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Carbon Capture, Utilization, and Storage

A Methodology for Modeling and Testing for Corrosion Rates and Selecting Corrosion Resistant Alloys for CCS Well Applications

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Why Evaluate for Corrosion?

- **Class VI wells must adhere to all construction requirements specified in 40 CFR 146.86**
  - Have sufficient structural strength and be designed for the life of the project
  - Be compatible with contacting fluids
  - Meet or exceed standards developed for well materials by the American Petroleum Institute (API), American Standards for Testing and Materials (ASTM) International, or comparable standards acceptable to the (EPA) Director.

- **Recent project experience (e.g. ADM) necessitates a careful design review**
- 13 chrome tubulars were found to be insufficient in highly saline (>100,000 mg/L) settings
- Corroded downhole equipment can create a leakage pathway between injection zone and shallower formations, especially in wells that are completed in multiple zones

Workflow

1. Establish minimum design and qualification criteria
2. Conduct preliminary corrosion modeling to qualify metallurgies
3. Conduct lab experiments to test selected metallurgies for process conditions
4. Compare modeling and lab results to re-calibrate models
5. ID suitable CRA for procurement
6. Finalize the CRA selection based on market conditions

Minimum Design Criteria

- There is no established standard for selecting corrosion resistant alloys (CRAs) for Class VI wells,
  - API's 5CT standard outlines that a maximum of 12.5% loss in wall thickness due to corrosion and other mechanical factors is acceptable to meet the load requirements along the wellbore.

- Generalized corrosion: **0.05 mm/year** was selected based on half of the minimum rate reported in literature (0.10 mm/year)
  - Wall loss of 5% by corrosion and a total of 10% to stay below the API 12.5%.
    - Assumed 5% wall loss for tubulars caused by installation and operations

- Localized corrosion: No indication of localized corrosion including pitting and crevice/cracking corrosion
  - Potential difference between re-passivation and corrosion must be positive (> 50mV desired)

Corrosion Modeling

- Consisted of modeling:
  - Thermodynamics of mixing, physical properties, and chemical properties including fluid phases, pH, viscosity, and speciation of electrochemically active species
  - Kinetics of anodic and cathodic reactions and corrosion potential to predict mass loss over time

- OLI's Studio was used to model the thermodynamics and mixing of the CO_2 stream and formation brine at bottomhole conditions
  - Stream Analyzer – Compute multiphase physical and chemical properties using equation of state and activity/mixing models
  - Corrosion Analyzer – Compute kinetics of anodic/cathodic reactions, generalized/localized corrosion potentials, and mass loss

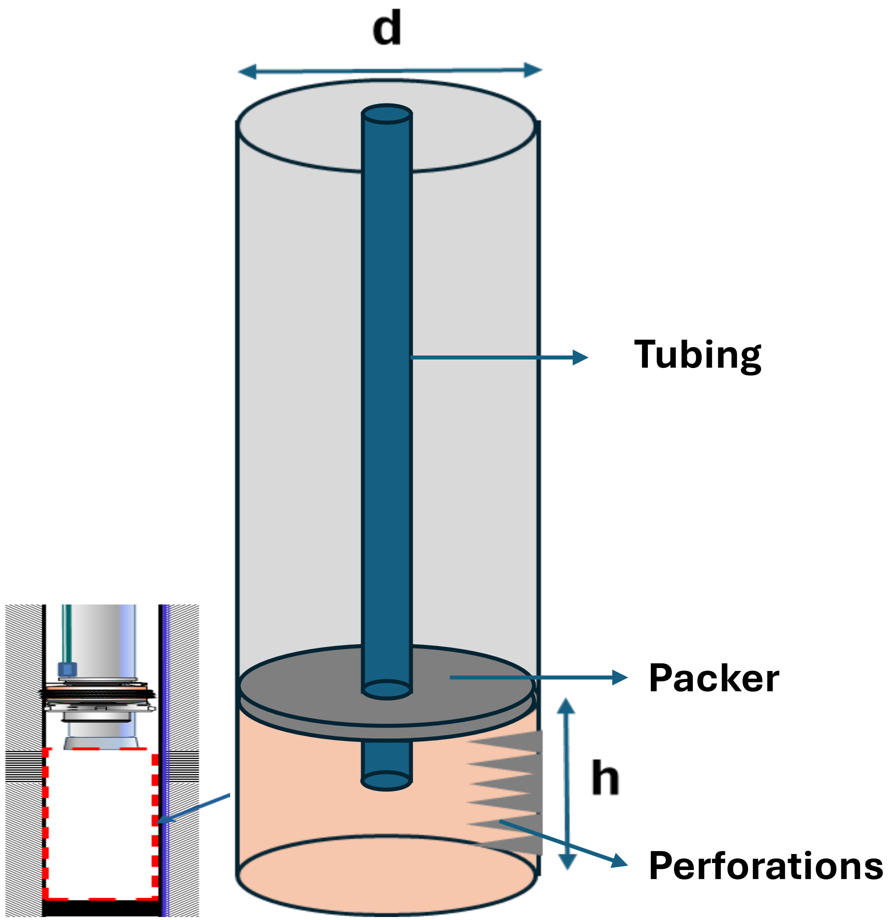
Computation Process	Model
Equation of State	Helgeson-Kirkham-Flowers
Thermodynamic Mixing Framework	Mixed Solvent Electrolyte (MSE) Model

Model Setup

- Physical conditions: ~3,000 psia, 100-150 deg. F
- Corrosion cell: Standing fluid volume below packer (see image)
  - Standing volume (V_{ST}) calculated as

$$V_{ST} = \pi d^2 h/4$$

  - Assumes inside of the casing above the perforations is sealed by a packer and not exposed to CO_2 or brine
- CRAs: 13 Cr, 15 Cr, 17 Cr, 22 Cr
- Fluid mixing
  - Operation: Wellbore section is 100% CO_2, no brine (100:0)
  - Shut-in: Brine flows back into the wellbore
    - Near well brine-water ratio is assumed as 50:50 vol/vol
    - Far-field brine-water ratio is assumed as 90:10 vol/vol



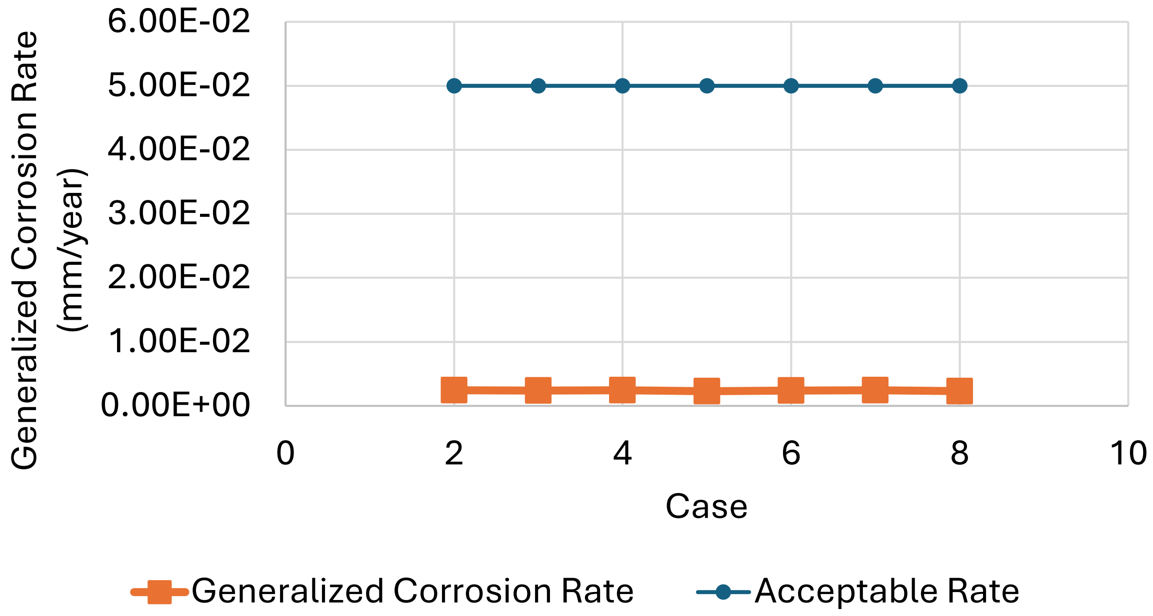
Model Cases

Case	Description	Location	CO_2 Stream	CO_2 Stream vol. fraction	Fm Brine vol. fraction
1	CO_2 Stream only	Injection well	Base	1	0
2	CO_2 Stream only	Injection well	HH	1	0
3	Mixing	Injection well	HH	0.9	0.1
4	Mixing	Injection well	HH	0.5	0.5
5	Mixing	Far-field	HH	0.1	0.9
6	Mixing	Injection well	LL	0.9	0.1
7	Mixing	Injection well	LL	0.5	0.5
8	Mixing	Far-field	LL	0.1	0.9

- *CO_2 stream composition used for modeling*
  - *CO_2: 95 vol%*
  - *O_2: 50 ppmv (L) or 100 ppmv (H)*
  - *SOx/NOx/H_2S: 300 ppmv*
  - *Water: 4 mass% (L) or 5 mass% (H)*
- *Formation brine composition used for modeling*
  - *Na^+: 20,000 mg/L*
  - *Mg^{+2}: 1,500 mg/L*
  - *Ca^{+2}: 4,500 mg/L*
  - *SO_4^{-2}: 2,000 mg/L*
  - *Cl^-: 80,000 mg/L*
  - *pH: 6*

Modeling Results – 13 Cr

- Generalized corrosion does not appear to be an issue for 13Cr for any of the tested cases
- Pitting is an issue at 50:50 mixing of CO_2 injectate and formation brine



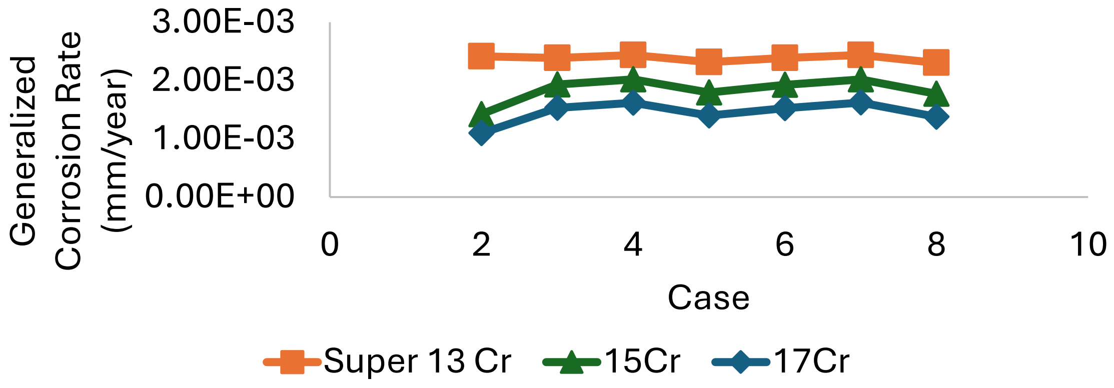
Case	Pitting Y/N	Safety margin for Pitting (mV)
2	No	>2000
3	No	36.55
4	Yes	
5	No	34.79
6	No	36.03
7	Yes	
8	No	37.06

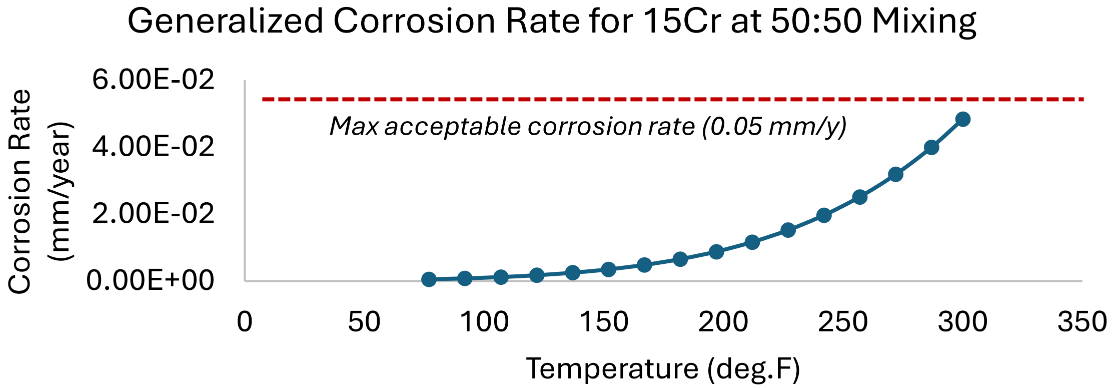
Results shown here correspond to complete agitation between standing fluid and tubular, which is the most aggressive corrosion case.

Modeling Results – Super Chrome Alloys

- Results for S13Cr, S15Cr, and S17Cr indicate a lower generalized corrosion rate than 13Cr
- No pitting corrosion was observed for any of the modeled cases
- Tested a temperature ramp for the most pessimistic mixing case for (50:50) between CO_2 stream and brine for S15Cr
  - Results indicated even at 300 °F, generalized corrosion was less than the acceptable rate
  - No pitting was observed at any of the test temperatures.

Results shown here correspond to complete agitation between standing fluid and tubular, which is the most aggressive corrosion case.





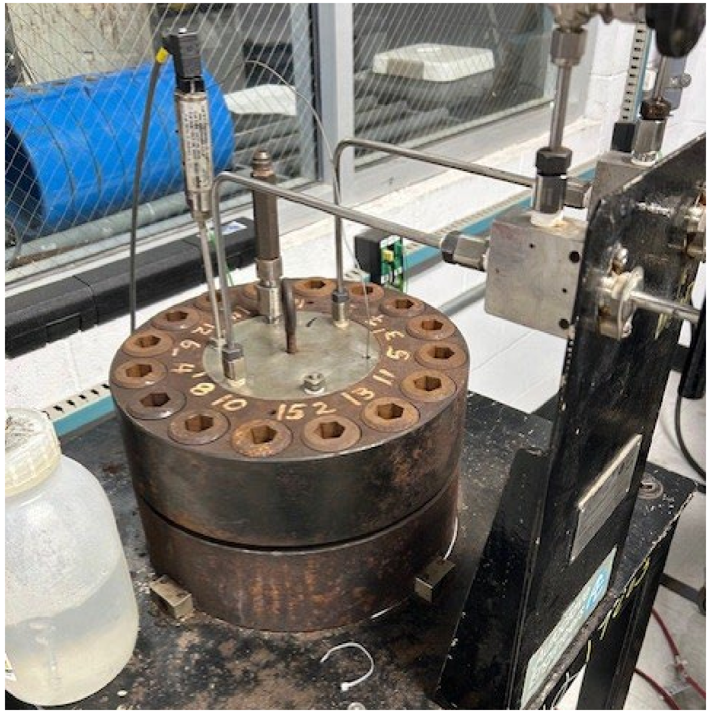
Lab Testing

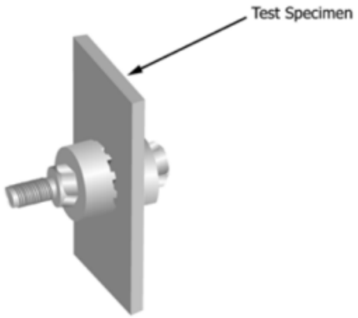
- Tested higher grade chrome alloys in a static setting
  - Commonly available variants of 15Cr (15-5PH) and 17Cr (17-7PH) were used
  - One duplex alloy (2205) was also tested
- Three bare coupons and three crevice coupons were tested for each material
- A 10-L C-276 autoclave (#6,000 psig/600°F) was used for 30-day exposure tests per ASTM G31 protocol
- Post-test analysis included visual inspection, metal loss, SEM-EDX imaging, and spent brine testing

Coupon	Weight of key metals %											
	C	Si	Mn	P	S	**Cr**	**Ni**	**Mo**	Ti	V	Al	N
S13Cr	0.01	0.24	0.42	0.015	0	**12.2**	**5.5**	**1.9**	0.1	0.05	-	-
15-5PH	0.04	0.4	0.64	0.022	0.4	**15.27**	**4.22**	**0.15**	0.001	-	-	-
17-7PH	0.07	0.32	0.87	0.021	0.0001	**16.81**	**7.22**	**-**	-	-	1.08	-
2205	0.024	0.48	1.76	0.027	0.0001	**22.4**	**5.75**	**3.11**	-	-	-	0.17

Lab Testing

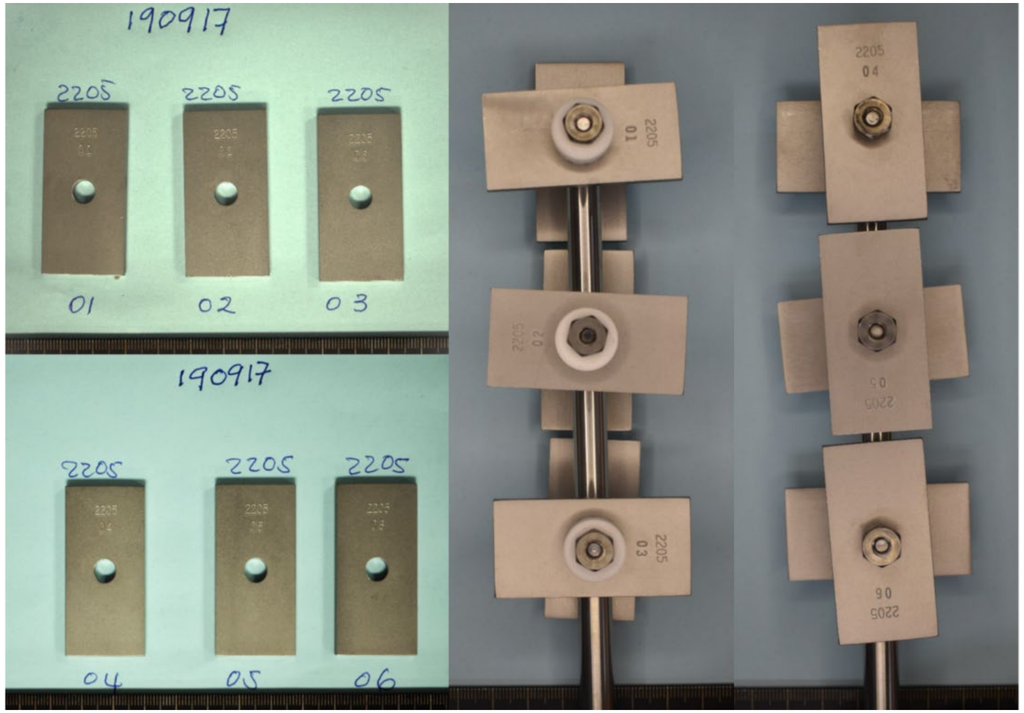
Autoclave Setup



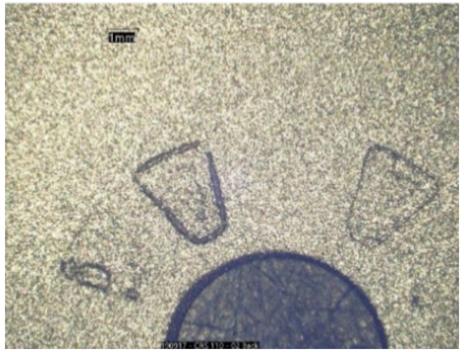


Two 12-tooth ceramic crevice washers were installed on both sides of metal coupons to hold in place

Loading configuration (2205 example)



Results – Visual Inspection



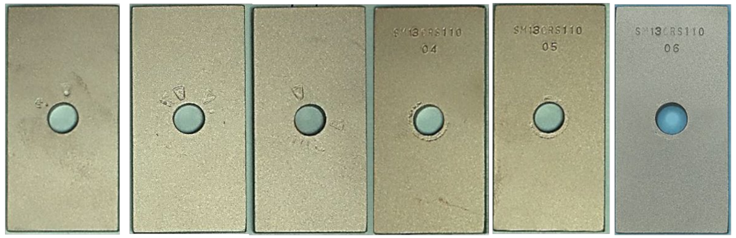
Closeup imaging showing mild crevice corrosion in S13Cr

13Cr CRS 110 Before exposure

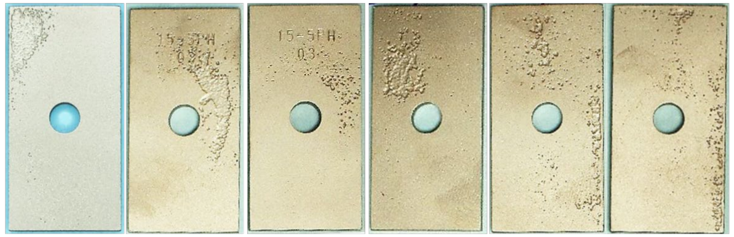
15Cr – 5PH Before exposure

13Cr CRS 110 After exposure (before cleaning)

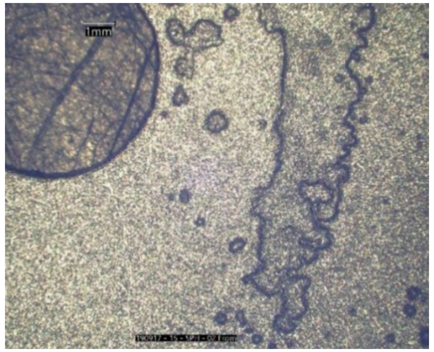
15Cr – 5PH After exposure (before cleaning)



13Cr CRS 110 After exposure (after cleaning)



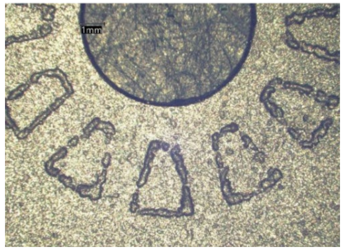
15Cr – 5PH After exposure (after cleaning)



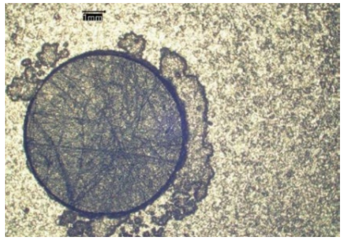
Closeup imaging showing pitting and crevice corrosion in 15-5PH

15-5PH appeared to have performed the worst in the visual inspection test

Results – Visual Inspection



Closeup imaging showing crevice and pitting corrosion in 17-7PH

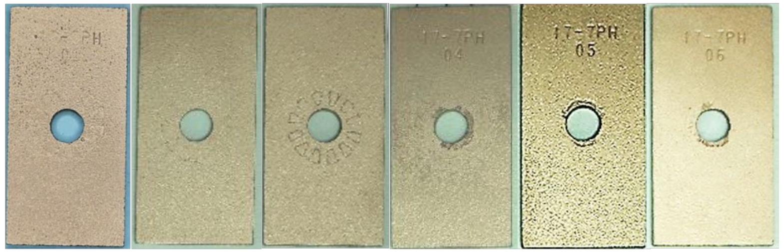


17Cr – 7PH Before exposure

22Cr 2205 Before exposure

17Cr – 7PH After exposure (before cleaning)

22Cr 2205 After exposure (before cleaning)



17Cr – 7PH After exposure (after cleaning)

22Cr 2205 After exposure (after cleaning)

2205 appeared to have performed the best in the visual inspection test (no pits/cervices)

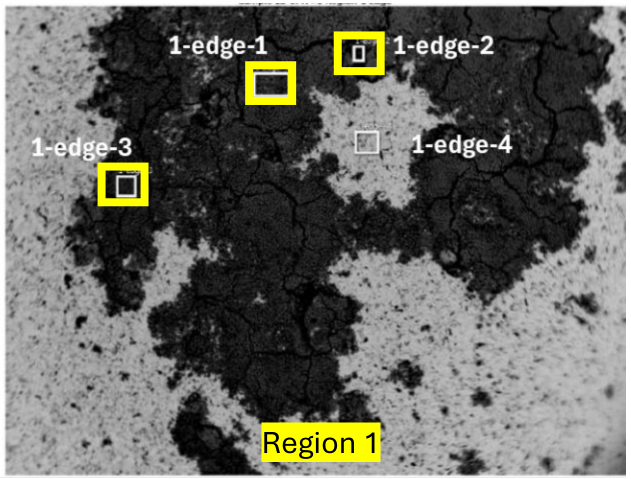
Results – Corrosion Rates

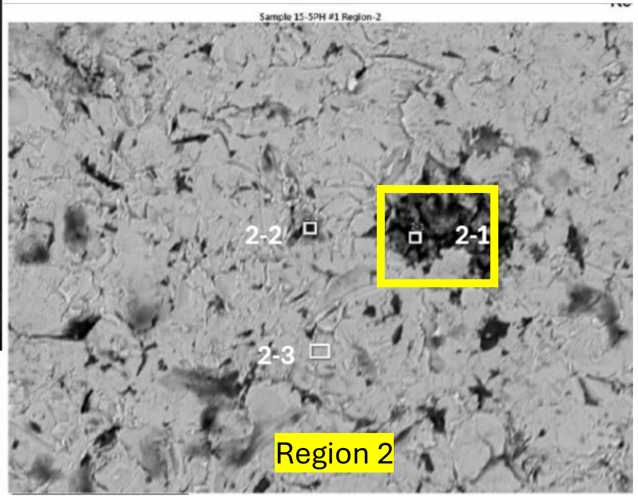
- Only S13Cr and 22Cr pass the generalized corrosion rate criteria (<0.05mm/year)

- From a pitting standpoint, only 22Cr met the minimum design criteria since all other metallurgies developed pits ranging from 1.0-1.3 mm/year.

Material	Average Corrosion Rate (mils/year)	Average Corrosion Rate (mm/year)	Average Pit/Crevice Depth (mils)	Average Pit/crevice growth rate (mils/year)
S13Cr	0.94	0.024	3.3	40.3
15-5PH	2.74	0.070	4.6	54.0
17-7PH	3.46	0.088	4.5	53.0
22Cr	0.80	0.020	-	-

Results – SEM-EDX (15-5PH)





Location	O	Cr	Fe	Ni	Cu
1-edge -1	29.2	31.0	4.1	3.1	20.8
1-edge -2	18.2	38.3	19.5	2.4	15.4
1-edge -3	31.8	30.9	0.6	3.6	21.0
1-edge -4	4.8	15.3	66.7	4.1	4.3

Higher Cu content detected in the film that coated the defect area

Cu-related second phase particles may have impeded re-passivation and accelerated localized corrosion

Location	O	Cr	Mn	Fe	Ni	Cu
2-1	3.0	15.0	0.7	7.1	21.4	44.7
2-2	6.1	15.6	0.7	60.0	4.9	4.8
2-3	2.5	15.1	0.8	72.2	4.4	3.5

Results – Spent Brine Analysis

- Initial pH (7.83) of formation brine was close to the final pH (7.03)
- Acidified (CO_2 mixed) brine pH was also comparable pre-test (4.42) and post-test (4.82)

Ionic Species	Pre-Test Composition (mg/L)	Post-Test Composition (mg/L)
Na^{+}	42,853	38,650
Mg^{+2}	1,600	1,392
Ca^{+2}	4,500	4,277
Fe^{+2}	-	28.1
Ni^{+2}	-	11
SO_4^{-2}	2,200	1,881
Cl^{-}	77,000	67,655
HCO_3^{-}	-	122

Concentration decreased suggesting salt/oxide deposition on metal coupons

Concentration increased suggesting dissolution from metal coupons

Ni provides pitting resistance but is not immune to dissolution into acidic brine (and accelerating pitting)

Bicarbonate formation likely buffered spent brine; may indicate longer exposure results in stronger buffering and lowering corrosion rates

Model-Lab Data Comparison

- Modeled as-tested stream in OLI to compare corrosion rates from model vs lab
  - Assumed a highly pessimistic (pH <3) case w/o any buffering
- Rates measured in the lab were noted to be an order of magnitude higher than those predicted by OLI for both corrosion rate and pitting depth rates
  - 30-day exposure test rates may average down over time (passivation, spent brine buffering)
- 15Cr and 17 Cr (as modeled in OLI) contained Mo while tested coupons did not which resulted in higher corrosion rates in lab
- Corrosion rates for 22Cr were extremely low as modeled and tested

Metallurgy	Corrosion Rate (mm/year)		Pitting rate (mm/year)	
	Model	Lab	Model	Lab
S13Cr	0.003	0.024	0.528	1.024
15Cr	0.002	0.070	0.130	1.372
17Cr	0.002	0.088	0.183	1.346
22Cr	0.001	0.020	0.046	0.000

Summary

- Corrosion modeling for project conditions
  - 13 chrome may be insufficient to withstand downhole corrosion in the modeled project setting
  - Higher grade chromium alloys (S13Cr, 15Cr, 17Cr, 22Cr) passed minimum design criteria
- Lab testing (ASTM G31)
  - S13Cr passed generalized corrosion criteria but exhibited crevice corrosion
  - Particle hardened martensitic steels like15Cr (15-5PH) and 17Cr (17-7PH) exhibited surprising results with higher corrosion rates than S13Cr → Likely due to lesser Mo content and higher Cu content
- Model-lab comparison
  - Rates were off by an order of magnitude with lab tests (30-day exposure) neglecting long-term buffering and passivation effects
- Duplex steel (2205) was qualified as the ideal metallurgy for this setting.

General Findings

- Establishing design criteria for CCUS tubulars requires more field tests and comparison with lab/modeled data sets and existing well construction standards
  - Current knowledge base points to a gap in establishing such criteria
- Corrosion models are empirically trained
  - Every project poses a new challenge and opportunity to re-train models
- Lab tests are subject to testing time limitations which do not fully capture passivation and buffering effects
- Higher Cr content may not translate to better corrosion resistance
  - Metals like Ni and Mo play a critical role in resisting localized corrosion
- Local defects in metals like elevated Cu content and their impact on accelerating corrosion needs to be studied further

References

- Craig, B., Rowe, A., Warmack, M., Doll, E., Stevens, C., and Connors, K., 2023. Guidelines for the selection of corrosion resistant alloys for CCS and CCUS injection wells. International Journal of Greenhouse Gas Control 129 (2023) 103988.
- Moreland, B.H., Dugstad, A., and Svenningsen, G., 2022. Experimental based CO2 transport specification ensuring material integrity. International Journal of Greenhouse Gas Control 119 (2022) 103697.
- Abu Bakar, M.A., Mohammad, W.A.W., Wahi, M.W.M., and Amir, M.S.E., 2021. Material Selection and Corrosion Rate Analysis for CO2 Injection Well: A Case Study of K1 Field CO2 Sequestration Project. Paper presented at the International Petroleum Technology Conference held virtually between 23 March – 1 April.
- OLI Systems, 108 American Road, Morris Plaines, New Jersey, 0795 0; www.olisystems.com.
- Zhang, Y. G. (2012). Modeling steel corrosion under supercritical CO2 conditions. Materials and Corrosion (63). doi:10.1002/maco.201106382
- I.S. Cole, D.A. Paterson, P. Corrigan, S. Sim, N. Birbilis, State of the aqueous phase in liquid and supercritical CO2 as relevant to CCS pipelines, Int. J. Greenhouse Gas Control, 7 (2012) 82.
- Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures - Parts I through IV. American Journal of Science.
- Tanger IV, J.C., 1986. Doctoral Thesis. Calculation of the Standard Partial Molal Thermodynamic Properties of Aqueous Ions and Electrolytes at High Pressures and Temperatures. University of California at Berkley.
- Wang, P., Anderko, A., Springer, R.D., Young, R.D., 2006. Modeling phase equilibria and speciation in mixed-solvent electrolyte systems: II. Liquid–liquid equilibria and properties of associating electrolyte solutions. Journal of Molecular Liquids 2006 125 (1), pp. 37-44.

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