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 CO_2 and H_2S 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 **vibrationnal 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.
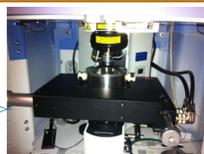
➡ The aim of this work is to explore the potentialities of this technique to characterize *in situ* corrosion products formed in CO_2 and H_2S environments

Experimental

Methodology

Design of the cell taking into account the Raman 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

Validation of the analysis cell on a simple case :
- Study of a steel specimen under pure CO_2 pressure
- Study of a steel specimen under pure H_2S pressure

Apparatus

Raman analyses were carried out on a Horiba LabRam Aramis using a frequency-doubled Nd:YAG laser (λ_{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 μm).
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 CO_2 + H_2S
- Strict de-aeration conditions

Results

Validation in pure CO_2 at 80° C
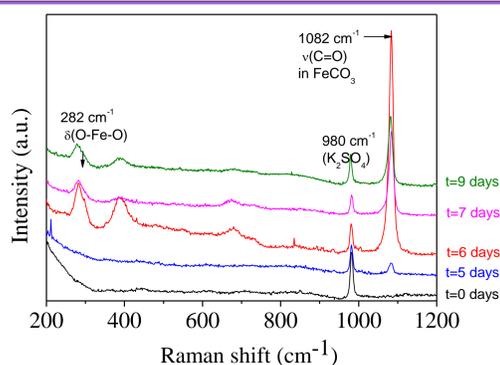
→ 2days : no iron salts detected
2 → 9 days : bands at 282 and 1082 cm^{-1} ⇨ $FeCO_3$

Validation in pure H_2S at ambient T°

No signal of S_8 at 480 cm^{-1} : ⇒ laser power is not too high
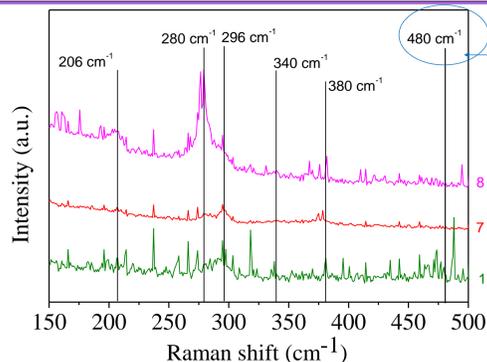
1 → 7 days : well crystallized mackinawite (296 cm^{-1}) + pyrite (340 and 380 cm^{-1})
8 days : formation of nano-mackinawite (280 cm^{-1}) in addition to the previous species

### *Ex situ* study of the heterogeneity (specimen with iron sulfides + iron carbonates)
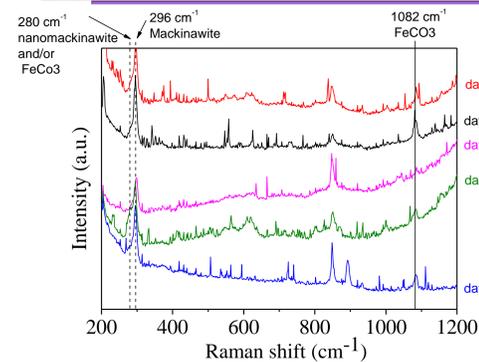
- 1 measure every day during 5 days
- cell is kept under vacuum between 2 spectra

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 H_2S/CO_2
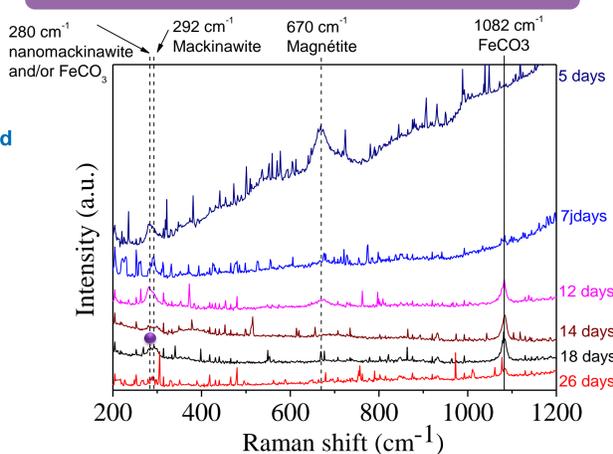
Ambient T° - 1000 ppm H_2S/CO_2
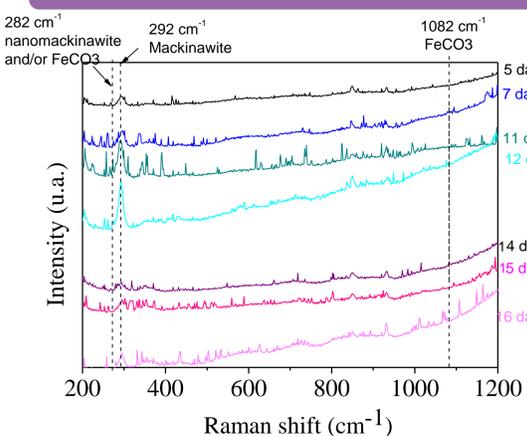
0 → 5 days : no iron salts detected
> 5 days : only a band at 282 cm^{-1} is detected ⇒ FeS in a Mackinawite structure

Under these conditions and with CO_2 / H_2S = 10^3 sulfides appear first and carbonates are not observed

Ambient T° - 100 ppm H_2S/CO_2

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 CO_2 / H_2S = 10^4 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 H_2S and CO_2 environments in a qualitative way.
- For a 1000 ppm H_2S/CO_2 atmosphere, only iron sulfides are detected
- For a 100 ppm H_2S/CO_2 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)

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[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. Rémazeilles, R. Sabot, and P. Refait, Journal of Raman Spectroscopy, 2011, 42, 496-504
[4] MC. Bernard, S. Duval, S. Joiret, M. Keddam, F. Ropital, and H. Takenouti, Progress in Organic Coatings, 2002, 45, 399-404