



IFA - CEA Program

Electrochemical study of iron monosulfide dissolution

Studiul electrochimic al dizolvarii monosulfurilor de fier

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General objectives

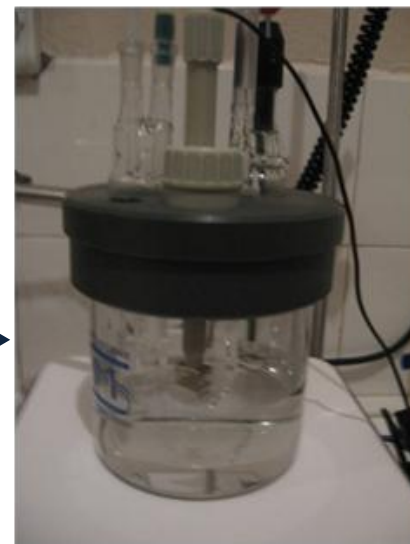
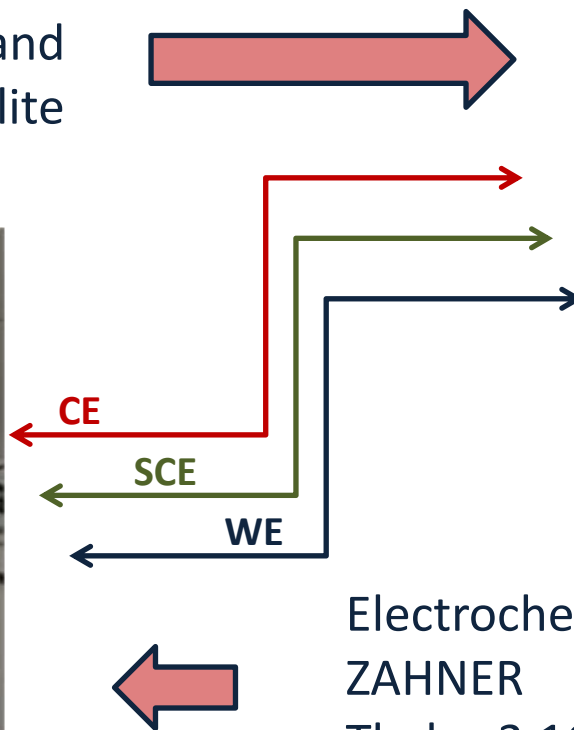
- Study of the reaction kinetics and mechanisms of iron monosulfide (IMS) dissolution
- Analysis of the impact of redox active species transport in media around radionuclide repositories

Activities

- Electrochemical investigation of IMS dissolution reactions
- Characterization of solid reaction products formed on surface of IMS electrodes using specific surface science techniques
- Identification of the main factors controlling IMS dissolution
- Development of theoretical models to estimate the redox buffer potential of IMS

Experiments

Three-electrodes electrochemical cell with a Pt counter electrode and SCE. Working electrode was troilite with 1 cm² exposed area

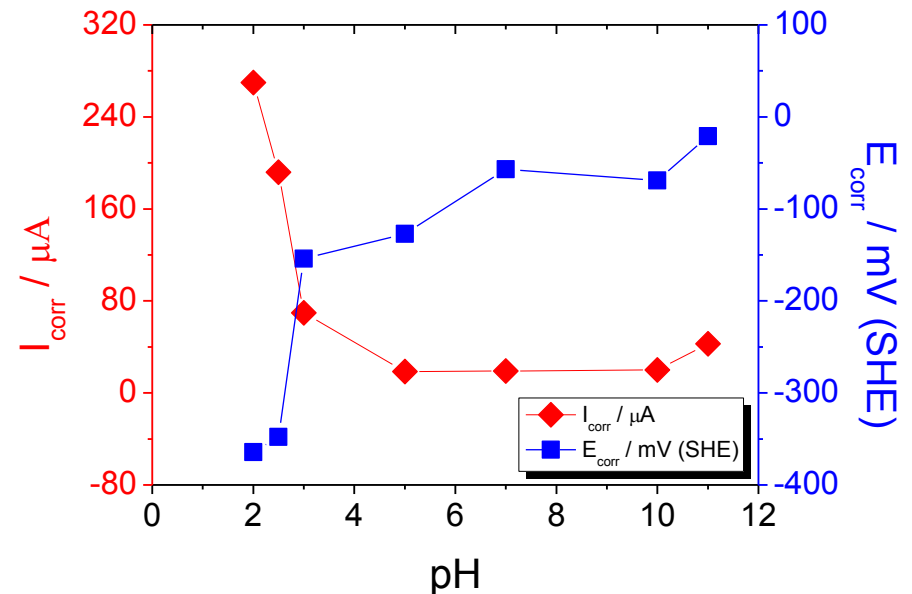
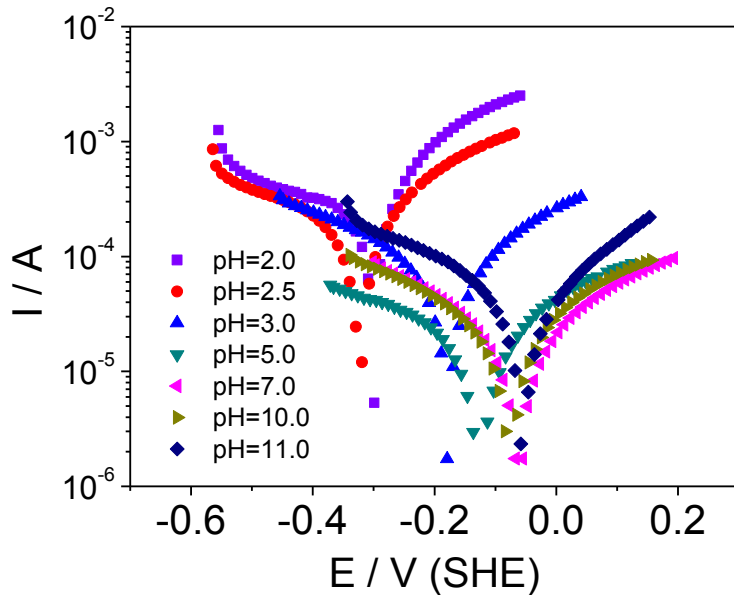


Electrochemical Workstation
ZAHNER IM6ex controlled by
Thales 3.16 Software

➔ The characterization of IMS samples was performed by thermal analysis (TG and DSC), XRD, BET method and Raman spectroscopy in CEA laboratories (French team) (Project C1-04 (2012) Technical Report II. IFA-CEA Program.)

Electrochemical study of IMS dissolution in presence of H_2O_2 : pH effect

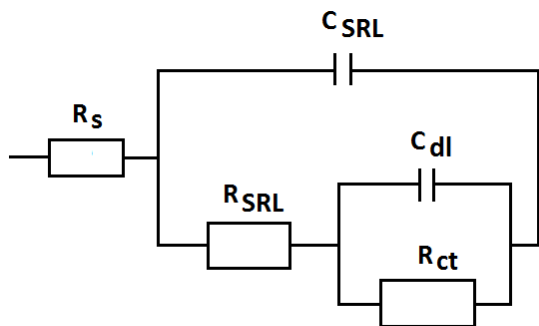
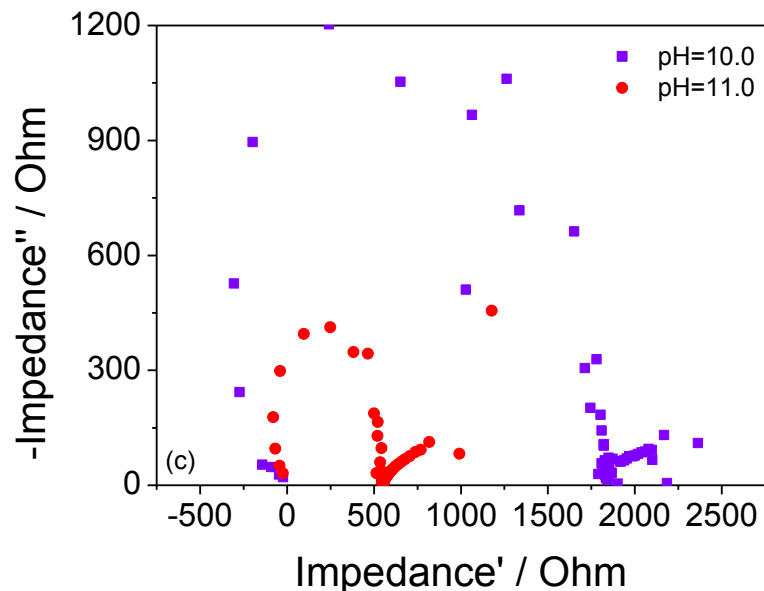
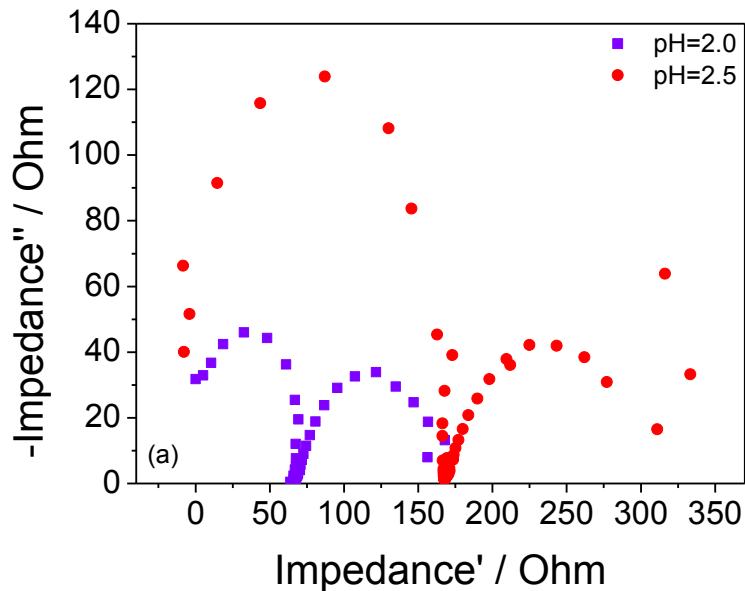
→ $[\text{H}_2\text{O}_2]=0.005 \text{ M}$ and 30°C



- I_{corr} decreases, and E_{corr} increases when pH increases up to pH 5
- Thereafter, I_{corr} and E_{corr} remain roughly constant up to pH 10

IMS dissolution in presence of $\text{H}_2\text{O}_{2(aq)}$: Electrochemical Impedance Spectroscopy (EIS)

➔ $[\text{H}_2\text{O}_2]=0.005\text{ M}$; 30°C and different pHs

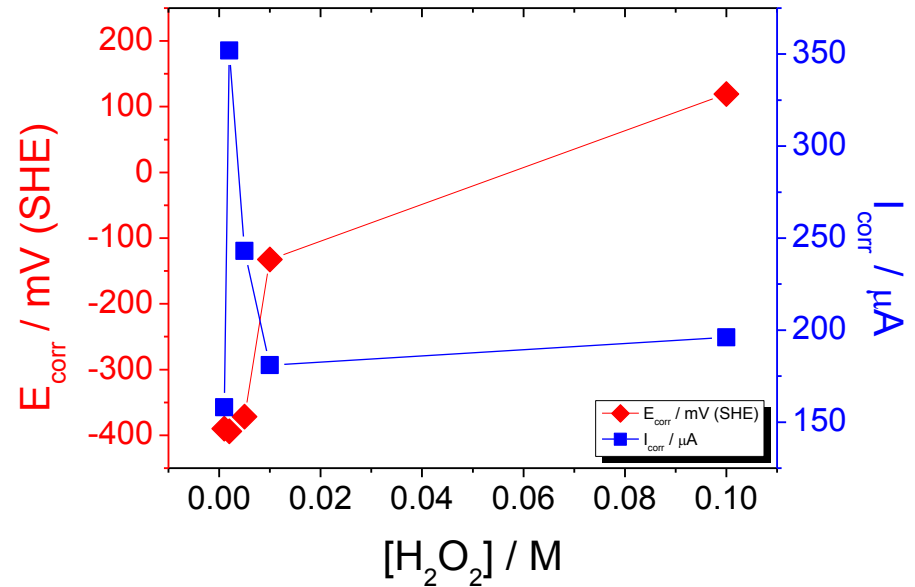
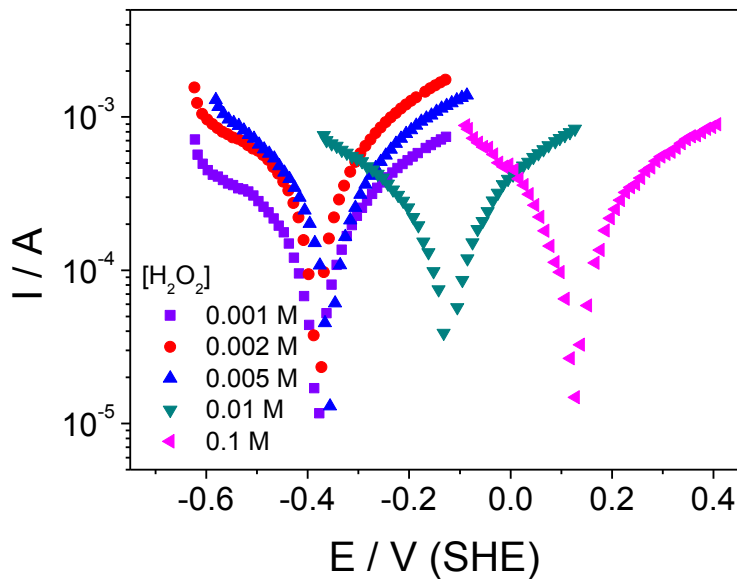


- LF loop gives information about the SRL formed on IMS
- HF loop indicates the charge transfer resistance (R_{ct})

← Equivalent circuit

IMS dissolution in presence of $\text{H}_2\text{O}_{2(aq)}$: [H_2O_2] effect

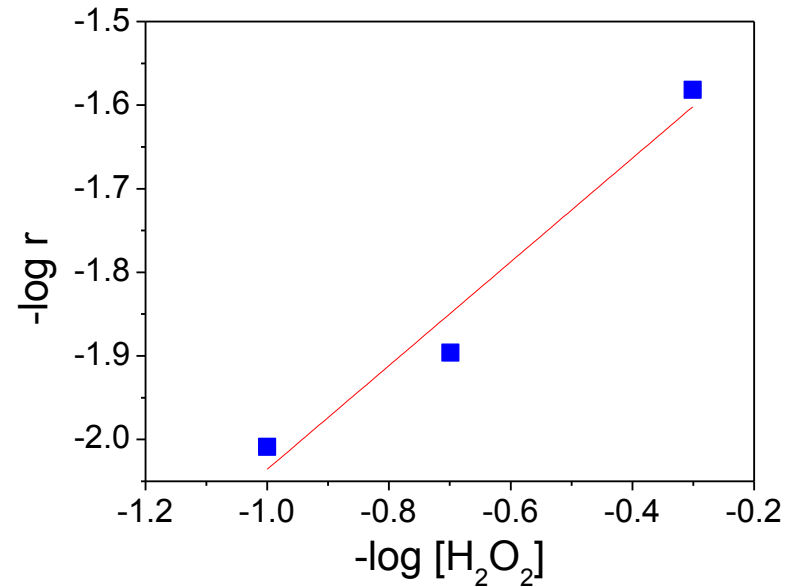
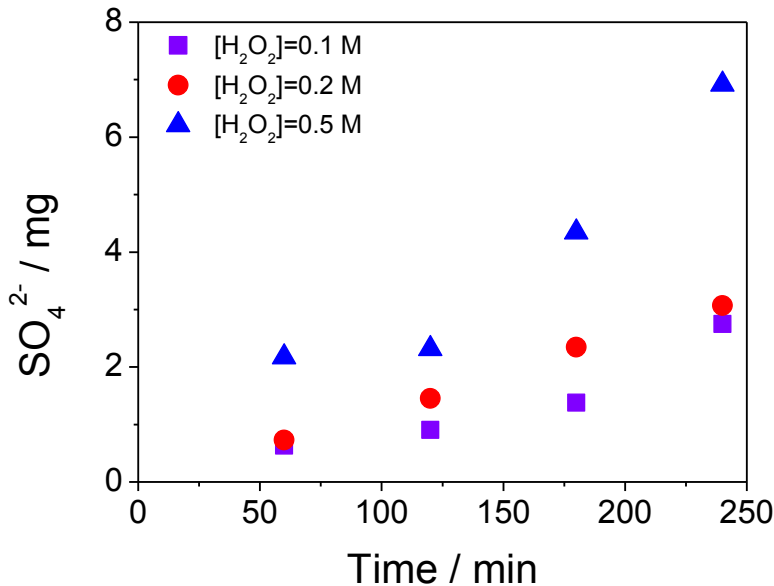
→ pH=2.5 and 45°C



- E_{corr} increases when [H_2O_2] increases
- I_{corr} increases up to [H_2O_2]=0.002 M, then decreases down to [H_2O_2]=0.01 M and remains roughly constant up to [H_2O_2]=0.1 M

Effect of $[H_2O_2]$ on IMS dissolution: Batch dissolution experiments

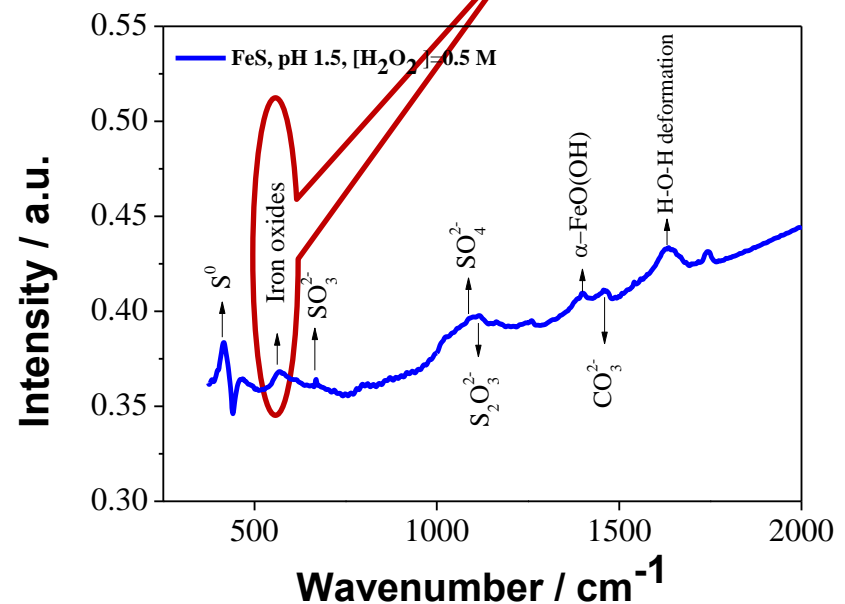
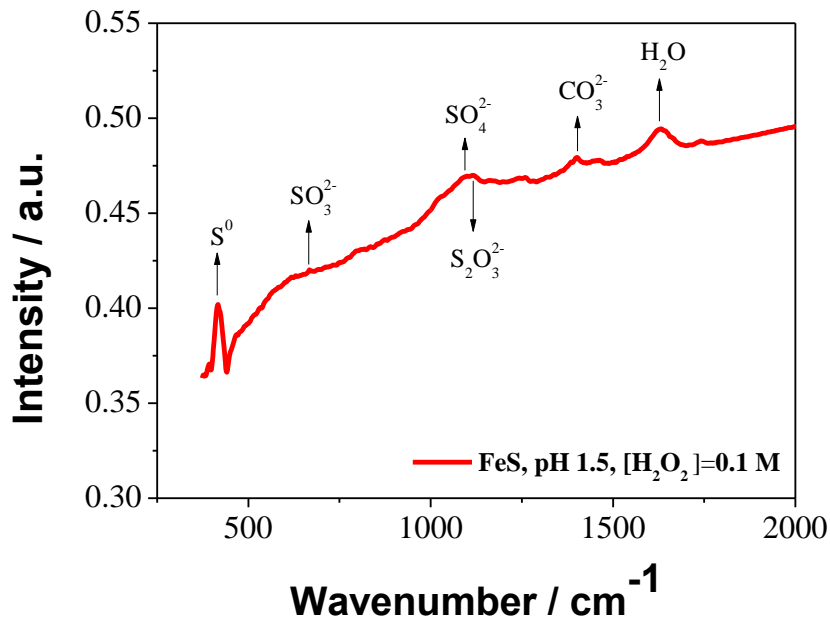
➔ $[H_2O_2]$ in range 0.1-0.5 M; pH=1.5 and 25°C



- The dissolution extent of troilite increases with time
- The rate of troilite oxidative dissolution increase when $[H_2O_2]$ increases
➔ the reaction order with respect to $[H_2O_2]$ is 0.62

Effect of $[H_2O_2]$ on IMS dissolution: FTIR spectroscopy

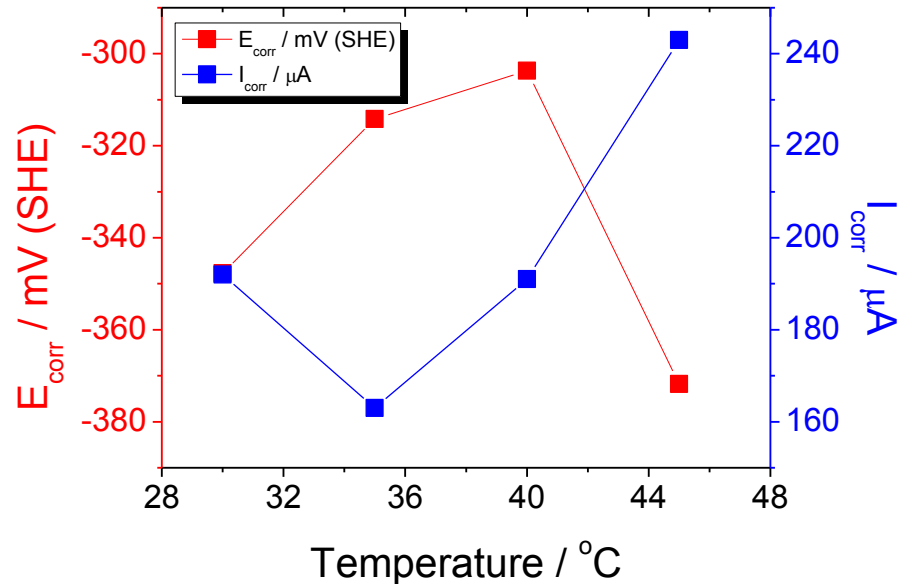
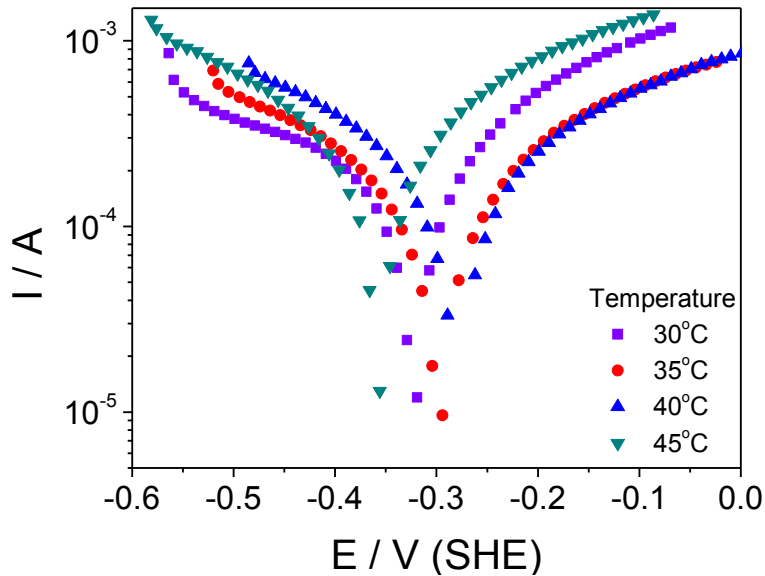
The bands failing in the region 520 to 570 cm^{-1} can be attributed to amorphous or poorly crystalline Fe-O phases (Mikhlin et al., 2002) from SRL



Mikhlin Yu.L, Kuklinskiy A.V, Pavlenko N.I, Varnek V.A, Asanov I.P, Okotrub A.V, Selyutin G.E, Solovyev L.A (2002) Spectroscopic and XRD studies of the air degradation of acid-reacted pyrrhotites. *Geochimica et Cosmochimica Acta*, 66(23) 4057-4067.

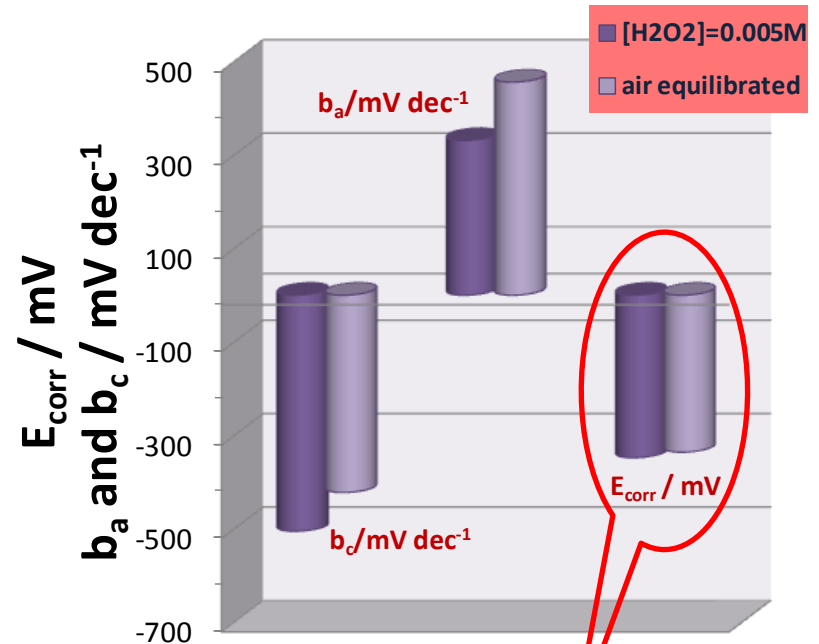
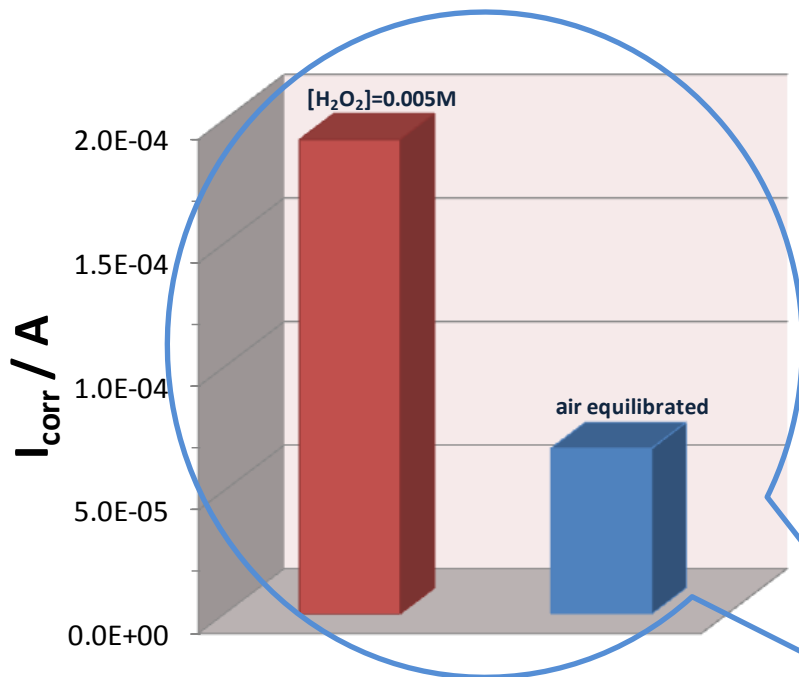
IMS dissolution in presence of H_2O_2 : Temperature effect

→ pH=2.5 and $[\text{H}_2\text{O}_2]=0.005\text{ M}$



- E_{corr} and I_{corr} have a complex (nonlinear) variation with temperature
- E_{corr} (I_{corr}) increases up to 40 $^{\circ}\text{C}$ (decreases down to 35 $^{\circ}\text{C}$), then decreases (increases)

H₂O₂ versus dissolved oxygen



The results indicate that IMS may *react more rapidly* with hydrogen peroxide than with dissolved oxygen (FeS may act as an *effective redox buffer* (Chirita and Schlegel, 2012; Constantin et al., 2012))

Chirita P., Schlegel M.L. (2012) Reaction of FeS with Fe(III)-bearing acidic solutions. **Chemical Geology** (in press).

Constantin C.A., Chirita P., Schlegel M.L. (2012) The electrochemical study of FeS oxidation by dissolved oxygen. **Mineralogical Magazine** (in press).

Summary and conclusions*

- IMS dissolution in presence of H_2O_2 is influenced by pH, $[\text{H}_2\text{O}_2]$ and temperature
- The variation of I_{corr} , E_{corr} and Tafel slopes follows a complex (nonlinear) variation with respect to pH, $[\text{H}_2\text{O}_2]$ (0.001-0.1 M) and temperature
- The reaction order with respect to $[\text{H}_2\text{O}_2]$ is 0.62 ($[\text{H}_2\text{O}_2]=0.1-0.5$ M)
- In quasi-similar conditions (30°C and pH 2.5) the reactivity of IMS in the presence of hydrogen peroxide ($[\text{H}_2\text{O}_2]=0.005$ M) is greater than that in the presence of dissolved oxygen
- 4 presentations to international conferences and 3 accepted publications in international journals

***The results interpretation was made by the two teams (Romanian and French)**

Perspectives of cooperation

- ❑ Further of the electrochemical study of IMS dissolution in the presence of H_2O_2
- ❑ Investigation of the IMS oxidative dissolution kinetics and mechanisms in the presence of $\text{Fe}^{3+}_{(\text{aq})}$
- ❑ Development of common research topics, with elaboration of joint proposals under international and European Programs and Initiatives
- ❑ Exchange of scientists and specialists between CEA and UCV

Support from IFA-CEA Program (Project C1-04)

Thank you