



# Providing solutions for the most critical sour environments

Today, we are often confronted with extreme corrosive conditions in "Sour Service" environments. These can be due to high concentrations of Hydrogen Sulfides (H<sub>2</sub>S), as found in certain extremely sour fields in the Middle East and central Asia; or to the presence of H<sub>2</sub>S in high pressure environments, such as ultra deep wells, HP/HT fields in the Gulf of Mexico and the North Sea, the pre-salt fields of Brazil and Africa, the Arctic fields in Canada and so on, all face the challenges of extreme corrosive conditions. Vallourec has developed and continues to develop a full range of Sour Service grades for OCTG to support Oil & Gas companies, providing solutions for the most critical conditions.

# → Research & Development

Our ambition is to provide innovative solutions for our customers.

- > 3 international R&D centers dedicated to OCTG developments
- > Permanent membership of international research institutes for corrosion, fatigue and creep testing
- > Participation to JIPs for Sour Service developments
- > Extensive database of NACE test results
- > Unique hot-rolling laboratory for new material development

# **Vallourec Quality Assured**

## Worldwide presence

- Production facilities in Europe, North America, South America, the Middle East, Asia and China
- Optimized production routes to offer shorter lead times and cost effective solutions

## Metallurgy

- > Fully integrated steel production process from raw material to finished products
- > New metallurgy concept for superior corrosion performance:
  - Low sulfur and phosphorous content
  - Homogeneous fine grained steel microstructure
  - Improved size and nature of precipitates
- > Advanced grades for superior mechanical properties

#### **Expertise**

- Internal corrosion laboratory with extensive database of NACE test results
- In-depth metallurgical expertise to offer material qualification testing in special conditions
- > Know-how to propose tailor-made cost effective solutions

## In-house testing

- > NDE inspection
- Ultra sonic phased-array technology

# **Operational Challenges**

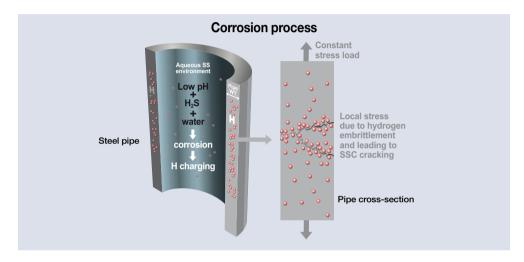
Sour Service refers to well environments containing Hydrogen Sulfides (H<sub>2</sub>S), which is naturally associated with acidic conditions. Even if not sour at the onset, some wells become sour over time.

The physical phenomenon associated with "Sour Service" environments is known as Sulfide Stress Cracking (SSC). It will appear when 3 different types of activating factors are combined together:

- > Environmental: temperature, pH, H<sub>2</sub>S partial pressure (ppH<sub>2</sub>S)
- > Material: mechanical properties and microstructure
- > Stress loading: external and internal stress

 $H_2S$  in combination with water and low pH will release free hydrogen. Due to its small sizes the hydrogen particles are absorbed by the material and interact with the steel which becomes brittle (embrittlement). Under unfavorable combination of all these factors, a crack can initiate in the material and propagate until catastrophic failure.

It is important to note that these crack failures can occur with stresses below the elastic limit of the material.



# → Material testing

Testing standards and methodologies for Sour Service environments are defined in NACE TM0177. It defines and normalizes four test methods (from A to D), methods A and D are most commonly used. These two tests are complementary as they assess the material resistance against crack initiation as well as crack propagation under H<sub>2</sub>S containing environments.

➤ NACE A test objective is to determine the risk of crack initiation during the first 720 hours (30 days) of testing. A smooth cylindrical tensile specimen is emerged into H₂S containing environment with a constant applied load (commonly 80% or 85% of Specified Minimum Yield Strength SMYS for API grades and 90% of SMYS for Vallourec proprietary grades).

➤ NACE D test objective is to determine fracture toughness of the material in H₂S containing environment by using Double Cantilever Beam (DCB) specimen. The test provides a critical stress intensity factor value (K₁ssc); it represents the material's resistance to crack propagation. This factor is used today for well design based on fracture mechanics theory. Acceptance criterion defines the minimum acceptable value for K₁ssc for each Product Specification (grade). The standard test duration is 336h (14 days).



NACE A testing



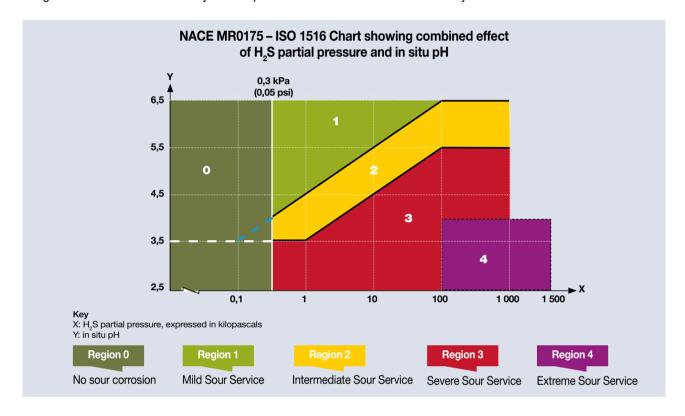
NACE D testing

## Sour Service standards and guidelines for OCTG

The National Association of Corrosion Engineers (NACE) together with the International Organization for Standardization (ISO) as well as European Federation of Corrosion (EFC) work together to provide guidelines for material selection and testing methodologies for use in H<sub>2</sub>S-containing environments for oil and gas production.

# → H<sub>2</sub>S Partial Pressure

Taking into account the combined effects of H<sub>2</sub>S partial pressure and in situ pH, NACE MR0175 – ISO 15156-2 identifies 4 regions of environmental severity with respect to the SSC of carbon and low-alloy steels.



According to Table 1 from NACE MR0175 / ISO 15156-2 standard, testing condition for SSC region 3 qualification is defined to 100kPa (1 bar). In reality however, certain environments can be more severe, combining low pH level (pH < 4) with higher H<sub>2</sub>S pressures.

Vallourec has defined this SSC domain as Extreme Sour Service and named it Region 4.

**Vallourec's new VM110XS grade has been specifically developed for extreme Sour Service.** Fully tested and qualified for the highest H<sub>2</sub>S pressure, up to 1500kPa (15bar) in full H<sub>2</sub>S environment, with NACE-A SSC testing at 90% AYS), this premium high strength carbon steel grade is ideally suited for Region 4 domain.

# → Temperature

Temperature is another environmental factor which influences the embrittlement phenomenon.

Although high temperature, associated with HP/HT wells, reduces the risk of hydrogen embrittlement, the risk for HP/HT actually lies at the top of the well, where pressure is still high, but temperature has decreased due to thermal losses, thus activating sulfide stress cracking (SSC).

The impact of low temperature on material selection also needs to be considered in the event of a well shut-in.

OCTG materials according to API 5CT/ISO 11960 are qualified by NACE MR0175 – ISO 15156-2 for  $H_2S$  environments as a function of temperature.

Vallourec Sour Service grades are available in minimum yield strengths ranging from 80Ksi to 125Ksi

## Vallourec's solution - Sour Service grades

Vallourec designs Sour Service grades for oil and gas operations in environments containing H<sub>2</sub>S. Our proprietary grades present improved corrosion resistance when compared to standard API grades by carefully designing and controlling the following parameters from the steel production, hot rolling, precise heat-treatment through to NDT control:

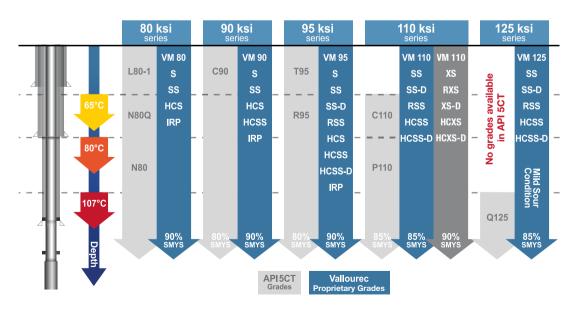
- > Cleanliness: to avoid inclusion and segregation
- > Grain size: Fine martensitic microstructure (finer than ASTM 7)
- > Homogeneous microstructure: fine and controlled precipitation level to enhance hydrogen trapping
- > Stability: Complete release of quenching stresses

Our OCTG product dimensional range is from OD of 2 3/8" to 26" with wall thickness above 2.3".

# Our Sour Service range of proprietary grades is composed of 5 series:

- **>** S series: standard Sour Service production route and qualified at region 3 according to NACE MR0175/ ISO 1516-2 standard Annex B Table A.3. SSC resistance is proven by mill quality record (PCP) implementation which allows for shorter lead time.
- **> SS series:** enhanced API grades, qualified at region 3 according to NACE MR0175/ISO 1516-2 standard Annex B Table A.3. showing better SSC resistance under applied stress, proven by NACE method A testing.
- **XS series:** enhanced Proprietary grades qualified for extreme sour application (SSC region 4) showing better SSC resistance, when compared to SS series, proven by NACE method A testing.
- **SS-D series:** enhanced API grades showing better SSC resistance proven by NACE method D testing.
- > IRP series: enhanced SS grade compliant with IRP standard proven by both NACE method A and method D testing.

# → Our sour service grades are available in minimum yield strengths ranging from 80Ksi to 125Ksi



# **Sour Service Resistance**

VALLOUREC PROPRIETARY GRADE			VM 80	VM 90	VM 95	VM 100	VM 110	VM 125
DOMAIN OF SSC RESISTANCE (*)			Region 3 at 90 % AYS / NACE sol. A	Region 3 at 90 % AYS / NACE sol. A	Region 4 at 90 % AYS / NACE sol. A	Region 4 at 90 % AYS / NACE sol. A	SS/SS-D: Region 3 at 80 % AYS / NACE sol. A XS: Region 4 at 90 % AYS / NACE sol. A	0,03 bar ppH <sub>2</sub> S / initial pH 3,5 at 90 % AYS NACE sol. A for method D
YIELD STRENGTH (KSI)  min  max		80	90	95	100	110	125	
		max	95	105	110	110	120	135
TENSILE STRENGTH (KSI)		min	95	100	105	105	115	130
S SERIES	Hardness (HRC)	reading	23.0	26.0	27.0	-	-	-
		average	22.0	24.0	25.0	-	-	-
SS SERIES	Hardness (HRC)	reading	23.0	26.0	27.0	27.0	31.0	36.0
		average	22.0	24.0	25.0	25.4	29.0	34.0
	NACE A SSC QA/QC	% of SMYS	90	90	90	85	85	85
XS SERIES	Hardness (HRC)	reading	-	-	-	-	31.0	-
		average	-	-	-	-	29.0	-
	NACE A SSC QA/QC	% of SMYS	-	-	-	-	90	-
SS-D SERIES	Hardness (HRC)	reading	-	-	27.0	27.0	31.0	36.0
		average	-	-	25.4	25.4	29.0	34.0
	NACE-D K <sub>1ssc</sub> (MPa√m)	reading	-	-	33.0	30.0	24.2	16.0
		average	-	-	36.0	33.0	26.4	18.0
IRP SERIES	Hardness (HRC)	reading	23.0	25.4	25.4	-	-	-
		average	22.0	25.0	25.0	-	-	-
	NACE A SSC QA/QC	% of SMYS	90	90	90	-	-	-
	NACE-D K <sub>1SSC</sub> (MPa√m)	reading	29.7	29.7	29.7	-	-	-
		average	33.0	33.0	33.0	-	-	-

(\*) as per domain of severity of NACE MR0175/ISO 1516-2 standard figure 1 and qualified according to Annex B Table A.3



Fully integrated steel production process

- > Customer well service conditions: Vallourec has large knowledge of qualification testing accumulating a large experience and data base on specific field conditions.
- ➤ All Sour Service grades are offered with high collapse and riser properties. Dedicated product specifications can be designed according to customer requirements.

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