

Corrosion Resistant Alloys (CRAs) in the oil and gas industry – selection guidelines update

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– selection guidelines update

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Environmental Note:

Stainless steels and nickel alloys offer important environmental benefits. Properly selected, they permit safe containment of oil and gas process fluids. Their durability ensures long life: replacement, and the resource demand that makes, is minimized as operating efficiencies are improved. At the end of the life of the structure, the nickel alloys are completely recyclable. Overall, stainless steels and nickel alloys are exceptional life cycle performers in both the environmental and economic senses.

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Introduction

Corrosion Resistant Alloys (CRAs) are essential for providing long term resistance to corrosion for many components exposed to oil and gas production environments. Components include downhole tubing and safety critical elements, wellhead and Xmas tree components and valves, pipelines, piping, valves, vessels, heat exchangers and many other pieces of equipment in facilities. There are many CRAs to select from, and they can be characterised by their resistance to specific environments.

Key environmental parameters influencing the corrosion properties of CRAs are:

- **Temperature**
- **Chloride ion concentration**
- **Partial pressure CO₂**
- **Partial pressure H₂S**
- **Environment pH**
- **Presence or absence of Sulphur**

Between them these parameters influence

- **the stability of the passive film (initiation of pitting or general corrosion)**
- **ease of repassivation of initiated pits**
- **rates of dissolution of metal from pits**
- **the risk of Stress Corrosion Cracking (SCC) initiating and propagating**

This guide for selection of CRAs for particular environments was originally published in 1998 and authored by Bruce Craig. It was one of the first to attempt to show that a material's corrosion properties are influenced by many environmental parameters simultaneously.

The 3D graphs show the safe operating envelope of the alloys as a function of 3 parameters e.g. T, H₂S, pCO₂. Since most of the underlying data has been for high chloride ion concentrations there is effectively a 4th parameter incorporated as well.

The publication has stood the test of time and continues to provide reliable guidelines on materials performance. However, the gradual accumulation of positive field experience at the "limits", or just beyond, combined with the accumulation of laboratory data from testing of materials in increasingly aggressive solutions, means that there is justification established for using some materials within a wider safe operating range.

Methods for Selecting CRAs

The selection of Corrosion Resistant Alloys, CRAs, for producing and transporting corrosive oil and gas can be a complex procedure and if improperly carried out can lead to mistakes in application and misunder-

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standing about the performance of a CRA in a specific service environment.

There are a variety of ways individuals and companies select CRAs for anticipated well and flowline conditions. Companies with large research facilities typically initiate a test program that involves simulating the particular part of the field environment under study (i.e. flowlines versus downhole). Then a group of alloys, based on information available, is selected that represents a possible range of alternatives. Rather than test all alloys all the time, it is more cost effective and less time consuming to test only a few CRAs that are likely candidates. This approach can easily require 1-3 years to accomplish at considerable expense.

Another selection procedure is to review the literature for corrosion data that generally applies to the anticipated field conditions. This can result in elimination of those CRAs that are not good candidates and, thus, narrow the number of candidate alloys for testing. The selected CRAs are then tested under very specific conditions to fill gaps in literature data and/or field experience.

Care must be taken when using this approach because, for example, the corrosion resistance of many CRAs at one temperature is not necessarily indicative of their corrosion resistance at other temperatures. Likewise, changes in critical environmental components such as elemental sulphur can have a profound impact on the resistance to stress corrosion cracking (SCC), another important factor in alloy selection.

Other resources for materials selection are also available such as the 2003 ISO 15156 publication which was derived from the previous NACE 0175 publication for “sour service” and the EFC16 publication which incorporated the influence of environment pH on the suitability of materials for sour service. The ISO15156 standard covers different alloy types with separate tables for different applications; though field experience in many cases has shown that alloys will withstand more aggressive conditions. Corrigenda are published from time to time to update its contents and so it is important to obtain the latest version and corrigenda.

The quickest and least expensive alloy selection method is simply to review the literature, and existing or similar field data, and make the selection. This method can be quite unsatisfactory since certain critical factors or conditions will not be known and must be assumed. A greater chance for error exists in this selection approach, introducing a potential for failure of the CRA or use of a more expensive alloy than is required. It is advisable, if this method is used, to consult with someone who has a working knowledge of CRAs and their applications.

Finally, a CRA selection method that is not recommended but is often used is to select a CRA that is readily available or most economical, without regard to its corrosion resistance in the intended environment. Misapplication of CRAs is becoming more common for this reason and has resulted in corrosion and cracking problems of the inappropriately selected alloys.

However, it is recognized that before extensive efforts are made to make a final CRA selection for a specific application it is often desirable, if not necessary, to make preliminary selections of candidate CRAs to test in a simulated field environment or to perform an economic analysis to judge the cost effectiveness of several corrosion control alternatives (i.e. carbon steel plus inhibitors, CRAs, etc.). It is for these latter needs that these guideline diagrams are offered and should only be used in that fashion. More detailed testing and analysis is often required in order to make a final selection. Moreover, these diagrams are based almost entirely on laboratory data since they are often more conservative than field conditions and because laboratory data are more quantitative and frequently more accurate. The diagrams are based on corrosion rates for the alloys of less than or equal to 0.05 mm/y (2 mils/year) and resistance to sulphide stress cracking (SSC) and SCC. In this regard it should be noted that none of the diagrams indicate strength level. Generally, if NACE MR0175/ISO 15156 requirements are met, strength (and hardness) will not be an issue. However, it must always be borne in mind that increasing strength of an alloy will generally increase susceptibility to SSC and SCC.

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Limitations of data

In some cases the diagram limits presented are not necessarily real limitations of the alloys but only limits of the available test data. For example, the limits of temperature and H₂S content for Alloy C-276 and Alloy 625 are essentially unknown at this time but the test data stops short of defining a true limit of applicability.

In order to make these diagrams generic and not specific to any one manufacturer or alloy producer, the alloys are referred to by their common names. Each diagram has three axes, one of which is always temperature. Temperature is one of the most critical factors in the resistance or susceptibility of any alloy to corrosion and cracking. In order to make the temperature scale universal, degrees centigrade (°C) is used. For the other axes the partial pressure of the gas in the gas phase is provided in pounds per square inch, psi, since well pressures are most commonly reported in those units. The chloride content is reported as sodium chloride since most laboratory testing has been carried out using NaCl and is reported in that fashion (i.e. gram/litre or percent).

Finally, care should be taken not to give too much credence to a specific datum point on a graph since not every point represents a laboratory tested value. Since laboratory data are actually quite sparse for many points, a weighting function based on the value of eight nearest neighbour points was used to develop the 3-D topography. Thus, as stated earlier, these diagrams are primarily to demonstrate the limitations of CRAs in certain environments and act as guidelines. Moreover, they are only strictly applicable to oil and gas environments and do not address external environments such as seawater or packer fluids. The absence of oxygen is essential for the application of these alloys under the conditions shown. If these alloys are to be considered for oxygenated environments (typically greater than 10 parts per billion), then other criteria should be used for selection. If the anticipated operating conditions are close to or outside the boundaries of these diagrams, then the user is advised to confirm the suitability of the material by testing to a standard protocol such as EFC 17.

The table below provides the nominal composition of the CRAs discussed in this publication.

Nominal chemical composition of alloys (Wt. %)								
Alloy (UNS No.)	Cr	Ni	Mo	Fe	Mn	C	N	Other
13 Cr (S42000) to API Standard	13	-	-	Bal.	0.8	0.2	-	-
S13Cr (typical ranges)	11-13	1-6	1-2	Bal.	0.2-0.5	0.025	-	0-2.0 Cu, Ti trace
316L (S31603)	17	12	2.5	Bal.	1	0.02	-	-
22 Cr duplex(*)	22	5	3	Bal.	1	0.02	0.15	-
25 Cr duplex (*)	25	7	4	Bal.	1	0.02	0.28	-
28 (N08028)	27	31	3.5	Bal.	1	0.01	-	1.0 Cu
825 (N08825)	22	42	3	Bal.	0.5	0.03	-	0.9 Ti, 2 Cu
2550 (N06975)	25	50	6	Bal.	0.5	0.03	-	1.2 Ti
625 (N06625)	22	Bal.	9	2	0.2	0.05	-	3.5 Nb
C-276 (N10276)	15.5	Bal.	16	6	0.5	0.01	-	3.5 W

* There are a variety of 22 Cr and 25 Cr duplex stainless steels with different UNS numbers.

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Comments for Specific Diagrams

There are several factors specific to each diagram that are important to consider when using them in order to correctly apply each as a guideline.

13 Cr (Martensitic Stainless Steel)

Figure 1 represents the generally acceptable regions of performance for 13 Cr stainless steel exposed to wet CO₂ containing NaCl. This figure is only applicable in the absence of oxygen and hydrogen sulphide (H₂S). Small amounts of oxygen can cause severe pitting of 13 Cr in the presence of chlorides. This is one reason that proper storage of 13 Cr is critical to its long-term corrosion resistance. Generally, in downhole primary producing environments 13 Cr does not encounter sufficient oxygen to be a problem. However, for surface equipment it must be considered and the diagram in Figure 1 will not be applicable.

Review of published data suggests that the proprietary S13Cr alloys, referred to as Super 13Cr, Hyper 13Cr or Modified 13Cr and generally stronger than the basic API 13Cr grade, are suitable up to about 30°C higher operating temperature than the standard 13Cr grades in H₂S-free environments.

In sour conditions many workers have investigated the impact of H₂S on its performance. The latest consensus from laboratory work and field data shows that standard API 13Cr L80 can tolerate a little higher H₂S than early publications seemed to suggest. Figure 2 shows the range of conditions where data indicates the material is resistant to sulphide stress cracking (SSC) and the region at low pH or higher H₂S where the material will crack in standard SSC test conditions.

The higher strength S13Cr grade has been found to be more susceptible to H₂S than the standard 13Cr grade, probably reflecting its higher strength. One publication indicates the influence of material yield strength on performance, illustrating that the present of 'cold work' in the material is a risk for enhanced initiation of pitting, hydrogen embrittlement and sulphide stress cracking (Figure 3).

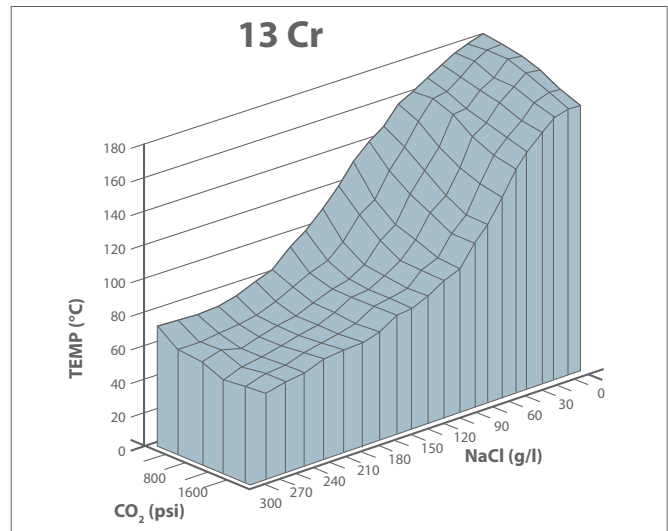


Figure 1 Safe operating temperature of 13 Cr stainless steel as a function of sodium chloride content and partial pressure of CO₂.

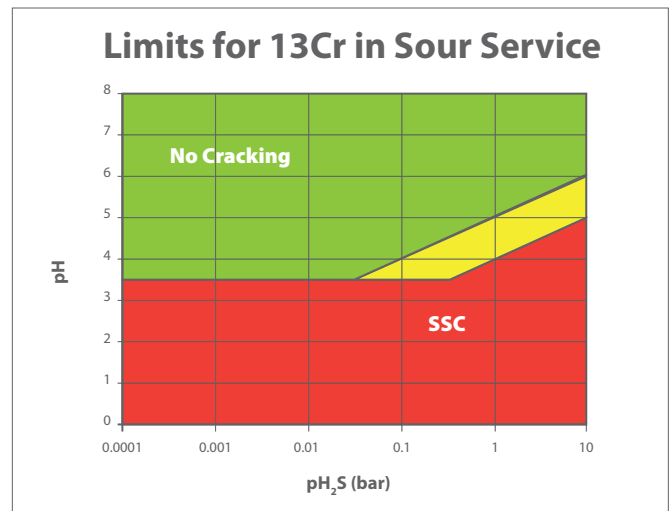


Figure 2 The red area indicates conditions where API L80 13Cr material may show susceptibility to sulphide stress cracking while the green area indicates conditions where it is resistant to SSC. The yellow area represents conditions requiring further checking of alloy behaviour.

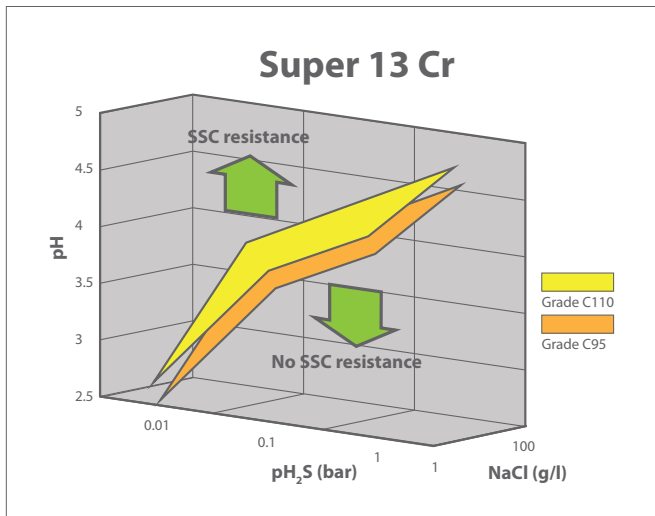


Figure 3 3-Dimensional SSC susceptibility diagram of a Super 13% Cr SS (specimens were stressed at 90% Actual Yield Strength). Ref. Marchebois, Leyer and Orleans-Joilet, NACE 07, Paper 07090

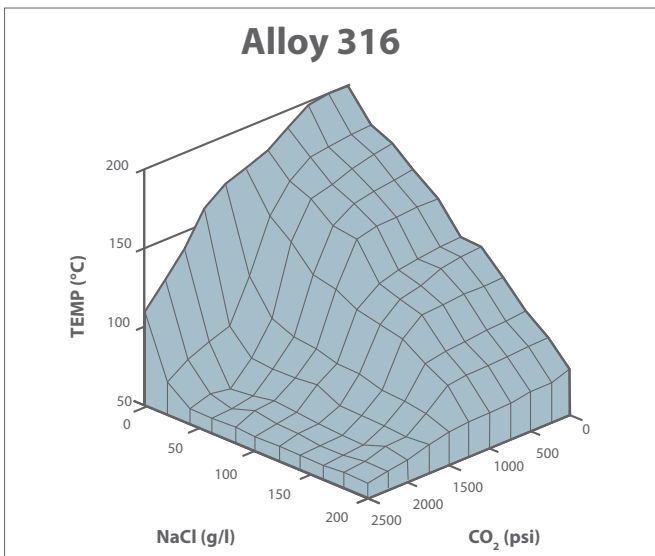


Figure 4 The corrosion resistance of Alloy 316/316L stainless steel in CO₂/NaCl environments in the absence of oxygen and H₂S. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

316L (Austenitic Stainless Steel)

Alloy 316L (Figure 4) shows the resistance of AISI 316L to deaerated, non-H₂S containing conditions. Since Alloy 316L is widely used for surface piping, vessel cladding and clad linepipe, care must be taken to ensure the application is completely deaerated. In the presence of oxygen, 316L will pit, for example, if exposed to even cold seawater.

In conditions containing H₂S, the performance of AISI 316L is very sensitive to the presence of chloride ions. In chloride-free environments (<50ppm chloride), 316L has given reliable service in sour gas handling facilities, but pitting is readily initiated when chloride ions are present. The reader is advised to consult latest test data and ISO 15156 corrigenda or make an evaluation based on testing for the specific application.

22 Cr (Duplex Stainless Steel)

Comparing Figures 1, 4 and 5 it can be seen that the resistance of 22Cr duplex stainless steel is significantly greater in non-H₂S environments up to higher temperatures than 13Cr and 316L.

The Superduplex 25Cr steels have a greater resistance to pitting than the 22Cr duplex steels, increasing the usability range by about 30 °C generally for any set of conditions compared to the 22Cr grade.

At more extreme chloride ion concentrations than Figure 5, made from mixed sodium, magnesium and calcium chloride salts evaporated to form a concentrated brine slurry (e.g. 230 g/l chloride ion concentration), it was shown that both 22Cr and 25Cr duplex stainless steels were susceptible to stress corrosion cracking in the absence of oxygen at 140 °C. These conditions were estimated to have arisen in some duplex stainless steel topside piping which was downstream of a choke valve with a high pressure drop and carrying a small volume of concentrated brine in the gas stream. Internal stress corrosion cracking was observed associated with the concentrated brine formed by evaporation of the produced water (Huizinga et al, NACE 2005, Paper 05474). The cracking problem was mitigated by upgrading the material to Alloy 625.

In conditions containing H₂S, the performance of duplex stainless steels is sensitive to the presence of

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chloride ions. The reader is advised to consult the latest test data and ISO 15156 corrigenda or make an evaluation based on testing for the specific application.

In some applications, the duplex stainless steels are cold worked for increased strength. This is not considered to affect their resistance to corrosion in CO_2/NaCl but can have a considerable detrimental effect on their resistance in H_2S service. So it is important to test the correct material condition as well as the expected environmental conditions.

Alloy 28

Alloy 28 has been successfully used for downhole tubing and casing liners in many oil and gas wells. **Figure 6** shows the envelope of applicability for Alloy 28 which is highly resistant to environments containing H_2S in contrast to the other stainless steels. Alloy 28 has limited resistance to SCC from elemental sulphur and applications that contain sulphur in combination with chlorides and H_2S and thus should be evaluated further in those environments.

Alloys 825, 2550, 625 and C-276

These alloys (**Figures 7,8,9, and 10**), as exemplified by **Figure 9** for Alloy 625, have increasing resistance to corrosion from H_2S with increasing temperature. They are generally immune to all concentrations of CO_2 and, therefore, are limited only by H_2S content and temperature. They are also not very sensitive to chloride concentration except at quite high chloride levels. However, this is a detail that should be explored before a final selection of one of these alloys is made. These diagrams are based on data derived from environments containing relatively high chloride levels (i.e. approximately 25,000 to 100,000 ppm). Alloy 2550 is also similar to several Alloy G type materials.

A component of some gas streams that has a profound effect on these alloys is elemental sulphur, also referred to as free sulphur. Sulphur has been found to cause severe pitting and catastrophic cracking of these alloys under certain conditions although Alloy C-276 is by far the most resistant, but not immune, alloy to this type of corrosion and cracking.

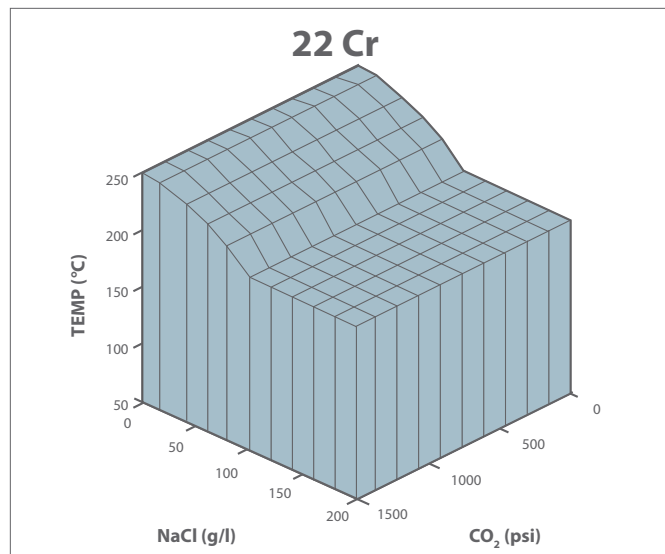


Figure 5 The corrosion resistance of 22Cr duplex stainless steel in CO_2/NaCl environments in the absence of oxygen and H_2S . Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

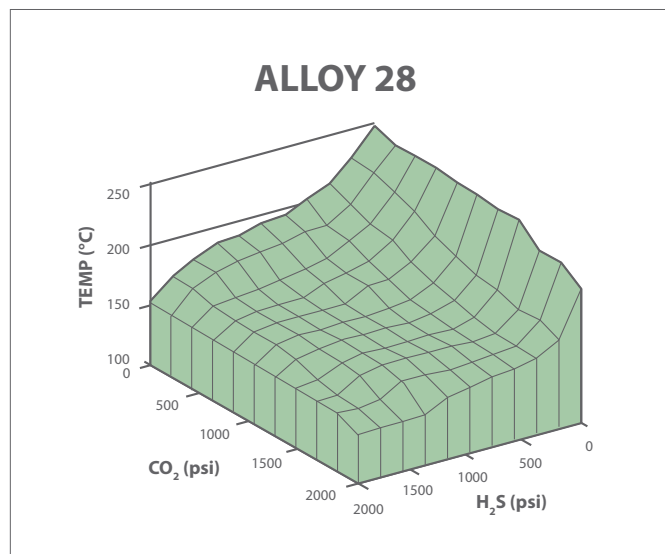


Figure 6 The corrosion resistance of Alloy 28 in $\text{H}_2\text{S}/\text{CO}_2$ environments in the absence of elemental sulphur. Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

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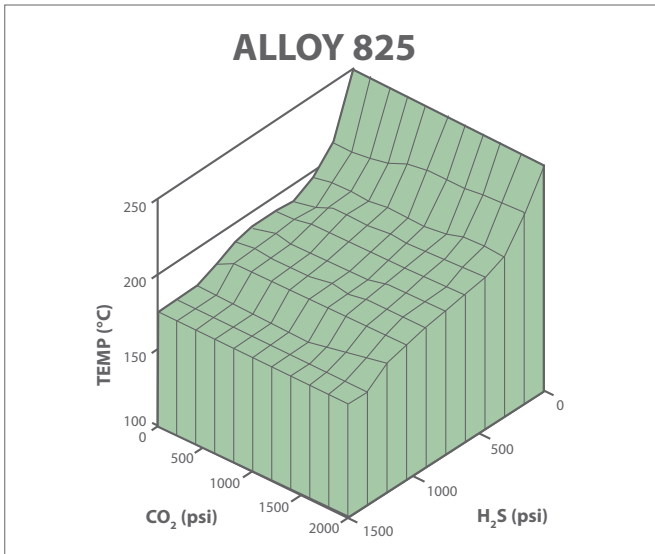


Figure 7 The corrosion resistance of Alloy 825 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

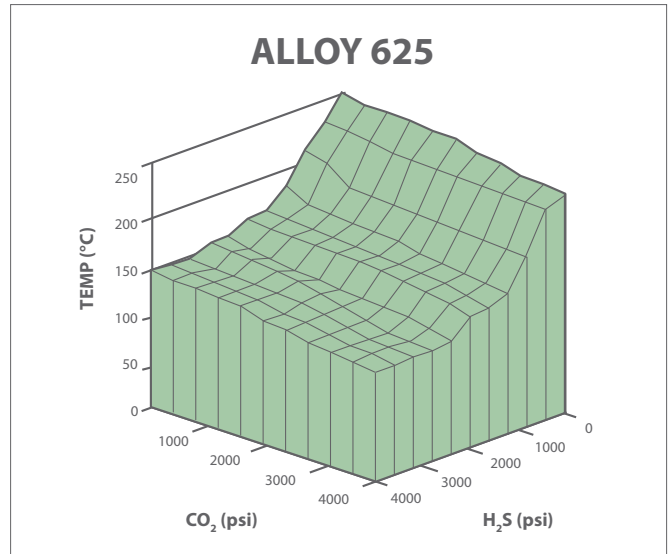


Figure 9 The corrosion resistance of Alloy 625 stainless steel in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

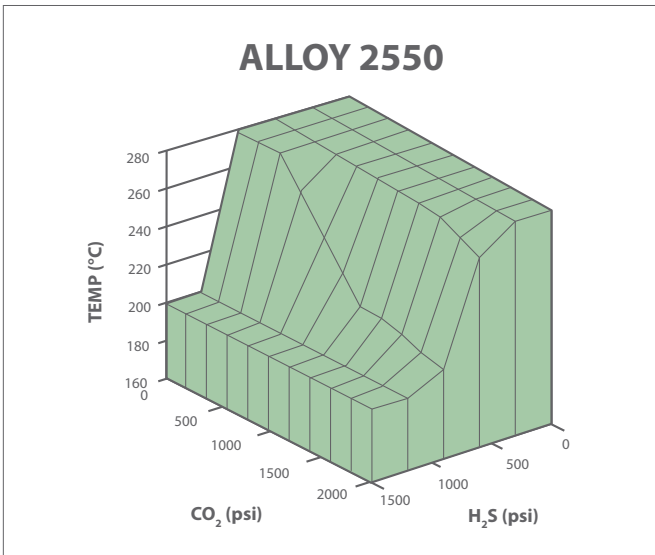


Figure 8 The corrosion resistance of Alloy 2550 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

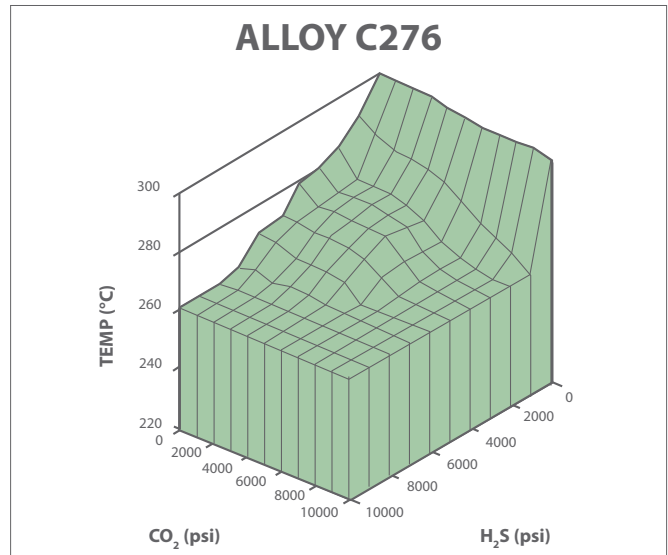


Figure 10 The corrosion resistance of Alloy C276 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤ 0.05 mm/yr (2 mpy) and no SSC or SCC.

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Examples of Diagram Use

Consider a wellstream with a partial pressure of 500 psi CO₂ at 100 °C and associated water that contains 50g/l NaCl, with no H₂S. While all alloys could be considered, 13 Cr is the least expensive choice. Now consider the same conditions but that the NaCl content is expected to be 200g/l. The 13 Cr alloy would not be suitable but the 22 Cr would be acceptable.

Another example would be a flowline carrying gas containing 1000 psi CO₂ and 500 psi H₂S at 150 °C. Alloy 825 is found to be acceptable. However, if the temperature is increased to 225 °C, this alloy is not suitable but Alloy 2550, Alloy 625 or Alloy C-276 would be suitable.

Comments

While it is NI's hope these diagrams will act as useful guidelines for the petroleum industry, they take no responsibility for their use or any applications arising from them.

A short list of suggested reading is included that contains many references that will further aid in selecting CRAs.

Suggested Reading

1. B. D. Craig, **Sour Gas Design Considerations**, SPE Monograph No. 15, 1993.
2. NACE Technical Report 1F192 (1993 Revision), **Use of Corrosion Resistant Alloys in Oilfield Environments**, NACE, Houston, TX, 1993.
3. ISO15156/MR0175 Petroleum and natural gas industries – **Materials for use in H₂S-containing environments in oil and gas production – Part 2: Cracking-resistant CRAs (corrosion resistant alloys) and other alloys.**
4. R. S. Treseder and R. N. Tuttle, **Corrosion Update, No. 1 - CRAs in Oil and Gas Production**, NACE, Houston, TX, 1993.
5. J. Kolts and S. Ciaraldi, **"Corrosion Resistant Alloys in Oil and Gas Production"**, NACE, 1996.
6. NACE Report 1F196, **"Survey of CRA Tubular Usage"**, 1996.
7. European Federation of Corrosion Publications, No. 17. **"A Working Party Report on Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for H₂S Service"** 2002.
8. H. Marchebois, J. Leyer and B. Orleans-Joilet, **"SCC Performance of a Super 13%Cr Martensitic Stainless Steel for OCTG: Three-Dimensional Fitness-For-Purpose Mapping According to PH₂S, pH and Chloride Content"** NACE 2007, Paper 07090
9. S. Huizinga, J.G. de Jong, W.E. Like, B. McLoughlin and S.J. Paterson, **"Offshore 22Cr Duplex Stainless Steel Cracking – Failure and Prevention"**, NACE 2005 Paper 05474



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