Selection guidelines for corrosion resistant alloys in the oil and gas industry

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

There is 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 to 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.

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

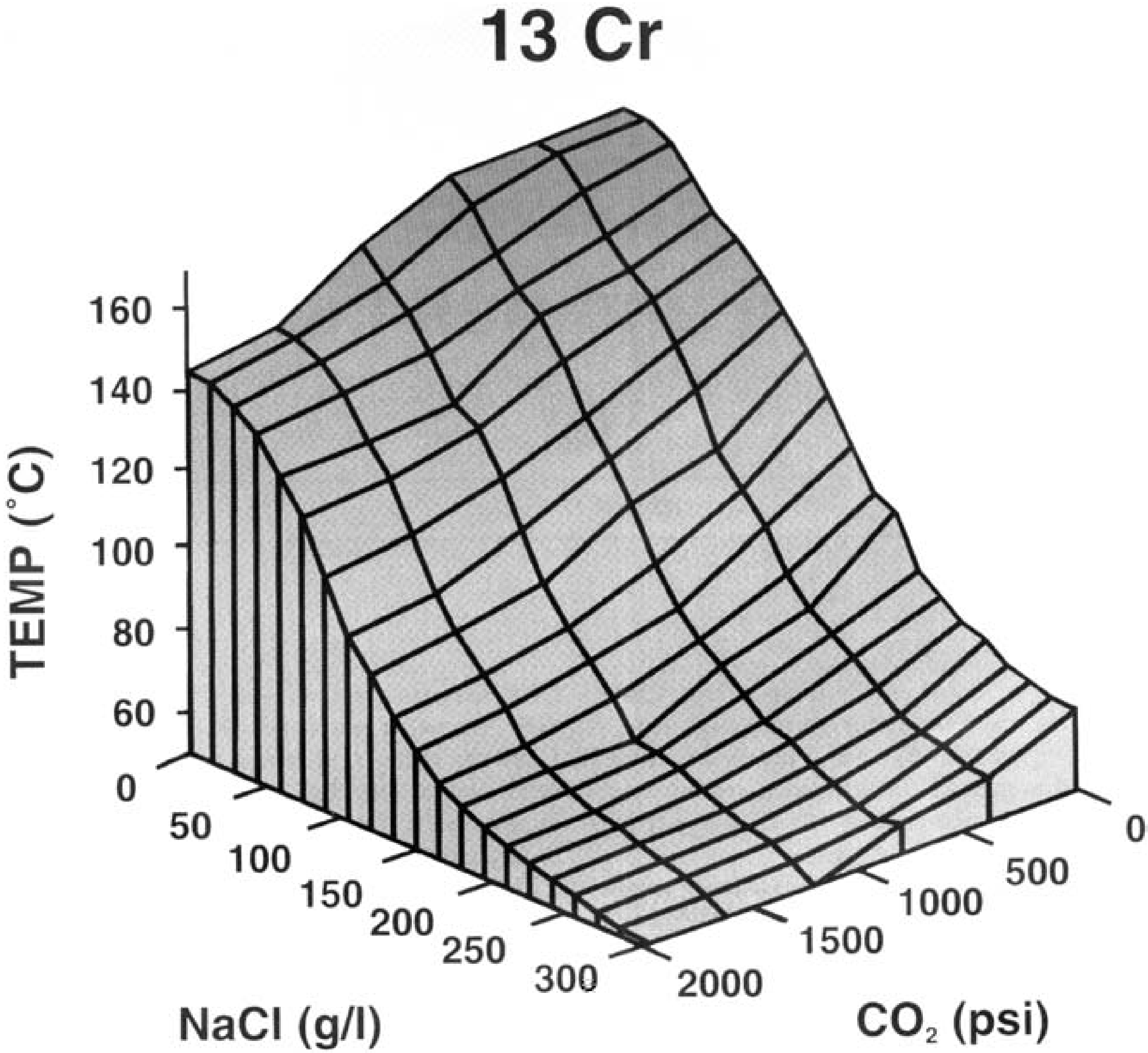

Figure 1 The corrosion resistance of 13Cr martensitic stainless steel in CO_2/NaCl environments in the absence of oxygen and H_2S. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

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 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.

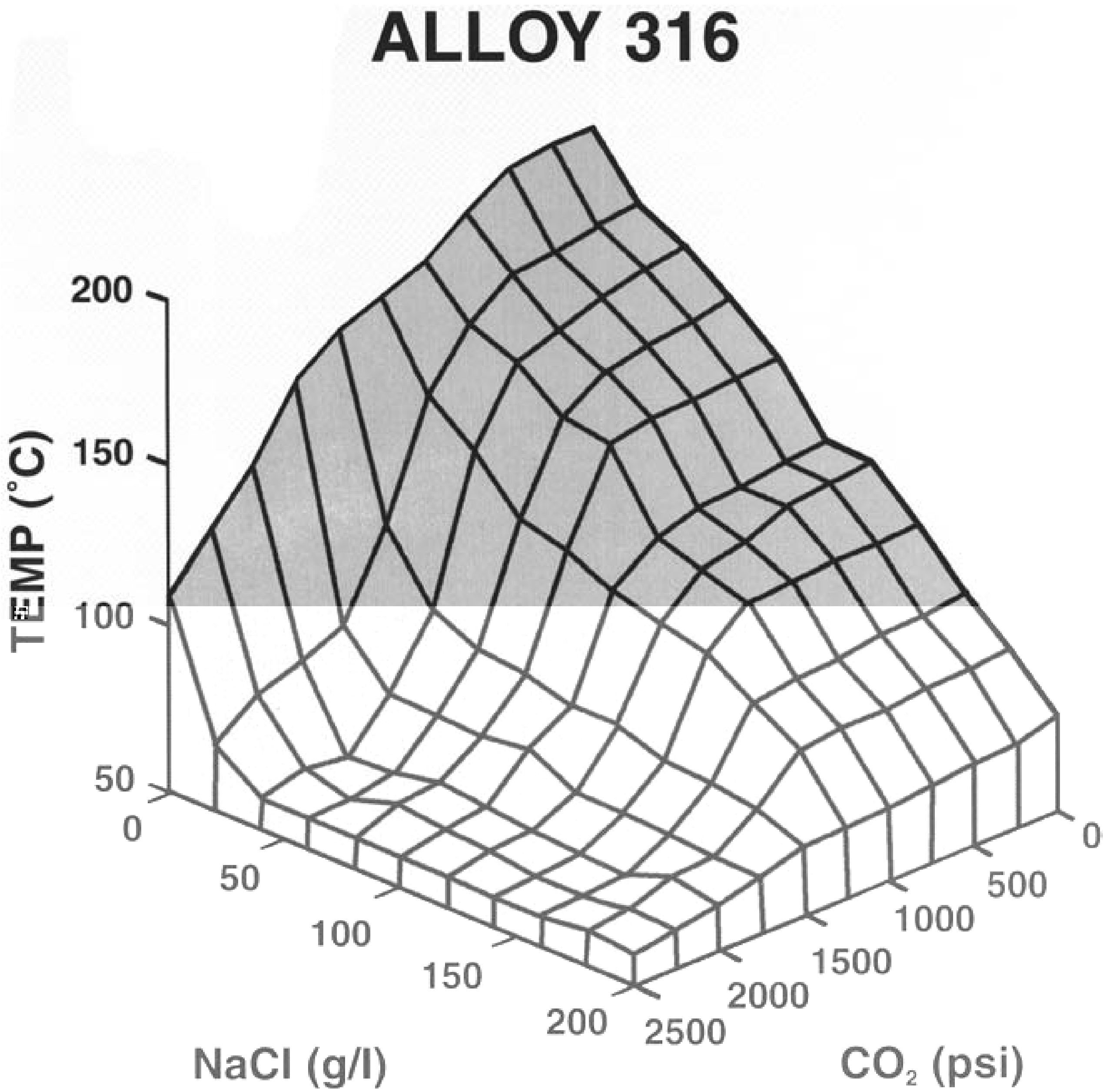

Figure 2 The corrosion resistance of Alloy 316 stainless steel in CO_2/NaCl environments in the absence of oxygen and H_2S. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

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 H_2S 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. On the other hand, the limits of 13 Cr are generally well understood except for H_2S exposure; the same exists for 316 and the duplex stainless steels (22 Cr and 25 Cr). Therefore, a note is made for these diagrams regarding H_2S limits.

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

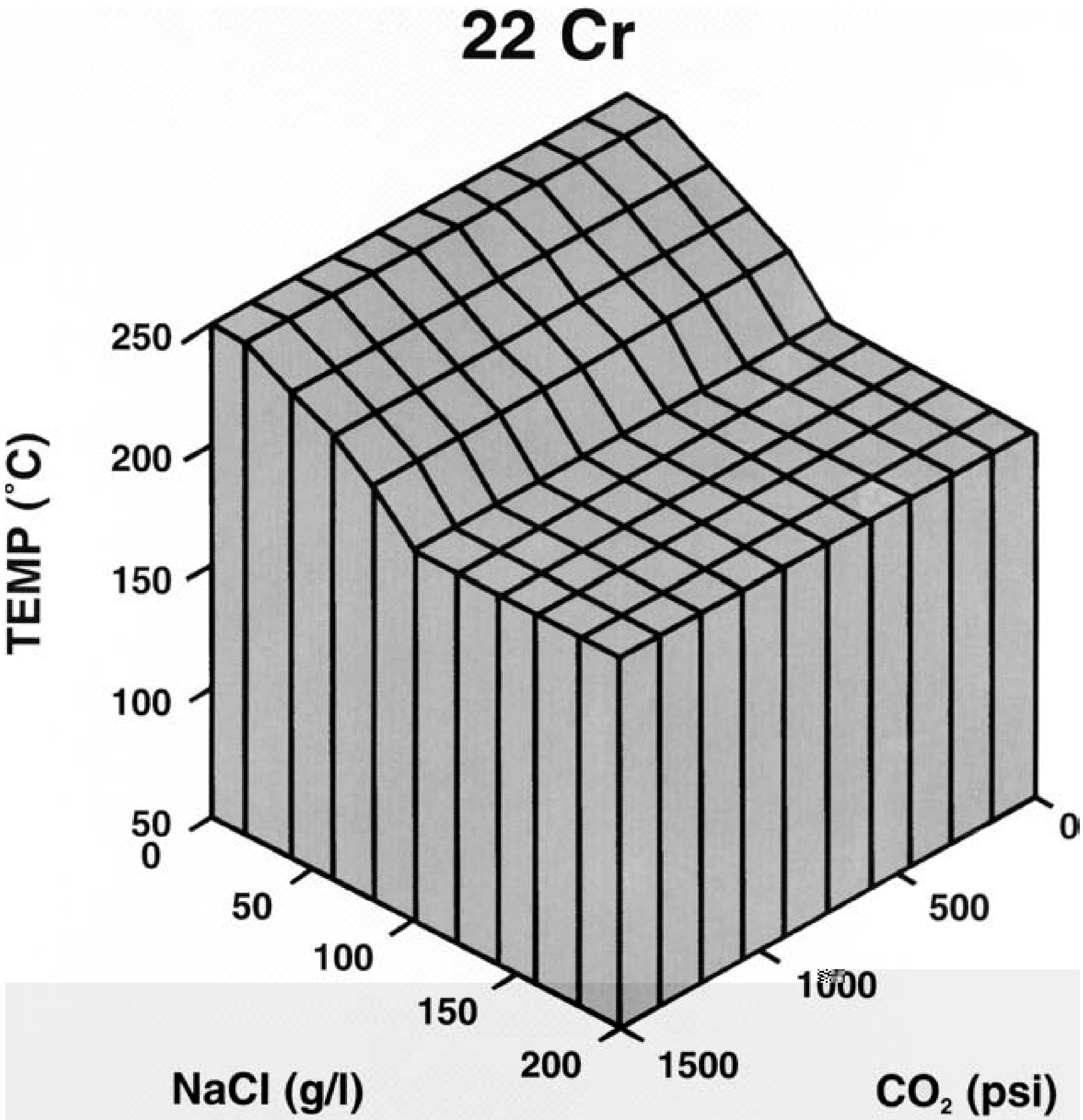

Figure 3 The corrosion resistance of 22Cr duplex stainless steel in CO_2/NaCl environments in the absence of oxygen and H_2S. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

cracking. In order to make the temperature scale universal, degrees centigrade 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 NaCI and is reported in that fashion (i.e., gram/litre or 5%, 20%, etc.). 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 3D 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 following table 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)	13	-	-	Bal.	0.8	0.2	-	-
316 (S31600)	17	12	2.5	Bal.	1	0.04	-	-
22 Cr (*)	22	5	3	Bal.	1	0.1	0.1	-
25 Cr (*)	25	7	4	Bal.	1	0.1	0.3	-
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.	-	0.03	-	1.2 Ti
625 (N06625)	22	Bal.	9	2	0.2	0.05	-	3.5 Cb
C 276 (N10276)	15	Bal.	16	6	-	0.01	-	2 Co, 3.5 W

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

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 CO_2 containing NaCl. This figure is only applicable in the absence of oxygen and hydrogen sulphide (H_2S). 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.

Hydrogen sulphide can also cause accelerated pitting corrosion of 13 Cr and lead to cracking. There is currently a controversy surrounding the acceptable limit of H_2S to which 13 Cr can be exposed without causing cracking or corrosion. The values range from 0 to 1.5 psia H_2S partial pressure. Therefore, the user must make a separate evaluation based on other data; however, a relatively conservative limit would be the NACE MR0175 concentration of 0.05 psia.

316 (Austenitic Stainless Steel)

Alloy 316 *(Figure 2)* or more commonly Type 316 stainless steel is frequently used for oilfield applications in the complete absence of oxygen. In deaerated environments the limiting factors are H_2S and chloride. As also explained in the sections for Alloys 13 Cr and 22 Cr, the H_2S resistance of Alloy 316 is marginal and in the presence of moderate chlorides can produce SSC and/or SCC. Therefore, *Figure 2* does not consider the

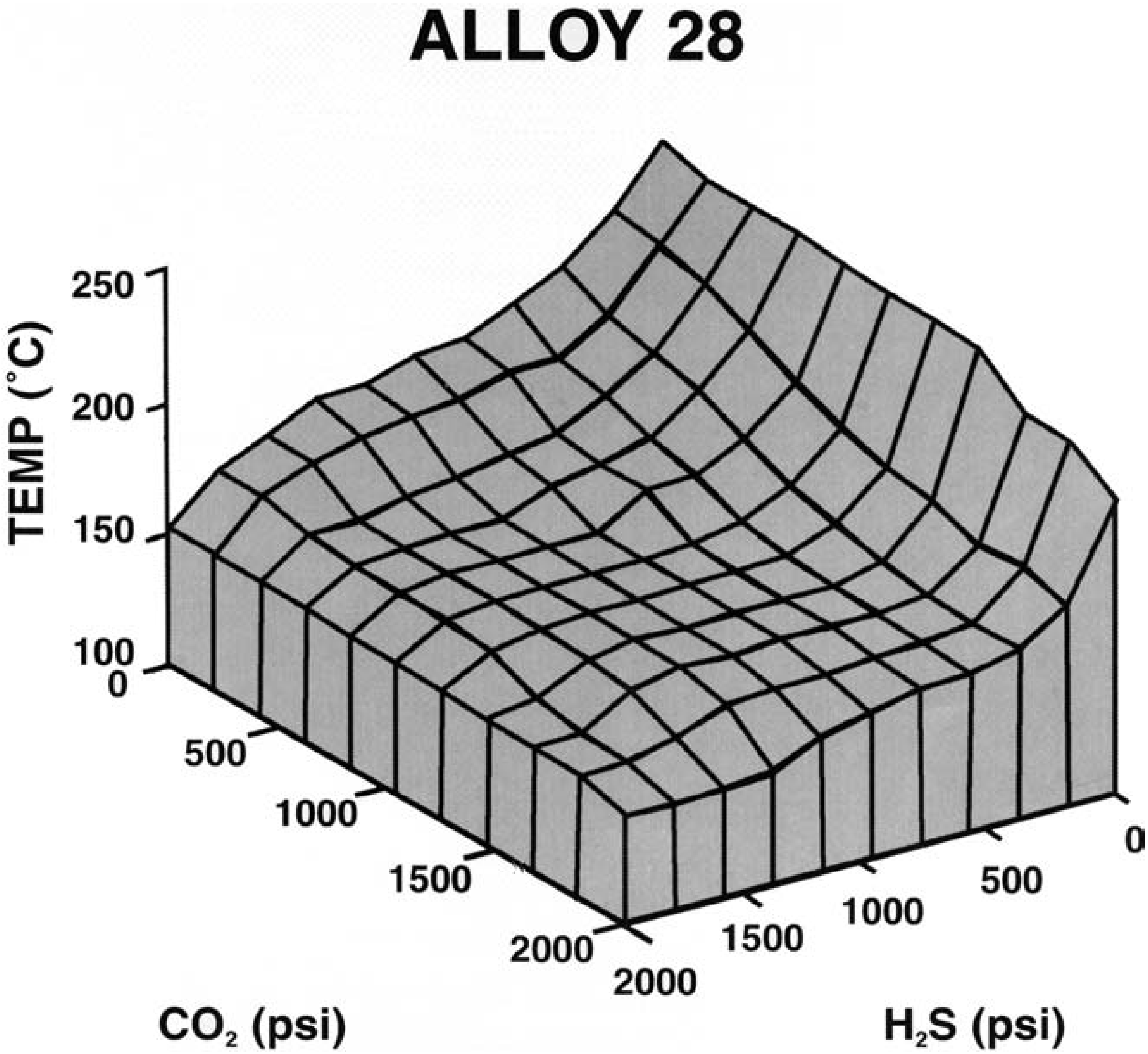

Figure 4 The corrosion resistance of Alloy 28 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

role of H_2S; rather the reader should make a separate evaluation based on testing for the specific application. Since Alloy 316 is widely used for surface piping, vessel cladding and clad line pipe, care must be taken to ensure the application is completely deaerated. *Figure 2* shows the broad range of applicability of this alloy at high chlorides and moderate temperatures but, for comparison, Alloy 316 when exposed to seawater (approximately 3.5% NaCl) which is aerated can easily fail from pitting at temperatures around 20°C and higher. Thus oxygen as well as H_2S in small concentrations have a profound effect on the resistance of Alloy 316 to corrosion and cracking.

22 Cr (Duplex Stainless Steel)

Comparing *Figure 3* with *Figures 1* and *2*, it can be

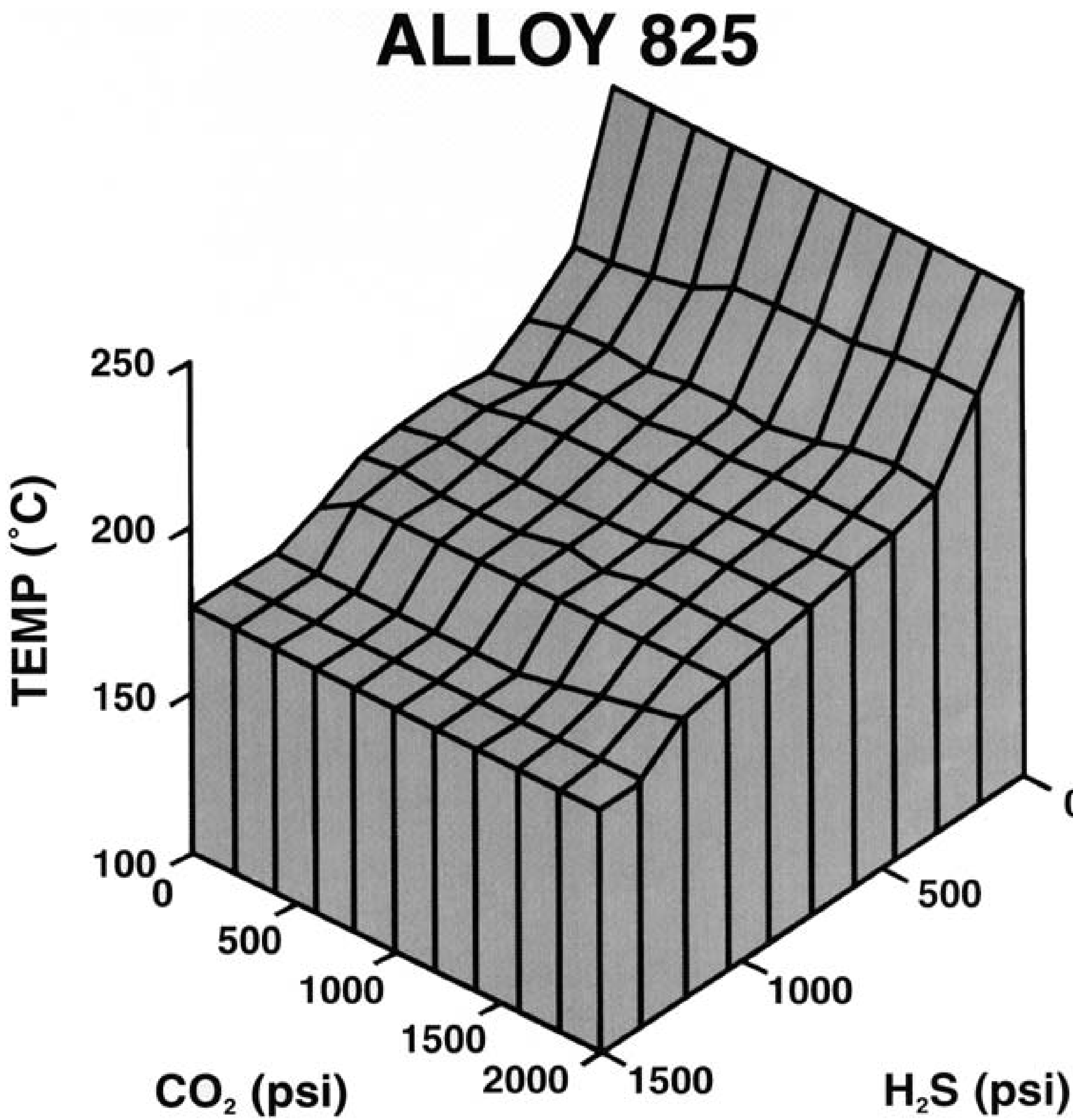

Figure 5 The corrosion resistance of Alloy 825 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

seen that the resistance of 22 Cr duplex stainless steel is significantly greater up to higher temperatures than for these other alloys. A diagram for 25 Cr duplex stainless steels is not presented because sufficient data are not currently available to develop one. However, the 25 Cr stainless steels are generally at least as corrosion resistant to CO_2 and NaCl as the 22 Cr, if not more so. Again as with 13 Cr and 316, the duplex stainless steels are susceptible to localized corrosion in the presence of small amounts of oxygen and H_2S. Moreover, cracking can occur in the presence of H_2S. Also, as with 13 Cr, controversy over the limit of H_2S leaves the decision to the user.

The duplex stainless steels are cold worked for strengthening which will not appreciably affect their resistance to corrosion in CO_2/NaCl but can have a considerable detrimental effect on their cracking resistance in H_2S.

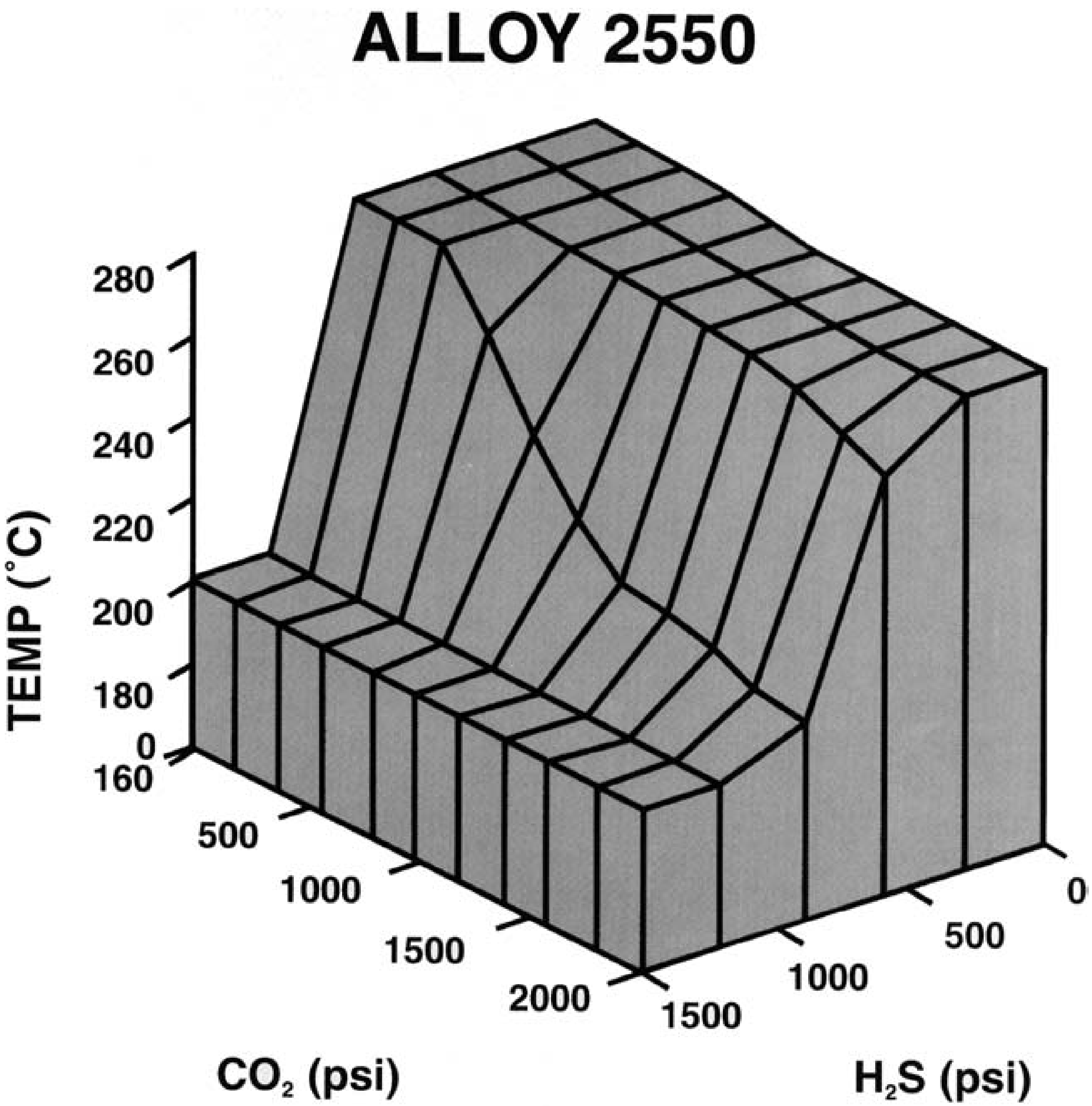

Figure 6 The corrosion resistance of Alloy 2550 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

Alloy 28

Alloy 28 has been successfully used for down-hole tubing and casing liners in many oil and gas wells. *Figure 4* shows the envelope of applicability for Alloy 28 which is highly resistant to environments containing H_2S in contrast to the stainless steels. Alloy 28 has limited resistant to SCC from elemental sulphur and applications that contain sulphur in combination with chlorides and H_2S should be evaluated further.

Alloys 825, 2550, 625 and C 276

These alloys *(Figures 5, 6, 7,* and *8*), as exemplified by *Figure 7*

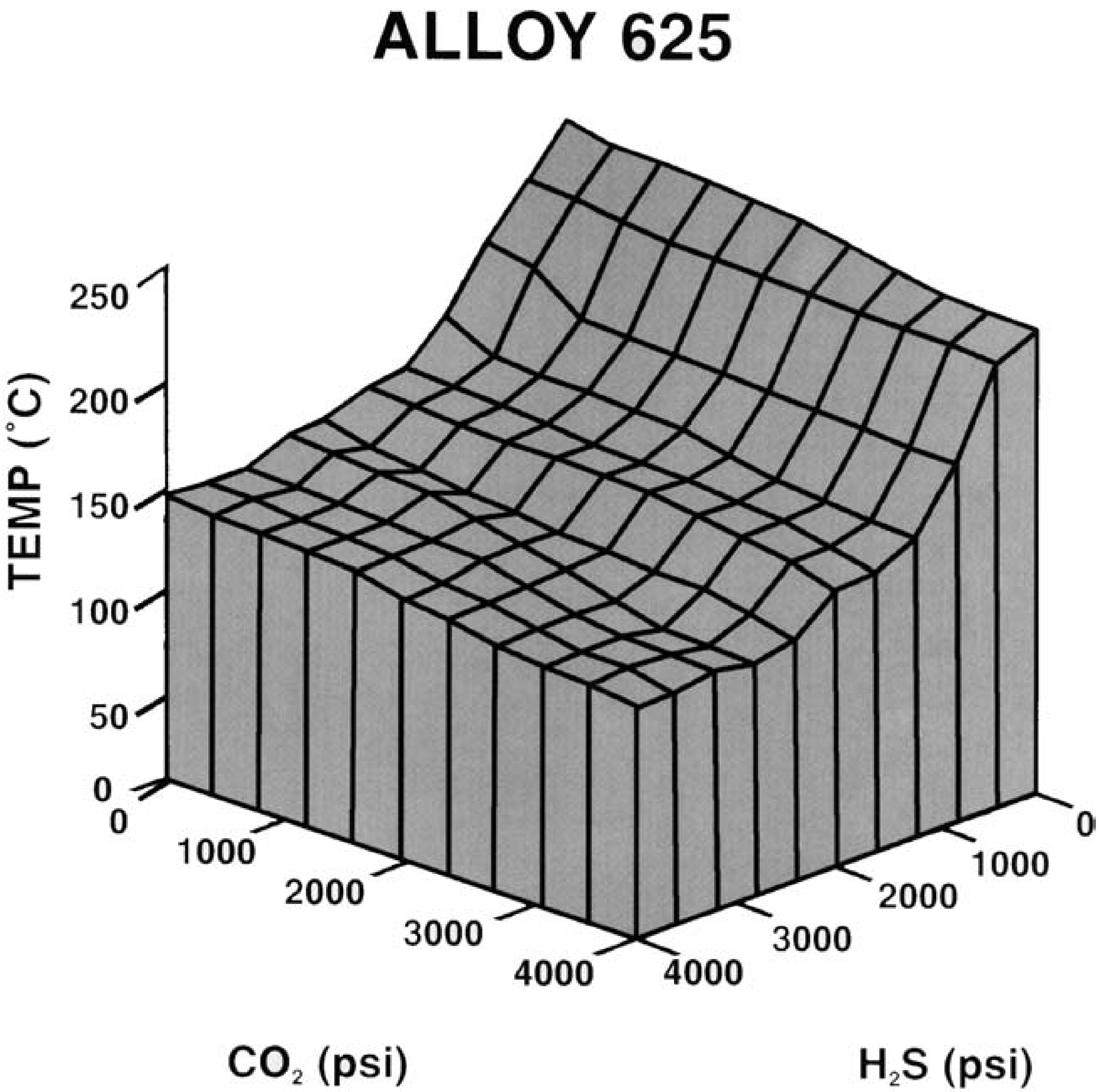

Figure 7 The corrosion resistance of Alloy 625 stainless steel in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

CO_2 and, therefore, are limited only by H_2S 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 ppm 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.

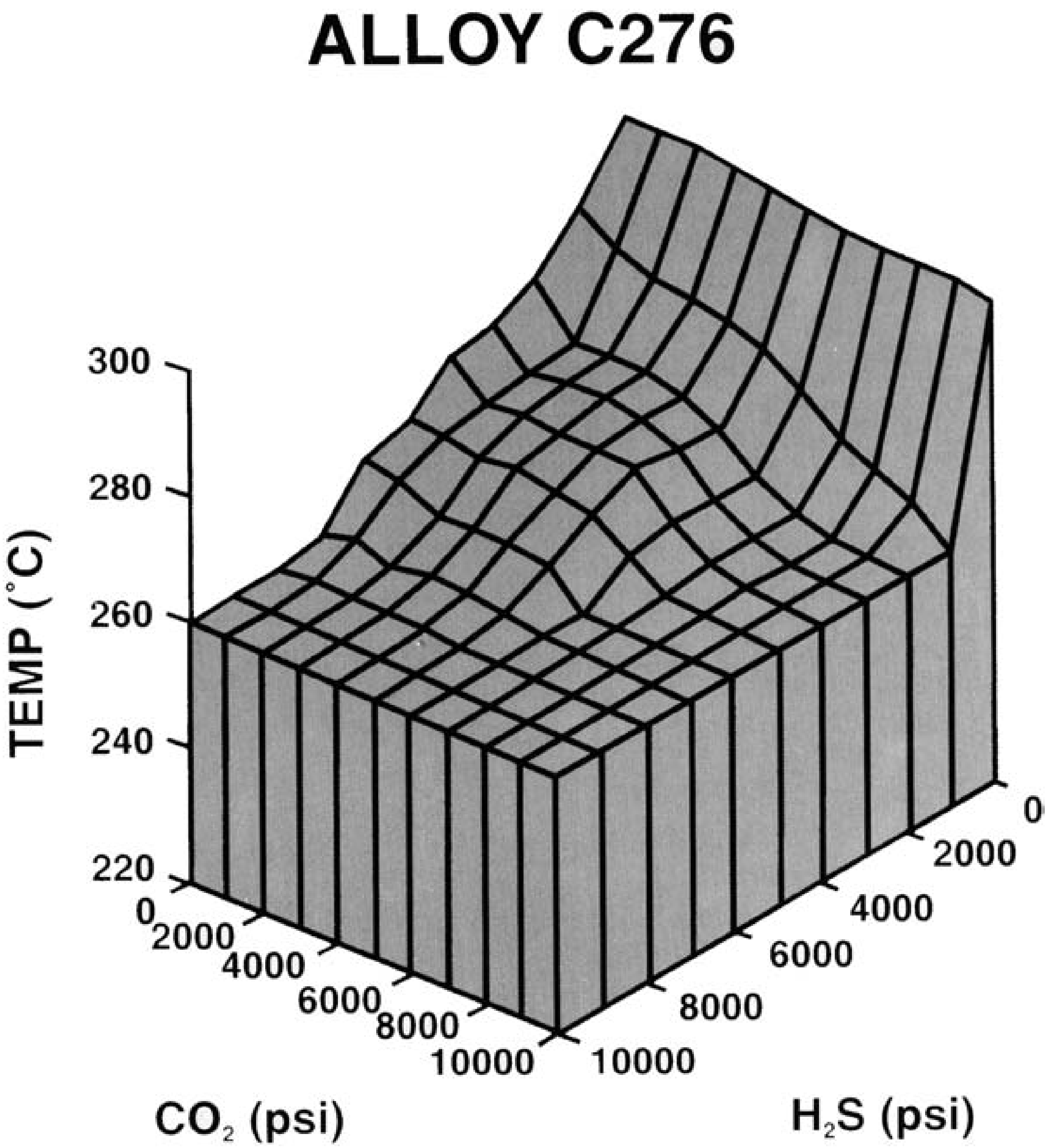

Figure 8 The corrosion resistance of Alloy C276 in H_2S/CO_2 environments in the absence of elemental sulphur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.

Examples of Diagram Use

Consider a wellstream with a partial pressure of 500 Psi CO_2 at 100°C and associated water that contains 50g/1 NaCl, with no H_2S. 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/1. 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 CO_2 and 500 psi H,S 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 2250, Alloy 625 or Alloy C 276 would be.

Comments

While it is NiDI'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. NACE Standard MR0175, Sulphide Stress Cracking Resistance Metallic Materials for Oilfield Equipment, NACE, 1999.
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 H_2S Service", 1996.