STRESS ENGINEERING SERVICES INC.

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Guideline for the Selection and Use of Corrosion Resistant Alloys in CCS and CCUS Projects

Final Report

Prepared for:
PCOR Partnership
Energy & Environmental Research Center
University of North Dakota
Grand Forks, ND

30 March 2023

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Prepared by: ______________________
Bruce Craig, PE, PhD
Subject Matter Expert

Prepared by: ______________________
Adam C. Rowe, PE
Principal

Reviewed by: Kimberly O. Flesner
Kimberly O. Flesner, PE
Subject Matter Expert

Stress Engineering Services, Inc.
13800 Westfair East Drive
Houston, Texas 77041-1101
Phone: 281-955-2900
Web: www.stress.com

Texas Registered Engineering Firm F-195

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Forward

Stress Engineering Services, Inc. (SES) was contracted by the PCOR Partnership to prepare this comprehensive guideline for the selection and use of corrosion resistant alloys (CRAs) in carbon capture and sequestration (CCS) and carbon capture utilization and storage (CCUS). The guideline was developed to provide PCOR membership with a basic guideline on considerations for selecting CRA material for use in CO_2 storage and utilization applications. This guideline represents the opinions of the authors and incorporates feedback from individual members of the PCOR Partnership who have reviewed this document and its provisions. The intent of this document is to summarize current best practices. It is not intended to replace education, experience, and the use of engineering judgment. Safety issues other than those expressly covered are not addressed in this document.

This guideline is strictly focused on the selection of CRAs for use in carbon dioxide (CO_2) injection wells. Pipelines used for transport of supercritical CO_2 are not addressed in this guideline since they are typically constructed of carbon steel.

It is of paramount importance to appreciate that for all the factors considered in this guideline, the most important is that only when a free water liquid phase is present will corrosion be of concern. In the absence of free water, when water is completely soluble in the supercritical CO_2 (SC-CO_2) and unlikely to break out, the fluid will not be corrosive, and standard carbon steel construction is sufficient.

It should be recognized throughout this guideline that, at the time of this writing, there is a complete lack of research data on performance of CRAs in SC-CO_2 containing impurities, with the exception of 13Cr stainless steel. Thus, the performance of CRAs is taken from allied industries with the expectation that the research data and service experience from these sources will be sufficiently similar to provide guidance for selection of CRAs for CCS and CCUS projects. Yet the specific CRAs for specific SC-CO_2 streams suggested in the guideline tables provided later in this report are only best estimates since no research data are available for most of the alloys highlighted herein.

The information detailed in this document provide comprehensive CRA guidance for operators and end users to consider in the design of CCS and CCUS systems. This guideline alone is not a substitute for review by a subject matter expert (SME), and it is recommended that material selection and procurement specifications be reviewed and accepted by an SME before equipment is ordered for construction.

This document represents the best knowledge and experience available at the time of its publication, but it is important to note that it is a starting point rather than a definitive standard. It is intended to provide guidance and recommendations, yet it is also designed to be adaptable and subject to revision as new information emerges.

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1. Introduction

At the request of the PCOR Partnership, the following comprehensive guideline was developed for the selection and use of corrosion resistant alloys (CRAs) in carbon capture and storage (CCS) and carbon capture utilization and storage (CCUS).

CCUS is defined as the process of capturing carbon dioxide (CO_2) to be recycled for further usage and differs from CCS in that CCUS is not intended for permanent geological storage of CO_2. Instead, the purpose of CCUS is to convert the captured CO_2 into more valuable substances or products – such as plastics, concrete, or biofuel – but retain the carbon neutrality of the production processes. Figure 1 shows the possible pathways for CO_2 utilization [1].

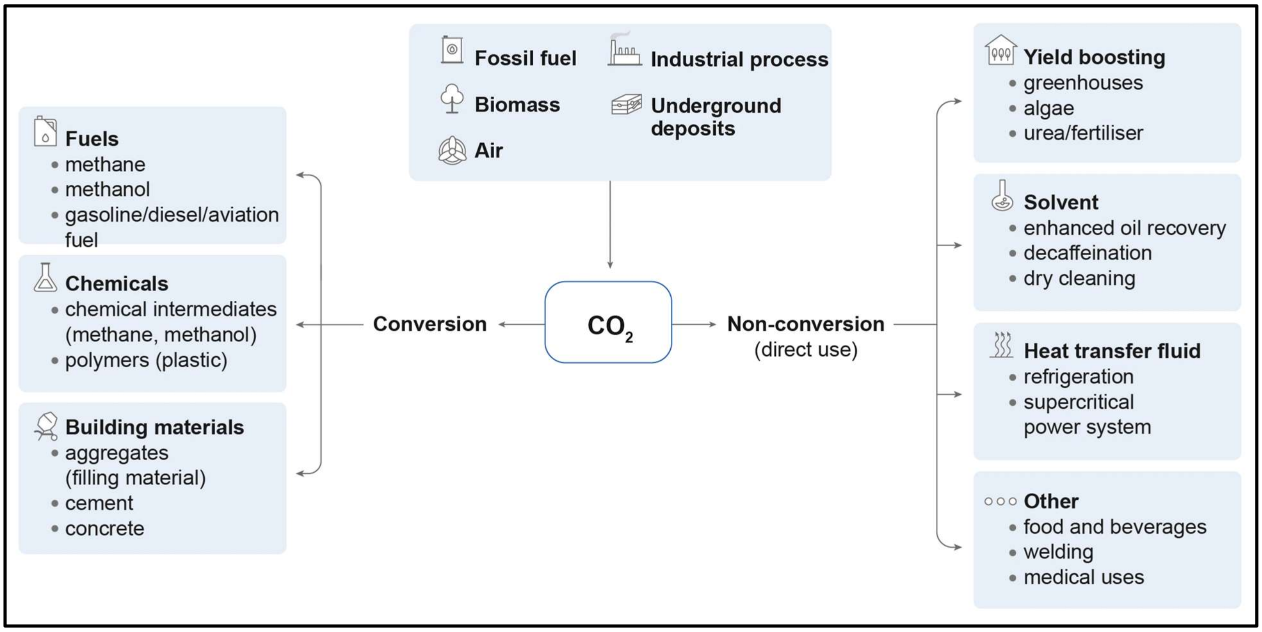


Figure 1. Possible pathways for CO_2 utilization.

There are so many possible uses for CO_2 under the CCUS definition such that the downstream processing is beyond the scope of this guideline. However, one pathway for CO_2 in CCUS is enhanced oil recovery (EOR), which will be considered in this guideline.

While the selection of a CRA material can be, and often is, based on common practices, each application requires an in-depth review of the complete system in order to determine the best material(s) for the application. The CRA material must withstand the length of time it will be in service to prevent migration of injected fluids out of the wellbore. Considerations include stream composition, reservoir fluids, flowing and static wellbore conditions, wellhead and surface equipment, downhole completion equipment, service life, etc.

It is of paramount importance to appreciate that for all the factors considered in this guideline, the most important is that only when a free water liquid phase is present will corrosion be of concern. **In the absence of free water**, when water is completely soluble in the supercritical CO_2 (SC-CO_2) and not at risk of breaking out, the fluid will not be corrosive, and standard carbon steel construction is sufficient. Operational experience has borne this out; petroleum industry enhanced oil recovery projects have been in operation for at least 40 years utilizing carbon steel pipelines for transport of SC-CO_2 with minimal issues. Therefore, for CCS where SC-CO_2 streams devoid of free water are transported and injected into non-water bearing formations, the entire system could be made from carbon steel equipment. Of course, this does not account for any potential leak from the tubing into the annulus that may be filled with a brine packer fluid, which is outside the scope of this guideline. However, for those CCS and CCUS systems where water is either anticipated to be present at some point such as injection into an aquifer or by virtue of incomplete dehydration, then CRAs must be a consideration.

Since carbon steel pipelines are standard practice for transport of SC-CO_2, and the use of CRA pipelines would be cost prohibitive, this guideline is strictly focused on the selection of CRAs which will be for injection wells.

It should be recognized throughout this guideline that, at the time of this writing, there is a complete lack of research data on performance of CRAs in SC-CO_2 containing impurities, with the exception of 13Cr stainless steel. Thus, the performance of CRAs is taken from allied industries with the expectation that the research data and service experience from these sources will be sufficiently similar to provide guidance for selection of CRAs for CCS and CCUS projects. Yet the specific CRAs for specific SC-CO_2 streams suggested in the guideline tables provided later in this report are only best estimates since very limited research data are available for most of the alloys highlighted herein.

2. Factors that Impact CRA Selection

When it is determined from process conditions that free water may be or will be present either during injection starting at the surface and/or due to a saline reservoir, the need for a CRA may be required to ensure sufficiently long service life. This section discusses the various factors that must be considered for selection of the most appropriate and cost effective CRA.

2.1 pH

The pH of the injected CO_2 if free water is present and/or the pH resulting from CO_2 contact with a saline formation is very important to the selection of an appropriate CRA. In these cases, the expected pH can be significantly lower than typically observed in oil and gas production.

Significant work has been performed by modeling the behavior and reactivity of dense phase CO_2 as it is injected into the well and the subsequent plume of CO_2 that develops around the wellbore over time. Since the mineralogy and properties of the reservoir are an important part of the models, it is common practice to select known reservoirs for study. B. Zerai [2] modeled the CO_2 sequestration in the Rose Run Sandstone, which is a candidate aquifer for CO_2 storage in the US. He found that the pH was lowest right at the wellbore but increased with both time and distance from the injection well. Figure 2 shows the results of three different CO_2 solubility models used by Zerai to predict pH. They all are very similar and show that regardless of time, the pH nearest the wellbore is always approximately 5.5. However, this is after a minimum time of 10 years. R. Smyth [3] found in laboratory studies that the pH initially dropped to 4.8 within hours after introduction of CO_2 but then quickly rebounded to and remained at 5.4, which is consistent with Figure 2. This was attributed to the mineral buffering from dissolution of Ca/Mg/Fe-bearing silicate minerals during CO_2 injection. Contrary to this, Lagneau [4] determined by modeling the Paris basin reservoir that, even after 10,000 years of injection, the pH at the wellbore would remain at 3.0 (see Figure 3).

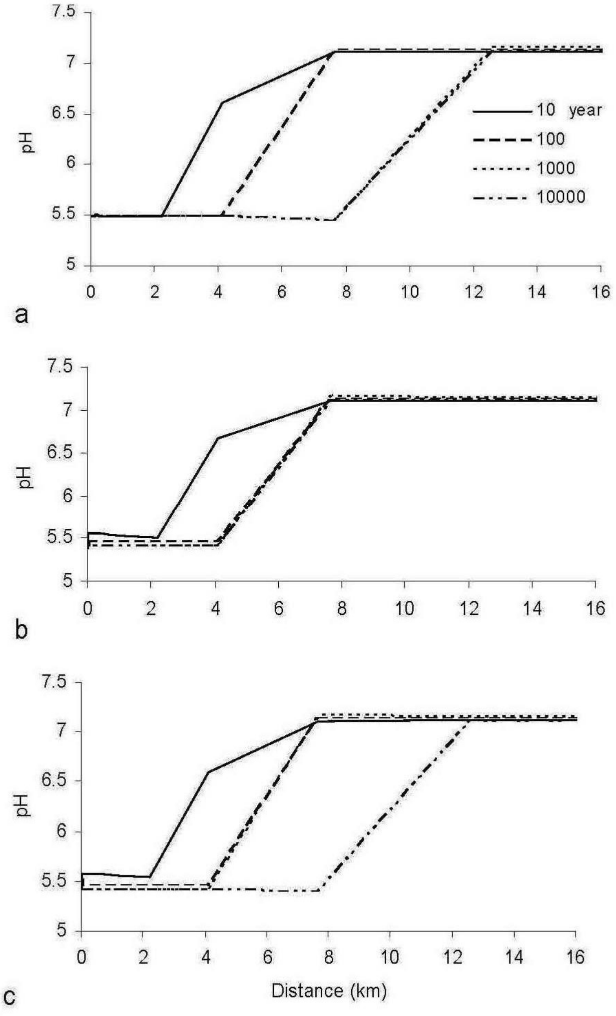


Figure 2. pH distribution as a function of time and distance from the injection well (km) for three different CO_2 solubility models (a, b, and c).

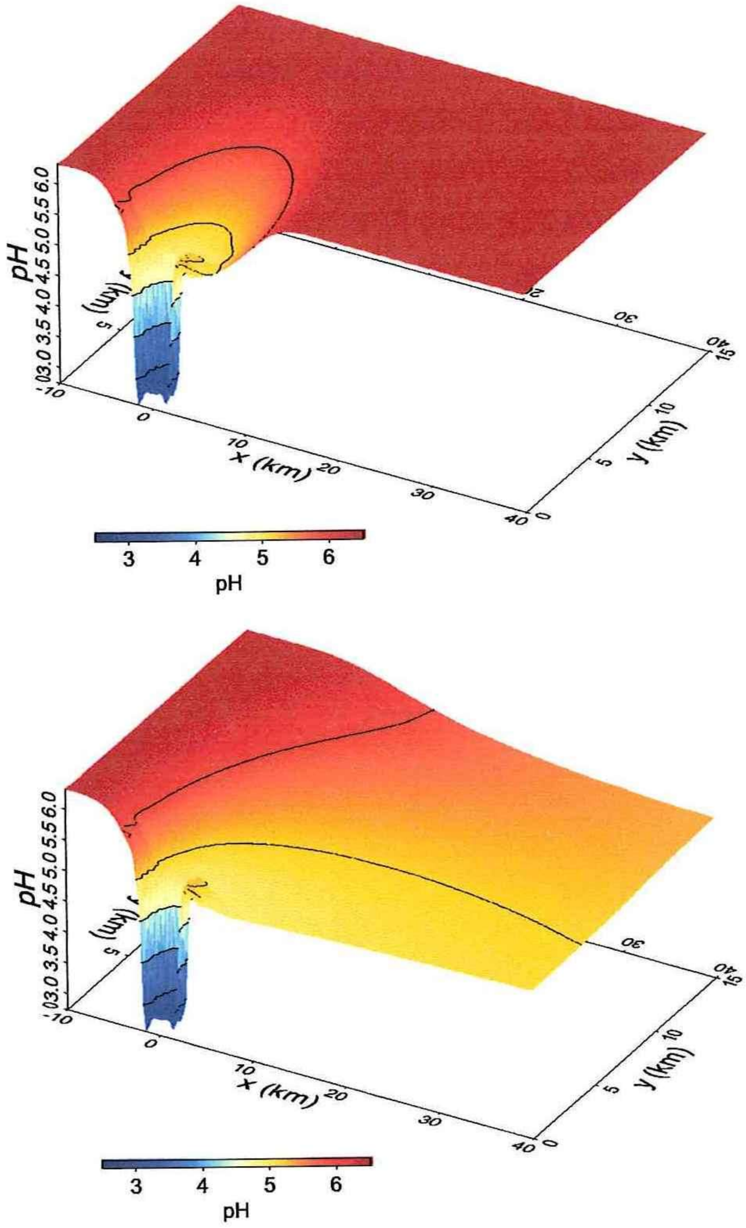


Figure 3. pH distribution model for CO_2 injection into the Dogger aquifer at 100 years (top figure) and 10,000 years (bottom figure). pH values less than 3 are a modeling error by the program according to the authors.

The extremely low pH predicted by Lagneau should be viewed with considerable skepticism based on more than 40 years of successful injection of supercritical CO_2 for EOR projects in the US. If the pH had been 3 for all these years, wellbores including the casing and cements should have been completely disintegrated by now, yet experience has shown that the casings and cements remain in place. Therefore, the moderate pH of 5.5 predicted by Zerai and measured by Smyth is probably more realistic, at least for the plume near wellbore. However, as shown later in this guideline, the pH of liquid (pure) water associated with SC-CO_2 is demonstrably around 3.0, which can lead to a very corrosive environment for injection equipment.

An important distinction between pH of producing oil and gas wells, for which most CRA selection guidelines are defined, and SC-CO_2 is the associated water phase is generally fresh with low total dissolved solids (TDS). As such, there is no buffering of pH in SC-CO_2 systems. Considerable work has been done at Ohio University studying this behavior and, as shown in Figure 4, the pH is 3.0 – 3.1 for SC-CO_2 at 1070 psi (73.8 bar) and 31 °C and above [5].

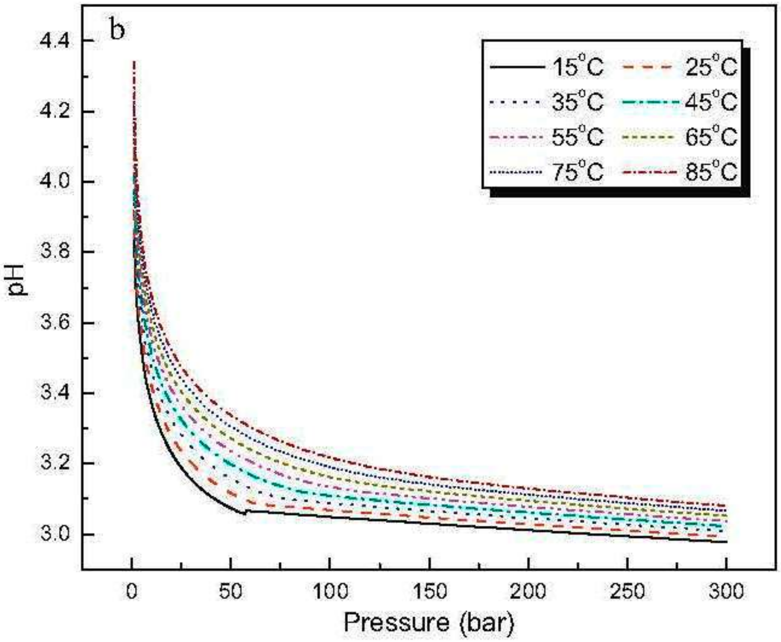


Figure 4. Variation of pH as a function of pressure and temperature.

Even more deleterious is the further drop in pH caused by impurities in the CO_2 such as SO_2 and NO_2. Ayello et al. found that adding as little as 100 ppm SO_2 to SC-CO_2 at 1,099 psi and 104 °F reduced the pH another decade below that shown in Figure 4 to approximately 2.5 [6].

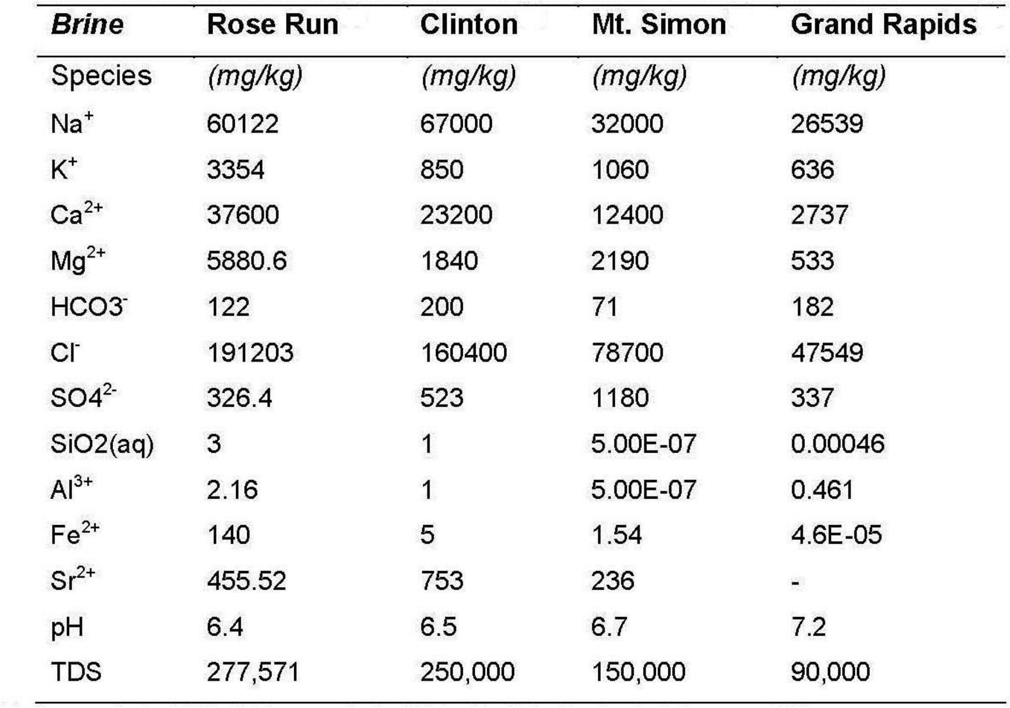
These are extremely low pH values rarely seen in oil and gas production and for which many CRAs have not been evaluated. Therefore, CRA selection in this guideline for such low pHs is based on some oil and gas well data, limited industry experience with alloys in SC-CO_2, plus the limited research data available for alloys in SC-CO_2.

2.2 Chloride Content

The chloride content of the water phase has a significant effect on the choice of CRAs, but the specific limits of CRAs to chlorides are a function of the temperature, pH, pH_2S, pCO_2, and the presence or absence of oxygen.

The chloride content in the reservoir near the wellbore is quite difficult to predict. According to Zerai, some typical brine compositions from reservoirs considered for CO_2 injection are presented in Table 1.

Table 1. Near Wellbore Brine Compositions of Different Reservoirs in Ohio and Michigan



Brine	**Rose Run**	**Clinton**	**Mt. Simon**	**Grand Rapids**
Species	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*
Na$^+$	60122	67000	32000	26539
K$^+$	3354	850	1060	636
Ca^{2+}	37600	23200	12400	2737
Mg^{2+}	5880.6	1840	2190	533
HCO3$^-$	122	200	71	182
Cl$^-$	191203	160400	78700	47549
SO4^{2-}	326.4	523	1180	337
SiO2(aq)	3	1	5.00E-07	0.00046
Al^{3+}	2.16	1	5.00E-07	0.461
Fe^{2+}	140	5	1.54	4.6E-05
Sr^{2+}	455.52	753	236	-
pH	6.4	6.5	6.7	7.2
TDS	277,571	250,000	150,000	90,000

The chloride content in the above table ranges from 47,549 to 191,203 ppm, which is a significant range. However, as modeled by Prevost et al. [7], close to the injection well the solubility of salt will be reduced due to evaporation of water into the CO_2 causing the precipitation of solid salt at the wellbore. Therefore, the chloride content will probably range from greater than 10,000 ppm initially to possibly saturation (approximately 200,000 ppm). For comparison, Table 2 provides the water composition for the Rose Run, Inyan Kara, Broom Creek, and Deadwood formations in North Dakota. As can be seen there is a wide variation in the chloride content from one formation to another. This is an important factor when selecting the appropriate CRA.

Table 2. Comparison of Several Formation Water Chemistries in North Dakota

Species	Rose Run		JLOC #1 (EERC Analysis)					
			Inyan Kara		Broom Creek		Deadwood	
	mg/L	% of TDS	mg/L	% of TDS	mg/L	% of TDS	mg/L	% of TDS
Na^+	60,122	21.7%	1,180	35.1%	16,900	34.5%	91,000	35.5%
K^+	3,354	1.2%	4.6	0.1%	3,002	6.1%	1,800	0.7%
Ca^{2+}	37,600	13.5%	13.9	0.4%	2,030	4.1%	8,340	3.3%
Mg^{2-}	2,880.6	1.0%	1	0.0%	404	0.8%	1,260	0.5%
HCO_3^-	122	0.0%	501	14.9%	67	0.1%	33.1	0.0%
Cl^-	191,203	68.9%	451	13.4%	26,400	53.9%	153,000	59.8%
SO_4^{2-}	326.4	0.1%	1,330	39.6%	3,060	6.2%	504	0.2%
$SiO_2(aq)$	3	0.0%	12	0.4%	1.0	0.0%	10.0	0.0%
AL^{3+}	2.2	0.0%	78	2.3%	263	0.5%	1,000.0	0.4%
Fe^{2+}	140	0.1%	1.0	0.0%	1.0	0.0%	25.20	0.0%
Sr^{2+}	455.5	0.2%	1.0	0.0%	49	0.1%	248.00	0.1%
pH	6.4		8.6		7.3		6.0	
TDS	277,571		3,360		49,000		256,000	

2.3 Temperature

Temperature is an extremely important parameter for defining CRA suitability but cannot be assigned without all the other corresponding factors such as chlorides, pH_2S, pCO_2, pH, etc.

2.4 Pressure

As with temperature, pressure is an important parameter; however, unlike oil and gas where partial pressure is commonly used to describe the effect of CO_2 on alloys, for SC-CO_2 dense phase fluids, fugacity is the correct term to describe the activity of CO_2. Figure 5 shows the corrosion rate of steel as a function of the pressure shown in brackets and the fugacity [8]. Fugacity is a measure of the actual partial pressure of a gas in comparison to an ideal gas. For an ideal gas at low pressure, partial pressures are an acceptable means of defining the effect of each component in the gas phase. Fugacity is the effective partial pressure and thus a measure of thermodynamic activity and also a measure of chemical potential. Note that increasing pressure of CO_2 does not have a one-to-one correspondence to fugacity. Rather, above the critical point (73.8 bar) the fugacity begins to level off compared to increasing pressure. The actual corrosion rates in Figure 5 are not relevant to CRAs, but it needs to be understood that CO_2 fugacity, rather than partial pressure, is the more important factor when evaluating the corrosivity of the fluid.

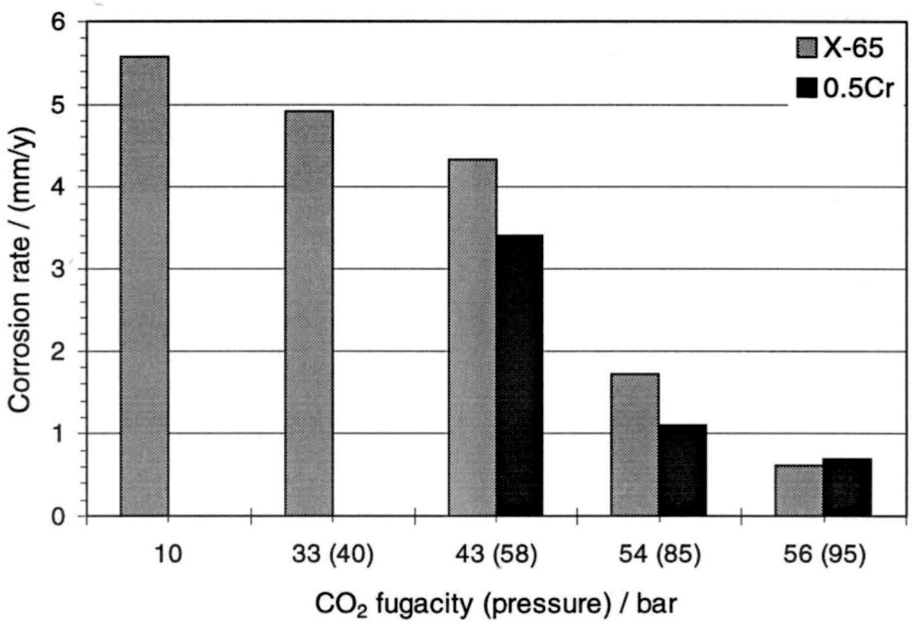


Figure 5. Average corrosion rate for two steels at 40 °C in water equilibrated with CO_2 at fugacity (pressure) shown.

Recently, with the drilling and producing of high pressure oil and gas wells, the need for evaluating CRAs as a function of fugacity has become important. Limited data are available for some alloys in this regard.

2.5 Hydrogen Sulfide, Sulfur, and Sulfur Dioxide

There are numerous forms of sulfur compounds, many of which do not impact CRAs. However, two that are important are elemental sulfur (S) and H_2S. Sulfur can induce stress corrosion cracking (SCC) and pitting in CRAs; however, at present there are no known sources of sulfur in CCS and CCUS systems so this threat can be ignored. H_2S on the other hand is a major factor in the selection of CRAs both from a cracking standpoint and possible pitting attack. This is a huge area of research and investigation leading to thousands of papers and technical reports that address the limits of CRAs exposed to H_2S, primarily with respect to sulfide stress cracking (SSC). The resistance of CRAs to SSC is covered in an industry standard, NACE MR0175/ISO 15156 which is too lengthy to detail here but should be referred to during any CRA selection process. However, this standard is applicable to production of oil and gas, and it remains to be determined whether CCS and CCUS operations are similar enough to apply this guide or if SC-CO_2 warrants different limits. For this guideline, the NACE MR0175/ISO 15156 standard was applied as best as could be for the conditions in CCS and CCUS wells.

It has also been determined that the presence of SO_2 in SC-CO_2 will promote the formation of sulfuric acid, dropping the pH to more acidic levels of one pH unit or more.

2.6 Oxygen

Producing oil and gas wells do not produce molecular oxygen (O_2), either as a gas or dissolved in produced fluids, so material selection methods for downhole tubulars in producing oil and gas wells do not account for oxygen exposure. In injection wells used for enhanced oil recovery, depending on the source of the stream, some oxygen may be entrained in injected fluids and must be considered in the material selection.

It is theorized that oxygen (and other contaminant gases) may lower the water solubility in high pressure CO_2, but this relationship has not been fully characterized. Oxygen dissolves into the water phase, increasing corrosivity to carbon steels and possible pitting and crevice corrosion in CRAs. Some CRAs may be susceptible to stress corrosion cracking when oxygen is present, even if they are not otherwise susceptible in oxygen-free production environments. Because only a very small amount of oxygen (10-20 ppb measured in the water phase) is needed to promote accelerated corrosion, reliable oxygen removal is not typically feasible in injection systems. For this reason, carbon steel injection tubing is not suitable when O_2 and water are present.

For CRAs, the pitting resistance equivalent number (PREN) is a helpful tool for ranking resistance to pitting and crevice corrosion in aerated brine. PREN is defined as follows:

$$PREN = \%Cr + 3.3 \times (\%Mo + 0.5\%W) + 16 \times \%N$$

For reference, it is generally accepted that a CRA needs to have a PREN ≥ 40 to be immune to pitting and crevice corrosion in aerated seawater. Injected CO_2 streams have few chlorides in the condensed water phase, so CRAs with lower PRENs, such as austenitic stainless steels, may be suitable if other parameters allow. As discussed in Section 2.2, the specific limits of CRAs exposed to chlorides in aerated water are a function of the temperature, pH, pH_2S, and pCO_2. For example, when a CRA is exposed to a saline aquifer, the lower PREN alloys would not likely be acceptable when O_2 is present due to the combination of chloride and temperature.

The presence of O_2 in SC-CO_2 streams presents a significant problem to the selection of CRAs since, unlike H_2S and CO_2 that are characterized by their partial pressures (or fugacities), the corrosivity from O_2 is defined by the concentration in the water phase. In order to define the O_2 content in water associated with SC-CO_2 or in contact with a saline reservoir, the concentration of O_2 would have to be modeled in the CO_2 phase as a fugacity in equilibrium with the liquid water phase in order to determine the likely O_2 content dissolved in the water phase for selection of an appropriate CRA. Currently, these data are not readily available.

2.7 Nitrogen

The presence of nitrogen (N_2) as an impurity in SC-CO_2 streams has no effect on corrosion and therefore is of no concern from a CRA selection standpoint. However, when NO_x is present as NO_2 ,which is highly soluble in water, the reaction with water produces nitric acid which can significantly lower pH. When both NO_2 and SO_2 are present, NO_2 catalyzes the oxidation of SO_2 to form sulfuric acid, again causing a significant drop in pH, typically on the order of one decade.

2.8 Hydrogen

Most oil wells do not produce molecular hydrogen (H_2), either as a gas or dissolved in produced fluids; however, it is not uncommon to find some small amounts of H_2 in producing gas wells. H_2 is typically not present in conventional injection systems for enhanced oil recovery (i.e., CO_2 flooding, alkaline, micellular, etc.). Therefore, CRA selection methods for downhole tubulars in oil and gas wells do not account for H_2 exposure, but most do account for H_2S exposure (see Section 2.5). The potential for H_2 to drive atomic hydrogen into the metal matrix is typically lower than for H_2S, so in general, CRAs resistant to environmentally assisted cracking (SSC) in the presence of H_2S are likely equally if not more resistant to cracking in the presence of H_2.

Hydrogen compatibility work performed by Sandia National Laboratory has shown that annealed type 316 austenitic stainless steel and solid solution nickel-chromium CRAs exhibited excellent resistance to hydrogen embrittlement in gaseous hydrogen environments. Duplex stainless steels (i.e., 22Cr and 25Cr alloys) and martensitic stainless steels (i.e., 13Cr alloys) have been shown to be susceptible to hydrogen embrittlement, the severity of which depends on the temperature and hydrogen pressure.

The impact of hydrogen on CRAs has not been investigated experimentally in CCS and CCUS systems, but H_2 is not expected to be of significant concern for CRA selection in most CCS and CCUS systems due to the low partial pressures (fugacities) of H_2 and low operating temperatures relative to where hydrogen degradation is normally observed. For applications where substantial H_2 is expected, material selection should be reviewed by a subject matter expert familiar with hydrogen damage phenomena and may require laboratory testing.

2.9 Water Content and Chemistry

Water chemistry is an important factor in the determination of the corrosivity of a process environment. In the absence of a free water phase there is no corrosion. Thus, SC-CO_2 that has been dehydrated will not be corrosive to steels or any other alloys which is why the transportation of SC-CO_2 can be accomplished using carbon steel pipelines. However, once free water is present, the corrosivity of the water phase determines what alloys are susceptible to corrosion and those which are not. The corrosivity is defined by the temperature, the pressure, water chemistry (i.e., total dissolved solids, chloride content, buffering species such as bicarbonate, acetate, etc.) and the thermodynamic activity of H_2S and CO_2 in solution. These latter parameters are not easily determined, especially from any water analyses or field measurements.

Many years ago, the oil and gas industry adopted a way to approximate the effect of such thermodynamic activities by applying the ideal gas law and assuming the partial pressure of acid gases was sufficient to define the role of H_2S and CO_2 on corrosion. Today this is still the most widely applied method, but recent developments in deep oil and gas reservoirs have dictated that the more thermodynamically correct term of fugacity is more appropriate. However, calculation of partial pressure is far easier than calculating the fugacity of H_2S and CO_2 in the appropriate phases. Specific software programs are required to determine the fugacity of these species; therefore, this guideline will continue to use partial pressures, which is considered more conservative than applying fugacity.

Once the acid gases are in solution in the water phase, the pH is defined by the concentration of their presence as well as the buffering capacity of the water, which is dependent on the total alkalinity, specifically such species as bicarbonate and organic acids (acetate, formate, etc.), that reduce the effect the acid gases have on the pH. Therefore, in order to properly determine the best CRA for a system, a complete water analysis must be provided and used as input to software programs to calculate the pH. However, the majority of corrosion testing and presentation of results for CRA limits is shown as partial pressures of acid gases and rarely related to pH as is shown in Section 3.4.

As stated earlier, one other important consideration is the presence of oxygen. In contrast to the use of partial pressures for H_2S and CO_2 the resistance of CRAs to corrosion in the presence of O_2 is related to the dissolved O_2 content (DO) in the water phase. A large body of data has been generated for CRAs and their resistance to attack from DO. The two primary forms of attack are referred to as pitting and crevice corrosion and are represented as temperature limits above which attack occurs and below which it does not. Thus, for pitting the value is represented as CPT (critical pitting temperature) and for crevice attack as CCT (critical crevice temperature). Table 3 is an example of these limits in seawater, which is approximately 20,000 ppm chloride. This is similar to many saline water formations but less than those shown earlier in Table 1. These limits mean that at temperatures above the CPT and CCT, the alloy will likely corrode.

Table 3. CPT and CCT for Select CRAs in Seawater

Alloy	CPT, °C	CCT, °C
304 SS	2	-15
316 SS	10	-10
22Cr DSS	40	20
25Cr SDSS	80	70

In the absence of chlorides (i.e., fresh condensed water from SC-CO_2) there will be no pitting or crevice attack.

CPT and CCT will be different in different fluids. No research or testing work has been done to define these limits when O_2 is present in SC-CO_2 streams for CRAs.

2.10 Annular Wellbore Fluids

Annular wellbore fluids should be carefully selected to be compatible with the CRA materials used in well construction. The annular fluids are typically halide salts of a specified density, often supplied with a package of additives (corrosion inhibitors, etc.). Under normal operating conditions, the impact of annular fluids on CRAs in CCS and CCUS injection wells will be similar to that of oil and gas production wells and EOR injection wells. In the case of a tubing leak where CO_2 from the injection stream commingles with halide brine, the resulting environment may become more corrosive, which may also present a stress corrosion cracking risk to certain CRAs.

Annular fluid selection is outside the scope of this guideline and should be reviewed by a subject matter expert. The review should include any additives to be supplied with the annular fluid. CRAs that do not have demonstrated compatibility with the specified annular fluids may require qualification by laboratory testing.

2.11 Service Life

The use of CRAs for corrosive well applications has been predominantly developed for oil and gas wells. Some shallow low pressure hazardous waste and disposal wells have utilized CRAs, typically type 316 stainless steel, but are not considered applicable to the injection of SC-CO_2, which because of the greater depths and pressures require higher strength CRAs. Therefore, the wide use of CRAs in the petroleum industry provides the best means to qualitatively estimate service life. Yet some of these alloys have only been in service for just over 40 years (i.e., 25Cr) while the industry experience with other CRAs such as 13Cr indicate they may only be suitable for 10-15 years. Moreover, there are currently no means to predict service life of CRAs due to the highly localized forms of corrosion attack that occurs rather than a uniform wall loss more common to carbon steel equipment that can be modeled and predicted. While the excellent history of CRAs in the oil industry is encouraging, at present the predicted life of these alloys cannot be considered to be more than 50 years for some of the higher CRAs (i.e., 25Cr and nickel-based alloys) and shorter for those such as 13Cr simply because there is no history for these alloys in environments sufficiently similar to petroleum production.

2.12 Other Pertinent Industry Experience with CRAs

One other CRA application that is useful for comparison to CCS materials selection is the wide use of acid gas injection (AGI) wells to dispose of CO_2 and H_2S. The injection of acid gas typically from gas processing plant is also handled using dense phase properties. Like CCS, AGI fluids also contain water vapor.

The ability to model the phase behavior of these acid gas injection streams has been quite good and is the key to materials selection for the acid gas injection equipment. If the associated water is found to be entirely soluble in the acid gas stream or the stream is dehydrated, then corrosion from H_2S and/or CO_2 will not occur. However, if the potential for a liquid water phase is moderate to light, then corrosion may be a problem. Contrary to oil and gas production containing H_2S and CO_2, the conditions are not as severe since the acid gas stream will contain little or no chlorides and the temperatures are often far lower than in deep wells. Moreover, it is common practice to pump the CO_2/H_2S stream as a dense phase to the injection well, in which case the water solubility is much higher than in the gaseous phase. Therefore, carbon steels and stainless steels are often used for acid gas injection equipment with great success. It is customary and prudent, however, to specify that all acid gas injection equipment be purchased to and fabricated in accordance with NACE MR0175/ISO 15156 since SSC can occur very quickly even during a minor upset when liquid water precipitates. There has been considerable and successful experience with acid gas re-injection in Canada and the US so that the materials of construction are very well established from years of injection. The excellent history of AGI in North America has been the result of proper dehydration of the fluids so corrosion is minimized. However, some operators jeopardize these successes by commingling produced water and/or cooling tower water with acid gas.

Much the same as for transport of SC-CO_2, the materials for the injection flowline are decided based on whether the dense phase acid gas is fully dehydrated at this point and will not drop out water on the way to the injection well or not. Since there will be essentially no chlorides at this point, the choice becomes carbon steel or type 316 stainless steel. Most often the flowlines are made from carbon steel and welded to meet NACE MR0175/ISO 15156; no other special precautions are taken. However, some companies feel an extra level of reliability is needed and use type 316 stainless steel for injection lines. For injection wells, the injection tree is typically steel trimmed with stainless steel, frequently the lower master valve is clad with alloy 625 (API 6A HH) to guarantee that the well can always be shut in. In some cases, only the seat pockets are inlaid with alloy 625 and the seats and gates and stems are alloy 625 or 718. A subsurface check valve is placed at the bottom of the tubing string to prevent back flow of the acid gases. The tubing string is either J55 or L80 and may be bare. Some companies prefer to internally plastic coat the tubing, which is generally not useful since plastic coatings often experience breaks in the coating from running in the well or after years of service and are not reliable for more than about 10 years.

Packers are most often constructed from a CRA material. Casing below the packer is generally recommended to be a CRA (i.e., G3/2550) due to the risk of high chloride contact with formation water or completion fluids left in the wellbore. In some cases, the tubing below the packer is also a CRA. One important difference between AGI and CCS and CCUS is that AGI wells do not have dense phase streams with O_2 present. This unknown for CCS and CCUS wells is an important distinction and makes selection of CRAs very difficult.

2.13 Other Factors to Consider

Downhole environments are complex, and there are numerous factors outside the scope of this guideline that can affect the performance of the systems.

2.13.1 Environmental Cracking

One such additional factor that should be considered when designing CCS and CCUS systems but for which there are no specific test data is the risk of environmental cracking. While there are many mechanisms of this highly localized form of damage the two likely mechanisms are sulfide stress cracking (SSC) and stress corrosion cracking (SCC), more specifically SCC from chlorides in low pH fluids. The former mechanism, SSC, is well codified in NACE MR0175/ISO 15156. While this mechanism and the resistance of alloys for wells is well defined, it is applicable to oil and gas production and no studies have been performed to define if the same performance occurs in SC-CO_2. It is assumed for this guideline that the NACE MR0175/ISO 15156 standard is sufficiently suitable for SC-CO_2 and as such has been incorporated into this document. Contrary to SSC, there is no industry standard for alloy resistance to chloride SCC. SCC is mechanistically different from SSC; SSC is a hydrogen cracking mechanism, while SCC is an anodic cracking mechanism in the presence of chlorides. The susceptibility to SCC of alloys is a function of a specific ion or species in solution and a particular metal. For example, carbon steels are not susceptible to SCC from chlorides whereas austenitic stainless steels can be. Moreover, for many CRAs acidic environments coupled with specific ions can further exacerbate SCC. Very limited work has been done to identify any risks to CRAs in CCS and CCUS from environmental cracking.

2.13.2 Cement

There is considerable concern in the CCS and CCUS community over the long-term stability of cements used to anchor casing in CO_2 injection wells. The chemical reaction of CO_2 with Portland cement is complex, involving the dissolution of portlandite, dissolution of calcium silicate hydrate (the primary structural material in cement), and the precipitation of calcium carbonate ($CaCO_3$). If the first two reactions predominate, the flux of CO_2 will increase with time as the cement sheath deteriorates. If, however, precipitation of $CaCO_3$ is significant, possible CO_2-leakage paths may self-seal and ultimately limit the flux of CO_2. The reaction of cements with CO_2 and brine is currently a very active area of research. A particularly good review of oil well cements and their resistance to supercritical CO_2 has been presented by R. Nygaard [9]. A complete review and set of guidelines for cementing practices is beyond the scope of this report.

2.13.3 Geology

Various geological formations may be used to store CO_2. Reservoir geology is important to consider in the overall system design, but geological implications are beyond the scope of this material selection guideline. However, aqueous reservoir fluids exposed to the wellbore within the geologic storage zones will need to be considered (see Section 3.3).

2.13.4 Threaded Connections

It is common practice when selecting CRAs for casing, tubing, and accessories to choose a gas-tight premium connection rather than a standard API connection. There are numerous premium connections in the industry such as from VAM, JFE, Tenaris, etc.; however, the specific CRA connection appropriate for any application is beyond the scope of this guideline. Best practices for CCS and CCUS wells is to require gas tight premium connections of CRA tubulars.

3. Definition of Limits for CRAs

3.1 Temperature – Pressure Correlation

Temperature is an important factor for defining the limits of CRAs, but it alone is not sufficient since all the other factors reviewed in Section 2 must be considered at the same time. This is because they are all dependent variables. Moreover, with a few exceptions, essentially all the CRA data that describe the envelopes of acceptability are based on partial pressure of acid gases (i.e., pCO_2 and pH_2S) but SC-CO_2 streams are not correctly defined by partial pressure; rather, the CO_2 and impurities are correctly defined by fugacity. At present, there are few available data that would allow CRA selection based on fugacity; therefore, the limits described below are from laboratory testing based on partial pressures. At this time it is believed, based on recent efforts in the petroleum industry comparing partial pressures and fugacity for high pressure wells, that using partial pressure instead of fugacity will be conservative and will not lead to a significant difference in performance.

3.2 CO2 Stream Composition

It is common practice when discussing CO_2 stream compositions to refer to the various methods for removing CO_2 from the specific plant generating this gas and the associated impurities. These methods are:

- Post-combustion capture
- Pre-combustion capture
- Oxyfuel combustion capture

However, more pertinent to this guideline is the composition of the final stream to be injected. As such, some examples of the streams from various sources are summarized in Table 4, keeping in mind the typical analysis is for CO_2 > 95% with no free water present (usually expressed as < 30 lb/MMscfd). These examples are not exhaustive and are presented solely for comparison. Many other industry sources are not included in the table. Exact conditions cannot be provided since each case will depend on the source of the CO_2 and the methods used to process it for injection.

Table 4. Examples of the Streams from Various Sources

Industries	Typical Impurities
Power Generation – Coal Fired Plants *(IPCC, Carbon Capture and Storage, Working Group III, 2005)*	0-0.5% SO_2, ~ 0.01% NO, 0-0.6 % H_2S, 0- 2.0 % H_2, 0-0.4 % CO, 0.01-3.7 % $N_2/Ar/O_2$
Power Generation – Gas Fired Plants (*IPCC, Carbon Capture and Storage, Working Group III, 2005*)	0-0.1 % SO_2, ~ 0.01% NO, < 0.01 % H_2S, 0-1.0 % H_2, 0-0.04 % CO, 0.01-4.1 % $N_2/Ar/O_2$
Chemical Plants	N_2, O_2 and H_2O
Other Industries such as natural gas plants (but primarily for EOR)	0 – 1 % H_2S, 2% CH4, 0-4% N_2, 0-10 ppm O_2, ≤ 0.1% H_2O
Ethanol plants	0% SO_2, ~ 1.5% N_2, < 2% O_2
Fertilizer plants	0.07% H_2, 0.44% N_2, 0.055% O_2, 0.01% Ar, 2.4 wt % H_2O

The ranges of various impurities shown in Table 4, while typical of design conditions, are in many cases too wide for CRA selection criteria. For example, O_2 given as < 2% or in combination of $N_2/Ar/O_2$ are insufficient to make an informed CRA choice since one alloy may be suitable for zero O_2 while another may be required if O_2 is 1%. The summary guidelines presented in Appendix A are based on the ranges shown in Table 4. Any significant changes will require re-evaluation, and the guideline Tables A.1, A.2, and A.3 may not be applicable.

3.3 Storage Zone Fluids

Injection wells entering storage zones with aqueous reservoir fluids must account for the composition of the reservoir fluids. The combination of salinity, pH, temperature, and other parameters of the reservoir fluids may degrade certain CRA materials within the storage zones.

In the US, several groups consisting of government and industry along with universities have formed partnerships to characterize the best regional locations for carbon sequestration. As part of their regional characterization, the Regional Carbon Sequestration Partnerships (RCSP's) identified and examined the location of potential geologic storage in basins throughout each region. High level resource estimates were calculated for the primary storage formations and these estimates will continue to be refined as the RCSP's continue to validate storage potential in their respective region. The conservative estimates of storage potential in North America, calculated in gigatons, are shown in Table 5 below [10].

Table 5. Estimates of Storage Potential in North America

Reservoir Types	Low (Billion Metric Tons)	High (Billion Metric Tons)
Saline Formations	1,653	20,213
Oil and Gas Reservoirs	143	143
Unmineable Coal Areas	60	117

There are pros and cons to the type of reservoir selected for carbon storage; however, saline formations offer the greatest potential for carbon storage and therefore will be the likely storage location for future CCS projects both in the US and Canada. Since these are saline formations, water is present along with chlorides, which could adversely affect the integrity of those portions of casing and tubing exposed to the saline waters and thus may require CRAs in these intervals.

3.4 Typical CRA Selection Diagrams for Selection of Alloys for Oil and Gas Wells

As stated throughout this guideline, the closest analogy to selecting CRAs for SC-CO_2 is from the oil and gas industry where a wealth of data resides for the various CRAs. Figure 6, Figure 7, and Figure 8 show some typical diagrams used to initially select stainless steel CRAs based on pCO_2, temperature, and chlorides [11].

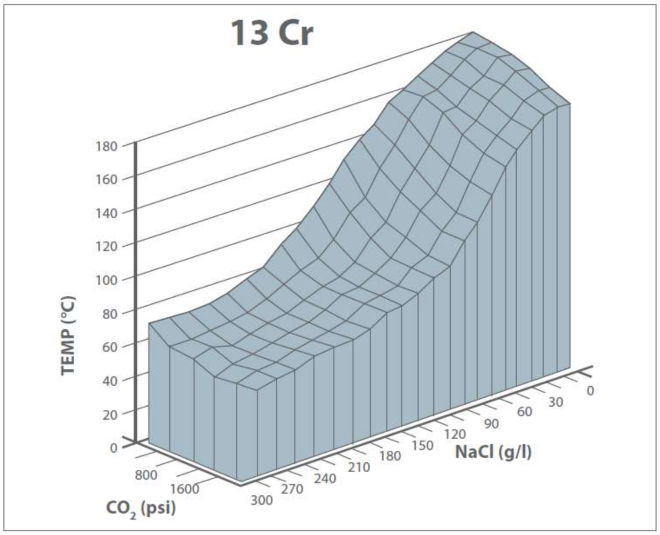


Figure 6. Envelope of acceptable conditions for L80 13Cr

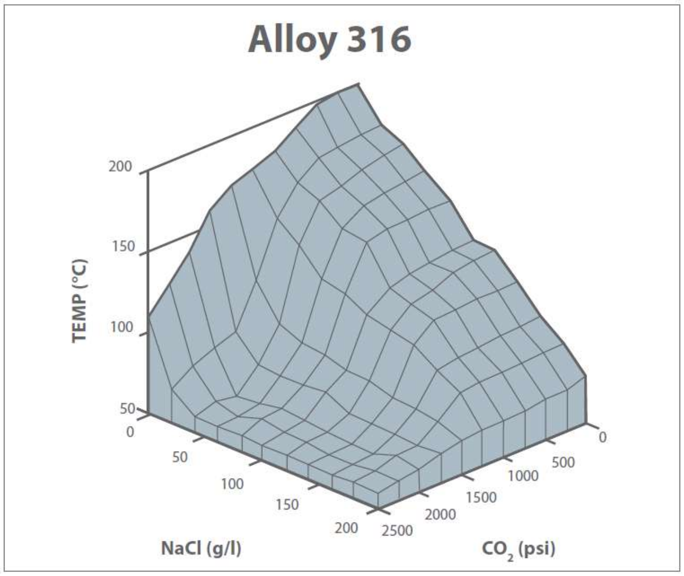


Figure 7. Limits for type 316 stainless steel

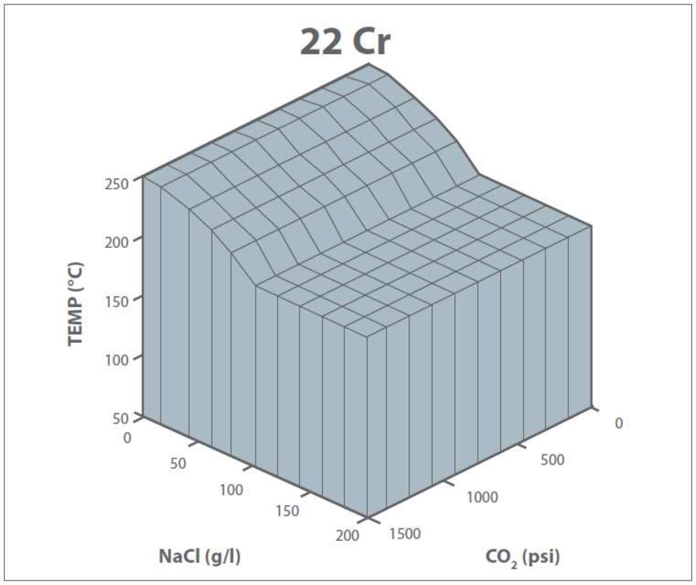


Figure 8. Limits for 22Cr duplex stainless steel

It is important to recognize that these figures do not show restrictions when H_2S and/or O_2 are present. H_2S must be accounted for according to NACE MR0175/ISO 15156, and in the presence of O_2 the CPT limits can be applied, but none of these selection diagrams are suitable for mixtures of CO_2-H_2S-O_2 streams. However, they do offer guidance for CRA selection in high CO_2 without impurities but in the presence of chlorides.

3.5 Research Results Specific to CRAs in SC-CO_2

While the volume of work done on CRAs exposed to SC-CO_2 with various impurities is small compared to the significant research over the years for oil and gas, there are pertinent data that are useful to guide further selection of CRAs in SC-CO_2. Again, all of these data were generated in the presence of water. Most of the CRA research for SC-CO_2 has focused on the use of 13Cr stainless steel (e.g., AISI 420 martensitic stainless steel) which is generally available as API Specification 5CT Grade 13Cr L80 and API Specification 5CRA Group 1. Following are examples of test results on 13Cr that would be considered for tubing and possibly casing liners.

Zhang et al. evaluated 13Cr in CO_2 at 1,956 psi and 176 °F for 96 hours [12]. Table 6 shows the results as a function of impurity contents.

Table 6. 13Cr Corrosion Rates vs. Impurities

Impurity Concentration, ppm	Corrosion Rate, mils/year		
	O_2	CO	H_2S
0	12.6	12.6	12.6
3-5	10.2	12.6	16.5
300-400	7.1	12.6	22.5
2,300-2,500	2.4	12.6	Not tested

These results show a beneficial effect of O_2 on corrosion of 13Cr and a detrimental effect from H_2S but no effect when CO is present. It should be noted that even with no impurities, 13Cr showed a measurable corrosion rate which would not be acceptable for a lifetime design of 50 years or more.

Luo et al. tested 13Cr in a mixture of 181 psi CO_2 and 181 psi O_2 with 30,000 ppm chlorides at various temperatures [13]. Although these conditions are not supercritical, they do demonstrate the important effect of temperature. Figure 9 shows their results. Under these conditions, the corrosion rate of 13Cr at 140 °C would be unacceptable for tubing. Even at 100 °C, the corrosion rate would be approximately 1 mm/y (40 mpy), also unacceptable for long term service.

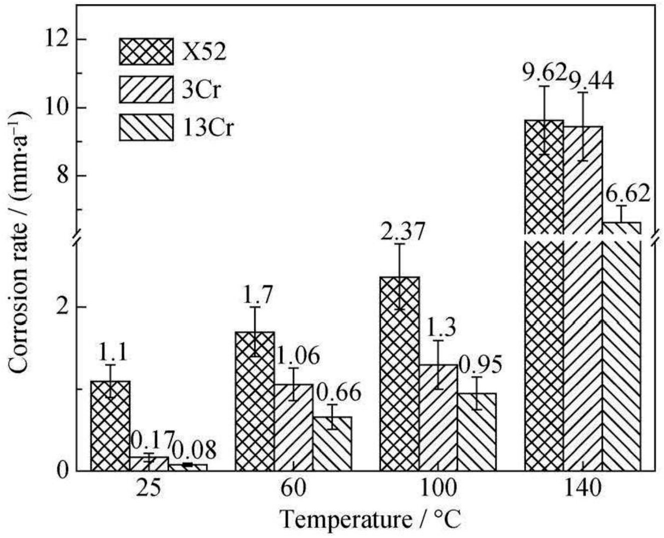


Figure 9. Corrosion rates of X52, 3Cr, and 13Cr at various temperatures. The error bars show the max and min values. The corrosion rate is in mm/y (1 mm/y = 40 mpy).

Hassani et al. evaluated the corrosion of several alloys including 13Cr in SC-CO_2 at 1,160 psi and 176 °F [14]. Figure 10 shows the results based on two measurement techniques, weight loss (WL) and electrochemical. The tests were only performed for 48 hours but show the corrosion rate of 13Cr to be near zero; however, the actual steady state value was approximately 0.1 mm/y (4 mpy).

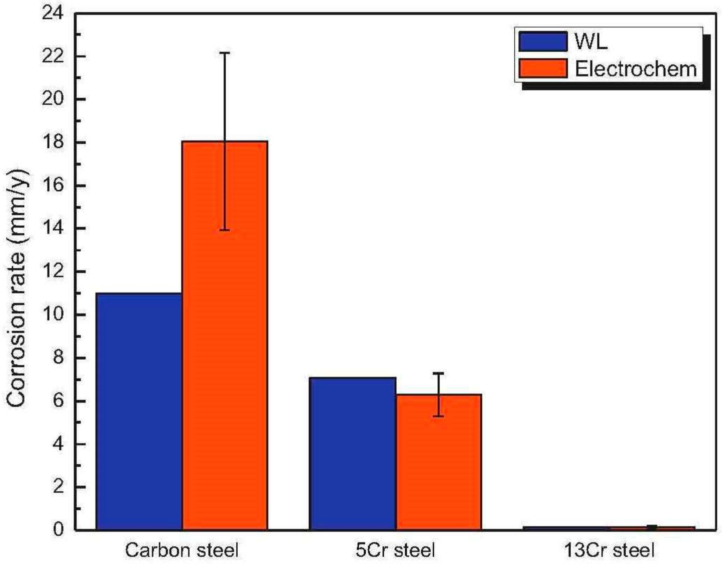


Figure 10. Comparison of corrosion rates from two measurement techniques for different alloys at 1,160 psi and 176 °F.

Hashizume et al. evaluated two 13Cr stainless steels in SC-CO_2. One was standard 13Cr and the other what is referred to in the industry as Super 13Cr (containing nominally 5% Ni and 2% Mo) [15]. In the absence of O_2, they tested these two alloys at 212 °F in a solution containing 30,000 ppm chlorides at different pressures of CO_2. The corrosion rate of 13Cr ranged from 2.8 mpy to 6.3 mpy at 4,350 psi and 2,175 psi, respectively. The S13Cr showed no localized corrosion in the same range of pressures except for localized corrosion of 0.4 mpy at 3,625 psi. Table 7 shows their results when O_2 was included, which resulted in more aggressive corrosion. Under the same conditions in Table 7, when crevice samples were tested, both alloys displayed crevice attack in almost all environments.

Table 7. 13Cr and S13Cr Corrosion in the Presence of O_2

Test Condition	13Cr	S13Cr
2,175 psi CO_2 0.03 psi O_2	9.9 mpy localized attack	1.6 mpy localized attack
4,350 psi CO_2 0.03 psi O_2	13.4 mpy localized attack	2.8 mpy localized attack
2,175 psi CO_2 0.003 psi O_2	3.2 mpy localized attack	0.4 mpy no localized attack
4,350 psi CO_2 0.003 psi O_2	2.8 mpy negligible localized attack	0.8 mpy no localized attack

Pfenning et al. tested 13Cr in CO_2 at 140 °F and atmospheric pressure and in SC-CO_2 at 140 °F and 1450 psi in contact with a simulated saline aquifer containing approximately 59,000 ppm chlorides [16]. Figure 11 shows their results demonstrating that the corrosion rates were an order of magnitude less in the supercritical conditions for 13Cr and declined with time. But the number of pits for the supercritical case reached a steady state of about 150 pits/m^2 in the liquid phase, indicating the 13Cr under these conditions would be prone to pitting when in contact with saline reservoir fluids.

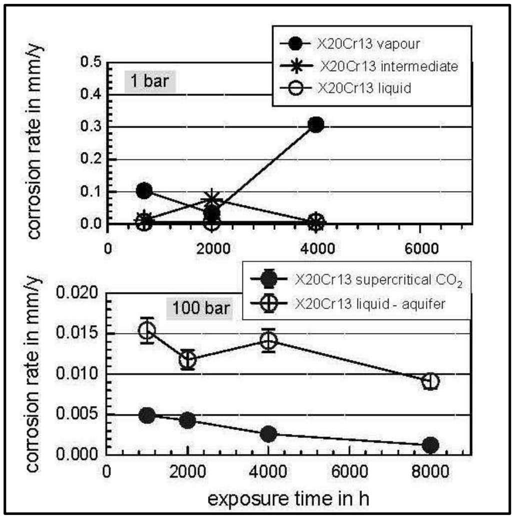
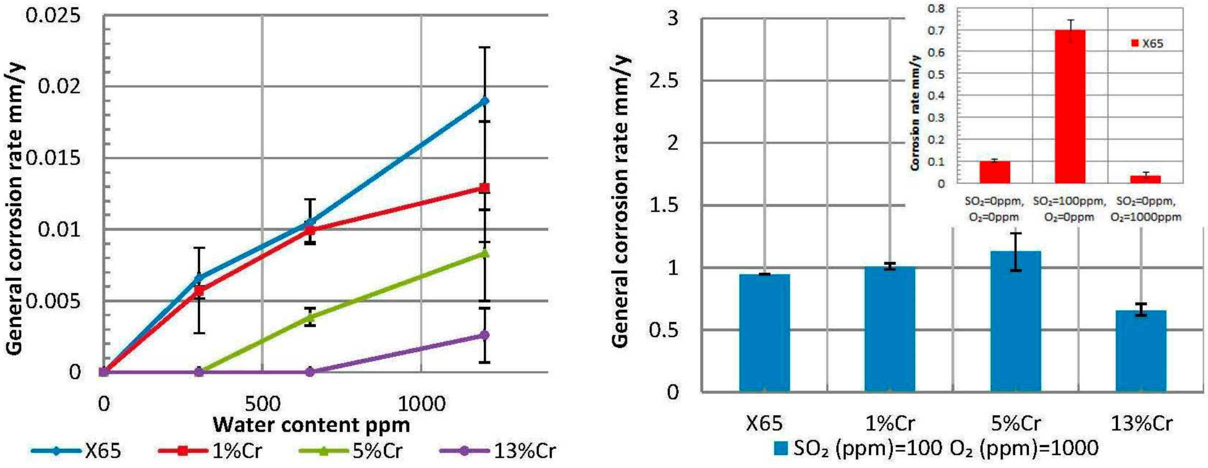


Figure 11. Corrosion rates of 13Cr in liquid and vapor/supercritical phase exposed to aquifer brine at 140 °F.

Hua evaluated 13Cr in supercritical CO_2 undersaturated with water as well as saturated with water in the presence of SO_2 and O_2 impurities [17]. Figure 12 shows when the SC-CO_2 is undersaturated at 95 °F and 1,160 psi for water content less than about 600 ppm, the corrosion rate of 13Cr is essentially zero. However, when the conditions are saturated and include O_2 and SO_2, the corrosion rate of 13Cr is about 23.6 mpy.



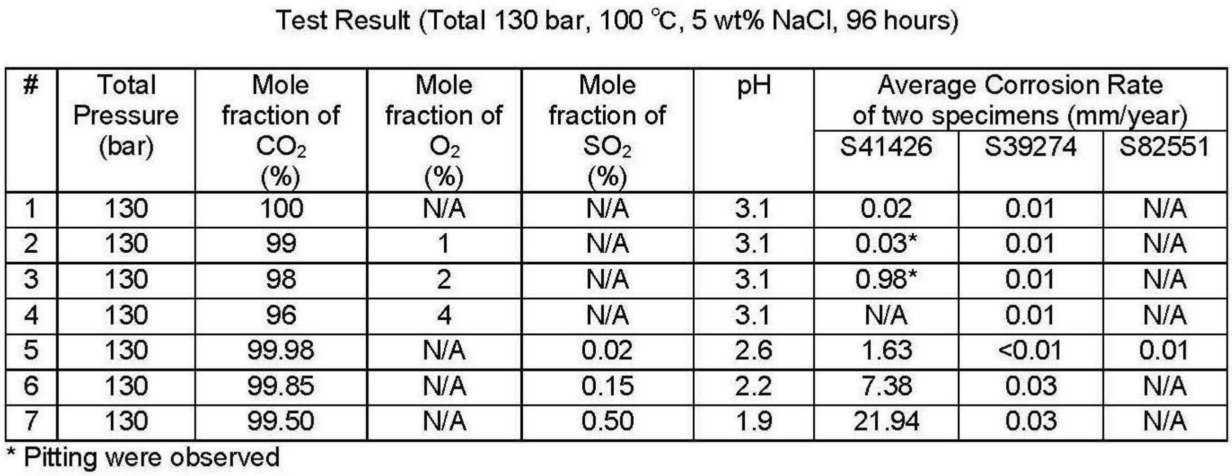
(a) (b)

Figure 12. Corrosion rates of X65/1Cr/5Cr/13Cr samples in water-containing supercritical CO_2 phase at 1,160 psi and 95 °F over an exposure time of 48 hours (a) under-saturated, (b) water-saturated conditions in the presence of 100 ppm SO_2 and 1000 ppm O_2.

These various results for corrosion of 13Cr in SC-CO_2 indicate that water saturation is an important factor in the corrosion of this alloy as well as contact with chloride-containing waters and all are dependent on the temperature. Thus, in the absence of water saturation, 13Cr is a possible candidate alloy for SC-CO_2. However, the presence of water even at under-saturation coupled with chlorides and impurities such as H_2S, O_2, and SO_2 cause measurable corrosion of this alloy and would not be suitable for long term service.

Very limited work has been done on high CRAs in SC-CO_2. Zhang showed that 22Cr duplex stainless steel (DSS) exposed to SC-CO_2 with water as a mist exhibited a corrosion rate of essentially zero for all temperatures up to 266 °F, but when a separate water phase was present, the corrosion rate exceeded 4 mpy at 176 and 230 °F [18]. D. Matsuo tested Super 13Cr and 25Cr superduplex stainless steel (SDSS) in SC-CO_2 with impurities of SO_2 and O_2 [19]. Table 8 below shows their results. The alloy S41426 is a Super 13Cr, S39274 is a 25Cr SDSS, and S82551 is a 25Cr DSS. In the absence of any impurities, the S13Cr alloy is corrosion resistant; however, for all amounts of O_2 and SO_2 tested, the S13Cr was not suitable, but the 25Cr SDSS was corrosion resistant. S82551 25Cr DSS was not tested under most conditions.

Table 8. S41426 and S39274 Corrosion in SC-CO_2 with O_2 and SO_2 Impurities



Test Result (Total 130 bar, 100 °C, 5 wt% NaCl, 96 hours)

#	Total Pressure (bar)	Mole fraction of CO_2 (%)	Mole fraction of O_2 (%)	Mole fraction of SO_2 (%)	pH	Average Corrosion Rate of two specimens (mm/year)		
						S41426	S39274	S82551
1	130	100	N/A	N/A	3.1	0.02	0.01	N/A
2	130	99	1	N/A	3.1	0.03*	0.01	N/A
3	130	98	2	N/A	3.1	0.98*	0.01	N/A
4	130	96	4	N/A	3.1	N/A	0.01	N/A
5	130	99.98	N/A	0.02	2.6	1.63	<0.01	0.01
6	130	99.85	N/A	0.15	2.2	7.38	0.03	N/A
7	130	99.50	N/A	0.50	1.9	21.94	0.03	N/A

* Pitting were observed

3.6 Service Life

As indicated in Section 2.11, the analogous oil and gas industry experience with CRAs is less than 50 years. As such, it is impossible to make finite predictions for the service life of any CRA beyond this time. Moreover, unlike steels that generally corrode at a predictable rate such that service life can be estimated based on some uniform wall loss, CRAs do not corrode uniformly. Rather, CRAs corrode in a highly localized manner such as pitting, crevice corrosion, or stress corrosion cracking, the rates of which are not currently predictable.

The service life for CCS and CCUS applications will depend on the specific application. EOR projects having a life expectancy of 10-20 years can utilize the lower cost CRA materials described in Section 4.2. However, for wells with longer design lives to meet regulatory well integrity measures, extended corrosion resistance is needed and thus the use of more costly alloys will be required.

3.7 Limitation on Injection Rates

Injection rate limits are a function of numerous variables, most of which are beyond the scope of this guideline, but one important mechanism that pertains to fluid flow is the possibility of erosion-corrosion. Historically the oil and gas industry has applied API Recommended Practice (RP) 14E to the design and flow limits in wells and surface equipment to avoid erosion-corrosion. This is not erosion from the presence of sand and/or solids but simply from liquid droplets in a gas phase or high velocities of liquid phases. Once a critical velocity, Vc, is exceeded, the degradation rate can be extremely high. Since there does not appear to be any significant study of erosion-corrosion in SC-CO_2 streams, the best available analog is to apply API RP 14E.

API RP 14E provides an equation to calculate the critical velocity, Vc, above which erosion-corrosion may occur and below which it is safe to operate free from erosion-corrosion effects. The equation is:

$$V_c = \frac{C}{\sqrt{\rho}}$$

Where:
Vc = fluid erosional velocity, ft/sec
ρ = gas/liquid mixture density, lbs/ft^3
C = constant

It is important to note that the density, ρ, is a mixture density and not the density for one phase, which is an important consideration. There is also the presence of the constant, C, also known as a “C factor”. API RP 14E presents the following C factors based on industry experience (see Table 9).

Table 9. C Factors According to API RP 14E

Alloy	Environment	C Factor
Steel	Solids free continuous service	100
Steel	Intermittent service	125
Steel	Solids free <u>intermittent</u> service without corrosion or when corrosion is controlled with inhibition	150-200
Steel	Solids free <u>intermittent</u> service without corrosion or when corrosion is controlled with inhibition	250
CRAs	Solids free <u>continuous</u> service without corrosion or when corrosion is controlled with inhibition	150-200

Alloy	Environment	C Factor
CRAs	Solids free intermittent service without corrosion or when corrosion is controlled with inhibition	250

Although the erosional velocity equation and the associated C factors are widely used by the petroleum industry, there has been significant criticism of it and its use. There is no documentation for where the equation came from or the C factors. Moreover, the latest version of API RP 14E includes C factors for CRAs but does not reference their origin. Additionally, the term CRA is not further defined, so no distinction between stainless steels, nickel-based alloys, or other CRAs is made, which is a very important shortcoming.

Individual companies have established their own in-house guidelines such as the example from Chevron Corporation [20]. Chevron ranks production in three categories:

1. Sand free production (SFP)
2. Nominal sands free production (NSFP) - defined as sand/solids content at ≤ 0.1 lb/MMscfd
3. Excessive sand production (ESP) > 0.1 lb/MMcfd

Sand free production does not have flow rate limits as long as the shear stress is below the critical tubing wall shear stress and the maximum does not exceed the liquid impingement threshold for alloys shown below in Table 10.

Table 10. Erosional Velocities for Select Materials

Material	Vc (ft/sec)
High alloy CRAs	295-410
12% Cr (same as 13%Cr)	390
Polymethylmethacrylate	682
High alloy CRAs (per DNV RP0501)	<230-262

The actual mechanism of erosion-corrosion remains to be clarified. Regardless of the specific mechanism, erosion-corrosion manifests itself as shown schematically in Figure 13 [21]. The sudden change in slope with increasing velocity is the critical velocity, Vc. Erosion-corrosion in the absence of solids is generally less severe than when solids are present and lends itself to more simple modeling compared to when solids are present. Sand erosion of elbows in piping systems and bends in pipelines is a well-known problem in the petroleum industry and, as such, considerable modeling has been developed to address this problem.

Until research on erosion-corrosion limits for SC-CO_2 is established, it is best practice to follow the API 14E guidelines for developing CCS and CCUS projects.

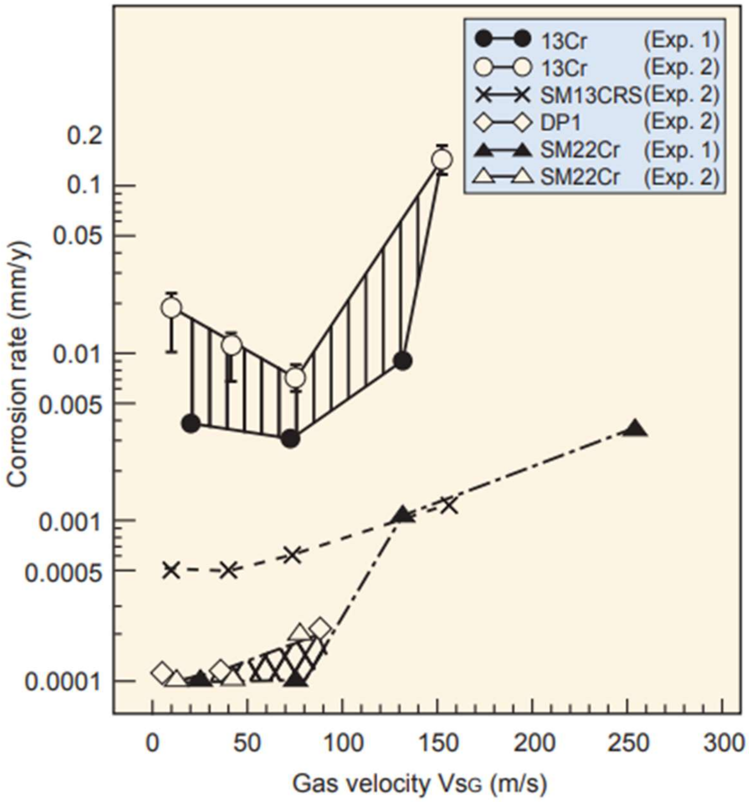


Figure 13. The sudden increase in metal loss at a critical velocity caused by erosion corrosion of 13Cr and 22Cr stainless steels.

4. Considerations for Various Equipment

At present there is no single accepted method for well design or completion for CO_2 injection wells. Not only does it depend on the location and depth of the well but eventually may also depend on national and local governmental regulations for CO_2 storage. Much remains to be decided about well design and completions. Even the often referenced work by the IPCC [22] only makes a general reference to CO_2 injections wells as follows:

> *"The design of a CO_2 injection well is very similar to that of a gas injection well in an oil field or natural gas storage project. Most downhole components need to be upgraded for higher pressure ratings and corrosion resistance."*

While bottomhole temperature is higher than the surface temperature, CO_2 injection into reservoirs has some behaviors that may be different from typical oil and gas well production.

CO_2 injection in deep saline formations induces temperature changes owing to processes such as Joule-Thomson cooling, endothermic water vaporization, exothermic CO_2 dissolution, and, according to some, CO_2 injectate will most likely reach the formation at a lower temperature than that corresponding to the geothermal gradient [23]. The conventional expectation is for injectate temperature to rise as it flows downhole. So, the following considerations for appropriate metallurgy assume that surface equipment will not be exposed to temperatures in excess of 200 °F (94 °C) and injection well equipment will not be exposed to temperatures in excess of 300 °F (149 °C).

The first and most important step in selecting compatible alloys for SC-CO_2 streams is to determine if free water will be present in the injectate on a more or less frequent basis. If free water is not present or the intermittent presence of water will be infrequent and of short duration, then carbon steel with a corrosion allowance, typically 1/8 inch, is suitable. However, if water will be present most or all of the time, then the next step is to determine the water chemistry. If it is fresh condensed water, the pH will be very low, typically around 3.1, and the other factors discussed in this guideline must be considered. If the water is saline or formation water, then the chloride content will be important as well, and a complete water analysis is required to begin the selection process.

One further consideration is the fundamental metallurgical fact that CRAs are not all processed the same way. For example, stainless steel alloys with greater corrosion resistance than 13Cr, such as 22Cr and 25Cr, are not able to be strengthened by heat treatment and therefore must be cold worked to achieve the desired strength levels. This can limit the particular product form (i.e., plate, tube, bar, etc.) that can be obtained. Likewise, certain nickel alloys such as Alloys 825, G3/2550, C276 must be cold worked, but Alloys 718, 925, and 725 can be heat treated (age-hardened). Because of these differences in processing, some alloys are better suited for casing and tubing and others for items such as packers and tubing hangers.

It cannot be overstated enough that there is insufficient test data and field experience to make complete materials choices without seeking the aid of a subject matter expert (SME) and, even more necessarily, performing laboratory tests to confirm the alloys selected are suitable for the specific well environment.

4.1. Casing

The selection criteria for casing depends on whether saline or other formations will be in contact with the casing that is inserted into the formation. If the injection zone is not water-bearing then carbon steel casing is suitable; however, casing exposed to formation water and in the contact area with the SC-CO_2 stream will need to be selected accordingly, following the guidance previously mentioned. Although there have been very few reported casing/tubing programs for CCS/CCUS, one available example is the CO_2SINK project in Europe. The project involved one injection well and two observation wells drilled into a saline formation in Germany to study the issues with CO_2 injection and containment [24]. These wells used the following casing design as shown in Table 11.

Table 11. CO_2SINK Project Casing Design

String	Depth (m)	Casing OD (in.)	Material
Stand pipe	30	24	4140
Conductor	150	18-5/8	X56
Reserve	340	13-3/8	K-55
Intermediate	590	9-5/8	K-55
Production	800	5-1/2	13Cr80 (external plastic coating)
Injection Tubing	561	3-1/2	C-95 (internal plastic coating)

It can be seen that the tubing only runs to a depth of 561 m (1,840 ft.) and thus is not extended into the aquifer layer while the production casing that is 13Cr stainless steel is run into the aquifer. In fact, most completions for injection wells do not have the tubing extending into the target formation but only down to a packer that sits above the formation inside the casing.

4.2. Tubing

The selection of appropriate tubing materials is not only important but complex. For example, in low pressure shallow CO_2 EOR injection wells, low strength tubing materials have historically been used. In many of these cases, CO_2 for EOR is performed using the water alternating gas (WAG) method. A helpful summary of industry experience with CO_2 injection well technology was provided by J.P Meyer on behalf of API [25]. Table 12 from his report presents the materials of construction for CO_2 injection wells summarized from several operators. The use of type 316 stainless steel and glass reinforced epoxy (GRE) lined carbon steel is limited to lower pressures and hanging loads, so ideal for shallow low-pressure SC-CO_2 EOR projects. For deeper higher pressure CO_2 injection wells, these materials are not capable of handling the pressures and hanging loads and so higher alloy CRAs are required.

Table 12. Materials of Construction for CO_2 Injection Wells

Component	Material
Upstream Metering and Piping Runs	316 SS, Fiberglass
Wellhead and Christmas Tree Trim	316 SS, Nickel, Monel
Valve Packing and Seals	Teflon, Nylon
Tubing Hanger	316 SS, Incoloy
Tubing	GRE lined carbon steel, IPC steel, CRA
Tubing Joint Seals	GRE seal ring, IPC threads and collars
On/Off tool, Profile Nipple	316 SS, Nickel plated

Component	Material
Packers	Nickel plated wetted parts, Internally coated hardened rubber (Buna-N)
Cements and Cement Additives	API cements and/or acid resistant specialty cements and additives

In addition to the above, this report also noted some other useful operators' experience:

- Use of corrosion protection of the casing strings via impressed and passive currents and chemically inhibited (oxygen, biocide, corrosion inhibitor) fluid in the casing-tubing annulus
- Use of special procedures for handling and installing the production tubing to provide gas tight seals between adjacent tubing joints and eliminate coating or liner damage
- Use of tubing and casing leak detection methods and repair techniques, using both resin and cement squeeze technologies as well as insertion of fiberglass and steel liners
- Formulation and implementation of criteria unique to siting wells in or near populated areas incorporating fencing, monitoring, and atmospheric dispersion monitoring elements to protect public safety

The longest running CO_2 storage project was established in Norway in 1996 by StatoilHydro into a saline formation at the Sleipner field approximately 2600 ft below the seabed [26]. The tubing alloy selected was 7" 25Cr SDSS, and the portion of the 9-5/8" casing exposed to the combined aquifer fluids and CO_2 was also 25Cr SDSS. The CO_2 stream could also contain as much as 150 ppm H_2S.

The largest CO_2 injection project to date is the Gorgon CO_2 injection project in Australia. Nine wells were drilled to a depth of 2576 m with all parts of the well system exposed to CO_2 completed with 25Cr SDSS tubulars and accessories [27].

The following general guidelines for tubing can be made:

1. No free water, no water wet components, and completely undersaturated all the time – carbon steel plus either IPC or GRE lined tubing for infrequent periodic upsets when some water might be present. GRE lined tubing is generally limited to a maximum of 230 °F. If the SC-CO_2 does not contain impurities such as H_2S and/or O_2, then 13Cr is suitable above 230 °F, but not exposed to saline formations.

2. Tubing/casing used for injection into saline formations when some part of the tubing and/or casing is in the aquifer – if no free water is present, then carbon steel down to just above the water interface is suitable and crossover to a CRA is acceptable. In this case there will be no risk of galvanic corrosion. However, if there is O_2 in the CO_2 stream and free water could be present, the potential for galvanic corrosion exists at the steel/CRA junction in the tubing and must be evaluated. The selection of the appropriate CRA depends on the design life of the well. If it is short

lived (i.e., less than 20 years) and there are no impurities such as O_2, H_2S, etc. and the temperature does not exceed approximately 212 °F (100 °C), then 13Cr tubing and exposed casing is suitable. However, if the desired design life is 20 - 50 years and H_2S is present in the SC-CO_2 but not O_2, 25Cr SDSS is acceptable.

3. In recent years, efforts have been made to develop corrosion inhibitors to deal with free water in contact with SC-CO_2. At present these inhibitors are not effective, nor are they reliable for the long-term life required for SC-CO_2 injection wells.

4.3. Packers and Downhole Equipment

It is common practice and good for reliability to select CRAs for the wetted parts of packers and downhole equipment to be similar to the tubing alloys. Thus, for fresh condensed water from SC-CO_2, if present, the same CRA as the tubing should be selected, or if the presence of water will be infrequent and steel tubing is run then 13Cr or S13Cr packers are suitable. However, if the SC-CO_2 injectate contains impurities and/or the packer and other downhole equipment are exposed to the saline formation, selection of the appropriate CRA should follow the guidelines in Appendix A.

4.4. Wellheads and Surface Equipment

4.4.1 Wellhead/Tree Equipment

Wellhead/tree equipment is stipulated in accordance with API Specification 6A. The primary equipment is defined in API 6A as the lower master valve, tubing head, tubing hanger, and tubing-head adapter. These components are critical to the tree for long term performance. It is generally considered that in all cases for SC-CO_2 injection the stream will be dehydrated, with the exception of WAG EOR wells; however, during the life of any well there are periods of shut-in which could drop water out in the tree. Therefore, considering the moderate wellhead temperatures, these primary components can be made according to the guideline table in Appendix A. For design lives of greater than 20 years and in the presence of impurities, as described in this guideline, the primary equipment should be Class HH (CRA on fluid-wetted surfaces).

4.4.2 Surface Equipment

There are numerous pieces of equipment that can be considered surface equipment, too many to address in this guideline, therefore, the focus here is on vessels, pumps, valves, and piping. For low pressure and temperatures of 140 °F and less in the absence of oxygen these components can be made from stainless steels such as type 316 and type 410. However, if H_2S is present, then compliance with the limits for these alloys laid out in NACE MR0175/ISO 15156 Part 3 is recommended. If O_2 is present and/or the temperature exceeds 140 °F, alloys such as Alloy 825 and Alloy 625 are recommended. In many cases vendors of certain specific components such as valves do not offer a variety of CRAs, so if type 316 stainless steel is not acceptable, then higher alloys such as Hastelloy C22 or Hastelloy C276 may be the only option. At this point a subject matter expert (SME) should be consulted to aid in determining the best and most economical alloys.

5. Summary of Materials Selection as a Function of Service Environment

The tables in Appendix A are guidelines for materials selection based on the service environment. They are by no means comprehensive, so the user must take into consideration all of the factors and issues addressed in the entire guideline to properly reach an appropriate materials selection. The specific limits provided in the tables are not exact but based on various data from other industries including the limits set forth in ISO 15156. Since there are no actual research data for CRAs under these various conditions nor any reported field experience, the limits can only be considered suggestions.

In many of the more severe conditions where numerous impurities are present and contact with a saline aquifer is likely, it may be necessary to perform laboratory corrosion testing to confirm the suitability of various alloys for that service.

For injection wells, precipitation hardening alloys such as 718 and 925 are not available as tubulars but are specific to items such as packers and tubing hangers. Other listed alloys such as 825, G3/2550, etc. are provided in the cold worked condition for tubulars. Alloys such as 825 and 625 can also be supplied as piping for surface equipment.

6. Handling, Running and Storage Guidelines for CRA Materials

By and large all procedures for handling, running, and storage of CRAs are similar regardless of the alloy. An example of such from NSSMC (formerly Sumitomo Metals) is provided in Appendix B.

7. Mixing of Carbon Steel (CS) and CRA materials

It has been demonstrated quite often in the oil and gas industry that in couples of carbon steel and CRAs, and of CRAs of different nobility, there is no galvanic corrosion when O_2 is not present. The majority of oil and gas operations around the world do not contain O_2 during the producing life and thus wells are frequently completed with a mixture of alloys with no adverse effects. However, in water injection wells when O_2 is present in the injected fluids, galvanic corrosion can be a significant problem. It is therefore assumed the same will be true for CO_2 injection.

7.1 Possible Compatibility Issues

7.1.1 Casing, Tubing, Packers and Other Downhole Equipment

In the absence of O_2 in the injection stream there should not be any issues with coupling carbon steel to any CRAs for casing, tubing, or any of the downhole equipment. However, if O_2 is present in the stream, then the junction of the carbon steel with the CRA should be made above any liquid water phase such as the saline reservoir fluids. If this cannot be accomplished, for example at a packer tubing interface, then all components in this zone must be made from the same CRA.

7.1.2 Wellhead and Other Surface Equipment

There are generally no galvanic problems for wellheads as long as the main run of the tree is all the same metallurgy. For example, Class FF will be all the same type of stainless steel and will not present a couple between carbon steel and stainless steel.

For surface equipment, again, if there is no O_2 present in the stream, then coupling carbon steel to CRAs is not an issue, especially when water is not present. However, in the presence of water and O_2, the surface equipment must be designed so that no junction between carbon steel and CRA occurs. Contrary to some ideas, plastic coatings will not provide a barrier against galvanic corrosion under these circumstances.

8. Inspection Methods

The most suitable inspection methods for CRAs is a very large topic to cover and cannot be simply addressed in this guideline. Vessel inspections, pump inspections, piping, and downhole equipment must all meet various industry standards which can become quite complex. As an example, the following notes are aimed at CRA injection well tubulars to demonstrate the various requirements. For downhole tubulars such as carbon steel casing and CRA tubing there are two primary considerations: whether the pipe is ordered from stock or a distributor or whether the pipe is ordered as a full mill run.

For the former, the pipe is in a yard or warehouse and has already been inspected during mill production to various industry standards such as API 5CT or API 5CRA, in which case few additional tests are advised as long as mill test reports are available for the alloys and satisfactory inspections have already been performed. It is certainly prudent to perform a visual inspection at the pipe location and in some cases random lengths of pipe might be selected for further tests such as ultrasonics, positive material inspection (PMI), etc.

For the latter, it is common in the industry to add supplemental requirements to existing industry standards to ensure the final product is fit for purpose. A sample supplemental manufacturing and inspection plan for 13Cr is presented in Appendix C.

9. Internal Coatings and Liners

9.1 Internal Plastic Coatings (IPCs)

Internal plastic coated (IPC) pipe and tubing (including other internal polymeric coatings) have a long history of use for water injection and are commonly used for CO_2 service. The coating acts as a barrier between the underlying carbon steel and liquid water, so as long as the integrity of the coating is maintained, the internal surface of the steel is protected from corrosion. Damage to the coating is therefore the most pervasive corrosion risk to the steel. Damage can occur during manufacturing, installation, or service, so proper handling and installation procedures are critical to ensure long-term performance. Coating near mechanical connections is of particular risk, and coating damage resulting from wireline runs has historically been a major source of corrosion. The coatings also require sound application, so it is recommended that supplier procedures for manufacturing IPC pipe and tubing be properly qualified to ensure that products are free of blisters and holidays and that proper handling and running procedures be followed when running these products.

The temperature limits of IPC pipe and tubing depend on the specific compound used for coatings. Refer to technical data sheets for the specific coating system for temperature ratings supplied by the manufacturers. Both the upper and lower temperature limits are important for the integrity of plastic and polymer coatings. If a temperature rating for a coating system in high pressure CO_2 or SC-CO_2 has not been established, service limits can be established through testing. CO_2 absorption can cause swelling of the coating in some conditions. It is recommended that qualification and validation of coatings systems include compatibility testing in CO_2 containing impurities that may be present in the fluid.

IPC pipe may be acceptable for short term applications, but due to the coating integrity concerns, they should not be relied on for the long-term service lives typically specified for CCS and CCUS equipment.

9.2 Ceramic Liners

The combination of abrasion and corrosion resistance make ceramic liners an attractive option for equipment protection. However, ceramic liners, even those with better-than-average toughness, are brittle and exhibit poor impact resistance. Standard handling, installation, and operation procedures may cause fissures to form in the liner, allowing corrosive fluids to contact the steel wall. Most CCS and CCUS fluids are not abrasive enough to warrant ceramic liners, and there are more reliable options for corrosion resistance. Ceramic liners are not recommended for most CCS and CCUS applications.

9.3 Fiberglass (FG) Liners

Fiberglass in this guideline should be understood to include both glass fiber reinforced epoxy (GRE) and glass fiber reinforced plastic (GRP). Fiberglass and fiberglass-lined tubing is frequently used for shallow CO_2 injection wells. However, it may not be appropriate for deep wells where the temperature exceeds 90 °C (194 °F) or high-pressure wells where the pressure exceeds 340 bar (4900 psi). Possible reduced injection volumes due to constricted injection tubing inside diameters also need to be considered when using fiberglass.

9.4 Cement Liners

Cement liners are commonly used in water pipelines and water injection facilities, and for these purposes they have historically been effective. Cement liners are brittle and prone to fissuring, which can allow fluids to contact the underlying steel. High pressure and supercritical CO_2 service presents an additional integrity risk of degradation to the cement liner material itself. The brief discussion of cement used to anchor casing in CO_2 injection wells presented in Section 2.13.2 is also relevant to cement used as liners for corrosion protection. While cement liners can offer steel tubulars initial protection from wet-CO_2

corrosion, prolonged exposure to CO_2 and water results in carbonation and deterioration of the cement. The severity of carbonation depends on a number of factors, particularly temperature and partial pressure of CO_2. Work performed by Han et al. [28] at Los Alamos National Laboratory concluded that no corrosion protection is provided once the cement is fully carbonated. Other work performed by Duguid et al. [29] found that cements exposed to flowing CO_2-saturated brine experienced rapid degradation on the order of weeks.

For these reasons, cement liners should be avoided in equipment handling CO_2-saturated brines or other conditions expected to expose the liner to substantial quantities of carbonic acid. Acid resistant cements are available but unproven for internal protection of CCS/CCUS systems where brine is present. The use of cement liners for corrosion protection of steel equipment in high pressure and supercritical CO_2 needs to be considered carefully and reviewed by a subject matter expert. Due to the complexity of the carbonation reaction and resulting effect on liner integrity, specific recommendations are outside the scope of this guideline.

10. Subject Matter Expert (SME) Review

The information detailed in this document provide comprehensive CRA guidance for operators and end users to consider in the design of CCS and CCUS systems. This guideline alone is not a substitute for review by a subject matter expert (SME), and it is recommended that material selection and procurement specifications be reviewed and accepted by an SME before equipment is ordered for construction.

11. Summary

Since this is a general guideline, no specific conclusions can be presented. However, certain key points can be reiterated.

1. In the absence of free water, when water is completely soluble in the supercritical CO_2 (SC-CO_2) and unlikely to break out, the fluid will not be corrosive, and standard carbon steel construction is sufficient.

2. When free water is determined to present, and/or when CO_2 is being injected into a water-bearing formation, the selection of an appropriate CRA for specific CO_2 injection well projects requires consideration of:

    a. The water chemistry of any saline formation being considered for storage.

    b. The impurities in the CO_2 stream and their effect on corrosion and the potential for cracking if H_2S is present. If oxygen is present, the suitable CRA maybe entirely different than for a stream without oxygen.

    c. Well conditions such as injection temperature and bottomhole temperature also effect the choice of CRAs.

3. There is insufficient test data and field experience to make complete materials choices without seeking the aid of a subject matter expert (SME) and, even more necessarily, performing laboratory tests to confirm the alloys selected are suitable for the specific well environment.

This guideline is intended to be a living document, regularly reviewed and revised as data and experience evolve. Its purpose is to provide guidance on current best practices in CCS/CCUS injection facilities to mitigate corrosion damage over the life of the facilities. As new information become available, this guide will be updated to ensure that it remains an accurate reflection of industry standards. Users are invited to provide feedback, suggestions, and comments to ensure that this document remains a reliable and up-to-date source of technical guidance.

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Appendix A: Guidelines for CRA Selection

Table A.1

Guidelines for CRA Selection – Surface Equipment (Ambient Temperature to 200 °F)1,2

Impurities	Concentration	CO_2 SOURCES					
		Power Generation		Chemical Plants	Natural Gas Plants and Other Industries	Ethanol Plants	Fertilizer Plants
		Coal Fired	Gas Fired				
O_2		Present[4]	Present[4]	Present[4]	10 ppm	< 2%	550 ppm
SO_2		≤ 0.5%	≤ 0.1%	-	-	-	-
NO_X		0.01 % NO	0.01 % NO	-	-	-	-
H_2S		≤ 0.6 %	< 0.01%	-	≤ 1%	-	-
H_2		≤ 2%	≤ 1%	-	-	-	700 ppm
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~ 0 ppm only condensed water from the SC-CO_2[3]	316 SS, T=200 °F Max.	316 SS, T=200 °F max.	316 SS, T=200 °F max.	316 SS, T=200 °F max.	316 SS, T=200 °F max.	316 SS, T=200 °F max.
	≤ 1000 ppm	316 SS, T=190 °F max.	316 SS, T=190 °F max.	316 SS, T=190 °F max.	316 SS, T=190 °F max.	316 SS, T=160 °F max.	316 SS, T=160 °F max.
	> 1000 ppm	316 SS, T=70 °F max. 25Cr temp 180 °F max. Alloys 825, 654 SMO and 625 no Temp limit	316 SS, T=70 °F max. 25Cr temp 180 °F max. Alloys 825, 654 SMO and 625 no Temp limit	316 SS, T=70 °F max. 25Cr temp 400 °F max. Alloys 825, 654 SMO and 625 no Temp limit	25Cr T= 400 °F max at 500 ppm H2S max. Alloys 825, 654 SMO and 625 no Temp limit	316 SS, T=70 °F max. 25Cr temp 180 °F max. Alloys 825, 654 SMO and 625 no Temp limit	316 SS, T=70 °F max. 25Cr temp 180 °F max. Alloys 825, 654 SMO and 625 no Temp limit

Notes:

1. Implicit in this table is the primary stream of SC-CO_2 at > 95% CO_2.
2. There are numerous other CRAs that are similar to those shown in the table but require an SME to determine their equivalency.
3. Also including incomplete dehydration of the CO_2 so free water may be present.
4. This assumes less than or equal to 10 ppm O_2. If O_2 content is expected to be higher, contact an SME.

Table A.2
Guidelines for CRA Selection – Tree/Wellhead Equipment (Ambient Temperature to 200 °F)[1]

Impurities	Concentration	CO_2 SOURCES					
		Power Generation		**Chemical Plants**	**Natural Gas Plants and Other Industries**	**Ethanol Plants**	**Fertilizer Plants**
		Coal Fired	**Gas Fired**				
O_2		Present[3]	Present[3]	Present[3]	10 ppm	< 2%	550 ppm
SO_2		≤ 0.5%	≤ 0.1%	-	-	-	-
NO_X		0.01 % NO	0.01 % NO	-	-	-	-
H_2S		≤ 0.6 %	< 0.01%	-	≤ 1%	-	-
H_2		≤ 2%	≤ 1%	-	-	-	700 ppm
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~ 0 ppm only condensed water from the SC-CO_2	Class EE	Class EE	Class CC[2]	Class EE-NL	Class CC[2]	Class CC[2]
	≤ 1000 ppm	Class EE	Class EE	Class CC[2]	Class EE-NL	Class CC[2], Master Valve Class HH	Class CC[2], Master Valve Class HH
	> 1000 ppm	Class FF-NL, Master Valve Class HH	Class FF-NL, Master Valve Class HH	Class FF-NL, Master Valve Class HH	Class FF-NL, Master Valve Class HH	Class HH	Class HH

Notes:

1. All of the alloy classes in this table are referenced to API Specification 6A for wellheads and trees.
2. In some cases, for very low-pressure injection, some vendors may offer type 316 stainless steel trees for Class CC, which could be acceptable depending on the specific well conditions.
3. This assumes less than or equal to 10 ppm O_2. If O_2 content is expected to be higher, contact an SME.

Table A.3

Guidelines for CRA Selection – Downhole Equipment (Ambient Temperature to 300 °F)[1,2,3]

Impurities	**Concentration**	**CO_2 SOURCES**					
		Power Generation		**Chemical Plants**	**Natural Gas Plants and Other Industries**	**Ethanol Plants**	**Fertilizer Plants**
		Coal Fired	**Gas Fired**				
O_2		Present[4]	Present[4]	Present[4]	10 ppm	< 2%	550 ppm
SO_2		≤ 0.5%	≤ 0.1%	-	-	-	-
NO_X		0.01 % NO	0.01 % NO	-	-	-	-
H_2S		≤ 0.6 %	< 0.01%	-	≤ 1%	-	-
H_2		≤ 2%	≤ 1%	-	-	-	700 ppm
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~ 0 ppm only condensed water from the SC-CO_2	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS	IPC/GRE steel tubing T < 230 °F, 25Cr SDSS
	≤ 1000 ppm	25Cr SDSS	25Cr SDSS	25Cr SDSS	25Cr SDSS	25Cr SDSS	25Cr SDSS
Saline aquifer contact	< 50,000 ppm Cl	Alloys G3, 2550, C22 or C276	Alloys G3, 2550, C22 or C276	Alloy G3/2550	Alloy G3/2550	Alloy C22 or C276	Alloy C22 or C276
	> 50,000 ppm Cl	Alloy C22 or C276	Alloy C22 or C276	Alloy C22 or C276	Alloy C22 or C276	Alloy C22 or C276	Alloy C22 or C276

Notes:

1. Implicit in this table is the primary stream of SC-CO_2 at > 95% CO_2. Maximum pressure is 3,000 psi.
2. For higher pressures and impurities outside these ranges contact SME.
3. There are numerous other CRAs that are similar to those shown in the table but require an SME to determine their equivalency.
4. This assumes less than or equal to 10 ppm O_2. If O_2 content is expected to be higher, contact an SME.

Appendix B: Example Procedure for Handling, Running, and Storage of CRAs

General

This appendix provides the recommended practices applicable to handling, running and storage of CRAs. These materials used for different types of corrosive applications are split into 3 main groups:

- Martensitic: **13Cr, SM13CrS, SM13CrM, SM13CrI**
- Duplex: **SM22Cr, SM25Cr, SM25CRW**
- Austenitic and Ni based: **SM2535, SM2242, SM2550, SM2050, SMC276**

While the basic recommendations detailed in API RP 5C1 remain the foundation for handling, storing, and running practices, this document is a compilation of best practices based on prior experiences in handling storing and running high alloy materials. The key issues differentiating handling and running of High alloy materials versus Carbon or low alloy steels are:

- Atmospheric corrosion susceptibility of the martensitic materials
- Localized corrosion susceptibility in combined presence of oxygen and chlorides
- Specific care to be maintained at all times while handling as well as while in storage to reduce potential spot hardening and carbon steel contamination since this may affect the corrosion resistance of the material.
- Galling susceptibility of thread and seals while making up and breaking out.

General information for martensitic materials (13Cr, SM13CrS, SM13CrM, SM13CrI)

13Cr (martensitic stainless steels) have been in usage for the last 30 years to address down hole CO_2 corrosion problems. In the last 15 years “modified” 13Crs were developed to address specific conditions synthesized as:

- Low cost 13Cr: SM13CrI
- High strength sweet service: SM13CrM
- Combined conditions containing CO2, marginal H2S & Cl-: SM13CrS.

Martensitic stainless steels are susceptible to corrosion while in storage in a wet and saline atmosphere. Storage away from the seashore or indoors in dry conditions is highly recommendable.

Typically, the pipe OD will be un-de-scaled and coated, while the ID will be de-scaled and coated. The remaining OD scale will provide some protection against atmospheric corrosion while in storage, however routine control of coating OD & ID condition will be carried out to ensure the absence of corrosion initiation. The control frequency will be adjusted depending upon the specific storage conditions.

General information for Duplex, Austenitic and Ni based CRAs

Duplex, Austenitic and Ni based materials were developed to address increasing corrosive application severity, that is SCC and pitting corrosion in high temperature chloride & H_2S containing environments.

Because of their high PREN index these materials can be considered to be corrosion resistant to atmospheric conditions.

The applied surface preparation is de-scaled, uncoated OD & ID

The galling susceptibility of these materials is commensurate with their alloying elements (specifically Cr & Mo), and consequently require an even tighter control while running or pulling than the martensitic materials.

Transportation, Handling and Storage

General

In order to retain the original material's corrosion resistance properties, adherence to this procedure's requirements and recommendations is highly recommendable. CRAs are manufactured under stringent quality control to obtain the desired corrosion resistance. Improper handling may result in affecting the material performances and by extension their corrosion resistance. It is then recommended that operators strictly adhere to the recommendations detailed in this document.

1. **Never use direct-flame heating or welding**
2. **Do not attempt to straighten a bent pipe. Please consult with an SMI rep.**
3. **Use non marking tong system and lifting equipment inclusive of slips**
4. **Never hammer the pipe**

Corrosion resistance of high alloy materials can be influenced by produced/injected fluids, packer fluids, completion fluids, acidizing media, as well combination with other material metallurgies. The forms of potential corrosion attacks may be general corrosion, galvanic corrosion, bimetallic corrosion, crevice corrosion, etc. Therefore, it is highly recommendable to investigate the expected sequence of exposures to avoid occurrence of corrosion initiation before running the string.

Transportation

1. All pipe transportations shall be carried out using the original mill packing system to prevent mechanical damage leading to material spot hardening.

   Never use steel band or wire slings directly on these materials. Instead, usage of either textile, or nylon slings, or encapsulated wire slings is recommended.

   In situations where local regulations prohibit usage of non-metallic slings for offshore handling, usage of lifting frames approved by the local authority (i.e., Ferguson Seacabs, MSI Rhino lifting U frame) can be considered. Adequate dunnage between these transport frames and the pipes must be used.

Never use metal protectors for these materials Instead usage of either plastic or composite or epoxy coated steel protectors is required.

2. Pipes packed in special packaging should be transported on flat bed insuring good support at all times. The packaging type will be selected based on pipe size, type of material, and customer specific requirements, and may be:
    - Bare & Loose pipes with spacer rings
    - Pipes with spacer rings bundle wrapped, and pre-slung.
    - RAP frame system
    - Care shall be exercised to avoid for box ends to hang over.
3. Adequate supervision should be exercised at any point of loading and unloading

Handling

1. Prevention of Iron Contamination
   Usage of unpadded hooks, chains, rails, unprotected wire slings is prohibited, and contact between pipes and carbon steel shall be avoided,

2. Prevention of Spot Hardening
   Stress concentration induced by spot hardening has a detrimental influence on the SSCC/SCC resistance of materials. To prevent such damages, it is recommended that materials should be kept in the original packing system until its usage. All pipe movements should be carried out in such a way to avoid damage.

3. The following precautions should be taken in handling pipe during unloading, loading, and inspection:

    a. Before any pipe movement insure of no untied protector.
    In case of handling small size loose R3 tubing in order to prevent bending, usage of a lift bar is recommendable.

    b. Loose pipe handling should be restricted to 3 or 4 pipes maximum at any given time to avoid pipe striking against each other.
    Set on racks protected with hard wood or plastic dunnage. Concerning hard wood quality please refer to I-3-2

    c. Do not drop pipe down onto racks while unloading. The pipes should be handled carefully with lifting only one joint/bundle/RAP frame at a time and set on racks with proper supports.
    d. Avoid rough handling, which may produce damages.

In case any transportation damage is detected upon arrival of the pipe cargo, it is recommended to quarantine the suspect material for additional inspection.

Storage

The following storage and related handling precautions shall be maintained at all times:

1. Never unload pipe directly onto ground, steel rail or bar, or concrete floors. To keep moisture and dirt away from pipe, the first tier of pipes should be stored to a sufficient height (at least 18 inches) from the ground.

   In desert conditions this height may be increased to avoid sand drifts to reach the bottom pipe row.

2. Wooden stringers or strips fumigated by products containing either chlorine or bromide are unsuitable as dunnage, and its usage prohibited.

3. Pipe should rest on skid racks properly spaced to prevent bending of pipe or damages to threads. For R3 length a 4 supports skid rack will be used.

   Dunnage must be placed between each row of pipe to prevent metal to metal contact of pipes and couplings. Dunnage shall be thick enough to allow for lifting slings or padded forklift arms to fit in.

4. For loose pipes, stagger adjoining pipes by a coupling length to allow each layer to remain parallel.

5. Block each loose pipe row by nailing a wedge block at both ends of the dunnage spacer.

6. For RAP frames stacking height will be restricted to 3 frames, and the frame elements staggered for good weight distribution.

7. If open end protectors are used, in order for rainwater to drain, the rack supports will be sloped by 2% minimum. The pin end will be located down slope.

8. The storage recommendations are dependent upon the climate and environmental conditions of the storage yard.

   Example of critical conditions requiring corrective action (non-exhaustive)

   - Air borne Industrial pollutants (cement dust, chemicals)
   - Sea spray, or air borne beach sand
   - Sand drifts reaching the bottom pipe row.

   Under the above conditions either the storage location needs to be reconsidered such as indoor warehouse, or if applicable usage of tarpaulins to prevent water wetting of the pipes.

Storage management

a. The Yard shall be managed on a First In-First Out basis.

b. Whenever possible pipes should be stored as far away as possible from C steel pipe in order to prevent air borne iron contamination.

c. Identification marks shall be kept legible and if required re-applied.

Inspection

The purpose of inspecting stored material is to maintain material traceability, and ensure that protection against corrosion remains efficient.

1. The stored material will be inspected on an established frequency to be defined based on the type of material, and the storage conditions. The following proposed frequencies are for information purpose only.
    - For martensitic the inspection frequency may be every 3 months
    - For Duplex, austenitic & Ni based material that frequency may be every 12 months
2. Storage being the most dangerous period of Martensitic material life cycle, specific attention will be given to corrosion initiation of the OD, ID, and threaded ends. Typically, 10% of the protectors (not the same 10% at each inspection cycle) will be removed to verify threaded end and pipe ID condition.
3. Applicable to all material types, remedial action will be taken when either dried storage dope, fading identification marks and untied protectors are found.

Running of Premium Connections on CRAs

Adherence to the procedures detailed in the below sections is highly recommended. The following are critical bullet points:

1. Prior to doping, threads and thread protectors must be absolutely clean, free of grit, nicks, or any other debris or iron powder from magnetic particle inspection
2. Avoid thread damage by keeping protectors in place during all handling operations
3. Only Use clean approved thread compound
   Use soft bristle brush for applying dope. Never use any type of metal brush.
4. Prior to running or pulling out, ensure that the elevator/traveling block are correctly aligned with the rotary table. If substantial misalignment is found, it is advisable to request a rig trim up.
   Alignment is a critical criterion when running high alloy material.
5. Stab vertically.

Ideally make up to hand-tight position by hand or pipe wrench (strap wrench) Alternatively whenever local regulations do not allow for operators' presence on the rig floor, rotate counter clockwise with power tong until the pin bumps up, then reverse the make-up direction

6. Usage of weight compensator is advisable for R2/R3 length pipes and highly recommendable for multiple lengths (stands).
7. Keep the rotation speed below 5 RPM and adhere to the recommended torque values.
8. Verify that the torque gauge has been calibrated recently (< 2 months).
9. It is advisable for critical or new material applications, to contract VAM Services engineer to help the operators crew in going through the learning curve in handling and running "High value" materials.

Preparation before Running

Preparation of Equipment and Materials

1. **Handling**

   The procedures detailed in Paragraphs I-2 (Handling) & I-3 (storage) apply. Ideally a pickup/lay down machine to bring the joint up to the rig is to be used.

   Alternatively, the V door, and Samson posts will be padded with non-metallic material, to avoid direct metal to metal contact and C. Steel contamination.

2. **Elevators and Slips**
   - ***Slip type elevator must be used,***
     Ideally the elevator and slips should be non-marking type. Alternatively standard slips and slip type elevator can be used provided they meet the following criteria
     - Long slip body to distribute the load of the string over a wide area.
     - Fine tooth and curved face slip inserts to reduce sharp tooth penetration.
     - Inside diameter of gripping surfaces shall match uniformly the pipe O.D

3. **Power Tong and Back-up Tong**
   - The power tong shall be suitable for the job at hand. Torque capacity should be about 1.5 times the optimum torque of the connection(s) to run; not too much nor too low.
     Never use drill pipe tong or rig tong for make-up or breakout.
   - The Power tong and back up will be equipped with non-marking dies.
   - The power tong will be equipped with an accurate and recently calibrated torque gauge and a monitoring system having the following functions:
     - Load cell with electronic strain gauge
     - Hydraulic dump valve system activated automatically, when reaching the preset optimum torque.
     - Monitoring system that graphically displays the torque – turn

4. **Stabbing Guide**
    - Stabbing guide shall be used when running or pulling high alloy materials.

5. **Thread Compound**
    - Only Use clean approved thread compound
    - Never use any type of compound containing Teflon particles
    - Never mix the thread compound with any chemical.

6. **Cleaning materials**
    - Clean thread and seal area completely using preferably steam gun or approved solvent.
    - Do not use oil-based solvent such as gasoline or diesel.
    - Use rags or bristle brush when cleaning.
    - Blow dry the threads and seals insuring that no foreign material remains in the thread root.

Preparation Procedure of Pipes

Details of preparation procedure are as follows:

Unpacking

1. Pipes should be transferred to well site in the original packing system.

Pick up Pipes

1. Use non-metallic or nylon encapsulated slings to lift the pipe.
2. Pipe should be put on rack allowing space to permit for easy access for cleaning and inspection
3. Use dunnage for the rack and between each pipe row

Remove Protectors

1. Blow out the inside of pipe from box end to pin end to remove eventual foreign particles.
2. Protectors should be cleaned, dried with compressed air, and kept clean for re-use.

Drift

1. Drift from box end to pin end being careful not to damage threads, seal, or shoulder. Usage of a Teflon coated drift or non-metallic mandrel is mandatory. Drift through the protector in place when open end driftable protectors are used.

   Keep the drift clean

Measuring Length

1. Measure pipe end to pipe (from coupling end to pin end)

2. Subtract the Make-up loss value indicated in the “VAM Running Book”

Clean Thread

1. Clean thoroughly pin and box threads
    - Use steam, fresh water, or solvents
    - Do not use oil or wire brush for cleaning
2. Dry thread ends, and protectors using compressed air

Inspection

1. Inspect visually thread, seal, and shoulder.
2. Minor thread damage can be field repaired by a qualified VAM Service or SMI representative.
3. Any damage on the seal area is a cause for reject.

Apply Thread Dope (If running is imminent, doping can be omitted)

1. Stir the dope thoroughly before usage.
2. Apply approved thread Compound on pin (1/3) and box (2/3) uniformly using a soft bristle brush

Install Protector

1. Install clean thread protector

Preparation of Accessories

Since accessories (hangers, safety valves, flow couplings, pup joints, crossovers) lengths are substantially shorter than standard pipe length, as well as often made from different metallurgies, material strengths, the standard practice is to make up these accessories into sub-assemblies prior to the completion running, using a quality buck on machine. Usually, the made up sub-assemblies are pressure tested prior to their release.

Running Procedure

Details of CRA running procedure for these materials are as follows:

Pick up Joint to V-door

1. Pick up one joint at a time following the procedure in paragraph II-1-1

Pick Joint to Rig Floor

1. Pick up the joint using pick up elevator

Check Thread and Seal

1. Remove the pin protector just before stabbing
2. If undoped, visually check the pin thread and seal for any damage
3. If already doped check the pin thread and seal by running a finger over the surface.
4. If undoped, apply dope.

Stabbing

1. Install stabbing guide before stabbing the pin in.
2. Stab vertically & slowly with stabbers' assistance (if applicable) in maintaining alignment.
3. In conditions where rules and regulations prohibit the presence of a stabber, control, and maintenance of pipe alignment throughout stabbing, and thread engagement will be exercised by every possible mean.

Making-up

1. **Hand Tight (Preferred)**

   Tighten up the joint several turns by hand or strap wrench until difficult to turn

2. **Whenever hand tight is not possible**

   Rotate counter clockwise with power tong until the pin bumps up, then reverse the make-up direction, at 5 rpm Max or lower if the running conditions are not ideal (misalignment).

3. Power Tight

   make up in low gear at 5 rpm Max and make up to the recommended torque value.

4. Ensure that pipe is properly aligned during the whole make up phase.
5. Check torque value and torque-turn curve.

   Assemblies showing incorrect make up torque value or abnormal torque-turn pattern must be broken out, both threaded ends cleaned and visually inspected.

6. When using standard dies, check for tong die marks and slip marks on pipe. If the die penetration is too important, take corrective action

Breaking-out Procedure

Break-out

1. Set the back-up tong on the lower half of the coupling
2. Break out in low gear for first two turns at 2 RPM Max
3. Ideally, at final breakout stage, switch from power tong to strap wrench to disengage the threads. Alternatively, spin out at Max 5rpm or lower if the running conditions are not ideal (misalignment), until the pin bumps into the box.
4. Ensure that pipe is properly aligned during the whole break out phase with stabber's assistance if applicable.
5. Install stabbing guide before lifting up the pin end from the box.
   Lift pipe slowly while avoiding damage to the pin seal area.

Install Thread Protector

1. Install clean thread protector

Lay Down/ Stand Back

1. Stand back pipe on wooden matting

Cleaning As soon as practical

1. Rinse pipe internally and externally with fresh water
2. Dry out pipe using compressed air
3. Check thread and pipe body internally and externally
4. Apply thread dope or storage compound on pin and box thread completely

Appendix C: Example Supplemental Manufacturing and Inspection Requirements for 13Cr Tubulars

SCOPE

This specification defines the requirements for seamless 13Cr tubing produced in accordance with API 5CT L8013Cr and API 5CRA using the latest editions and requirements of these specifications.

MANUFACTURE

Material shall be melted by electric furnace or vacuum degassing process.

Material shall be produced by any of the following methods: pilgering, cold rolling, hot rolling, extruding, or drawing. It is the vendor's option which method or methods to use in order to meet the dimension requirements stated on the purchase order unless specifically stated on the purchase order. Method(s) used shall be reported.

CHEMICAL REQUIREMENTS

The following base elements and residual elements shall be met and reported.

Supplemental specs often tighten the chemistry limits for various reasons

Elements	Min.	Max.
C	0.15	0.22
Mn	0.25	1.00
Si	0	1.00
S	0	0.005
P	0	0.020
Cr	12.00	14.00
Ni	0	0.20
Cu	0	0.25

One ladle and (2) two product analyses shall be reported per heat of steel.

Grain size is to be 5 or finer. Grain size is to be reported.

Ferrite level is to be less than 5%. Ferrite level is to be reported

HEAT TREATMENT

The vendor has the option which method or methods to be use in order to meet the physical requirements stated on the purchase order unless stated otherwise on the purchase order.

All heat treatment used, including temperatures and times at temperature, shall be reported.

If a second temper is applied, it shall be at 50oF below the first temper.

All material shall be hot rotary straightened or stress relieved after cold straightening.

MECHANICAL PROPERTIES

After completion of all heat treat cycles a Qualification Test Coupon (QTC) shall be removed and tested.

All testing shall be done in accordance with the latest edition of ASTM A370 or equivalent.

The QTC shall be a prolongation removed from two or more of the production pieces. Perform minimum two (2) complete series of tests per heat /lot,

The QTC shall be of sufficient length to perform all required testing.

The dimensions, orientations and test temperatures of the specimen tested shall be reported. Results of tests shall conform to the following requirements:

In this example table more restrictive limits are typically provided as required.

Yield Strength	**80,000 psi min.**	**95,000 psi max.**
Tensile Strength	**95,000 psi min.**	
Elongation in 2 in.	**19.5% min.**	
Reduction of Area, %	**35 min.**	
Hardness	**23 HRC max.**	

The hardness values shall be reported in a 9 point - 4 quad thru wall hardness survey in HRC. OD surface hardness readings shall be reported in Brinell hardness scale. All readings of the survey and OD readings shall be reported.

The Charpy V notch impacts, tested at 32 °F shall meet the requirements of API 5CRA. **However, more restrictive requirements would be included in the supplemental spec.**

NON DESTRUCTIVE INSPECTION

All material shall be Ultrasonically inspected to 5% notch requirements in the longitudinal and transverse directions for body wall defects. Full body shall be inspected 100% Reports shall state inspection criteria and that material has passed inspection.

If tighter inspection criteria are deemed necessary, they are so stated

MARKINGS AND PACKAGING

Reference all dimensions in U. S. standard units (inches, pounds, etc.)

Each production piece shall be marked with a continuous line paint stencil identifying the size, grade, specification, mill heat number (with heat treat lot number if any) and purchase order number.

The heat number (and heat treat lot number if applicable) shall be steel stamped on one end of each tube, using low stress dot faced stamps.

End caps shall be installed.

CERTIFICATION AND DOCUMENTATION

A certified test report shall be produced and accompany all shipments for each mill heat.

All Information required in API 5CRA must be stated on the certified test report and if additional information is required it would be stated herein.