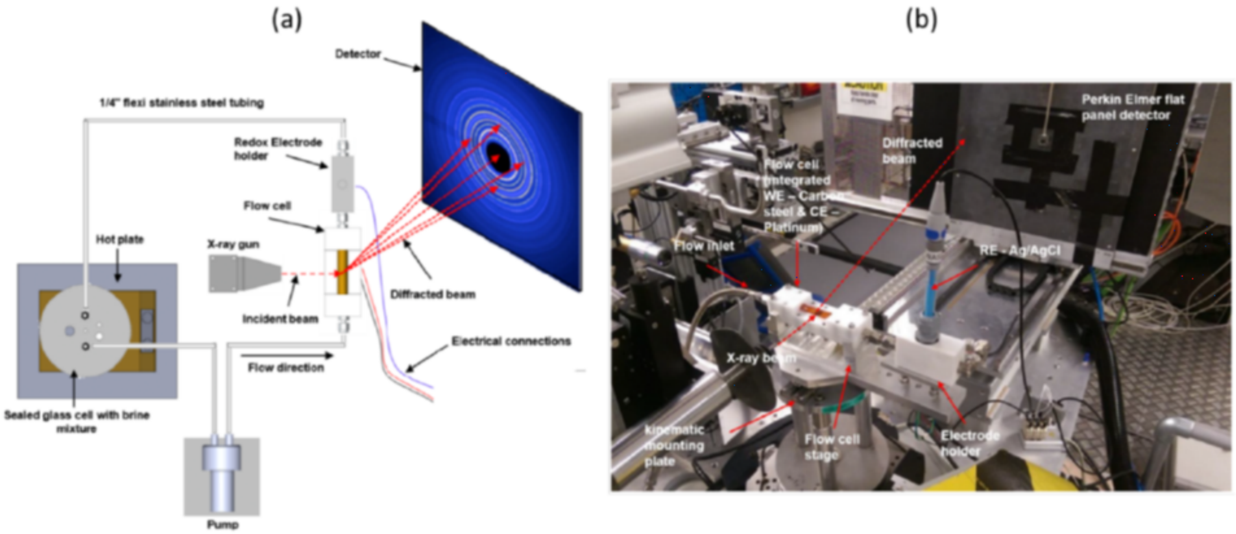

Figure 5:(a) Illustration and(b) configuration of the flow cell used on the Diamond Light Source beamline (Oxford) [3]

The protectivity (reflected by a nobler open circuit potential) observed during ”pseudo-passivation” is strongly linked to the accumulation of iron carbonate ($FeCO_3$) on the steel surface (figure 6). The chukanovite $Fe_2(OH)_2CO_3$ was only detected at higher anodic potentials (associated with a rapid steel dissolution rate), outside the pseudo passive protection domain (figure 7): this phase thus appears to be associated with the active dissolution of carbon steel [3].

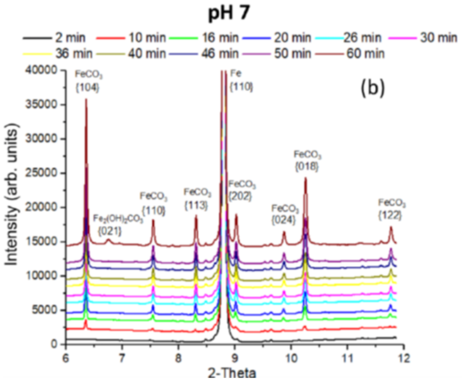

Figure 6: In situ XRD analysis of an X65 carbon steel coupon at 80°C at 0.54 bar of CO2, flowing at a velocity of 0.1 m/s through a flow cell at pH 7. Individual diffraction peaks evolving with time over the course of a test duration of around 1 hour [3].

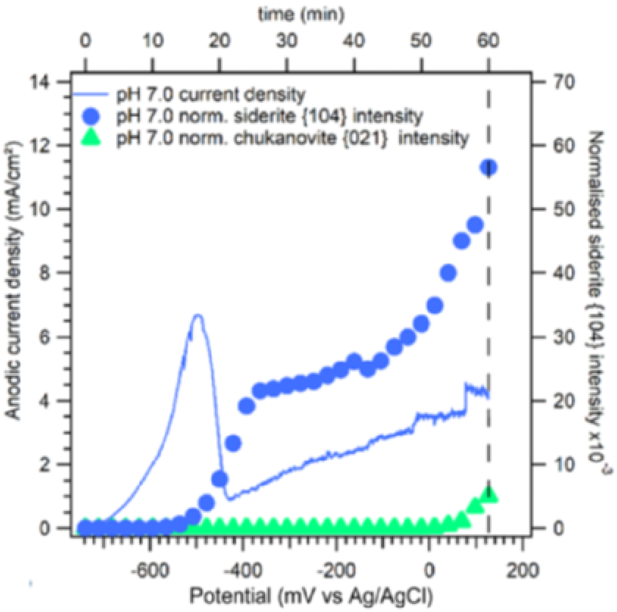

Figure 7: Normalized FeCO3 (104) and Fe2(OH)2CO3 (021) lattice plane intensity during potentiodynamic polarization in the anodic domain of the X65 carbon steel coupon in an 80 ?C and 3.5 wt% NaCl solution saturated with CO2 at 0.54 bar pCO2, flowing at a velocity of 0.1 m/s through the flow cell at pH 7 [3].

## Conclusion

This collaborative fundamental research led to a better understanding of the protection mechanisms association with the “pseudo passivation” of carbon steel in aqueous environments containing carbon dioxide. It also demonstrates the interest of the methodologies implemented, in particular **in situ electrochemistry in a synchrotron**. These methodologies were also used to study the reinforcement of protection by the incorporation of magnetite in the pseudo passive layer [4-5], as well as the impact of contaminants, such as oxygen, on the duration of pseudo passivation. [6-7]

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