NACE MR0175/ISO 15156-3 Proposal for Change

SUBMITTING COMPANY: Weatherford

SUBMITTED BY: Robert Badrak

MAILING ADDRESS: 11909 Spencer Rd (FM 529), Houston, TX 77041

TELEPHONE NUMBER: 713-983-5308

E-MAIL ADDRESS: robert.badrak@weatherford.com

MATERIAL: 17-4PH stainless steel

UNS NUMBER (IF KNOWN): UNS S17400

SUGGESTED ALTERATION TO NACE MR0175/ISO 15156 (latest edition):

The proposed change is to add a note further limiting the application window of 17-4PH. The proposed change is in NACE MR0175 / ISO 15156-3 Table A.27.

The existing unchanged Table is shown below:

Table 1 — Environmental and materials limits for martensitic precipitation-hardened stainless steels used for wellhead and christmas tree components (excluding bodies and bonnets), valves and chokes (excluding bodies and bonnets) and packers and other subsurface equipment

Individual alloy UNS number	Temperature	Partial pressure H_2S p_{H_2S}	Chloride conc.	pH	Sulfur-resistant?	Remarks
	max. °C (°F)	max. kPa (psi)	max. mg/L			
UNS S17400	See "Remarks" column	3.4 (0.5)	See "Remarks" column	≥ 4.5	NDS[a]	Any combination of temperature and chloride concentration occurring in production environments is acceptable.
UNS S45000	See "Remarks" column	10 (1.5)	See "Remarks" column	≥ 3.5	NDS[a]	

For these applications, these materials shall also comply with the following.

a) Wrought UNS S17400 precipitation-hardening martensitic stainless steels shall have a maximum hardness of 33 HRC and shall have been heat-treated in accordance with either 1) or 2), as follows:

   1) double age-hardening process at 620 °C (1 150 °F):
      — solution-anneal at (1 040 ± 14) °C [(1 900 ± 25) °F] and air-cool or liquid-quench to below 32 °C (90 °F);
      — first precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F); and
      — second precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F).
   2) modified double age-hardening process
      — solution-anneal at (1 040 ± 14) °C [(1 900 ± 25) °F], then air-cool or liquid-quench to below 32 °C (90 °F);
      — first precipitation-hardening cycle at (760 ± 14) °C [(1 400 ± 25) °F] for 2 h minimum at temperature and air-cool or liquid-quench to below 32 °C (90 °F); and
      — second precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F).

b) Wrought UNS S45000 molybdenum-modified martensitic precipitation-hardened stainless steel shall have a maximum hardness of 31 HRC (equivalent to 306 HBW for this alloy) and shall have undergone the following two-step heat-treatment procedure:

   1) solution-anneal;
   2) precipitation-harden at (620 ± 8) °C [(1 150 ± 15) °F] for 4 h minimum at temperature.

[a] No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment.

The proposed Table is shown below:

Table 2 — Environmental and materials limits for martensitic precipitation-hardened stainless steels used for wellhead and christmas tree components (excluding bodies and bonnets), valves and chokes (excluding bodies and bonnets) and packers and other subsurface equipment

Individual alloy UNS number	Temperature max. °C (°F)	Partial pressure H_2S p_{H_2S} max. kPa (psi)	Chloride conc. max. mg/L	pH	Sulfur-resistant?	Remarks
UNS S17400	See "Remarks" column	3.4 (0.5)	See "Remarks" column	≥ 4.5	NDS[a]	See note b; the safe use limits on chloride and temperature have not been defined.
UNS S45000	See "Remarks" column	10 (1.5)	See "Remarks" column	≥ 3.5	NDS[a]	Any combination of temperature and chloride concentration occurring in production environments is acceptable.

For these applications, these materials shall also comply with the following.

a) Wrought UNS S17400 precipitation-hardening martensitic stainless steels shall have a maximum hardness of 33 HRC and shall have been heat-treated in accordance with either 1) or 2), as follows:

1) double age-hardening process at 620 °C (1 150 °F):
   - solution-anneal at (1 040 ± 14) °C [(1 900 ± 25) °F] and air-cool or liquid-quench to below 32 °C (90 °F);
   - first precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F); and
   - second precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F).

2) modified double age-hardening process
   - solution-anneal at (1 040 ± 14) °C [(1 900 ± 25) °F], then air-cool or liquid-quench to below 32 °C (90 °F);
   - first precipitation-hardening cycle at (760 ± 14) °C [(1 400 ± 25) °F] for 2 h minimum at temperature and air-cool or liquid-quench to below 32 °C (90 °F); and
   - second precipitation-hardening cycle at (620 ± 14) °C [(1 150 ± 25) °F] for 4 h minimum at temperature, then air-cool or liquid-quench to below 32 °C (90 °F).

b) Wrought UNS S45000 molybdenum-modified martensitic precipitation-hardened stainless steel shall have a maximum hardness of 31 HRC (equivalent to 306 HBW for this alloy) and shall have undergone the following two-step heat-treatment procedure:

1) solution-anneal;

2) precipitation-harden at (620 ± 8) °C [(1 150 ± 15) °F] for 4 h minimum at temperature.

[a] No data submitted to ascertain whether these materials are acceptable for service in the presence of elemental sulfur in the environment.

[b] The use of UNS S17400 is restricted to those applications where the sustained stress intensity is no more than 50% of the specified minimum yield strength (SMYS) or 380 MPa (55 ksi), whichever is less. The use of UNS S17400 is acceptable for wellhead components and valve components, such as stems, which are only subjected to higher stress intensity levels for very short periods of time during actuation or other field operations. The use of UNS S17400 is prohibited for components subjected to other or longer duration in-service stress intensities above 50% of the specified minimum yield strength (SMYS) or 380 MPa (55 ksi), whichever is less.

Justification based on Laboratory Testing:

(1) Historical data - Figure 2 below from R.R. Gaugh, Materials Performance (1977)

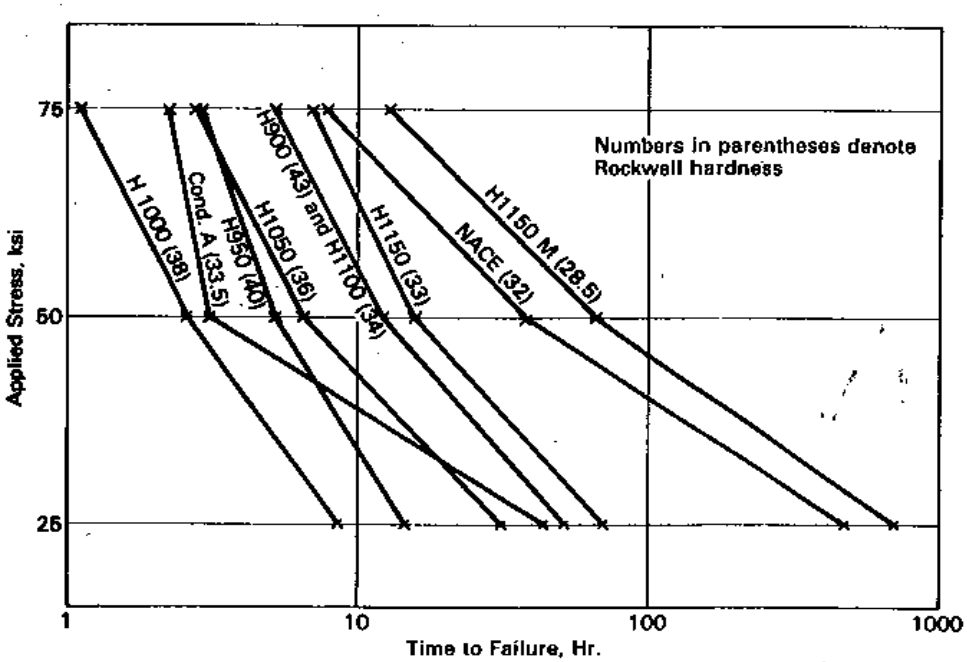

FIGURE 2 — Sulfide stress cracking of S17400. Numbers in parentheses denote Rockwell hardness.

Data shows failure at 600 hours for 25 ksi applied stress in NACE TM0177 test for UNS S17400 in the DH1150 condition. Note this is 1 bar H2S with 5% NaCl, 0.5% HAc with an unconfirmed but most likely pH in the 2.8 – 3.8 range.

(2) Historical data – Table 10 below from Corrosion 2003 Paper # 03102 (Cassagne et al).

TABLE 10
SSC TESTS IN 1G/L NACL UNDER 40 MBAR H_2S (0.6 PSI)
NUMBER OF FAILURES FROM 3 SAMPLES, AND TIME TO FAILURE (IN DAYS)

material	A		B		D	
pH	3.2	4.2	3.2	4.2	3.2	4.2
52 % SMYS*	0	NT**	2 (14, 18 d)	NT**	0	NT**
72 % SMYS*	3 (5, 5, 10 d)	0	1 (4 d)	2 (4, 6 d)	2 (6, 6 d)	0
90 % AYS	2 (< 3 d)	1 (4 d)	3 (< 3 d)	3 (<3, <3, 7 d)	3 (4, 4, 21 d)	2 (8, 15 d)

* SMYS = 724 MPa (105 ksi) ** NT = not tested

Data at 4.2 pH shows no failures at 52% of SMYS (724 MPa, 105 ksi) with 0.6 psi H_2S but failures at 72% SMYS.

(3) Historical Data – Tables 4 and 5 from Corrosion 2005 paper 05091 (Nice & Martin)

TABLE 4
ALLOY 17-4 PH A RESULTS FROM THE SSC TESTS

pH	NaCl	H_2S	Pass / Fail
3.5	1000 ppm	1%	Pass
3.5	1000 ppm	10%	Fail
4.0	1000 ppm	5%	Fail
4.5	1000 ppm	5%	Fail
4.5	20%	0.5%	Fail
4.5	20%	1%	Fail
5.0	20%	1%	Fail
5.0	20%	5%	Fail
5.5	20%	10%	Pass

TABLE 5
ALLOY 17-4 PH B RESULTS FROM THE SSC TESTS

pH	NaCl	H_2S	Pass / Fail
4.5	20%	5%	Fail
5.0	20%	0.5%	Fail
5.0	20%	1%	Fail
5.0	20%	10%	Fail

These results are with stress levels that are 90% of the AYS; the data demonstrates that there are no useful limits that can be recommended for this alloy in applications with very high sustained tensile loads (stress levels).

(4) Historical Data – Table, data extracted from Corrosion 2008 paper 08099 (Kane)

H2S	Chloride	pH	YS	Load	Results
1.5 psi	30000ppm	4.5	118 ksi	100% ays	fail
1.5 psi	30000ppm	5	118 ksi	100% ays	fail
0.15 psi	30000ppm	5	118 ksi	100% ays	fail

These results also demonstrate that high tensile stress levels cannot be used with this alloy in H_2S containing environments.

(5) New test data – see Tables below

Table 1: Testing parameters (720 hour tests)

series	Condition	Test temperature, °C	H_2S Concentration, psi	Stress Level, %SMYS	pH initial value	pH value after testing
1	As-received	25	0.5	50	4.54	4.58
				75	4.54	4.58
				100	4.54	4.59
2	Re-Heat treated	25	0.5	50	4.53	4.57
				75	4.53	4.57
				100	4.53	4.58

Table 2: Chemical Composition

C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Nb	Ta
0.041	0.38	0.73	0.019	0.001	15.98	0.10	4.46	3.31	0.265	0.009

Table 3: Material Properties

	Yield Strength, ksi	Tensile Strength, ksi	Elongation, %	RoA, %
As-received	135.2	148.6	19.5	53.2
Re-heat treated	119.8	147.6	19.6	55.6

Table 4: Test Results

series	Condition	Stress Level, %SMYS	Results

1	As-received	50	Pass – no cracks
		75	No cracks but small black pits noted
		100	Cracks observed
2	Re-Heat treated	50	Pass – no cracks
		75	No cracks but small black pits noted
		100	Cracks observed

The SMYS basis was 724 MPa (105 ksi) in the above tests. The results indicate that 50% SMYS was safe for the materials and conditions tested. Though the 75% SMYS tests actually passed since no cracks were detected, the presence of small black pits indicated a risk of cracking after longer (than 720 hrs) exposure periods.