Assessing corrosion at the cement-steel interface in aqueous CO$_2$ environments

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Leakage Pathways in Wellbore Systems
Interface Experiments

Carey et al 2010; IJGGC
Corrosion electrochemistry

- **Half cell reactions:**
  - **Cathodic reactions:**
    \[
    2\text{H}_2\text{CO}_3(aq.) + 2e^- \rightarrow \text{H}_2(g.) + 2\text{HCO}_3^-(aq.) \\
    2\text{H}^+(aq.) + 2e^- \rightarrow \text{H}_2(g.) \\
    2\text{H}_2\text{O}(l.) + 2e^- \rightarrow \text{H}_2(g.) + 2\text{OH}^-(aq.)
    \]
  - **Anodic reaction:**
    \[
    \text{Fe (s.)} \rightarrow \text{Fe}^{2+}(aq.) + 2e^-
    \]
Corrosion kinetics

- Chemical reaction kinetics:

\[ r_r = k \cdot C_i^x \cdot e^{\left(\frac{E_a}{R \cdot T}\right)} \]

- Electrochemical reaction kinetics:

\[ i_r = F \cdot C_i^x \cdot e^{\left(\frac{E_a}{R \cdot T}\right)} \cdot e^{\left(\frac{\alpha \cdot n \cdot F \Delta E}{R \cdot T}\right)} \]
Corrosion measurements

- **Overall Reaction kinetics: Measurement**

\[
    i_{net} = i_0 e^{\left[ \frac{\beta_a \cdot n \cdot F}{R \cdot T} \cdot (E - E_{rev}^a) \right]} - i_0 e^{\left[ \frac{\beta_c \cdot n \cdot F}{R \cdot T} \cdot (E - E_{rev}^c) \right]}
\]
Corrosion measurements

- Electrode-solution

- Measurements:
  - LPR: $R_t = R_s + R_c$
  - EIS:
    - $R_s$ at high frequency
  - $R_c = R_t - R_s$
pH measurement in cement micro-environment
Cement-steel interface design

- Cement
- Steel
- Cement

Brine +/- CO2

Fluid attacks at interfaces
Experiments: Electrochemical glass cell

- **Electrodes**
  - Working electrode: steel sample
  - Reference electrode: calomel
  - Counter electrode: Titanium

- **Continuously stirred**

- **Positive CO₂ gas flow**

- **Electrochemical impedance spectroscopy**
  - Aqueous system resistivity

- **Linear polarization resistance**
  - Total system resistance
Local pH in cement

$T=25 \, ^\circ C, \omega=300 \, \text{rpm}, P_{total} = 1\text{bar}$
Results: Local pH in cement

\[ T=25 \, ^\circ\text{C}, \, \omega=300 \, \text{rpm}, \, P_{\text{total}}=1\text{bar} \]
Corrosion - interface gap size effect

![Graph showing corrosion rate vs. time for different interface gap sizes. The graph includes data points for 0 μm, 20 μm, 100 μm, 200 μm, 500 μm, 1000 μm, and 'open'. The conditions are T=25 °C, ω=300 rpm, P_{total} = 1bar.]
Corrosion – interface gap size effect

Corrosion rate / (mm/yr)

Steel-cement Interface gap / μm

T=25 °C, P_{total} = 1bar

0
0.001
0.01
0.1
1

0
500
1000
open

Interface Gap (μm)

0 RPM
300 RPM

0.001
0.01
0.1
1

0
500
1000
open

Interface Gap (μm)

0 RPM
300 RPM
Corrosion – cement versus epoxy

T=25 °C, $P_{\text{total}}= 1$bar
Solid marks: steel-cement; Hollow marks: steel-epoxy
Corrosion – porosity of cement

Solution resistance at $T=25 \, ^\circ\mathrm{C}$, $\omega=300 \, \text{rpm}$, $P_{\text{total}}=1\,\text{bar}$
Conclusions

- **Local water chemistry in cement**
  - pH is > 12 in cement.
  - pH is decreased to <8 by CO$_2$.
  - pH is greater than bulk solution ($\approx 0.5$)

- **Corrosion rate increases as cement-steel interface gap size increase**
  - Corrosion is severe at large size (>100 $\mu$m)
  - Corrosion is minor at smaller size (>20 $\mu$m)
  - Porosity in cement allows corrosion to occur.
Future work

- Work started at *in situ* high-pressure autoclave
- Apply interface gap results to wellbore environments
  - Corrosion scale.
  - Passivation/depassivation
  - Localized corrosion
- Obtained information will be incorporated in wellbore integrity model for risk assessment
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- CO₂ Capture Project
Corrosion measurements

- **Reaction kinetics:**

\[
i_{\text{net}} = i_0 e^{\left[ \frac{\beta_a \cdot n \cdot F}{R \cdot T} \cdot (E - E_{\text{rev}}^a) \right]} - i_0 e^{\left[ \frac{\beta_c \cdot n \cdot F}{R \cdot T} \cdot (E - E_{\text{rev}}^c) \right]}
\]

- **Linear polarization resistance:** (<10 mV vs. OCP)

\[
i_{\text{corr}} = \frac{\Delta i}{\Delta E} \cdot \left( \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \right) = \frac{B}{R}
\]
Corrosion - reproducibility

Gap size=$\infty$ um (open)  
Gap size=200 um interface

T=25 °C, $\omega$=300 rpm, $P_{\text{total}}$ = 1bar