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Guidelines for the selection of corrosion resistant alloys for CCS and CCUS injection wells

Bruce Craig [a,*], Adam Rowe [a], Michael Warmack [b], Thomas E. Doll [b], Catherine Stevens [b], Kevin C. Connors [b]

[a] *Stress Engineering Services, Inc., 13800 Westfair East Dr, Houston, TX 77041, USA*
[b] *Energy & Environmental Research Center University of North Dakota, 15N. 23rd Street Stop 9018, Grand Forks, ND 58202-9018, USA*

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ABSTRACT

Carbon capture and sequestration (CCS) and carbon capture utilization and storage (CCUS) projects continue to develop as an effective method to reduce anthropogenic CO_2 emissions. Injection wells for these projects are often required to retain integrity over long operational lives, sometimes 50 years or longer. When it is determined from process conditions that free water may or will be present, either condensing from the CO_2 injectate itself or due to injection into a water-bearing formation, the need for a corrosion resistant alloy (CRA) is required to ensure sufficiently long service life. For well designers and operators, there is a growing need for comprehensive guidelines for the selection of suitable corrosion resistant alloys (CRAs). This paper summarizes important parameters developed through the Plains CO_2 Reduction (PCOR) Partnership that need to be considered for general materials selection for use within CO_2 injection wells based on available data.

1. Introduction

Carbon capture utilization and storage (CCUS) is defined as the process of capturing carbon dioxide (CO_2) to be recycled for further usage and differs from carbon capture and sequestration (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. Possible pathways for CO_2 utilization include conversion to fuels, chemicals, and building materials as well as direct use as solvent, heat transfer fluid, industrial gas, and enhanced oil recovery (EOR).

The purpose of this paper is to present guidelines, developed through the Plains CO_2 Reduction (PCOR) Partnership, for the use of corrosion resistant alloys (CRAs) in CCS and CCUS projects, specifically in long term downhole injection and storage facilities. This equipment needs to maintain integrity for long periods of time, sometimes 50+ years, in order to ensure sequestered CO_2 remains in the storage reservoir. Current well design standards do not adequately address the performance of CRAs in CCS and CCUS environments since most of these standards are based on oil and gas production, which are typically designed for lives of 30 years or less.

It is of paramount importance to appreciate that it is only when liquid water is present that corrosion will be of concern. In the absence of free water, when water is completely soluble in the supercritical CO_2 ($SC{-}CO_2$) stream and not at risk of breaking out, the fluid will not be corrosive, and standard carbon steel construction is sufficient.

For those CCS and CCUS systems where water is expected to be present at some point, such as injection into a saline formation or by virtue of incomplete dehydration, then carbon steel will corrode and CRAs must be considered. Since carbon steel pipelines are standard practice for transport of $SC{-}CO_2$, and have a- successful history, this paper is strictly focused on the selection of CRAs for injection wells.

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 job. Considerations include stream composition, reservoir fluids, flowing and static wellbore conditions, wellhead and surface equipment, downhole completion equipment, service life, etc.

It should be recognized throughout this paper that, at the time of this writing and with the exception of 13Cr stainless steel, there is a substantial lack of research data on the performance of CRAs in $SC{-}CO_2$ streams containing impurities. Thus, the performance of CRAs is taken from allied industries with the expectation that the research data and

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* Corresponding author.
E-mail address: bcraig@stress.com (B. Craig).

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service experience from these sources will be sufficiently similar to provide guidance for selection of CRAs for CCS and CCUS projects. The CRAs for specific SC—CO_2 streams suggested in the guideline Tables 3 and 4 at the end of this paper are only best estimates since no research data are available for most of the alloys considered.

2. Factors that impact CRA selection

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

2.1. Temperature

Temperature is considered first as it is an extremely important parameter for defining CRA suitability. The corrosivity of an environment can never be adequately described without consideration of the temperature. However, it is impact on corrosion cannot be reasonably discussed without all the other corresponding factors such as chlorides, partial pressure of H_2S (pH_2S), partial pressure of CO_2 (pCO_2), pH, impurities, etc., which are explored in the sections below. Within environmental conditions that cause an alloy to corrode, in general, increasing temperature will increase the corrosion rate of alloys.

2.2. 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. The lower the pH, the greater the risk for pitting and environmental cracking. In SC—CO_2 streams, the expected pH can be significantly lower than typically observed in oil and gas production.

An important distinction between pH of producing oil and gas wells, for which most CRA selection guidelines are defined, and SC—CO_2 streams is that the associated water phase is generally fresh with low total dissolved solids (TDS). As such, there is no buffering of condensed water pH in SC—CO_2 systems. Considerable work has been done at Ohio University studying this behavior, and it was found that the pH is 3.0–3.1 for SC—CO_2 at 73.8 bar and 31 °C and above (Choi and Nesic, 2011).

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 75.8 bar and 40 °C reduced the pH another decade to approximately 2.5 (Ayello et al., 2010).

These are extremely low pH values rarely seen in oil and gas production and for which many CRAs have not been evaluated. CRA selection for such low pHs must therefore be based on a combination of oil and gas well data, limited industry experience with alloys in SC—CO_2, limited research data available for alloys in SC—CO_2, and laboratory testing.

2.3. 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. In general, increasing chloride content of water will increase the corrosion rate and promote pitting corrosion of CRAs.

Data provided by the University of North Dakota Energy & Environmental Research Center (UND EERC), for some typical brine compositions from reservoirs considered for CO_2 injection are presented in Table 1. The chloride contents in these brines range from 451 to 153,000 ppm, which is a significant range. Zerai (2006) complied data for Rose Run, Clinton, Grand Rapids and Mt Simon brines which showed a range of chlorides from 47,549 to 191,203 ppm. The chloride content of the formation brine is the most important factor when selecting the appropriate CRA and can dramatically affect the alloying needed to resist corrosion.

Table 1
Examples of several brine compositions.

	Provided by UND EERC		
Species	Inyan Kara mg/L	Broom Creek mg/L	Deadwood mg/L
Na^+	1180	16,900	91,000
K^+	5	3002	1800
Ca^{2+}	14	2030	8340
Mg^{2-}	1	404	1260
HCO_3^-	501	67	33
Cl^-	451	26,400	153,000
SO_4^{2-}	1330	3060	504
SiO_2 (aq)	12	1	10
Al^{3+}	78	263	1000
Fe^{2+}	1	1	25
Sr^{2+}	1	49	248
pH	8.6	7.3	6.0
TDS	3360	49,000	256,000

2.4. Pressure

Pressure is an important parameter as greater pressures will drive more acid gasses and impurities to dissolve into the water phase. In oil and gas wells, partial pressure is commonly used to describe the effect of CO_2 on alloys. However, for SC—CO_2 dense phase fluids, fugacity is a more accurate term to describe the chemical activity of CO_2 and the resulting corrosivity of free water. This is because partial pressure defines the contribution of various gaseous components in a mixed gas to the total pressure. However, in dense phase CO_2 there is no gas phase, so the more thermodynamically correct term is fugacity.

In practice, calculating the partial pressure is far easier than calculating the fugacity of constituents such as H_2S and CO_2 in the appropriate phases. Because of the difficulty of determining the fugacity of these species, which requires specific software programs, partial pressure is used herein. At this time, it is believed that using partial pressure instead of fugacity will be conservative and not lead to a significant difference in performance.

2.5. Water chemistry

Water chemistry is an important factor in the determination of the corrosivity of a process environment. Once free water is present, the corrosivity of the water phase determines what alloys are susceptible to corrosion and those which are not. In addition to the parameters already discussed in this paper (temperature, chlorides, and CO_2), the corrosivity of the water is defined by contaminants (see following section), the total dissolved solids, and buffering species such as bicarbonate and organic acids. Chlorides and buffering species can be accurately measured through water analyzes. Acid gas contents and in situ pH are not easily determined, especially from any water analyzes or field measurements.

Once the acid gasses are in solution in the water phase, the pH is defined by the concentration as well as the buffering capacity of the water, which is dependent on the total alkalinity. 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.

It should be cautioned that numerous geochemical studies of CO_2 injection into reservoirs consider only the pH of plumes emanating from the wellbore and therefore predict higher pH than near the wellbore where CRA selection must be considered. At present it must be assumed that the initial contact of CO_2 into the saline water immediately at the casing surface will have insufficient water to completely dilute the CO_2, and any buffering from the water will not be able to quickly increase the pH. As indicated in the earlier pH discussion, the pH will be close to 3 in the near wellbore. The pH will rise as CO_2 spreads out into the formation as a plume, but the concern is the local pH close to the wellbore to which the materials are exposed

2.6. Stream contaminants

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, and oxyfuel combustion capture for capture from power generating facilities, with direct capture and treating from ethanol, fertilizer (ammonia), chemical and other industry facilities.

However, more pertinent to CRA selection is the composition of the final stream to be injected. As such, some examples of the streams from various sources are summarized in Table 2, keeping in mind the typical analysis is for $CO_2 > 95\%$ with no free water present (usually expressed as < 30 lb/MMscfd, < 480 mg/Sm^3). 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. However, it is imperative when considering the selection of CRAs for a specific application that more accurate stream compositions be defined.

The ranges of various impurities shown in Table 2, 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 CRA guidelines presented at the end of this paper are based on the ranges shown in Table 2 and are only applicable within the stated limits.

2.6.1. Oxygen

Oxygen dissolves into the water phase, increasing corrosivity to carbon steels and possible pitting and crevice corrosion in CRAs, especially in sealing areas. 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 in many alloys, reliable oxygen removal is not typically feasible in injection systems.

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:

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

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 typically have no or very low chlorides in the condensed water phase, so CRAs with lower PRENs such as austenitic stainless steels may be suitable depending on the temperature and presence of contaminates. When a CRA is exposed to a saline formation, the lower PREN alloys would not likely be acceptable when O_2 is present due to the combination of chlorides and temperature.

The presence of O_2 in SC—CO_2 streams presents a significant problem to the selection of CRAs. The corrosivity from O_2 is defined by the dissolved oxygen (DO) concentration in the water phase, which is difficult to model in complex systems. Currently, these data are not readily available for SC—CO_2 streams commingled with formation brines.

Table 2
Examples of 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% CH_4, 0–4% N_2, 0–10 ppm O_2, $\leq$ 0.1% H_2O
Ethanol plants	0% SO_2, ~ 1.5% N_2, < 2% O_2, < 50 ppm total sulfur
Fertilizer plants	0.07% H_2, 0.44% N_2, 0.055% O_2, 0.01% Ar, 2.4 wt% H_2O, H_2S may be present

2.6.2. SO_x and NO_x

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. 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. 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. Higher alloyed CRAs may be needed to resist corrosion and environmental cracking in lower pH waters resulting from SO_x and NO_x impurities.

2.6.3. Hydrogen sulfide and elemental sulfur

There are numerous forms of sulfur-bearing compounds, many of which do not impact CRAs. However, two that are important are elemental sulfur (S) and hydrogen sulfide (H_2S). Elemental sulfur can induce stress corrosion cracking (SCC) and pitting in CRAs; however, at present there are no known sources of elemental sulfur in CCS and CCUS systems, so this threat can typically be ignored except when H_2S and O_2 are present which may result in the formation of elemental sulfur. 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 the industry standard NACE MR0175/ISO 15156–3, which is too lengthy to detail here but should be referred to during any CRA selection process. It is important to recognize that this standard is specifically 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, particularly when oxygen is present.

2.6.4. Hydrogen and nitrogen

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 relative to where hydrogen gas degradation on CRAs is normally observed, typically several thousand psi. For unusual 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.

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.

Table 3
Guidelines for CRA Selection – Tree/Wellhead Equipment (Ambient Temperature to 93 °C)[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		$\leq 0.5\%$	$\leq 0.1\%$	-	-	-	-
NO_X		0.01% NO	0.01% NO	-	-	-	-
H_2S		$\leq 0.6\%$	$< 0.01\%$	-	$\leq 1\%$	-	-
H_2		$\leq 2\%$	$\leq 1\%$	-	-	-	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]
	$\leq$ 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 4
Guidelines for CRA selection – downhole equipment (ambient temperature to 149 °C) [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		$\leq 0.5\%$	$\leq 0.1\%$	-	-	-	-
NO_X		0.01% NO	0.01% NO	-	-	-	-
H_2S		$\leq 0.6\%$	$< 0.01\%$	-	$\leq 1\%$	-	-
H_2		$\leq 2\%$	$\leq 1\%$	-	-	-	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 $T < 230^\circ$F, 25Cr SDSS	IPC/GRE steel tubing $T < 230^\circ$F, 25Cr SDSS	IPC/GRE steel tubing $T < 230^\circ$F, 25Cr SDSS	IPC/GRE steel tubing $T < 230^\circ$F, 25Cr SDSS	IPC/GRE steel tubing $T < 230^\circ$F, 25Cr SDSS	IPC/GRE steel tubing $T < 230^\circ$F, 25Cr SDSS
	$\leq$ 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.

2.7. 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 because 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, the lives of these alloys cannot presently be predicted beyond 50 years for some of the higher CRAs (i.e., 25Cr and nickel-based alloys).

3. CRA limits in CSS/CCUS conditions

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 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. (2019) evaluated 13Cr in CO_2 at 135 bar and 80 °C for 96 h and recorded corrosion rates as a function of impurity contents. Their results showed a beneficial effect of O_2 on corrosion of 13Cr and a detrimental effect from H_2S but no effect when CO is present. However, the test duration was too short (96 h) to be considered valid for determining the effect of impurities on localized corrosion of CRAs and, therefore, may not be valid.

Hashizume et al. (2013) evaluated two 13Cr stainless steels in SC—CO_2. One was standard 13Cr and the other, referred to in the industry as Super 13Cr (S13Cr), which contains nominally 5% Ni and 2% Mo. In the absence of O_2, they tested these two alloys at 100 °C in a solution containing 30,000 ppm chlorides at different pressures of CO_2. The corrosion rate of 13Cr ranged from 0.07 mm/y to 0.16 mm/y at 300 bar and 150 bar, respectively. The S13Cr showed no localized corrosion in the same range of pressures except for localized corrosion of 0.01 mm/y at 250 bar. However, under the same conditions, both alloys displayed crevice attack in almost all environments.

Work by Hassani et al. (2014) demonstrated that 13Cr may work in SC—CO_2 in a 42,800 ppm chloride brine without oxygen or other impurities. The tests were only performed for 48 h, which again is too short to be considered a valid test, but showed the corrosion rate of 13Cr to be near zero; however, the actual steady state value was approximately 0.1 mm/y. Other work on 13Cr materials by Pfennig et al. (2021) and Luo et al. (2017) in SC—CO_2 conditions indicated that 13Cr may be prone to pitting in saline brine, both with and without oxygen. Hua et al. (2016) showed that when the SC—CO_2 is undersaturated at 35 °C and 80 bar 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 0.6 mm/y.

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.

In summary the results for 13Cr in SC—CO_2 with impurities are conflicting/inconclusive and more work is needed to better define the limits. In the meantime, it is well known that O_2 causes severe pitting of 13Cr in seawater, so conservatively 13Cr should not be used for SC—CO_2 environments containing O_2.

Very limited work has been done on high CRAs in SC—CO_2. Zhang (2011) 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 130 °C, but when a separate water phase was present, the corrosion rate exceeded 0.1 mm/y at 80 °C and 110 °C. Matsuo (2022) tested Super 13Cr and 25Cr superduplex stainless steel (SDSS) in SC—CO_2 with impurities of SO_2 and O_2. In the absence of any impurities, the S13Cr alloy was 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.

4. Consideration for specific equipment

In injection and storage wells, the casing, tubing, packer, tubing hanger, and tree may each be exposed to the combination of liquid water and the CO_2 stream. A generic well schematic is shown in Fig. 1 to illustrate the portions of the injection stream and storage formation that different equipment will see. The tree and tubing hanger at the surface would typically only see fresh condensed water that drops out of the SC—CO_2 stream, particularly during shut-in conditions. In some cases where exposure to formation water may extend to surface, the tubing hanger and main run of the tree may be exposed to saline water as well. The packer and portions of the tubing and casing strings that run across water-bearing storage formations will need to account for chlorides in the formation brine and be CRA material.

At present, there is not a standardized well design or completion for CO_2 injection wells. However, the CCS wells require a Class VI permit, which will list the requirements for the design of the well. 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 (2005) only makes a general reference to CO_2 injections wells as follows:

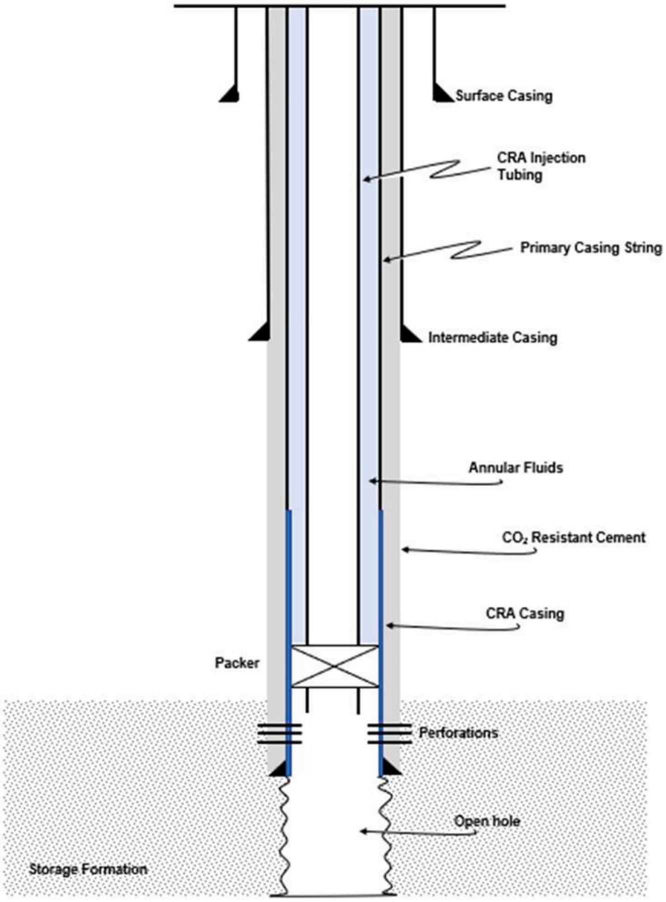

Fig. 1. Generic well schematic for CCS.

> *"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, and exothermic CO_2 dissolution. According to Han (2010), CO_2 injectate may reach the formation at a lower temperature than the corresponding geothermal gradient. However, this depends on the temperature of the CO_2 stream at the wellhead, and can follow the conventional expectation is for injectate temperature to rise as it flows downhole (if it is cooler than the wellbore temperature).

When selecting metallurgy for injection well equipment, it is important to recognize 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, 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. Solid solution nickel-based alloys such as Alloys 825, G3/2550, and C276 must also be cold worked. However, precipitation-hardened nickel-based alloys such as Alloys 718, 925, and 725 can be heat treated (age-hardened) for strength. 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.

4.1. Casing and tubing

The selection criteria for casing depends on whether saline or other water bearing 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.

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 such as type 316 stainless steel have historically been used. 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.

At present, 25Cr superduplex stainless steel (SDSS) has been successfully deployed in several CO_2 systems. 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 (Eiken 2011). The tubing alloy selected was 7″ 25Cr SDSS, and the portion of the 9–5/8″ casing exposed to the combined formation 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 (Trupp et al., 2021).

At present, there is a tendency to run carbon steel casing from the surface to just above the saline reservoir, at which point there is a crossover to CRA casing. This raises the question of whether galvanic corrosion might be an issue at the junction. Galvanic corrosion will not occur in the absence of water, specifically water containing dissolved oxygen, so the crossover should be made above the reservoir fluid contact. Furthermore, if the casing/tubing annulus has a packer fluid which contains an inhibitor package with oxygen scavenger, this should not be an issue. Also, for the external exposure of this junction, the cement column should restrict any water contacting this area. Therefore, galvanic corrosion is not expected to be a problem. Currently there are no other reliable methods to ensure long term isolation of such galvanic couples in casing.

4.2. 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 outlined in this paper.

4.3. Wellheads and Christmas trees

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 water free, with the exception of water alternating gas (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 guidelines presented in this paper. For design lives of greater than 20 years and in the presence of impurities, the primary equipment should be Class HH (CRA on fluid-wetted surfaces).

5. Conclusions

In conclusion,

- Impurities in the CO_2 stream and their effect on corrosion and the potential for cracking need to be considered carefully.
- If oxygen is present, the suitable CRA maybe entirely different than for a stream without oxygen. Well conditions such as injection temperature and bottomhole temperature also critically affect the choice of CRAs.
- Guidelines for injection well metallurgy are presented below in (tree/wellhead equipment), and (downhole equipment). These guidelines assume that surface equipment will not be exposed to temperatures in excess of 94 °C and injection well equipment will not be exposed to temperatures in excess of 149 °C.

These guidelines 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. 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.

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CRediT authorship contribution statement

Bruce Craig: Conceptualization, Methodology, Writing – original draft. **Adam Rowe:** Conceptualization, Methodology, Writing – original draft. **Michael Warmack:** Supervision, Writing – review & editing. **Thomas E. Doll:** Writing – review & editing. **Catherine Stevens:** Writing – review & editing. **Kevin C. Connors:** Writing – review & editing.

Declaration of Competing Interest

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Data availability

No data was used for the research described in the article.

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