Material Considerations for Sour Gas Systems

Breakfast Club Event
Organized by Swagelok Oklahoma / West Texas

WebEx Presentation
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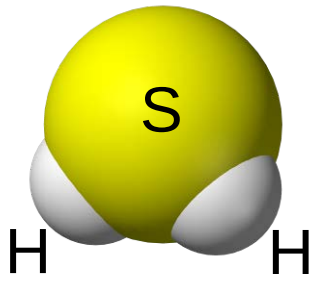
Sulfide stress cracking (SSC)



- Also known as sour gas cracking
  - Sour gas: hydrogen sulfide H_2S in unrefined fuels
  - H_2S: corrosive, toxic, flammable
  - Up to 20% H_2S in reservoirs of northern Caspian Sea
  - Aging reservoirs: sulfur compounds → H_2S
- Brittle failure by cracking under combined action of tensile stress and corrosion in the presence of water and H_2S
  - Metal + H_2S → Metal-sulfide + 2H
  - H-atom diffuses into metal
  - Special case of hydrogen embrittlement
- All materials susceptible to atomic hydrogen embrittlement are very susceptible to sulfide stress cracking

Higher risk of sulfide stress cracking

- Higher hardness, higher tensile strength
- Higher hydrogen ion concentration (lower pH-value)
- Higher H_2S partial pressure
- Higher total tensile stress (applied & residual)
- Lower temperature
- Longer exposure time

Selecting materials for sour gas service

- NACE Standard MR0175
- Standard Material Requirements Number 01, approved 1975
- Earlier title: Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment
- Last NACE revision: MR0175-2003
- 2003 NACE title: Metals for Sulfide Stress Cracking and Stress Corrosion Cracking Resistance in Sour Oilfield Environments

Selecting materials for sour gas service

- NACE MR0175/ISO 15156 (2003)
  - NACE standard is merged with ISO standard
- Title: Petroleum and natural gas industries – Materials for use in H_2S-containing environments in oil and gas production
- Part 1: General principles for selection of cracking-resistant material
- Part 2: Cracking-resistant carbon and low alloy steels, and the use of cast iron
- Part 3: Cracking-resistant CRA's (corrosion resistant alloys) and other alloys
- NACE MR0175/ISO 15156 revised in 2009 and 2015
  - No major changes

Selecting materials for sour gas service

- NACE MR0175/ISO 15156 standard addresses all mechanisms of cracking
  - sulfide stress cracking (H_2S)
  - stress corrosion cracking (Cl^-)
  - environmental cracking (synergistic, H_2S & Cl^-)
  - various hydrogen-induced cracking mechanisms

Important information in NACE standard

- Lists pre-qualified materials
  - Can be used without additional testing
  - Must have specific metallurgical characteristics (e.g., annealed)
  - Must meet property requirements (e.g., max. hardness)
- Identifies alloys by material groups or individual alloys
  - Within each group by materials type
- Refers to two types of applications
  - Components for general use
  - Components for downhole applications
- States environmental limits
  - H_2S partial pressure, temperature, chloride concentration, pH-value
    - Stricter limits for general use than downhole use

Alloy groups and types

Group #	Group Name	Type	Criterion	Typical Alloys
2	Austenitic Stainless Steels	n/a	≤0.08% C; ≥16% Cr; ≥8% Ni; ≤0.045% P; ≤0.04% S; ≤2.0% Mn; ≤2.0% Si	304, 316, 317, 321, 347
3	Highly Alloyed Aust. St. Steels	3a	(Ni + 2Mo) > 30% (with Mo ≥2%)	254 SMO, AL6XN
		3b	PREN > 40	
4	Solid Solution Nickel-Based Alloys	4a	≥19.0% Cr; ≥29.5% (Ni + Co); ≥2.5% Mo	825, 625, 276
		4b	≥14.5% Cr; ≥52% (Ni + Co); ≥12% Mo	276
		4c	≥19.5% Cr; ≥29.5% (Ni + Co); ≥2.5% Mo	825, 625
		4d	≥19.0% Cr; ≥45% (Ni + Co); ≥6% (Mo + W)	625, 276
		4e	≥14.5% Cr; ≥52% (Ni + Co); ≥12% Mo	276
7	Duplex Stainless Steels	a	30 < PREN < 40 (with Mo ≥ 1.5%)	2205
		b	40 < PREN ≤ 45	2507

Austenitic stainless steels (A.2)

---------- ANY EQUIPMENT ----------						
Material Requirements			**Environmental Limits**			
Heat treatment, microstructure, properties	Forming	Hard-ness	Max. temp-erature ºC (ºF)	Max. H2S partial pressure kPa (psi)	Max. chloride conc. mg/l	pH
solution-annealed and quenched, or annealed and thermally stabilized	free of cold work intended to enhance mechanical properties	22 HRC max.	60 (140)	100 (15)	no limit	no limit
			no limit	no limit	50	no limit
316, in as-above condition			93 (200)	10.2 (1.5)	5,000	≥ 5
316L, in as-above condition			149 (300)	10.2 (1.5)	1,000	≥ 4

There is no table for “Downhole Use” of these materials

Austenitic stainless steel fittings (A.4)

- Table A.4 allows use of 316 SS compression fittings
  - Material does not have to meet requirements of Table A2
    - Can be strain-hardened
  - No limits for temperature, H_2S partial pressure, chloride concentration, in situ pH
    - "…..some combinations of values of these parameters may not be acceptable."
  - Fittings can be used with instrument & control line tubing

- Pipe and weld fittings for use in "Any Equipment"
  - Material must be in solution-annealed delivery condition
  - Use "–SG" extension on Swagelok part number

Austenitic stainless steel (A.6)

---------- ANY EQUIPMENT ----------						
Material Requirements			**Environmental Limits**			
Heat treatment, microstructure, properties	Forming	Hard-ness	Max. temp-erature ºC (ºF)	Max. H2S partial pressure kPa (psi)	Max. chloride conc. mg/l	pH
solution-annealed and quenched, or annealed and thermally stabilized	free of cold work intended to enhance mechanical properties	22 HRC max.	no limit	no limit	no limit	no limit

For materials used in instrumentation and control devices, e.g., pressure gauges & transducers

Highly alloyed austenitic SS (A.8 & A.9)

	Material Requirements			Environmental Limits			
Group / Type (typical alloys)	Heat treatment, microstructure, properties	Forming	Hardness	Max. temperature ºC (ºF)	Max. H2S partial pressure kPa (psi)	Max. chloride conc. mg/l	
3a + 3b (254 SMO, AL6XN)	solution annealed			60 (140)	100 (15)	any	**ANY EQUIP-MENT (A8)**
				no limit	no limit	50	
3b (254 SMO, AL6XN)				121 (250)	700 (100)	5000	
				149 (300)	310 (45)		
				171 (340)	100 (15)		
3a + 3b (254 SMO, AL6XN)	must have been solution annealed	may have been cold worked	35 HRC max.	60 (140)	100 (15)	any	**DOWN-HOLE (A9)**
3b (254 SMO, AL6XN)				121 (250)	700 (100)	5000	
				149 (300)	310 (45)		
				171 (340)	100 (15)		

Fittings from highly alloyed austenitic SS

- Table A.11 allows use of compression fittings from highly alloyed austenitic stainless steel
  - Material to be of Type 3a or 3b (254 SMO, AL6XN)
  - No limits stated for temperature, H_2S partial pressure, chloride concentration, in situ pH
    - "…..some combinations of values of these parameters may not be acceptable."
  - Fittings can be used with instrument & control line tubing

- Pipe and weld fittings
  - NACE compliance to Table A.8 for "Any Equipment"
    - Requires solution annealed delivery condition
  - NACE compliance to Table A.9 for "Downhole Use"
    - Strain-hardened delivery condition allowed, 35 HRC max.

Conditions for nickel alloys (2003)

	Material Requirements			Environmental Limits			
Group / Type (typical alloys)	Heat treatment, microstructure, yield strength	Forming	Hardness	Max. temperature ºC (ºF)	Max. H2S partial pressure kPa (psi)	Max. chloride conc. mg/l	
4a (825, 625, 276)	solution-annealed or annealed			any combination of temperature, H2S partial pressure, chloride concentration and in situ pH			**ANY EQUIP-MENT**
4b (276)							
4c (825, 625)	≤ 1034 Mpa (150 ksi)	annealed and cold-worked	40 HRC max.	see standard			**DOWN-HOLE**
4d (625, 276)	≤ 1034 Mpa (150 ksi)						
4e (276)	≤ 1240 Mpa (180 ksi)						

Conditions for nickel alloys (Rev. 2005)

	Material Requirements			Environmental Limits			
Group / Type (typical alloys)	Heat treatment, microstructure, yield strength	Forming	Hardness	Max. temperature ºC (ºF)	Max. H2S partial pressure MPa (psi)	Max. chloride conc. mg/l	
4a (825, 625, 276)	solution-annealed or annealed			any	any	any	**ANY EQUIP-MENT (A13)**
4b (276)							
4c (825, 625)	≤ 1034 Mpa (150 ksi)	annealed and cold-worked	40 HRC max.	232 (450)	0.2 (30)	any	**ANY EQUIP-MENT (Corrig. 2005) (A14)**
				218 (425)	0.7 (100)		
				204 (400)	1 (150)		
				177 (350)	1.4 (200)		
				132 (270)	any		
4d (625, 276)	≤ 1034 Mpa (150 ksi)			218 (425)	2 (300)		
				149 (300)	any		
4e (276)	≤ 1240 Mpa (180 ksi)			232 (450)	7 (1000)		
				204 (400)	any		

Fittings from alloys 825, 625 and C-276

- Tube, pipe and weld fittings to Table A13 (“Any Equipment”)
  - Must be made from solution-annealed material
  - No limits for temperature, H_2S partial pressure, chloride concentration, in situ pH
- Tube, pipe and weld fittings to Table A14 (“Any Equipment”)
  - Can be made from strain-hardened material
    - Hardness 40 HRC max.
    - Tensile strength 150 ksi max. (825, 625), 180 ksi max. (C-276)
  - Limits for temperature and H_2S partial pressure
    - Higher temperature limit leads to lower H_2S limit
  - No limits for chloride concentration and in situ pH

Duplex stainless steels (A.24 & A.25)

	Material Requirements			Environmental Limits			
Group/ Type (typical alloy)	Heat treatment, micro-structure, properties	Forming	Hardness	Max. temperature ºC (ºF)	Max. H2S partial pressure kPa (psi)	Max. chloride conc. mg/l	
7a (2205)	solution-annealed and liquid quenched; 35% ≤ ferrite content ≤ 65%			232ºC (450ºF)	10 kPa (1.5 psi)	no limit	**ANY EQUIP-MENT (A24)**
7b (2507)					20 kPa (3psi)		
7a (2205)	solution annealed and liquid-quenched; 35% ≤ %ferrite ≤ 65%	may have been cold-worked	36 HRC max.	no limit	2 kPa (0.3 psi)	no limit	**DOWN-HOLE (A25)**
7b (2507)				no limit	20 kPa (3 psi)	120,000	

2507 tube fittings, any equipment, A.24

- Straight bodies
  - Machined from solution-annealed bar
- Forged bodies
  - Forgings in solution-annealed state
- Front ferrule
  - Made from cold-drawn bar
  - Nose under compression
    - Not subject to environmental cracking
- Nut, back ferrule
  - Made from cold-drawn bar
  - Not wetted by system fluid
- 2507-SG2 product data sheet: eDTR

2507-SG2

2507 weld & pipe fittings, any equ., A.24

- Machined from solution-annealed material
  - Bar
  - Forgings

2507 tubing meets NACE requirements

- Until recently, did **not** meet requirements
  - Standard required solution-annealing & water-quenching
  - Manufacturing process uses gas-quench method
- Now 2507 tubing **does** meet requirements
  - Standard was revised
  - ANSI/NACE MR0175/ISO 15156-3:2009/Cir.1:2011(E)
    - "Wrought and duplex stainless steels shall be solution annealed and liquid-quenched or rapidly cooled by other methods"