MATERIALS OF CONSTRUCTION FOR NACE APPLICATIONS

In 1975, the National Association of Corrosion Engineers (NACE) issued a standard that provided materials recommendations for sour services (i.e. applications containing hydrogen sulfide). This standard, referred to as "NACE MR0175", listed acceptable materials, heat treatments and hardness limits for sour services. The standard was primarily developed for sour oilfield applications, but was also adopted by the oil refining industry. One major distinction between oilfield and refinery applications not addressed by NACE prior to 2003 is that oilfield applications tend to contain salt water or brine. The resulting high level of chlorides in these oilfield applications creates additional corrosion problems particularly for stainless steels.

To address this basic difference between the two applications, NACE essentially split the original MR0175 into two specifications in 2003. The new standard NACE MR0103-2003 entitled "Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Environments" is very similar to NACE MR0175 prior to 2003. It is used for refinery applications or for other sour services where no brine or salt water is present. This standard is detailed under NACE MR0103-2003 Applicability later in this bulletin.

For oilfield applications containing brine or salt water, the revised NACE MR0175-2003 should be used. This specification is now titled "Metals for Sulfide Stress Cracking and Stress Corrosion Cracking Resistance in Sour Oilfield Environments" and is clearly focused on oilfield production. In this environment, not only is hydrogen sulfide stress cracking a concern, but the presence of brine or salt water introduces the additional issue of chloride stress corrosion cracking. This revision is a drastic change from its predecessor. Many of the materials allowed previously are either no longer permitted or severely restricted in their use. The end user must know a variety of environmental factors in order to select appropriate materials of construction. These include: Hydrogen Sulfide concentration, total system pressure, application temperature, existence of elemental sulfur, and chloride content. The use of this standard is detailed under NACE MR0175-2003 Applicability later in this bulletin.

DEFINITIONS

Throughout this bulletin the following terms are used:

- **Mol % H_2S:** The Mol (abbreviation for mole) percentage represents the relative concentration of H_2S in a system by volume. The Mol % is directly equivalent to ppm by the following relation: 1 Mol % H_2S = 10,000 ppm (by volume) H_2S. It is important to note that Mol % is not the same as mass or weight percentage. To convert from a mass percentage of H_2S to a mole percentage of H_2S, the mass percentage of each constituent must first be divided by its molecular weight (in grams/mole). The molecular weight is a physical characteristic of a particular liquid or gas, and can often be found on the MSDS sheet for the substance. The resulting value of moles calculated for each constituent is then converted into a percentage by dividing by the total sum of moles calculated for all the constituents. Example 1 shows how Mol % H_2S is calculated for one application.
- **Psia:** Refers to Absolute Pressure in pounds per square inch. Equals Gage Pressure (psig) + 14.7.
- **Partial Pressure:** Equals the Total System Pressure (psia) multiplied by the Mol % H_2S divided by 100. Note that the charts are plotted with Total System Pressure (psia) on the y-axis and Mol % H_2S on the x-axis, with lines of constant partial pressure also shown. In order to use these charts, the user needs to know either the partial pressure of the application, or a combination of the total system pressure (psia) and the Mol % H_2S. In other words, if the total system pressure (psia) and the Mol % H_2S are known, the user does not need to calculate the partial pressure.

NACE MR0103 - 2003

Applicability

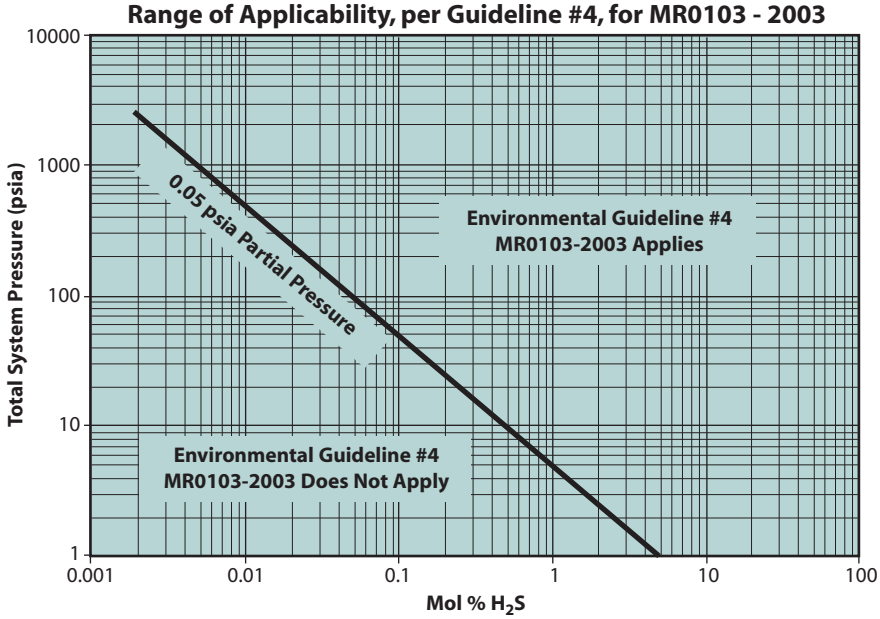
This standard applies to sour refinery applications and to other sour services where no brine or saltwater is present. The following paragraphs describe how to assist users in determining whether or not this specification is applicable for their application.

The standard is applicable if the application contains:

1. > 50 ppm by weight (**Note:** 50 ppmw = .005% weight concentration) dissolved Hydrogen Sulfide (H_2S) in free water (water in liquid phase), or
2. Free water with pH < 4 and some dissolved H_2S present, or
3. Free water with pH > 7.6 and 20 ppm (by weight) dissolved hydrogen cyanide (HCN) in the water and some dissolved H_2S present, or
4. Free water and > 0.05 psia partial pressure H_2S in the gas in processes with a gas phase.

Guideline #4 is illustrated in the chart below. Referring to the definition of partial pressure from page 1, recall that the user does not need to calculate this value if the total system pressure and the Mol % H_2S are known. In the latter case, the user could use this chart to determine if the application falls below or above the black 0.05 psia partial pressure line.

Range of Applicability, per Guideline #4, for MR0103 - 2003



The following example illustrates how to determine if MR0103 is applicable.

Example 1: *Determining Applicability of MR0103*

If my total system pressure is 1200 psia, the system pH is 6.5 and I have the following constituents in my application percentages by mass): 10% methane, 75% carbon dioxide, .0045% H_2S, .3% water and balanced nitrogen, how do I determine if NACE MR0103-2003 applies?

Example 1: *Solution*

First, the specification would not apply per the first 3 environmental conditions. The H_2S concentration is just below the level listed in environmental condition #1, and the pH is not an issue per conditions #2 and #3. Proceeding to the 4th condition, we must use the chart above. We first need to calculate Mol % H_2S:

Constituents	Mass % (A)	Molecular Weight (g/mole) (B)	# Moles (A/B)	Mol % # Moles/2.8688 * 100
Methane	10	16.044	0.6233	21.7262
Carbon Dioxide	75	44.01	1.7042	59.4028
Hydrogen Sulfide	0.0045	34.076	0.00013	0.0046
Water	0.3	18.0153	0.0167	0.5805
Nitrogen	14.696	28.0134	0.5246	18.2859
Total:	100		2.8688	100

The Mol % H_2S was found to be .0046%. We know that the total pressure is 1200 psia. Referring to the chart, this application is just above the boundary line. To be sure, we can calculate the partial pressure as .0046/100 * 1200 = .055 psia, which is greater than 0.05 psia. As a result, NACE MR0103-2003 would apply per guideline #4.

Acceptable Materials of Construction for NACE MR0103-2003		
Material	**Cast or Wrought**	**Restrictions**
Carbon Steel		
ASTM A216 Gr. WCB	Cast	22 HRC Max
Ductile Iron		
ASTM A395	Cast	When API, ANSI, and/or other industry standards approve its use
Austentic Stainless Steels		
ASTM A351 CF8M	Cast	22 HRC Max; Solution annealed
ASTM A351 CG8M	Cast	22 HRC Max; Solution annealed
ASTM A351 CF3M	Cast	22 HRC Max; Solution annealed
ASTM A351 CN7M	Cast	22 HRC Max; Solution annealed
S31600 (316)**	Wrought	22 HRC Max; Solution annealed
S31700 (317)**	Wrought	22 HRC Max; Solution annealed
S31603 (316L)**	Wrought	22 HRC Max; Solution annealed
N08020 (Alloy 20)**	Wrought	22 HRC Max; Solution annealed
S20910 (Nitronic 50)	Wrought	35 HRC Max; Solution annealed; Hot-rolled or cold-worked condition
Highly Alloyed Austentic Stainless Steels		
ASTM A351 CK-3MCuN	Cast	35 HRC Max; Solution annealed
S31254	Wrought	35 HRC Max; Solution annealed
Precipitation Hardenable Stainless Steels		
S17400	Wrought	33 HRC Max; H1150M condition
Nickel Alloys		
ASTM A494 M35-1	Cast	35 HRC Max
N10276	Wrought	35 HRC Max; Solution annealed
N05500	Wrought	35 HRC Max; Hot-worked and age-hardened, or solution annealed, or solution annealed and age-hardened
N07718	Wrought	35 HRC Max; Solution annealed or hot-worked or hot-worked and aged
N07718	Wrought	40 HRC Max; Solution annealed and aged

** Free of cold work that enhances mechanical properties

NACE MR0175 - 2003

Applicability

This standard applies to sour oilfield applications containing brine or salt water. The following paragraphs describe how to assist users in determining whether or not this specification is applicable for their application.

As with MR0103, MR0175-2003 always applies for applications containing water as a liquid with H_2S partial pressures equal to or greater than 0.05 psia.

This is shown in the chart below. Again, the user does not need to calculate partial pressure if the total system pressure and the Mol % H_2S are known. In the latter case, the user could use this chart to determine if the application falls below or above the black 0.05 psia partial pressure line.

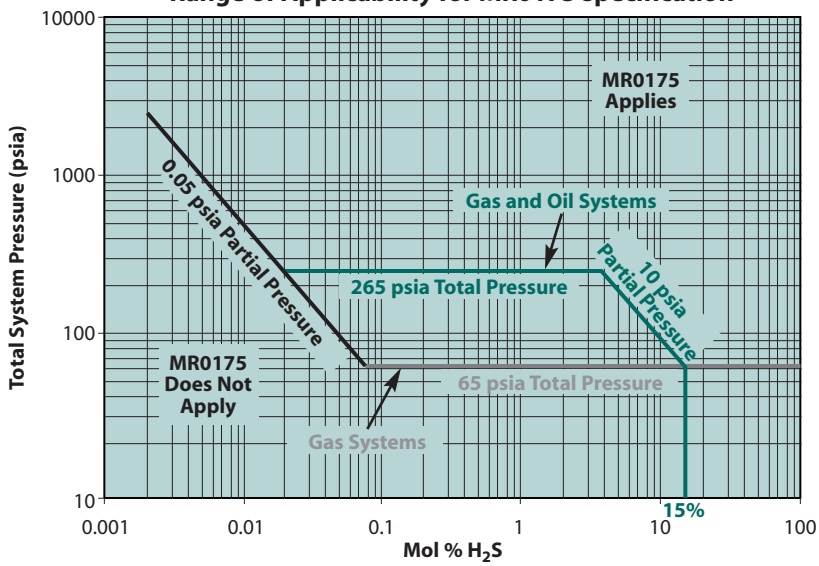
MR0175-2003 also has some situations where it does not apply. These specific cases are:

Gas Systems, if:
Total System Pressure < 65 psia
(Below the grey line on chart)

Gas and Oil Systems, if:
Total System Pressure < 265 psia,
and Partial Pressure < 10 psia,
and Mol % H_2S < 15
(Below and inside the blue line on chart)

Refer to example 1 on page 2 for an example showing how to determine the Mol % H_2S and the partial pressure of a system.

Range of Applicability for MR0175 specification



Determining Materials of Construction

After confirming that NACE MR0175-2003 is applicable for a given application, the following information is required in order to select materials of construction:

- H_2S Mol %
- Total system pressure
- Application temperature
- Existence of elemental sulfur
- Chloride content

} Or Partial Pressure (as discussed above)

Use the chart below to determine the appropriate zone for the application based on the total system pressure and the Mol % H_2S. Once the appropriate zone is determined, select the material combination from Tables 1 and 2 for Butterfly Valves and Tables 3 and 4 for Ball Valves.

The material options are denoted Tier 1, Tier 2 and Tier 3. Note that the Tier 1 combination is the least expensive option, Tier 2 is moderately priced, and Tier 3 is the most expensive. The user should select the appropriate materials of construction for an application.

Examples 2 and 3 illustrate how these graphs and tables are used to select the appropriate materials of construction for an application.

It is important to note that for some MR0175-2003 acceptable materials, the hardness and heat treatment requirements may be different from the same materials listed in MR0103-2003. Review the material requirements listed in this section carefully.

Application Zones for Butterfly and Ball Valve Usage

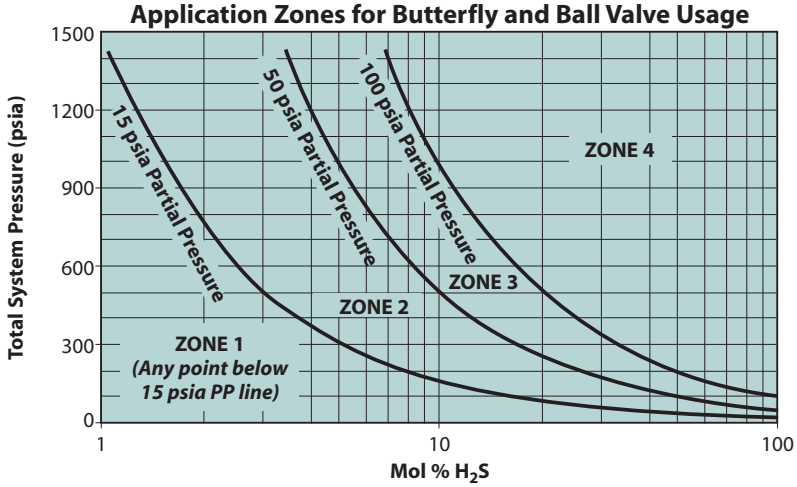


Table 1: Butterfly Valve Tier Selection for Zones 1 – 4
from Application Zones for Butterfly and Ball Valves chart on page 4 (Refer to Table 2 for Tier Definitions)

	Tier 1			Tier 2	Tier 3
	Max Temp	Elemental Sulfur	Max Cl Content		
Zone 1	140˚F	Not Allowed	No Limit	No Elemental Sulfur No Other Restrictions	No Restrictions
Zone 2	No Limit	No Limit	50 mg/L	No Elemental Sulfur No Other Restrictions	No Restrictions
Zone 3 & Zone 4	Not Permitted			No Elemental Sulfur No Other Restrictions	No Restrictions

Table 2: Tier Definitions for Butterfly Valves

	Tier 1	Tier 2	Tier 3
Body*	ASTM A216 WCB 22 HRC Max	ASTM A216 WCB 22 HRC Max	ASTM A216 WCB 22 HRC Max
Disc	ASTM A351 CF8M Solution Annealed 22 HRC Max	ASTM A351 CK-3MCuN Solution Annealed 100 HRB Max	ASTM A494 CW-12MW Solution Annealed 52% (Ni + Co) Min
Shaft	S20910 (Nitronic 50) Solution Annealed and Cold Worked; 35 HRC Max	S20910 (Nitronic 50) Solution Annealed and Cold Worked; 35 HRC Max	S20910 (Nitronic 50) Solution Annealed and Cold Worked; 35 HRC Max

* Disc material may be substituted for body material.

Table 3: Ball Valve Tier Selection for Zones 1 – 4
from Application Zones for Butterfly and Ball Valves chart on page 4 (Refer to Table 4 for Tier Definitions)

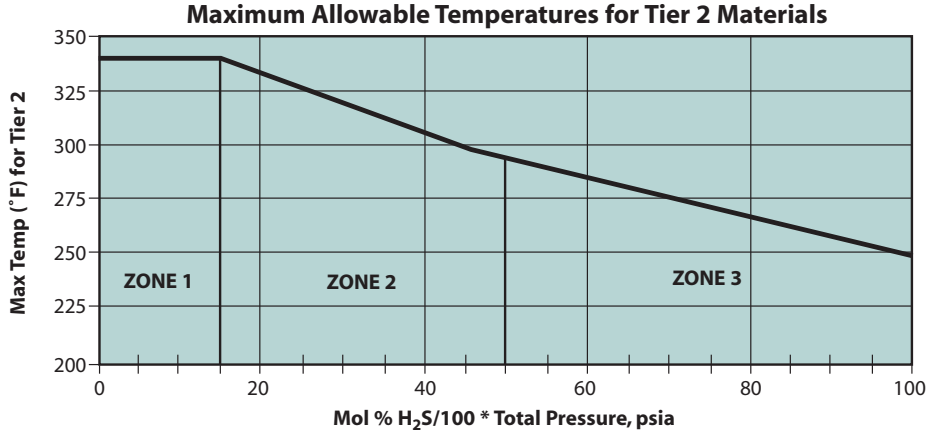
	Tier 1			Tier 2			Tier 3
	Max Temp	Elemental Sulfur	Max Cl Content	Max Temp	Elemental Sulfur	Max Cl Content	
Zone 1	140˚F	Not Allowed	No Limit	340˚F	Not Allowed	5000 mg/L	No Restrictions
Zone2	No Limit	No Limit	50 mg/L	Per Chart Below	Not Allowed	5000 mg/L	No Restrictions
Zone 3	Not Permitted			Per Chart Below	Not Allowed	5000 mg/L	No Restrictions
Zone 4	Not Permitted			Not Permitted			No Restrictions

Table 4: Tier Definitions for Ball Valves

	Tier 1	Tier 2	Tier 3
Body*	ASTM A216 WCB 22 HRC Max	ASTM A216 WCB 22 HRC Max	ASTM A216 WCB 22 HRC Max
Ball	ASTM A351 CF8M or ASTM A479 S31600** Solution Annealed 22 HRC Max	ASTM A351 CK-3MCuN Solution Annealed 100 HRB Max or ASTM A479 S31254 Solution Annealed	ASTM A494 CW-12MW or ASTM B574 N10276 Solution Annealed 52% (Ni + Co) Min
Stem	ASTM A479 S31600** Solution Annealed 22 HRC Max	S20910 (Nitronic 50) Solution Annealed and Cold Worked; 35 HRC Max	S20910 (Nitronic 50) Solution Annealed and Cold Worked; 35 HRC Max

* Ball material may be substituted for body material.
** Free of cold work that enhances mechanical properties.

Maximum Allowable Temperatures for Tier 2 Materials



Example 2: *MR0175 Materials of Construction for Butterfly Valves*

My application contains 2 Mol % H_2S @ 1200 psia. What materials of construction should I use for a butterfly valve if my application temperature is 300˚F, I have no elemental sulfur, and my chloride content is 1000 mg/L?

Example 2: *Solution*

We first refer to the **Application Zones for Butterfly and Ball Valves** chart on page 4. We find that the point comprised by 2 Mol % H_2S and 1200 psia appears to fall just above the green line into Zone 2. To confirm this, we simply calculate the partial pressure as 2/100 * 1200 = 24 psia, and we do find that the point falls above the 15 psia partial pressure boundary line.

We then go to Table 1, where we see that we have 3 material combination options depending on the application temperature, the presence of elemental sulfur and the chloride content. Tier 1 has no requirements on temperature and elemental sulfur, but the maximum chloride content allowed is 50 mg/L. Since our chloride content is 1000 mg/L, we cannot use Tier 1.

We next look at Tier 2, where we see that the only requirement is that there is no elemental sulfur in the system. Since we comply with this requirement, we can use Tier 2 for this application. Tier 3 may also be used for this application, since there are no restrictions on its use, however Tier 2 would be the most cost-effective option.

Example 3: *MR0175 Materials of Construction for Ball Valves*

For the application in Example 2, what materials of construction would I use for a ball valve?

Example 3: *Solution*

From Example 2, we know that our first step is to refer to the **Application Zones for Butterfly and Ball Valves** chart on page 4, and we know that for this application we fall into Zone 2.

We then go to Table 3 for ball valves, and look across the Zone 2 row at the material combinations available. To use Tier 1, the chloride content must be less than 50 mg/L. Since our application has 1000 mg/L, we cannot use this option.

Tier 2 has three requirements, that the maximum temperature adheres to the **Application Zones for Butterfly and Ball Valves** chart on page 4, that there is no elemental sulfur, and the chloride content is less than 5000 mg/L. For our application, we have no elemental sulfur and the chloride content is 1000 mg/L, but we do need to check the **Maximum Allowable Temperatures for Tier 2 Materials** chart on page 5 to determine whether our temperature complies with the requirements. At 2 Mol % H_2S and 1200 psia, the x-axis value in the **Application Zones for Butterfly and Ball Valves** chart is computed as 0.02 * 1200 = 24 psia. For this x-axis value, the maximum allowable temperature for Tier 2 is approximately 325˚F. Since our temperature is 300˚F, we comply with this requirement and also comply fully with the requirements for Tier 2.

Tier 3 may also be used since there are no restrictions on its use, however it is more cost-effective to use the lower Tier numbers whenever possible.

Metso Automation Inc.

Europe, Levytie 6, P.O. Box 310, 00811 Helsinki, Finland.
Tel. +358 20 483 150. Fax +358 20 483 151

North America, 44 Bowditch Drive, P.O. Box 8044, Shrewsbury, MA 01545, USA.
Tel. +1 508 852 0200. Fax +1 508 852 8172

Europe, 6-8 rue du Maine, 68271 Wittenheim Cedex, France.
Tel. +33 (0)3 89 50 64 00. Fax +33 (0)3 89 50 64 40

South America, Av. Independéncia, 2500- Iporanga, 18087-101, Sorocaba-São Paulo
Brazil. Tel. +55 15 2102 9700. Fax +55 15 2102 9748/49

Asia Pacific, 238A Thomson Road, #25-09 Novena Square Tower A, 307684 Singapore.
Tel. +65 6511 1011. Fax +65 6250 0830

China, 19/F, the Exchange Beijing, No. 118, Jianguo Lu Yi, Chaoyang Dist, 100022 Beijing, China.
Tel. +86-10-6566-6600. Fax +86-10-6566-2575

Middle East, Roundabout 8, Unit AB-07, P.O. Box 17175, Jebel Ali Freezone, Dubai,
United Arab Emirates. Tel. +971 4 883 6974. Fax +971 4 883 6836

www.metso.com/automation

metso