Vallourec Steel grades for Sour Service

SOUR SERVICE
S series
SS series
SS-D series
HCS series
HCSS series

HIGH COLLAPSE
13CR/SUPER13CR
### Sour Service Grades

<table>
<thead>
<tr>
<th>Size</th>
<th>OD</th>
<th>Wall Thickness</th>
<th>Yield Strength</th>
<th>Ultimate Strength</th>
<th>Hardness</th>
<th>Method A</th>
<th>Method D</th>
<th>HRC</th>
<th>QCC provided</th>
<th>Color Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4”</td>
<td>16.8</td>
<td>20.7</td>
<td>454</td>
<td>645</td>
<td>81</td>
<td>129</td>
<td>129</td>
<td>129</td>
<td>VM 90 S</td>
<td>-</td>
</tr>
<tr>
<td>1”</td>
<td>21.2</td>
<td>30.5</td>
<td>600</td>
<td>800</td>
<td>105</td>
<td>166</td>
<td>166</td>
<td>166</td>
<td>VM 90 S</td>
<td>-</td>
</tr>
<tr>
<td>1 1/2”</td>
<td>26.8</td>
<td>36.8</td>
<td>800</td>
<td>1070</td>
<td>139</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>VM 90 S</td>
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</tr>
<tr>
<td>2”</td>
<td>34.5</td>
<td>41.9</td>
<td>1100</td>
<td>1470</td>
<td>198</td>
<td>316</td>
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** VM 90 S and VM 110 SS-D follow the QA/QC philosophy of T95

### High Collapse & Sour Service Grades

<table>
<thead>
<tr>
<th>Size</th>
<th>OD</th>
<th>Wall Thickness</th>
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<th>Hardness</th>
<th>Method A</th>
<th>Method D</th>
<th>HRC</th>
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<td>VM 90 S</td>
<td>-</td>
</tr>
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</table>

** VM 90 S and VM 110 SS-D follow the QA/QC philosophy of T95
**Sour Service in OCTG**

“Sour Service” refers to a well environment containing Hydrogen Sulfide (H₂S), which is naturally associated with acidic conditions. H₂S comes from the decomposition of organic material, so that it is often found in oil & gas environments which derive from the same phenomenon. Even if not sour at the onset, some wells become sour over time, as (H₂S) bearing formation water starts to flow together with oil.

It is well known that H₂S is a hazard to human health, living organisms, and more generally to the environment. That is the reason why historically the wells found with “Sour” environment were often and carefully plugged and abandoned! With the first oil crisis in 1973, the need for other sources of supply and the high price of oil drove the technology to cope more systematically with this hazardous environment.

Today Sour Service environments provide further challenges with deeper wells, higher pressures and extreme corrosive conditions. Vallourec OCTG material suitable for Sour Service conditions provide solutions to push these limits on a safe and reliable manner.

### 1. Definition and Standards

The National Association of Corrosion Engineers (NACE) formed a committee in the 1950’s to help understand and avoid failures caused by H₂S. A first standard (MR0175) was published in 1975: It defined “Sour Service” conditions as a threshold on the partial pressure of H₂S: \( P[H₂S] > 0.05 \text{ psi} \).

Today, a new international standard, ISO 15156 has emerged. It combines the findings of the European Federation of Corrosion (EFC) with those of NACE. This standard defines the metallic material requirements to provide resistance to Sulfide Stress Cracking (SSC).

It introduced pH as an additional major factor influencing how critical the environment is, along with specific tests that have become standard in order to qualify material for “Sour Service” environment.

### 2. Sulfide Stress Cracking

The physical phenomenon associated with “Sour Service” environment is known as “Sulfide Stress Cracking” (SSC) or “H₂S embrittlement”. H₂S in combination with water and low pH, will release free hydrogen. Due to its small size the hydrogen particles are adsorbed by the material and interact with the steel which becomes brittle. Two key activating factors are low temperature and high stress state of the material. Under unfavourable combinations 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.

### 3. The major influence of Temperature

The key influence of H₂S partial pressure makes it clear that high pressure wells are more critical in Sour Service environments. But high pressure often relates to high temperature which is well known to be an inactivating factor of the embrittlement phenomenon.

The risk actually lays at the top of the well where the pressure is still high, but temperature has decreased due to thermal losses, thus activating the sulfide stress cracking.

In that regard, materials according to API 5CT (ISO 11960) do comply with NACE MR0175, as a function of temperature level. Outside these envelopes proprietary grades are required.
4. Material evaluation

The objective is to assess whether a given material is suitable for Sour Service conditions. NACE TM0177 has defined and normalized several tests: Methods A to D. They typically use a critical and normalized sour service environment called “environment A” (with the exception of Method B that does not require NaCl addition). They differ by the way the stress is applied to the test specimen and can fit into 2 categories:

- **Go / No Go** type tests provide a binary result: Either the material passes the test or not. NACE methods A, B and C belong to this first category.
- **Method D** provides a level of performance through the measurement of the crack propagation.

This allows comparison and continuous ranking of materials.

### Test Methods Overview

<table>
<thead>
<tr>
<th>Test Method</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress Application</td>
<td>Tension</td>
<td>Bending</td>
<td>Bending</td>
<td>Displacement</td>
</tr>
<tr>
<td>Environment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PH - 3</td>
<td>14.5 psi or 1 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl - 3</td>
<td>50 g/l (residual method)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td>75°F or 24°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration</td>
<td>720 hours (30 days)</td>
<td>360 hours (15 days)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Result</td>
<td>Go / No Go</td>
<td>Stress Intensity Factor $K_{1SSC}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To be considered suitable for Sour Service environments, a material has to pass at least one of these tests. Methods A and D are the most commonly used in the industry.

5. NACE Method “A”

Cylindrical samples are manufactured from the base material, taken longitudinally. Sample is enclosed into the sour environment, with tension load inducing commonly 80% of Specified Minimum Yield Strength (SMYS). Duration is 720 hours or 30 days.

6. NACE Method “D”

A Double Cantilever Beam (DCB) is manufactured from the base material, taken longitudinally. A tapered wedge is used to load the test specimen which is then, enclosed in the sour environment, for 360 hours (15 days).

The sample is then retrieved, failed open, and the crack length measured. The resistance to crack propagation $K_{1SSC}$ is calculated, providing a direct numerical rating. Acceptance criterion is defined by API 5CT, for example the $K_{1SSC}$ minimum average value for grade T95 should be not less than 30 ksiV in.

7. Standard Sour Service material

C90 and T95 are the dedicated API grades suitable for Sour Service environments. They comply with the following requirements:

- **Chemical composition**
- **Grain size finer than ASTM 5**
- **Hardness limitation**
- **NACE tests (TM 0177), methods A, B or D.**

Lower API grades including J55, K55, or L80 are also granted suitability.

8. Vallourec proprietary Sour Service grades

The know-how at Vallourec has demonstrated that material suitable for sour service environments should be designed and manufactured by carefully designing and controlling the following parameters:

- **Cleanliness** To avoid inclusion and segregation
- **Grain size** Fine martensitic microstructure
- **Homogeneity** Even distribution of characteristics
- **Stability** Complete release of quenching stresses

A unique expertise and extensive product offer have been developed based on:

- **Chromium - Molybdenum steel chemistry;**
- **Low Sulfur and Phosphorus content;**
- **Improved Grain size finer than ASTM 7;**
- **Dedicated quenching process, adapted to heavy pipe up to 2” in wall thickness (ID-OD quenching);**
- **100% Non-Destructive Examination (NDE);**
- **Extensive database of NACE test results.**
Vallourec Sour Service range is composed of 3 series to fulfill the customers’ requirements with regards to the mechanical properties and level of reliability:

<table>
<thead>
<tr>
<th>Time Saving Sour Service grades</th>
<th>SS series “Time Saving”</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 90 S</td>
<td>C95</td>
</tr>
<tr>
<td>VM 95 S</td>
<td>C95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Enhanced Sour Service grades</th>
<th>SS series “Enhanced API”</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 80 SS</td>
<td>L40</td>
</tr>
<tr>
<td>VM 90 SS</td>
<td>C90</td>
</tr>
<tr>
<td>VM 95 SS</td>
<td>T95</td>
</tr>
<tr>
<td>VM 110 SS *</td>
<td>T95*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NACE-D Sour Service grades</th>
<th>SS-D series “NACE-D”</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 95 SS-D</td>
<td>T95*</td>
</tr>
<tr>
<td>VM 110 SS-D</td>
<td>T95*</td>
</tr>
</tbody>
</table>

### 9. Sour Service & High Collapse grades

Vallourec has combined its expertise on Sour Service applications along with that on High Pressure environments to cope with the most demanding High Pressure - High Temperature (HP-HT) projects. This has led to the High Collapse & Sour Service product line:

<table>
<thead>
<tr>
<th>Time Saving High Collapse &amp; Sour Service grades</th>
<th>SS series “Time Saving”</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 90 HCS*</td>
<td>C95*</td>
</tr>
<tr>
<td>VM 95 HCS</td>
<td>C95*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Enhanced High Collapse &amp; Sour Service grades</th>
<th>SS-D series “NACE-D”</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM 80 HCSS</td>
<td>L40*</td>
</tr>
<tr>
<td>VM 90 HCSS</td>
<td>C90*</td>
</tr>
<tr>
<td>VM 95 HCSS</td>
<td>T95*</td>
</tr>
<tr>
<td>VM 110 HCSS *</td>
<td>T95*</td>
</tr>
</tbody>
</table>

### 10. Vallourec Sour Service grade added-value

Vallourec proprietary Sour Service grades can thus offer:

- A larger domain of application and an enhanced safety margin through the SSC resistance guaranteed and demonstrated up to 90% of the material Yield Strength vs. 80% with API (NACE method A test);
- Higher Strength materials, like VM110SS-D or VM110HCSS with 110 ksi Yield Strength;
- Enhanced reliability of the product and its delivery thanks to the improved Quality Control and Quality Assurance;
- Reduced lead time thanks to Vallourec proven success record in performing NACE testing, allowing parallel shipping of the material;
- Heavy pipe and coupling stock up to 2” in wall thickness, with the same Sour Service guaranty;
- Top performance and reliability in HP-HT wells, when combined with Vallourec High Collapse technology.

### 11. Fit-for-purpose approach

Beyond API and proprietary Sour Service grades, “taylor-made” products, services, or characterization may be required to fulfill customer highest profile projects.

Vallourec offers a complete engineering approach to satisfy specific needs including:

- Special sizes, for HP-HT wells in particular;
- Vallourec SSC data base with more than 10,000 test results, including DCB tests;
- 967 NACE-D test results on VM110SS-D,
- Special NACE testing with adapted objectives, parameters and targets;
- Close coordination with customers and material experts to fit the global Sour Service evaluation into an operating plan;
- Faster lead time approach extended to higher grades like VM80SS upon request and agreed quality plan.

There are more than 20 scientists and material experts working in our 3 Research & Development laboratories located in France and Germany. They can elaborate mini-heats on their own, perform more than 600 SSC tests per month at full thrust, and rely on the full support of 16 steel and pipe manufacturing mills around the world.

12. First class processing capacity

Steel elaboration is processed in 4 mills in France, USA, Brazil and Germany including the long-lasting relationship with first-class supplier HKM (Hüttenwerke KRUPPMANN-NESMANN), in which Vallourec holds a 30% share. Combined capacity and supply sources reach 3.5 million tons per year. Equipment includes electric furnaces fed from scrap, blast furnaces (BOF) fed with iron ore, vacuum degassing batches, continuous cast to produce steel rounds and forging equipment.

Pipe manufacturing is processed in 11 mills in France, Germany, UK, USA, Brazil and Indonesia with Citra Tubindo in which Vallourec holds a 25% share. Combined seamless capacity reaches 2.7 million tons per year. Equipment includes:

- Advanced hot-rolled processes: Pilger mill, continuous mandrel mill, plug rolling mill, ppm mill, …
- Heat treatments with computer controlled austenitizing and tempering furnaces, internal and / or external quenching units.
- Non-destructive evaluation on or off line, including the latest ultra-sonic technology like phased-array, capturing defects twice as small as API, and C-Scan.

Pipe finishing for OCTG market includes full length mill threading and stock management in 9 facilities around the world, in France, Germany, UK, USA, Canada, Mexico, Brazil and Indonesia, a VAM* Licensee network of more than 100 accessory and repair shops around the world and a quality, documentation and gauge rental system managed by VAM* Services.

13. Field records: A selection

Vallourec has been involved in the most critical Sour Service applications around the world. A high profile project in the Caspian Sea (*) provides a relevant example of critical conditions:
- **TD** = 13,000 ft (4000 m)
- **BHP** = 11,600 psi (800 bar)
- **H2S** = 16%, **CO2** = 3%, **pH** = 3 to 4
- **T** = 5°F to 230°F (-15°C to 110°C)

Vallourec large spectrum of experience is further illustrated below:

<table>
<thead>
<tr>
<th>Size</th>
<th>Wall Thickness</th>
<th>Material</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 1/2”</td>
<td>0.271”</td>
<td>VM 80 SS</td>
<td>North America</td>
</tr>
<tr>
<td>5”</td>
<td>0.408”</td>
<td>VM 95 HCS</td>
<td>Far East</td>
</tr>
<tr>
<td>6 5/8”</td>
<td>0.417”</td>
<td>VM 90 SS</td>
<td>Caspian Sea</td>
</tr>
<tr>
<td>7”</td>
<td>0.453”</td>
<td>VM 95 S</td>
<td>West Africa</td>
</tr>
<tr>
<td>7”</td>
<td>0.498”</td>
<td>VM 110 SS-D</td>
<td>North Sea</td>
</tr>
<tr>
<td>8 5/8”</td>
<td>0.850”</td>
<td>C90</td>
<td>Gulf of Mexico</td>
</tr>
<tr>
<td>9 5/8”</td>
<td>0.545”</td>
<td>VM 110 SS</td>
<td>Latin America</td>
</tr>
<tr>
<td>9 5/8”</td>
<td>0.595”</td>
<td>VM 110H CSS</td>
<td>Middle East</td>
</tr>
<tr>
<td>10 1/4”</td>
<td>0.800”</td>
<td>T95</td>
<td>Caspian Sea</td>
</tr>
<tr>
<td>10 3/4”</td>
<td>0.950”</td>
<td>VM 110 SS</td>
<td>North Sea</td>
</tr>
<tr>
<td>14”</td>
<td>0.800”</td>
<td>VM 95 SS-D</td>
<td>Caspian Sea*</td>
</tr>
</tbody>
</table>

14. Product mix to the market

Sour Service material typically accounts for 13% of Vallourec Premium pipe deliveries. Of this, 85% is Vallourec proprietary grades, including 20% of high-tech High Collapse & Sour Service material. Higher grades represent 90% of deliveries, including 30% of top-of-the-line 110 ksi Yield Strength material.

15. References

Vallourec offers a large range of OCTG material suitable for Sour Service environment where \( H_2S \) is present. It covers the requirements and parameters of such inhospitable conditions including high pressures, low temperatures, low \( pH \), and more. More than anywhere else, reliability is paramount and Vallourec provides the required top-of-the-class expertise and know how.

**Full range of products**

- Size range: 2 3/8” to 26” for OCTG
- Wall Thickness up to 2”
- Yield Strength: 55 to 150 ksi
- Grades: API and Vallourec proprietary grades
- Sour Service and High Collapse
- Connections: API and VAM®
- Taylor made products: Non standard OD, weight or grade upon request

**Integrated pipe manufacturer**

- Design, process and control of proprietary steel chemistries
- 5 steel mills in France, Germany, USA, Brazil and several pipe mills throughout the world dedicated to the production of OCTGs
- Connection threading integrated to the pipe mills or strategically located to serve a market
- In house metallurgical testing and Non-Destructive Examination

**Reliable Products and Services**

- Proprietary sour service grades with greater than API Sulfide Stress Cracking resistance
- Extensive NACE data bank for all NACE test methods
- Best-in-class quality control plan, including technologies with improved sensitivity to defects and enhanced control frequency

**BENEFITS**

- Full range of products
- Heavier and higher Yield Strength material
- Improved Sulfide Stress Cracking resistance
- Reliable quality and leadtime
- Fit-for-purpose approach
- Single source of your complete solution

**Expertise and know-how**

- Three Research & Development laboratories with more than 20 engineers and technicians dedicated to the design of improved steel chemistries
- Capacity to perform more than 600 corrosion tests per month
- All-in-one technical support: pipe, material, VAM® Premium connection and services

**Supply Chain Management**

- Full service provider: From steel making to pipe run in your well
- Reduced lead time thanks to NACE testing parallel to manufacturing process
- Extensive VAM® licensee network for field repairs or accessories
- VAM® Field Service International: Inspection and running services
World Leader in Premium Tubular Solution

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