

The Formation of Sulfide Scales on Carbon Steel in Saturated H₂S

Noora Al-Qahtani^{1,2}, Jiahui Qi¹, Aboubakr M. Abdullah², Nick Laycock³, and Mary Ryan¹

¹Department of Materials, Imperial College London, London SW1 7AZ, UK.

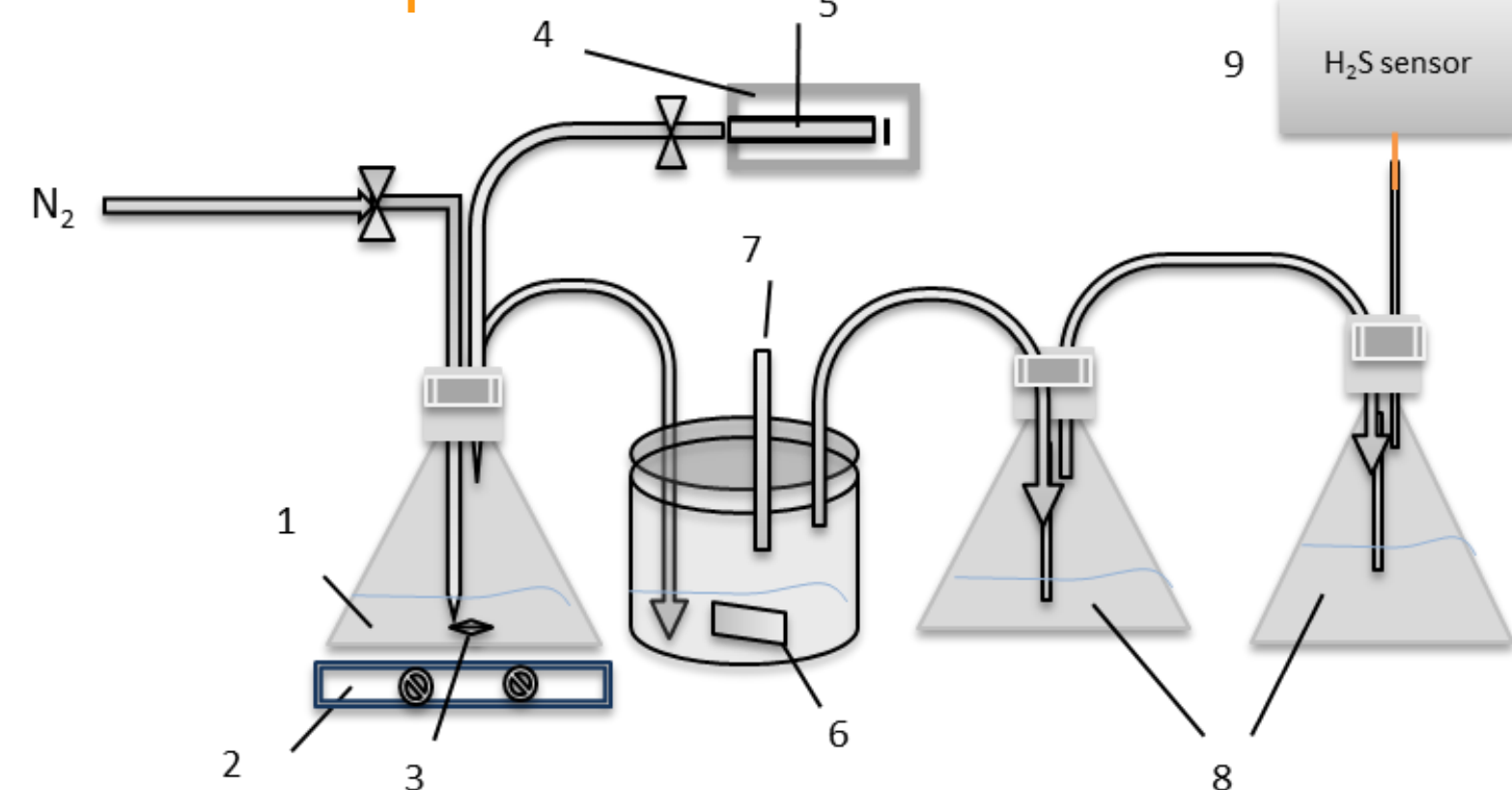
²Center for Advanced Materials, Qatar University, Doha P. O. Box 2713, Qatar.

³Qatar Shell Research and Technology Centre, Doha- Qatar.

Introduction

The damage caused by the building up of scale inside wellbores and pipelines costs millions of pounds each year. Better understanding of the mechanism of scale formation and the kinetics of the process is essential, for asset management in general and for the development of new protection approaches. Surface scale formation is one of the important factors related to the corrosion rate in sour systems. The internal corrosion of carbon steel in the presence of hydrogen sulfide represents a significant problem for both oil refineries and gas treatment facilities/pipelines. Many studies have revealed that the system is complex: more than one iron sulfide compound may form and its morphology is sensitively dependent on environmental conditions. However, the kinetics of scale formation, such as the nucleation and growth processes of the scale; and how corrosion inhibitors interact with nanoscale morphology of the scales are not at all well-understood.

Experimental setup



Ambient pressure set-up for in-situ H₂S generation

1 Sodium sulfide solution; 2 Stirring hot plate; 3 Stirrer bar; 4 Syringe pump; 5 Syringe filled with Diluted HNO₃ solution; 6 Iron sample; 7 pH meter; 8 H₂S scrubbers; 9 H₂S sensor.

The system allows for saturated hydrogen sulfide solution, temperature control, and export of the sample to high pressure environment for repeat assessment.

Results and Discussion

Scale formation was investigated as a function of temperature and time. Visual inspection reveals increasing apparent density with temperature and thickness of the scale with time.

Temp /Time	10 min	30 min	1 hr.	1.5 hr.	2hrs
RT					
50 °C					
80 °C					

pH measurement of the solution is essential because it affects the solubility metals such as iron, and in turn provides information about the saturation conditions of the system. At RT, pH drops in the first 20-30 min then rises and stabilizes at pH 4-5; at 50 °C, after an initial drop there is an increase pH 6-7, before stabilising at a similar value. This temporal variation strongly affects the rate Fe dissolution.

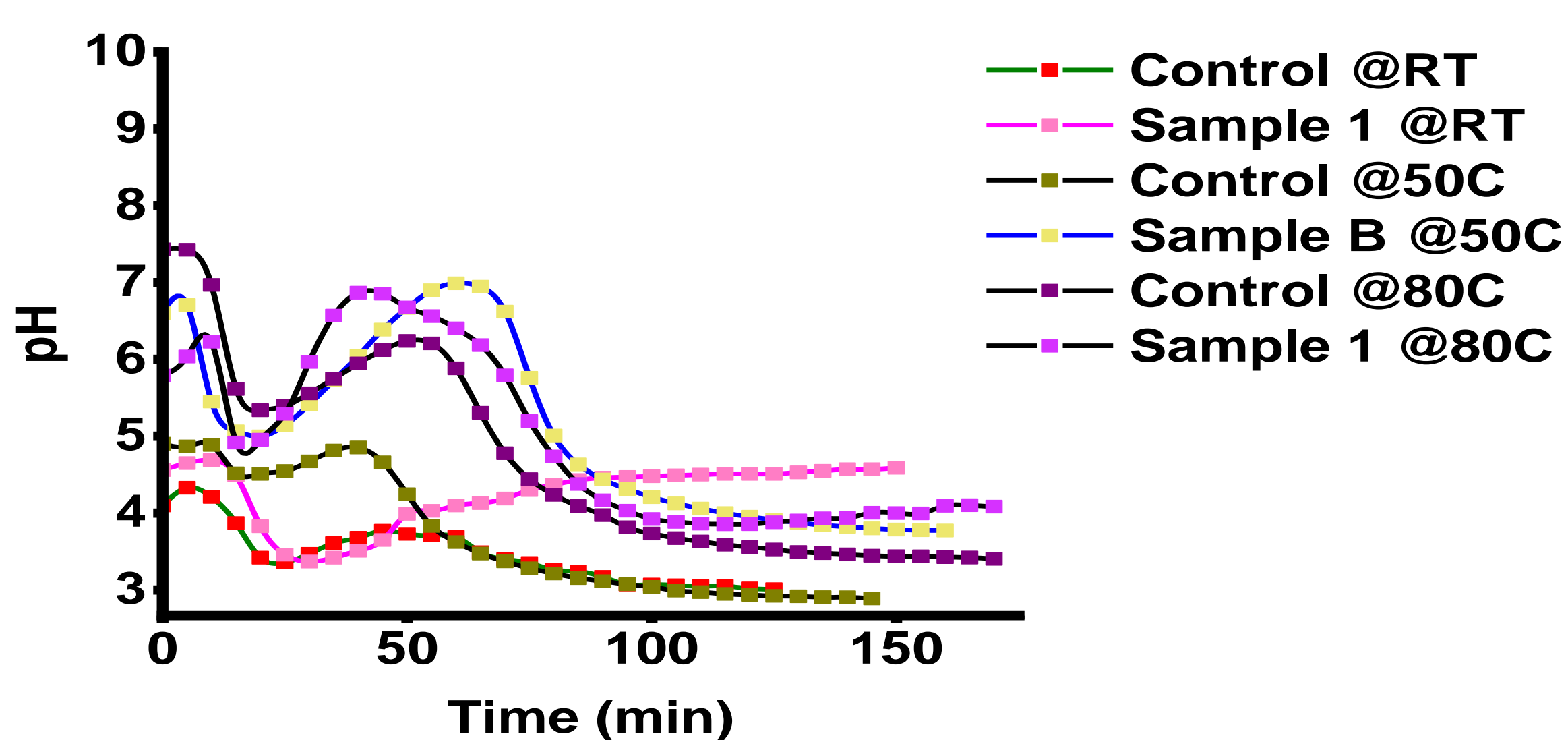


Figure 2: Solution pH change with time at different temperature: RT, 50 °C and 80 °C.

Advanced Characterization

Scanning Electron Microscopy (SEM) imaging was used to examine the surface morphology of the corrosion products formed on steel surfaces. It reveals the generation of porous structure on the surfaces.

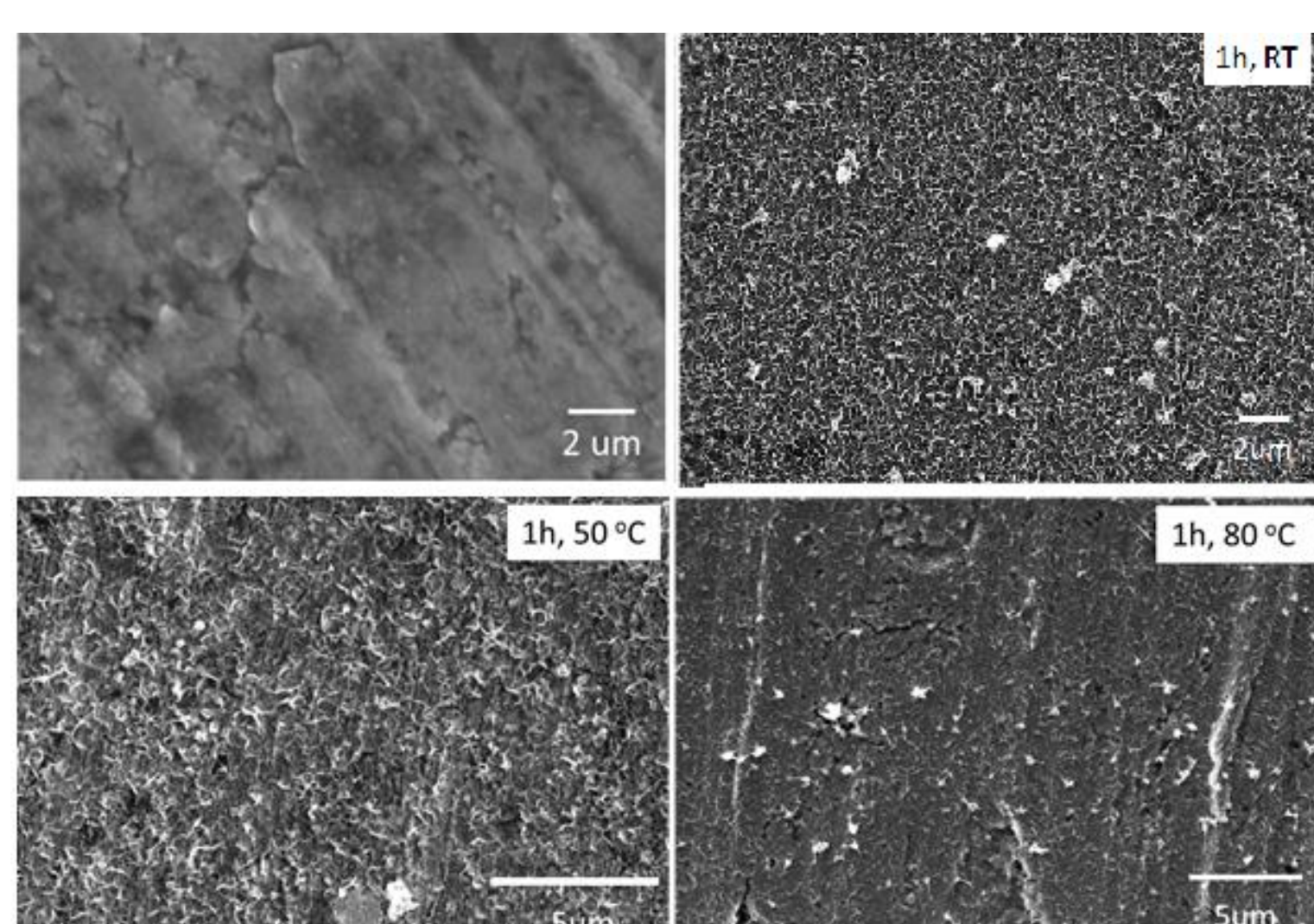


Figure 3: SEM imaging for: (A) unreacted carbon steel, (B) FeS at 1hr-RT, (C) FeS at 1hr-50 °C (D) FeS at 1hr-80 °C.

High resolution cross-sectional Transmission electron microscopy (TEM) reveals a complex multi-layer film formed with nanoscale porosity. Both the scale thickness and porosity are found to be temperature dependent.

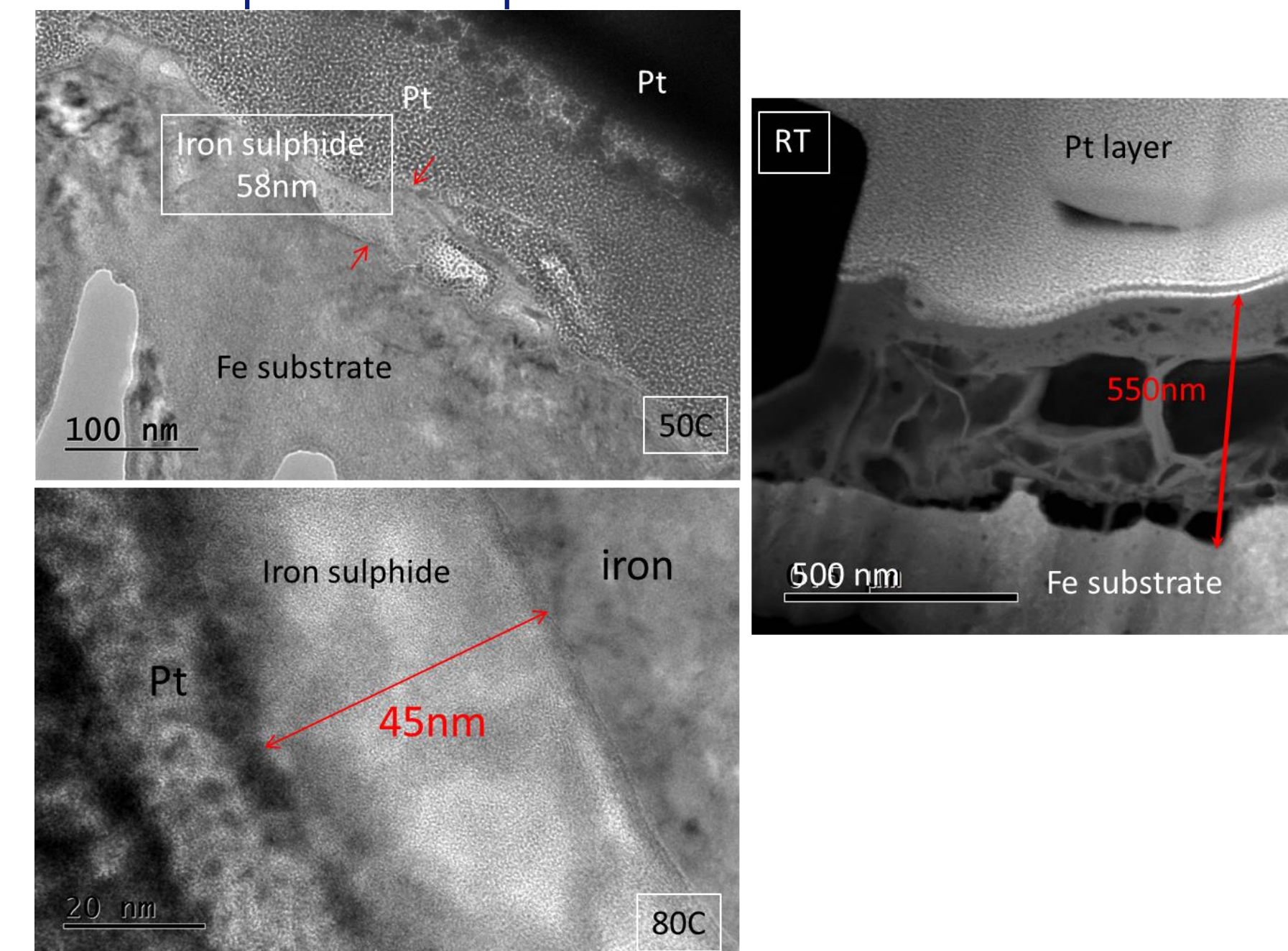


Figure 4: S/TEM images show the comparison of the thickness of the iron sulfide scale formed at RT, 50 °C and 80 °C, reaction time 1 hour for all (note the Pt layer is added to protect the surface during ion milling of the cross section)

In situ Raman Spectroscopy experiments have been carried out using a newly installed spectrometer from Renishaw (combined with ESEM and complementary optical system). The results from *ex situ* experiments showed a chemically heterogeneous surface, with different iron sulfide species. *In situ* data show a transition (possible crystallization) in the structure of the film formed with time.

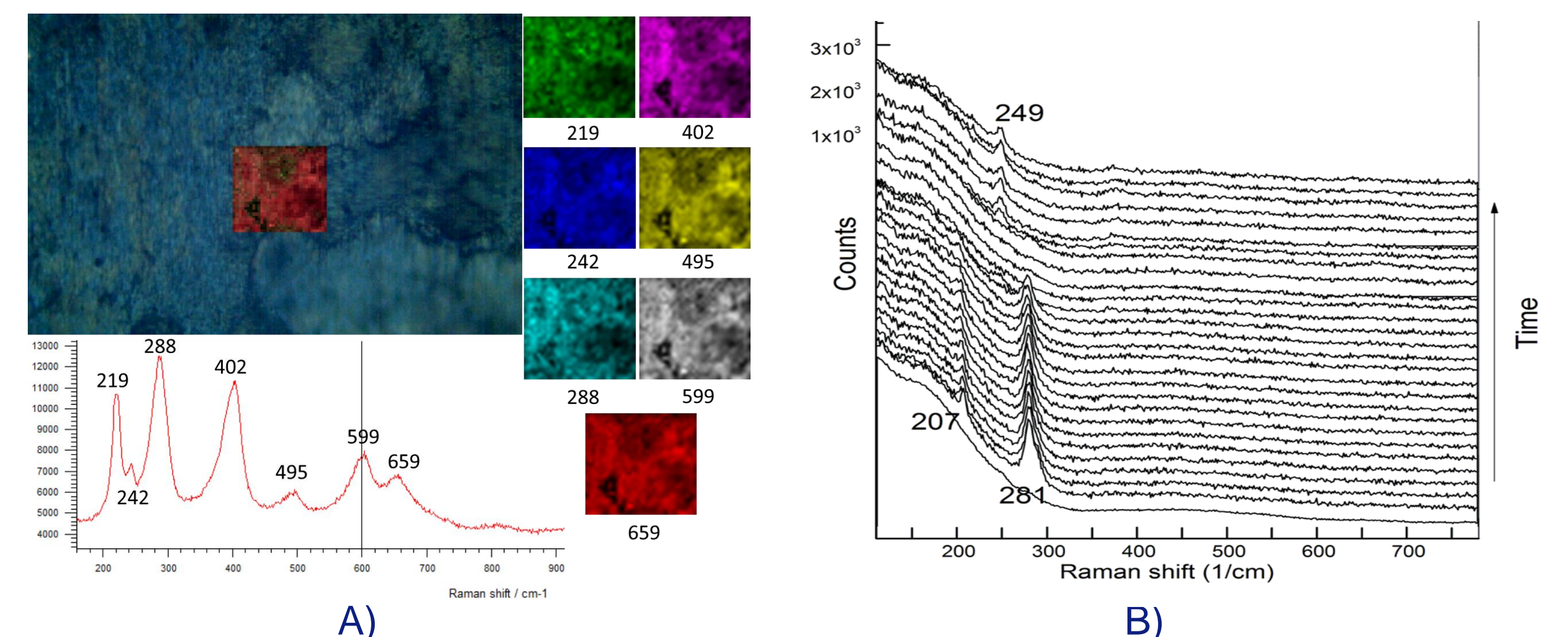


Figure 5: A) Raman maps show distribution of different forms, B) *In situ* Raman spectra showing early stage iron sulfide formation/evolution

Name	Chemical formula	Raman bands positions	reference
Nanocrystalline mackinawite	FeS	208; 282	(Bourdoiseau et al. 2008)
Well crystalline mackinawite	FeS	208; 250; 298	(Bourdoiseau et al. 2008)
Greigite	Fe ₃ S ₄	138; 188; 255; 350; 365	(Rémazeilles et al. 2010)
Pyrite	FeS ₂	343; 349; 430	(White, 2009)

Summary and Future Directions

- The morphology and chemical structure of iron sulfide formed on the Fe substrate have been investigated at different time scales by SEM, TEM and Raman Spectroscopy. A multi-layered nanoporous structure is formed on the surface of steel on exposure to saturated H₂S. The morphology and thickness of this scale are temperature dependent; linked to variations in the dissolution rate of iron with temperature. The initially formed structure is an amorphous or nanocrystalline structure.
- Further work is underway to determine, *in situ*, the morphology and structural evolution of iron sulfide with time; and the role of corrosion inhibitors in scale formation and stability.
- Combined electrochemical methods to measure the corrosion rate during H₂S exposure, along with methods to evaluate under deposit behaviour are being set up in our laboratories.

Acknowledgements

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