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A study by in situ Raman spectroscopy of carbon steel corrosion in CO₂ and H₂S environment

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Background and Objectives

Corrosion products formed in oil and gas exploration & production environments are very often composed of iron carbonate and / or iron sulfide. The impact of such deposits on corrosion largely depends on their composition, thus on the ratio between partial pressures of both gases. A classical rule-of-thumb considers a dividing line between sweet and sour corrosion where the ratio of CO₂ and H₂S partial pressure is 500. However, a recent review of thermodynamic calculations showed that the error band for the calculation of this ratio threshold was extremely large [1]. It is also well known that the composition of corrosion products observed in field exposures evolves over long periods of time, especially for iron sulfides that can change from mackinawite to pyrrhotite [2], the latter forming preferentially at higher temperature and high P_{H₂S}. Besides, most of sulfides species are very sensitive to oxydation after removal from the exposure environment. It is therefore useful to develop *in situ* methods.

Raman spectroscopy is a **vibrational spectroscopy** commonly used to describe iron sulfides with high resolution [3,4] and can carry out *in situ* analyses using immersion probe or a specific cell equipped with a window.

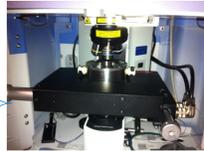
➔ The aim of this work is to explore the potentialities of this technique to characterize *in situ* corrosion products formed in CO₂ and H₂S environments

Experimental

Methodology

Design of the cell taking into account the motorized constraints :

- Dimensions : the cell must be put on the motorized mapping stage
- Focusing : distance sample <-> LWD objective ≤ 10 mm
- Signal quality : glass window must be as thin as possible



Apparatus

Raman analyses were carried out on a Horiba LabRam Raman using a frequency-doubled Nd:YAG laser ($\lambda_{exc}=532$ nm), an Olympus confocal microscope equipped with a 50X LWD (Long Working Distance) objective (-> the diameter of the studied zone is around 2 μ m). Then the Raman signal is collected by a back-scattering configuration and dispersed with a 1200/mm grating and collected by a CCD detector. The spectral resolution obtained is around 1.5 cm^{-1} . Finally, the analytical conditions depend on the species :

Carbonates species only :

- moderate acquisition time
- moderate to high laser power

Sulfides species :

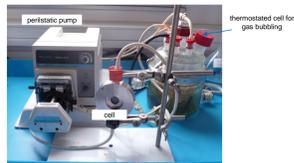
- long acquisition time
- low laser power

Corrosion experiment conditions

- Low alloy steel specimens
- Exposure in pure water saturated with CO₂ + H₂S
- Strict de-aeration conditions

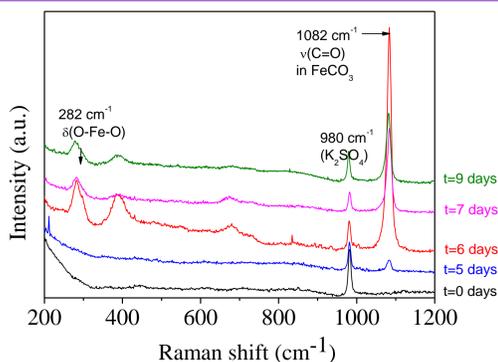
Validation of the analysis cell on a simple case :

- Study of a steel specimen under pure CO₂ pressure
- Study of a steel specimen under pure H₂S pressure



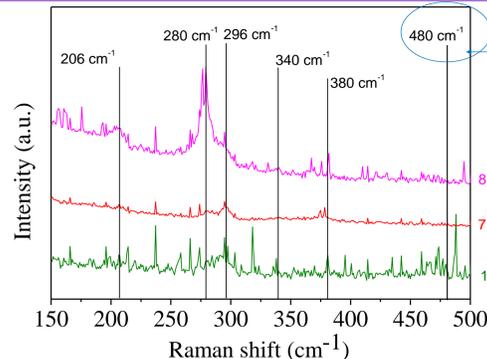
Results

Validation in pure CO₂ at 80° C



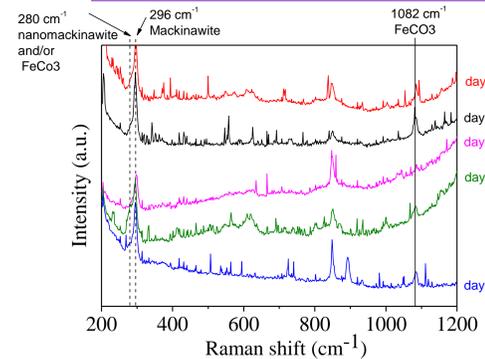
- ➔ 2 days : no iron salts detected
- ➔ 2 → 9 days : bands at 282 and 1082 cm^{-1} ⇒ FeCO₃

Validation in pure H₂S at ambient T°



- ➔ 1 → 7 days : well crystallized mackinawite (296 cm^{-1}) + pyrite (340 and 380 cm^{-1})
- ➔ 8 days : formation of nano-mackinawite (280 cm^{-1}) in addition to the previous species

Ex situ study of the heterogeneity (specimen with iron sulfides + iron carbonates)



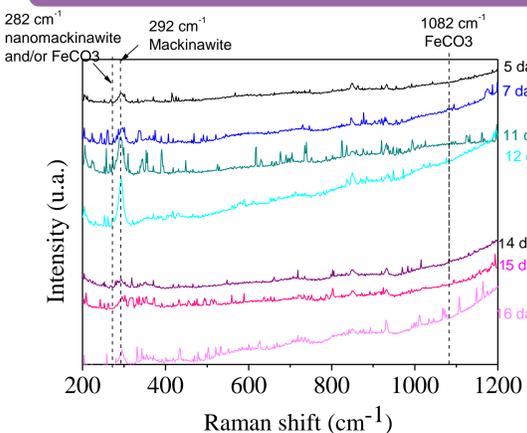
- 1 measure every day during 5 days
- cell is kept under vacuum between 2 spectra

Ratio of carbonates to sulfides depends on the spot :
⇒ surface coverage by corrosion scale is heterogenous
⇒ Analysis should be averaged with several spots

The cell and methodology is validated : this development permits to analyze *in situ* both sulfides and iron carbonates in a qualitative way

Study of the competition between sulfides and carbonates at 100 and 1000 ppm H₂S/CO₂

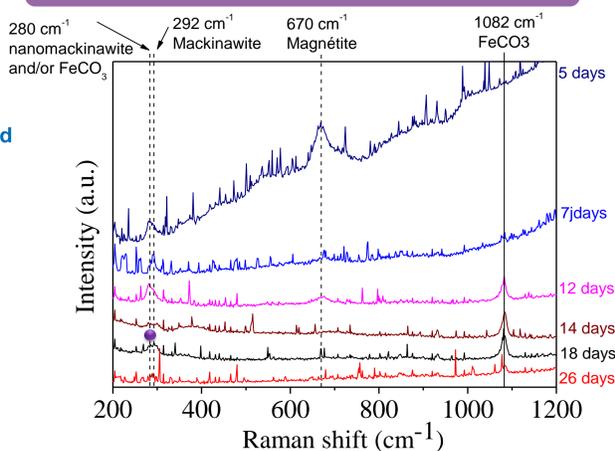
Ambient T° - 1000 ppm H₂S/CO₂



- ➔ 0 → 5 days : no iron salts detected
- ➔ > 5 days : only a band at 282 cm^{-1} is detected ⇒ FeS in a Mackinawite structure

Under these conditions and with CO₂ / H₂S = 10³ sulfides appear first and carbonates are not observed

Ambient T° - 100 ppm H₂S/CO₂



- ➔ 5 days : mackinawite (292 cm^{-1}) and magnetite (670 cm^{-1}) appeared
- ➔ 7 days : iron carbonates are suspected
- ➔ 12 days : iron carbonates are detected
- ➔ >12 days : magnetite has disappeared

Under these conditions and with CO₂ / H₂S = 10⁴ sulfides appear first and then both carbonate and sulfides are observed simultaneously

Conclusions

- ➔ Raman spectrometry permits *in situ* monitoring of the corrosion process under both H₂S and CO₂ environments in a qualitative way.
- ➔ For a 1000 ppm H₂S/CO₂ atmosphere, only iron sulfides are detected
- ➔ For a 100 ppm H₂S/CO₂ atmosphere, this methodology shows that iron sulfides appear first followed by iron carbonates
- ➔ The study of the heterogeneity puts in evidence the issue of the significativity of the measure. The analyzed area must be increased by using new mapping technologies such as Duoscan (Horiba) or Streamline (Renishaw)

[1] S.N. Smith, Discussion of the history and relevance of the CO₂/H₂S ratio, Corrosion/2011 paper no065, NACE International (2011) 811-818

[2] S.N. Smith, B. Brown, W. Sun, Corrosion at higher H₂S concentrations and moderate temperatures, Corrosion/2011 paper no081, NACE International (2011)

[3] J.A. Bourdoiseau, M. Jeannin, C. Rémaizeilles, R. Sabot, and P. Refait, Journal of Raman Spectroscopy, 2011, 42, 496-504

[4] M.C. Bernard, S. Duval, S. Joiret, M. Keddad, F. Ropital, and H. Takenouti, Progress in Organic Coatings, 2002, 45, 399-404