# Corrosion Resistant Alloys in $CO_2$ Injection Wells for CCS and CCUS Projects

AADE Houston - IETG Meeting

1972 50th ANNIVERSARY 2022

Date: 19 January 2023

Presenter: Adam C. Rowe, PE
Principal
Metallurgical Engineer
Stress Engineering Services, Inc.

STRESS ENGINEERING SERVICES INC.® an employee-owned company

# Confidentiality

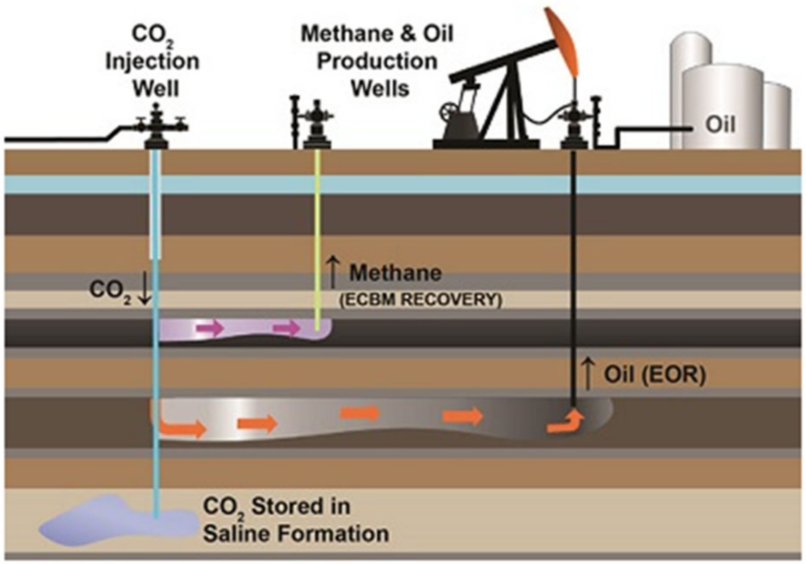
This presentation and the information contained herein is considered Confidential and Proprietary to Stress Engineering Services, Inc., and it is subject to copyright protection.

Any duplication or reproduction including, but not limited to, screenshots or video recording is strictly prohibited.

To request any information contained in this presentation, please contact: Adam Rowe at adam.rowe@stress.com.

# What is CCS and CCUS?

- Carbon capture and sequestration (CCS)
- Carbon capture utilization and storage (CCUS)
- This presentation will focus on $CO_2$ injection well metallurgy for storage wells




Source: https://netl.doe.gov/carbon-management/carbon-storage/faqs/carbon-storage-faqs

STRESS ENGINEERING SERVICES, INC.

# So What's the Problem?

- $CO_2$ pipelines have been successfully developed for many years without corrosion
- Pipelines are typically carbon steel
- No water → No corrosion
  - Carbon and low alloy steel okay
- Free water → Severe corrosion
  - CRAs needed
- Possible sources of water
  - Condensation
  - Formation water
  - Flowback

# Corrosion Assessment

- Major challenge → Limited data for many CRAs in SC-$CO_2$
- Can lean on related experience for guidance with significant limitations
  - Oil and gas production – No oxygen
  - Acid gas injection – Lower temperature, No oxygen
  - Seawater injection – Near neutral pH
  - $CO_2$ EOR
    - CCS wells are often deeper and hotter
    - CCS utilizes continuous injection, no WAG
    - CCS wells typically have longer design lives
    - CCS injectate may have additional contaminants



# Factors that Impact Corrosion in SC-$CO_2$

- Injectate composition and impurities in the SC-$CO_2$ stream
  - $H_2S$, $O_2$, $SO_x$, $NO_x$, $H_2$
- Water / water chemistry
  - No water → No corrosion
  - Fresh condensate → No buffering, no chlorides
  - Formation water → Buffering, chlorides
- Temperature
  - Important, but impact substantially dependent on other factors
  - Generally, higher temperature → higher corrosion rates to CRAs
- pH
  - Directly related to $CO_2$ pressure / fugacity
  - Generally, lower pH → higher corrosion rates

50th ANNIVERSARY
STRESS ENGINEERING SERVICES, INC.

# SC-$CO_2$ Stream Impurities

- Impurity contents vary substantially by source
- $H_2S$, $O_2$, $SO_x$, $NO_x$ of utmost interest for material selection
- Examples shown below, but many other sources and compositions exist
- These ranges are too broad for material selection criteria
  - Actual project stream specification needs to be considered

| Data Source | Industries | Typical Impurities |
|---|---|---|
| IPCC Special Report | Power Generation – Coal Fired Plants | 0-0.5% $SO_2$, 0-0.01% NO, 0-0.6% $H_2S$, 0.01-3.7% $N_2$/Ar/$O_2$ |
| IPCC Special Report | Power Generation – Gas Fired Plants | < 0.01% $SO_2$, < 0.01% NO, < 0.01% $H_2S$, 0.01-4.1% $N_2$/Ar/$O_2$ |
| Industry Experience | Natural Gas Processing | < 1% $H_2S$, < 10 ppm $O_2$ |
| Industry Experience | Ethanol plants | < 10 ppm H2S, < 2% $O_2$ |

# Effect of SC-$CO_2$ Stream Impurities

| Alloy | PREN (Typical) |
|---|---|
| 13Cr | 13 |
| 304 SS | 18 |
| 316 SS | 23 |
| 22Cr DSS | 36 |
| 25Cr SDSS | 42 |

- SOx and NOx
  - Sulfuric acid and/or nitric acid formation in water phase
    - pH reduction
  - When present together, $NO_2$ catalyzes oxidation of $SO_2$
- $H_2S$
  - Can promote cracking susceptibility
  - Has not been rigorously studied in SC-$CO_2$
  - ISO 15156 best available guideline
    - Based on experience in oxygen-free oilfield environments

Mixtures of $H_2S$ and $O_2$ can also form elemental sulfur!

- $O_2$
  - Dissolved oxygen in the water phase promotes susceptibility to pitting and crevice corrosion
  - Perhaps most significant difference between CCS and oil and gas production environments
  - PREN helpful tool for ranking stainless steels
    - *PREN = %Cr + 3.3 x (%Mo + 0.5%W) + 16 x %N*
    - *Relationship has not been established between PREN and corrosion resistance in SC-CO2 environments*
- Nitrogen ($N_2$) and Hydrocarbons not expected to influence material selection
  - Possible effects of Hydrogen ($H_2$) in CCS streams has not been explored and may warrant review

50th ANNIVERSARY STRESS ENGINEERING SERVICES, INC.

# Formation Water

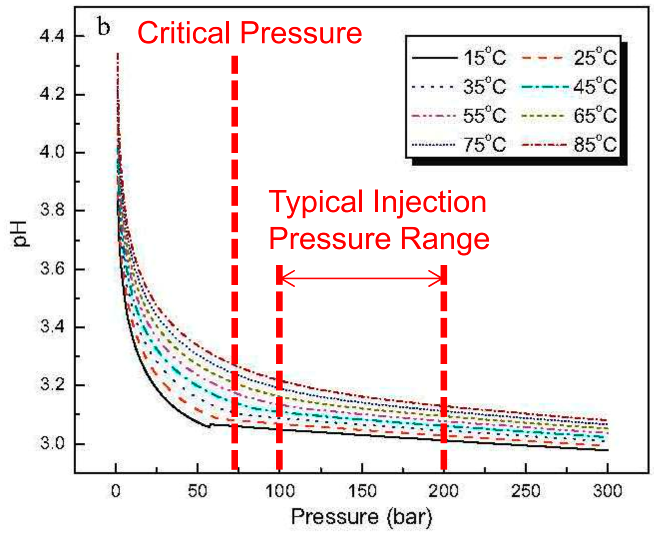
- For CRA selection, chloride is the critical constituent
- Chloride can vary substantially from formation to formation
  - Also sample to sample and test to test
- Ideally, material selection based on water analyses from several samples
- Sometimes preliminary recommendations are needed based only on estimated TDS
  - Conservative assumption is that TDS is entirely NaCl
- Formation water pH shown is ***BEFORE*** injection

| Species | Compiled by Zerai [CWRU, 2006] | | | | For Reference* |
|---|---|---|---|---|---|
| | Rose Run | Clinton | Mt. Simon | Grand Rapids | Typical Seawater |
| | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| $Na^+$ | 60,122 | 67,000 | 32,000 | 26,539 | 10,561 |
| $K^+$ | 3,354 | 850 | 1,060 | 636 | 380 |
| $Ca^{2+}$ | 37,600 | 23,200 | 12,400 | 2,737 | 400 |
| $Mg^{2-}$ | 5,881 | 1,840 | 2,190 | 533 | 1,272 |
| $HCO_3^-$ | 122 | 200 | 71 | 182 | 142 |
| $Cl^-$ | 191,203 | 160,400 | 78,700 | 47,549 | 18,980 |
| $SO_4^{2-}$ | 326 | 523 | 1,180 | 337 | 2,649 |
| $Sr^{2+}$ | 456 | 753 | 236 | - | 13 |
| pH | 6.4 | 6.5 | 6.7 | 7.2 | 8.2 |
| TDS | 277,571 | 250,000 | 150,000 | 90,000 | ~34,000 |

**Source: NACE Corrosion Engineer's Reference Book*

# pH Considerations

- As $CO_2$ pressure increases, the pH of present freshwater approaches 3
  - Can be demonstrated by modeling
- Adding as little as 100 ppm $SO_2$ can drop pH to 2.5
  - Recall that streams from coal-fired plants may have up to 5000 ppm $SO_2$
- These pH values are lower than most available corrosion data from oil and gas wells




Source: http://www.icmt.ohio.edu/documents/publications/8253.pdf

# pH Considerations (cont.)

- Injection plume models have predicted that the pH near the wellbore will remain low even after many years
- pH increases with distance from the wellbore due to dilution and buffering
- Monitoring wells may therefore see higher pH, and different metallurgy may be suitable

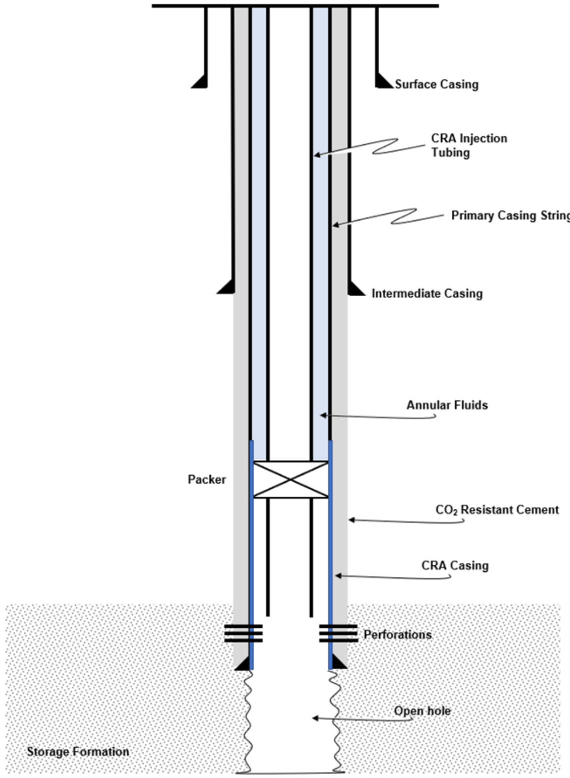
# Candidate Alloys – Many Options Available

- Casing and Tubing
  - Carbon and Low-alloy Steel
  - 13Cr/S13Cr
  - 15Cr/17Cr
  - 22Cr
  - 25Cr
  - Higher Cr options
  - Nickel-base (G3/2550/C22)
  - Titanium
- Packers and Tubing Hangers
  - Carbon and Low-alloy Steel
  - 22Cr and 25Cr – limited strength
  - PH Ni-base alloys
  - Titanium
- Wellheads/Trees
  - Low alloy steel – No water drop out
  - Class CC – Limited acceptable options
  - Class HH

STRESS ENGINEERING SERVICES, INC.

# How to Select?  Material Selection Philosophy

- Can exposure to water be reliably avoided over the life of the well?
  - If so, then carbon steel may be acceptable
  - Applies to non-wetted portions of the tree/wellhead and properly cemented casing above the packer
- Intermittent water warrants a risk assessment
  - Very corrosive when present
  - Balance equipment integrity against workover schedule
- Frequent or continuous water exposure requires CRA
  - Which CRA to choose?
  - Water from condensation or formation?
  - Cost typically increases substantially with corrosion resistance
  - Consultation with a Subject Matter Expert (SME) is needed




STRESS ENGINEERING SERVICES, INC.

# Martensitic Stainless Steels

- 13Cr, S13Cr, 15Cr, 17Cr
  - Strengthened by heat treatment, quenched and tempered
- 13Cr is commonly used in oil and gas production
  - AISI 420, L80 Type 13Cr
  - Available test data suggests that it is questionable for SC-$CO_2$, even without the presence of oxygen
- S13Cr
  - Alloyed with Mo for improved corrosion and cracking resistance
  - Better pitting resistance than 13Cr, but still limited in CCS environments
- 15Cr and 17Cr
  - No publicly available data in SC-$CO_2$
  - May be suitable in low $O_2$ – testing recommended
- Cracking resistance of these alloys has not been established at low pH expected in CCS when $H_2S$ is present
- Possible application in monitoring wells, but Subject Matter Expert review is recommended

# Duplex Stainless Steels

- 22Cr (e.g. SAF 2205, SM22CR, VM 22)
  - Good experience in oil and gas
  - Limited in $H_2S$ and $O_2$ bearing streams
- 25Cr (e.g. SAF 2507, SM25CR/CRW, VM 25S)
  - Exhibits some pitting resistance in dissolved oxygen
    - Demonstrated by good industry experience in offshore equipment and seawater injection
  - Critical pitting and crevice corrosion temperatures well established in saturated seawater and acidified ferric chloride
    - CCS limits not established
- Very limited CCS data available for 22Cr and 25Cr
- No public data for higher Cr DSS such as 3207
- Strengthened by cold-work, so may not be suitable for high strength hangers and packers with thick sections

CPT and CCT for Select CRAs in Seawater

| Alloy | CPT, °C | CCT, °C |
| --- | --- | --- |
| 304 SS | 2 | -15 |
| 316 SS | 10 | -10 |
| 22Cr DSS | 40 | 20 |
| 25Cr SDSS | 80 | 70 |

50th ANNIVERSARY STRESS ENGINEERING SERVICES, INC.

# Nickel Alloys

- Solid solution and cold-worked alloys for tubing and casing
  - Alloys 2535, G3, 2550, C276, C22
  - Tubulars may be offered in grades up to 125 ksi SMYS
- Precipitation-hardened (PH) alloys
  - Alloys 925, 718, 725, 625 Plus
  - Strengthened by heat treatment
  - PH nickel alloys may be needed for higher strength packers and hangers
- Almost no publicly available CCS data
  - Some CCS combinations of low pH, high T, and high $O_2$ may still be pitting risk

# Common Questions

- Will galvanic corrosion be a concern?
- Will this new alloy that my supplier is suggesting work for my well?
- What thread should we use for our downhole connections?
- What material requirements should we specify to the mill?

- Classic metallurgist response: “*It Depends!*” ¯_(ツ)_/¯

- These are all good questions that need to be carefully considered on a project-by-project basis with the input from subject matter experts from several disciplines

STRESS ENGINEERING SERVICES, INC.

# Other Considerations

- Injection rates
  - Consideration of critical erosional velocities
- Threaded connections
  - Gas-tight premium connections
  - Risk of low temperature event?
- Annular fluids
  - Typically halide brines with additive package including oxygen scavengers
  - Need to be compatible with CRA
  - Can become aggressive if comingled with $CO_2$ stream
- Acid jobs
  - Possible damage to equipment if not quickly circulated out
- Elastomers
  - Sealing elements used for production equipment may not be compatible in SC-$CO_2$
- Cements
  - Portland cement is not compatible with $CO_2$
  - Need $CO_2$-resistant cement for exposed portions of well

STRESS ENGINEERING SERVICES, INC.

# Final Thoughts on $CO_2$ Injection Well Metallurgy

- The information presented here is intended to bring attention to the parameters that need to be considered in material selection
- It is always recommended that material selection and procurement specifications be reviewed by a Subject Matter Expert prior to ordering equipment
- Free water is the most critical factor in a corrosion assessment, and standard steel construction is suitable so long as the water stays completely soluble in the supercritical $CO_2$ for the life of the well
- When free water is determined to be present, material selection should be reviewed by a Subject Matter Expert and should carefully consider the following:
  - The composition of the injectate and maximum allowable impurities in the stream
  - The composition of water in the injection zone, such as a saline formation
  - Maximum injection pressures and bottomhole temperatures

# Industry Needs as CCS Continues to Grow

- More corrosion data in SC-$CO_2$ environments
  - 2023 is expected to yield a large volume of new tests data
  - Temperature and impurity limits will need to be established for many CRAs
- Material selection guidelines
  - Currently, only a couple papers have been published touching on material selection guidelines for CCS injection wells
  - The PCOR Partnership and Stress Engineering have recently developed more comprehensive guidelines for CCS injections wells
    - Publication is in progress
- More field experience and case studies

# Thank You!