

V&M 13% Cr & Super 13% Cr steel grades for Sweet CO₂ corrosion service



*SOUR SERVICE
HIGH COLLAPSE*

13CR/SUPER13CR

VM 80 13Cr

VM 90 13Cr

VM 95 13Cr

VM 95 13CrSS

VM 110 13CrSS

VM 80 13ET

Vallourec Group






VALLOUREC & MANNESMANN TUBES



13% Cr & Super 13% Cr V&M grades

V & M Proprietary Grades	Mechanical properties			QC provided	Color Code
	Yield Strength	Ultimate Strength	Hardness	HRC	
	min - max (ksi) (Mpa)	min (ksi) (Mpa)	HRC (max)	(# Pipe)	


13% Cr Grades : Fully compatible with API

VM 80 13Cr	80 - 95	552 - 655	95	655	< 23	2/lot	
VM 90 13Cr	90 - 105	621 - 724	100	690	< 26	2/lot	
VM 95 13Cr	95 - 110	655 - 758	105	724	< 28	2/lot	

Super 13% Cr Grades : For higher yield strength and improved resistance to sweet CO₂

VM 95 13CrSS	95 - 110	655 - 758	105	724	< 30	10%	
VM 110 13CrSS	110 - 130	758 - 897	120	828	< 34	10%	

Expandables 13% Cr Grade : Reduced tolerances & specific quality checks

VM 80 13ET	80 - 95	552 - 655	95	655	< 23	3 / lot	
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Higher Performances V&M CRA grades

V&M Tubes offers also a full range of proprietary CRA materials for the more stringent corrosive environments. It includes the main OCTG duplex, super duplex, super austenitic and nickel base alloys like :

- **VM 22** **22%Cr duplex steel**
 - **VM 25** **25%Cr duplex steel**
 - **VM 25S** **25%Cr super duplex steel**
 - **VM 28** **28%Cr super austenitic steel**
 - **VM 825**
 - **VM G3**
 - **VM 50**
- } **Nickel base alloys**

CO₂ corrosion in OCTG

The growing demand of energy has resulted in a general need to produce fields with a tangible CO₂ content.

The presence of corrosive species such as CO₂, H₂S, organic acids, O₂ and chlorides has a pronounced effect on corrosion in producing wells. Carbon dioxide is almost always present and its effect on corrosion is primarily by decreasing the pH of the water phase. Carbon dioxide instigates general corrosion, localized corrosion or formation of hard iron carbonate scales.

For the last 25 years, the use of 13% Cr seamless steel pipes has been the most cost effective solution to protect against sweet wet CO₂ corrosion.

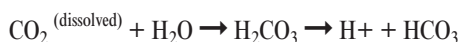
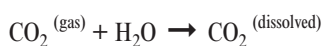


1. Mechanism of wet CO₂ corrosion

Corrosion arises because CO₂ gas dissolves into produced water. Therefore, the main parameters driving CO₂ corrosion are:

- actual CO₂ partial pressure (or maximum value at the bubble pressure in oil wells),
- actual pH of the water phase,
- actual temperature,
- weak acids,
- flow rate (for carbon and low alloy steel only).

CO₂ corrosion is related to the chemical reactions associated with the produced water.



The overall mechanism (described by De Waard and Milliams¹) when CO₂ gas is in contact with steel is:



It induces several types of corrosion attacks on steel materials.

2. Standard recommendations

The physical phenomenon associated with a sweet wet CO₂ corrosion is known as the uniform corrosion or the weight loss. In given conditions it has been demonstrated that the addition of a sufficient quantity of chromium in a steel alloy can dramatically reduce and even stop this phenomenon. Advanced 13% Cr stainless steels were developed in the 1970s, with martensitic microstructures. More recently, "Super" 13% Cr alloys were developed, with improved resistance to certain forms of corrosion: They combine low carbon content and additions of Ni and Mo.

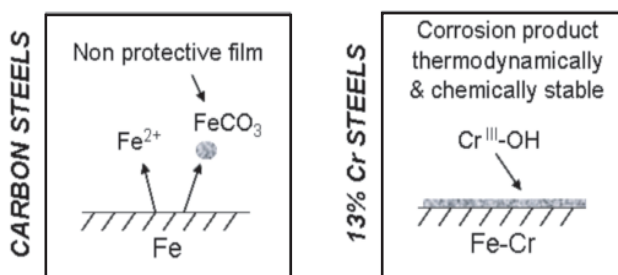
Alloys	C	Cr	Ni	Mo
13% Cr	0.2	13	0.15	0.02
Super 13% Cr	0.02	13	5	2

Table of main elements

NACE MR0175/ISO 15156-3², API 5CT/ISO 11960³ and ISO 13680⁴ international standards define the rules of selection and the material specifications for martensitic and super martensitic stainless steels.

3. Corrosion resistance

As shown on the picture below, carbon steel is subject to drastic general and local CO₂ corrosion while 13% Cr alloy remains protected thanks to its passive layer.

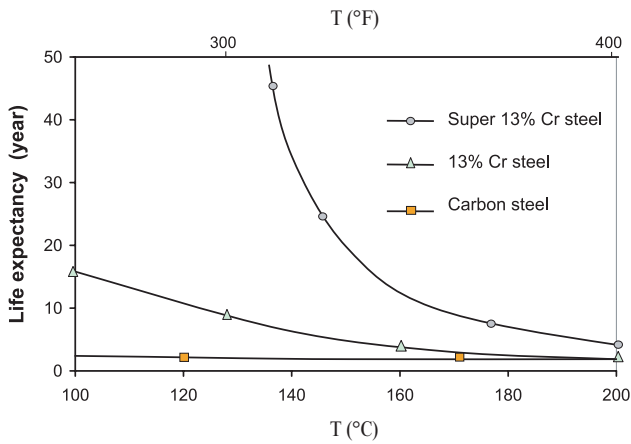


A lot of parameters may change the intensity and the speed of the above general mechanism.

Compilation of reference papers^{5, 6} shows the evolution of the corrosion rate versus temperature and chloride content.

The next graph displays the corrosion rate of a 5 1/2" 17 lb/ft. tubing in a sea water as a function of time. It illustrates the life expectancy of the tubing, based on a 50% wall thickness loss as

an acceptable limit. That graph clearly highlights the advantageous effect of 13% Cr.



CO₂ corrosion acts both through general weight loss and through acute localized attacks.

Localised corrosion of carbon steel consists of severe and deep dissolution of the metal at discrete areas. Three main forms are known:

- Pitting (no or moderate flow conditions)
- Mesa Attack (through unstable carbonate protective layer)
- Flow Induced (reinforced by high flowing conditions)

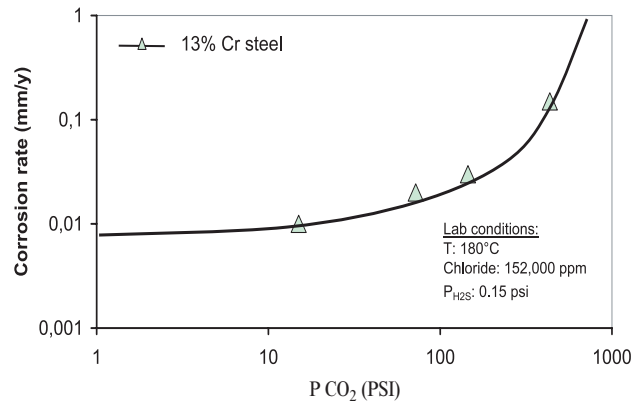


Example of CO₂ corrosion of Carbon Steel OCTG pipe

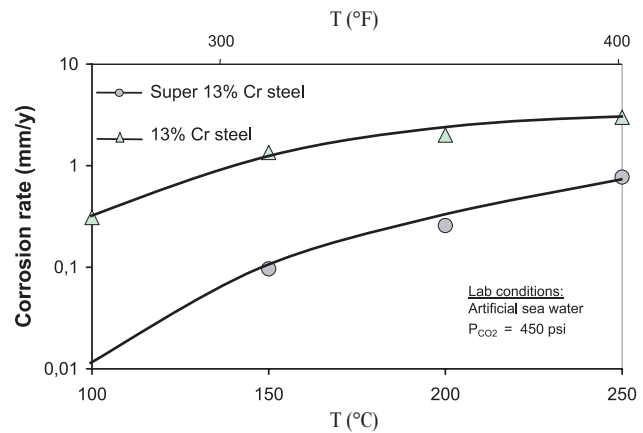
4. Limits of corrosion resistance

Field case histories provide the most reliable data base for the measurement of the efficiency of a material within a corrosive reservoir. Using such a V&M TUBES data base, our experts can analyse all the parameters in the well environment. To help their diagnosis, the effects of the main factors which provoke sweet corrosion have been studied in laboratory.

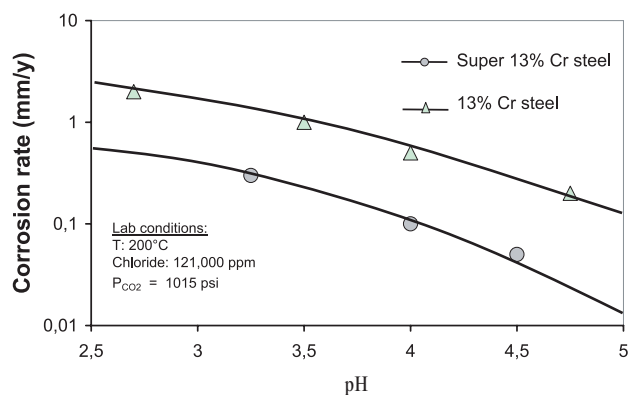
CO₂ Partial Pressure: CO₂ content determines the acidic conditions. Then the higher the CO₂ Partial Pressure the lower the corrosion resistance is.



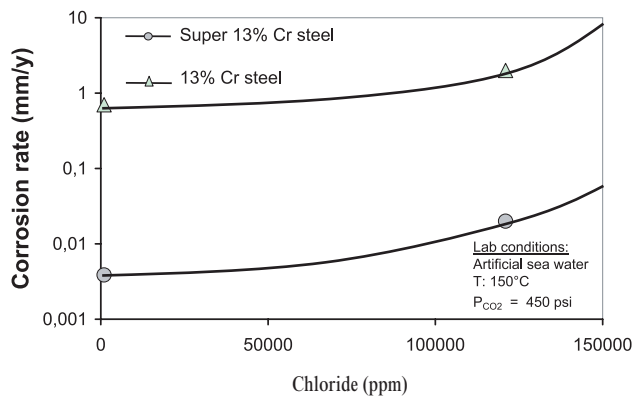
Temperature: The temperature is linked to the kinetics of the chemical reactions. An increase limits the corrosion resistance.



pH: As pH is mainly dictated by CO₂ Partial Pressure, the decrease of pH will decrease the corrosion resistance.



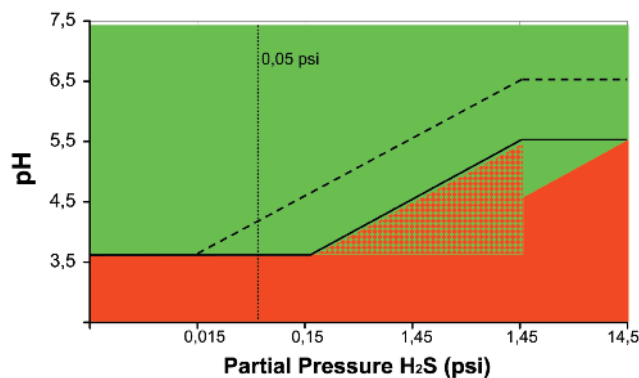
Chloride content: Recent studies have shown that the chloride content has a detrimental effect on the passivation layer. This leads to a decrease in the corrosion resistance.



5. Sulfide Stress Cracking resistance

The first standard published by NACE in 1975 defined Sour Service⁷ conditions above a threshold of Partial Pressure H₂S of 0.05 psi. NACE MR0175 / ISO 15156 standard has since emerged and defines Sour Service domains as a function of the Partial Pressure H₂S and the in-situ pH.

The NACE / ISO standard limits the use of 13% Cr alloys at a maximum H₂S partial pressure of 1.5 psi and pH ≥ 3.5. Crolet / Kermani in their paper⁸ define a wider domain of non sour service for L80 13% Cr if the actual yield strength of pipes is appropriate (green colour on the figure below). V&M TUBES' recommendation is to perform SSC tests according to well conditions with Partial Pressure H₂S between 0.15 and 14.5 psi and pH above 3.5 (red-green dotted area of the graph below).

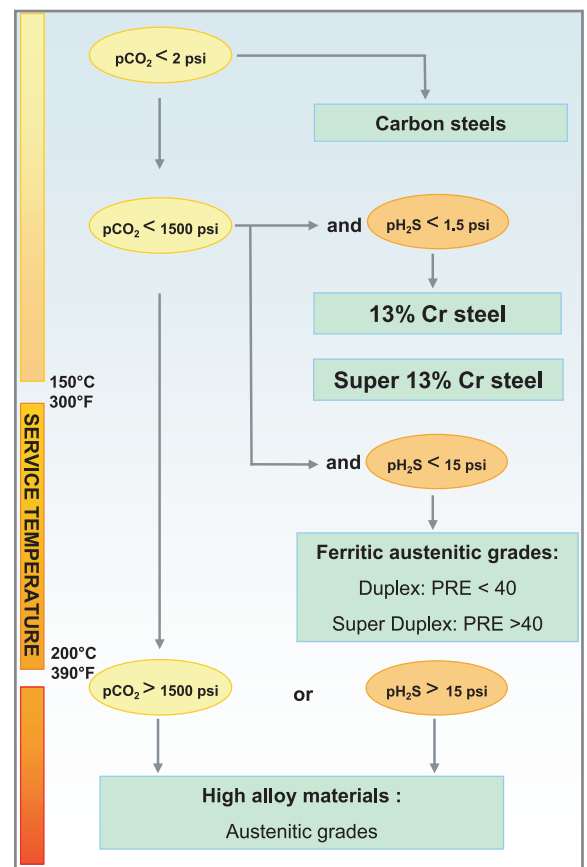


Note: According to the Fit-For-Purpose approach and since chloride content is an important parameter, two typical environments such as formation and condensed waters may be used for assessing the corrosion resistance of martensitic stainless steels. While formation water originates in the various geological horizons of oil and gas reservoirs, condensed water is produced in the tubing as the pressure and the temperature decrease. As mentioned in the literature a typical formation water extracted with the oil and gas effluent contains chloride ions with concentrations up to about 200,000 ppm with pH values close to 4.5. For a typical condensed

water the content will be about 1,000 ppm chloride without bicarbonates leading to a pH value between about 3.2 and 3.5 in this case.

6. 13% Cr Alloys Selection guidelines

The table below give some guidance to steel selection. That chart is conservative and has been based on a “worst case” philosophy. A full knowledge of the specific oilfield environment will often allow a larger range of use of the V&M steels.



7. Handling and storage

As a general rule pipe shall be stored and handled in accordance with API RP 5C1⁹ “Recommended Practice for Care and Use of Casing and Tubing”.

13% Cr and Super 13% Cr materials are sensitive to pitting initiated by confined or trapped humidity with the presence of chlorides. Nevertheless they do not suffer from routine rinsing (rain) providing that they are properly packed and stacked.

V&M TUBES ensures the condition of its 13% Cr goods by the use of appropriate procedures that cover the packaging, temporary protection, storage and transportation of its products.

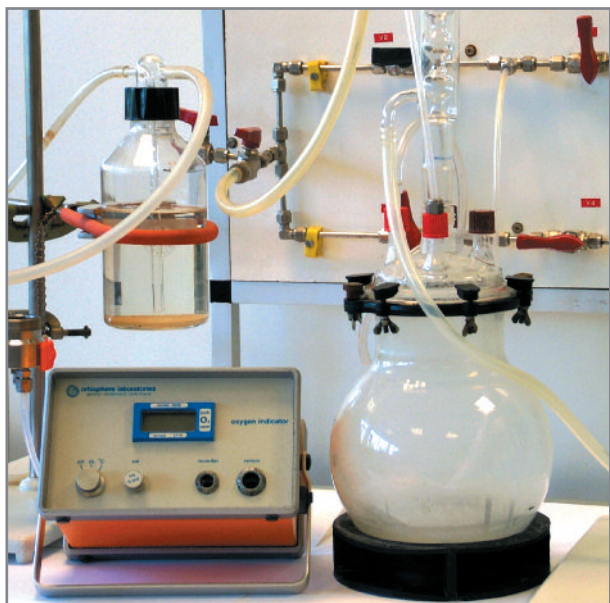
8. Competitiveness of 13% Cr alloys

13% Cr pipe presents a greater initial investment than carbon steel.

However, this effect is balanced by the higher Operational Expenditure of chemical inhibition or work over when carbon steels are used in sweet CO₂ environments. In many cases the economics presented by well environments and applications lead clearly to financial advantages of 13% Cr materials over carbon steel and inhibitors.



9. Corrosion expertise



There are more than twenty scientists and material experts working in our three Research & Development laboratories located in France and Germany. Their expertise in pipe corrosion prevention is based on more than fifty years of work with the Oil & Gas industry.

Our laboratories are equipped with efficient CO₂ and H₂S corrosion investigation tools such as electrochemical and autoclave equipments.

V&M TUBES is happy to aid your selection process and to demonstrate its validity.

10. First class processing

13% Cr and Super 13% Cr steel elaboration is processed in our Saint-Saulve steel plant in France or by expert steels maker partners. Equipments include electrical furnaces fed from scrap, blast furnaces fed with iron ore, vacuum degassing batches, continuous cast to produce steel rounds and forging equipment.

The 13% Cr and Super 13% Cr pipe is produced in four mills in France, Brazil and Germany. Overall capacity reaches up to forty thousand tons per year. Equipments include:

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

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

11. Field records

V&M TUBES has been involved in all the different types of sweet CO₂ applications all around the world during the last thirty years. Do not hesitate to ask us for a reference or a field records' list.

12. References

- ¹ C. de Waard and D.E. Williams "Carbonic acid corrosion of steel", Corrosion 1975, 31, 131
- ² NACE MR0175 / ISO 15156-3 "Petroleum and natural gas industries – Materials for use in H₂S-containing environments in oil and gas production – Part 3: Cracking-resistant CRAs (Corrosion Resistant Alloys) and other alloys", First Edition, December 15, 2003
- ³ API 5CT / ISO 11960 "Petroleum and natural gas industries – Steel pipes for use as casing or tubing for wells", Eighth Edition, July 1, 2005
- ⁴ ISO 13680 "Petroleum and natural gas industries – Corrosion-resistant alloy seamless tubes for use as casing, tubing and coupling stock – Technical delivery conditions", First Edition, July 1, 2000
- ⁵ EFC #13 "Predicting CO₂ corrosion in the Oil and Gas industry", 1994
- ⁶ EFC #23 "CO₂ corrosion control in Oil and Gas production", Edited by M. B. Kerrmani and L. M. Smith, 1997
- ⁷ "V&M Steel grades for Sour Service" leaflet, 2004
- ⁸ M.B. Kerrmani and D. Harrop – B.P. Research, M.L.R. Truchon and J.L. Crolet – Elf-Aquitaine "Experimental limit of Sour Service for Tubular Steels", Corrosion91, Paper #21, 1991
- ⁹ API RP 5C1 "Recommended Practice for Care and Use of Casing and Tubing", Eighteenth Edition, May 1999

V&M TUBES offers the best of OCTG suitable for Sweet CO₂ environment with limited H₂S presence. It covers the requirements and parameters of such inhospitable conditions including high pressures, high temperatures and more. More than anywhere else, reliability is paramount and V&M TUBES provides the required top-of-the-class expertise and know how.



Full range of products

- Size range for OCTG: 2 3/8" to 10 3/4"
- Wall Thickness up to 1"
- Yield Strength: 80 to 110 ksi
- Grades: API and V&M proprietary grades
- 13% Cr and Super 13% Cr
- VAM® Premium connections
- Tailor made products: Non standard OD and weight upon request



Integrated pipe manufacturer

- Design, process and control of proprietary steel chemistries
- 1 steel mill in France and several pipe mills in France, Germany, USA, Brazil dedicated to the production of OCTG goods
- 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 13% Cr and Super 13% Cr grades with tighter tolerances than API
- Extensive data bank for various 13% Cr and Super 13% Cr specific tests conditions
- Best-in-class quality control plan, including technologies with improved sensitivity to defects and enhanced control frequency

BENEFITS

- **Large range of products**
- **Reliable quality and leadtime**
- **Long term expertise**
- **Single source of your complete solution**
- **VAM® premium connections**



Expertise and know-how

- Three R&D 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

