Plains CO_2 Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

THE NEED FOR CORROSION-RESISTANT ALLOYS IN CO_2 INJECTION WELLS FOR CCS AND CCUS PROJECTS

White Paper

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EXECUTIVE SUMMARY

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 because of injection into a water-bearing formation, 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 CRAs. This paper summarizes important parameters that need to be considered for general materials selection based on available data. A more detailed and complete review is provided in the Plains CO_2 Reduction (PCOR) Partnership's "Guideline for the Selection and Use of Corrosion-Resistant Alloys in CCS and CCUS Projects."

Because of the limited public information available on the use of CRA materials with CO_2 streams containing impurities in saline environments, it is anticipated that the information presented in this document will be updated or refined as more information and test data become available in the future.

PCO2R Partnership

Plains CO_2 Reduction (PCOR) Partnership

Energy & Environmental Research Center (EERC)

THE NEED FOR CORROSION-RESISTANT ALLOYS IN CO_2 INJECTION WELLS FOR CCS AND CCUS PROJECTS

INTRODUCTION

Carbon capture, utilization, and storage (CCUS) is defined as the process of capturing 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 summarize guidelines that have been developed 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 extended 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 ($scCO_2$) stream and not at risk of breaking out, the fluid will not be corrosive and standard carbon steel construction is sufficient. As proof of this, EOR projects have been in operation for at least 40 years utilizing carbon steel pipelines for transport of $scCO_2$ with essentially no reported problems. Therefore, for CCS and CCUS where $scCO_2$ streams devoid of free water are transported and injected into non-water-bearing formations, the entire system could be made from carbon steel equipment.

For those CCS and CCUS systems where free 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. Through the interaction of water and CO_2, carbonic acid is formed and is corrosive to carbon steel. Since carbon steel pipelines are standard practice for transport of $scCO_2$ and have a long, successful history due to strict dehydration of the CO_2 stream so that no free water is present, 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 guideline 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 $scCO_2$ streams containing impurities. 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. The CRAs for specific $scCO_2$ streams suggested in the guideline tables at the end of this paper are only best estimates since no research data are available for most of the alloys considered. Because of the limited public information available on the use of CRA materials with CO_2 streams containing impurities in saline environments, it is anticipated that the information presented in this document will be updated or refined as more information and test data become available in the future.

This work was completed by Stress Engineering Services, Inc. (SES) and the University of North Dakota Energy & Environmental Research Center (EERC) through the Plains CO_2 Reduction (PCOR) Partnership. The PCOR Partnership, funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), the North Dakota Industrial Commission's (NDIC's) Oil and Gas Research Program and Lignite Research Program, and more than 240 public and private partners, is accelerating the deployment of CCUS technology. The PCOR Partnership is focused on a region comprising ten U.S. states and four Canadian provinces in the upper Great Plains and northwestern regions of North America. It is led by the EERC, with support from the University of Wyoming and the University of Alaska Fairbanks.

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 because of a saline reservoir, a CRA may be required to ensure sufficiently long service life. This section summarizes the various factors that must be considered for selection of the most appropriate and cost-effective CRA.

Temperature

Temperature is listed here 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 temperature. However, its 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. In general, increasing temperature will increase the corrosion rate of alloys.

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 are very important to the selection of an appropriate CRA. The lower the pH, the greater the risk for pitting and environmental cracking. In $scCO_2$ streams, the expected pH can be significantly lower than typically observed in oil and gas production.

An important distinction between the pH of producing oil and gas wells, for which most CRA selection guidelines are defined, and $scCO_2$ streams is that the associated water phase contained within $scCO_2$ streams is generally fresh with low total dissolved solids (TDS). This is a result of the capture process where only water vapor is maintained in the $scCO_2$ stream. As such, there is no buffering ofcondensed water pH in $scCO_2$ 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 $scCO_2$ at 1070 psi (73.8 bar) and 31°C (88°F) and above (1).

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 $scCO_2$ at 1099 psi (75.8 bar) and 104°F (40°C) reduced the pH another decade to approximately 2.5 (2).

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 $scCO_2$, limited research data available for alloys in $scCO_2$, and laboratory testing.

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 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.

Based on data collected by Zerai (3) and additional data provided by the EERC, 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 191,203 ppm, which is a significant range. This is a principal factor when selecting the appropriate CRA and can dramatically affect the alloying needed to resist corrosion. Contact with the chlorides within the water streams can occur in the tubulars upon initial start of injection, after well workovers, flowbacks, or extended shut-ins where the reservoir water can encroach back into the wellbore. The effects can be limited if appropriate check valves or precautions are planned/taken in the well design and construction.

Table 1. Examples of Several Brine Compositions

	Compiled by Zerai (3)				**Provided by the EERC**		
Species	**Rose Run, mg/kg**	**Clinton, mg/kg**	**Mt. Simon, mg/kg**	**Grand Rapids, mg/kg**	**Inyan Kara, mg/L**	**Broom Creek, mg/L**	**Deadwood, mg/L**
Na^+	60,122	67,000	32,000	26,539	1180	16,900	91,000
K^+	3354	850	1060	636	5	3002	1800
Ca^{2+}	37,600	23,200	12,400	2737	14	2030	8340
Mg^{2-}	5881	1840	2190	533	1	404	1260
HCO^{3-}	122	200	71	182	501	67	33
Cl^-	191,203	160,400	78,700	47,549	451	26,400	153,000
SO_4^{2-}	326	523	1180	337	1330	3060	504
SiO_2 (aq)	3	1	0	0	12	1	10
Al^{3+}	2	1	0	0	78	263	1000
Fe^{2+}	140	5	2	0	1	1	25
Sr^{2+}	456	753	236	–	1	49	248
pH	6.4	6.5	6.7	7.2	8.6	7.3	6.0
TDS	277,571	250,000	150,000	90,000	3360	49,000	256,000

Pressure

Pressure is an important parameter, as greater pressures will drive more acid gases and impurities to dissolve in the water phase. In oil and gas wells, partial pressure is commonly used to describe the effect of CO_2 on alloys. However, for scCO_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, there is no gas phase in dense-phase CO_2, so the more thermodynamically correct term is fugacity.

Fugacity is a complicated concept, and a detailed discussion of the relationship between fugacity and chemical activity is outside the scope of this paper. The important takeaway is that increasing pressure of CO_2 does not have a one-to-one correspondence to fugacity. Rather, above critical pressure (73.9 bar for pure CO_2), fugacity begins to level off with increasing pressure.

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, based on recent efforts in the petroleum industry comparing partial pressures and fugacity for high-pressure wells, it is believed that using partial pressure instead of fugacity will be conservative and will not lead to a significant difference in performance.

Water Chemistry

Water chemistry is a key 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 that 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), TDS, and buffering species such as bicarbonate and organic acids. Chlorides and buffering species can be accurately measured through water analyses. Acid gas contents and in situ pH are not easily determined, especially from any water analyses or field measurements.

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. The buffering capacity of the water is dependent on the total alkalinity, specifically, such species as bicarbonate and organic acids (acetate, formate, etc.) that reduce the effect acid gases have on 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.

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. It must be assumed that the initial contact of CO_2 into the saline water immediately at the casing surface and near-wellbore 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.

Stream Contaminants

It is customary practice when discussing CO_2 stream composition to refer to the various methods for removing CO_2 from the specific plant generating this gas and the associated impurities. These methods are postcombustion capture, precombustion capture, and oxyfuel combustion capture.

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). 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 $N_2/Ar/O_2$ is insufficient to make an informed CRA choice since one alloy may be

Table 2. Examples of Streams from Various Sources

Industries	Typical
Power Generation – Coal-Fired Plants (4)	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 (4)	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, ≤0.1% H_2O
Ethanol	0% SO_2, ~1.5% N_2, <2% O_2, <50 ppm total, H_2S may be present
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

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.

Oxygen

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

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 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:

$$\text{PREN} = \%\text{Cr} + 3.3 \times (\%\text{Mo} + 0.5\%\text{W}) + 16 \times \%\text{N} \qquad \text{[Eq. 1]}$$

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 contaminants. When a CRA is exposed to a saline formation, the lower-PREN alloys would not likely be acceptable when O_2 is present because of the combination of chlorides and temperature.

The presence of O_2 in $scCO_2$ streams presents a significant problem for 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 $scCO_2$ streams commingled with formation brines.

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). These limits mean that the alloy will likely corrode at temperatures above the CPT and CCT. Table 3 is an example of these limits in seawater, which has approximately 20,000 ppm chlorides. This is similar to some saline water formations, but many storage brines have much higher chloride contents, such as several of those presented earlier in Table 1.

Table 3. CPT and CCT for Select CRAs in Seawater

Alloy	Material	CPT, °C	CCT, °C
304 SS	Stainless steel (SS)	2	−15
316 SS	SS	10	−10
22Cr DSS	Duplex SS (DSS)	40	20
25Cr SDSS	Super duplex SS (SDSS)	80	70

It is important to note that CPT and CCT will be different in different fluids. Very limited research and testing work has been done to define these limits when O_2 is present in $scCO_2$ streams for CRAs.

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 $scCO_2$ will promote the formation of sulfuric acid, dropping the pH to more acidic levels of 1 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 1 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.

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 and 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. 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 National Association of Corrosion Engineers (NACE) Standard 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 $scCO_2$ warrants different limits, particularly when oxygen is present.

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 because of 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 (SME) familiar with hydrogen damage phenomena and may require laboratory testing. The presence of nitrogen as an impurity in $scCO_2$ streams has no effect on corrosion and, therefore, is of no concern from a CRA selection standpoint.

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 SS, but are not considered applicable to the injection of $scCO_2$ 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 industry experience with other CRAs, such as 13Cr, indicates they may only be suitable for 10–15 years. Moreover, there are currently no means to predict service life of CRAs because of the highly localized forms of corrosion attack that occur 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) and shorter for those such as 13Cr, simply because there is no history for these alloys in environments sufficiently similar to petroleum production. The service life for CCS and CCUS applications will depend on the specific application.

CRA LIMITS IN CCS/CCUS CONDITIONS

While the volume of work done on CRAs exposed to $scCO_2$ 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 $scCO_2$ in the presence of water. Most of the CRA research for $scCO_2$ has focused on the use of 13Cr SS (e.g., AISI 420 martensitic SS), which is generally available as API (American Petroleum Institute) Specification 5CT-grade 13Cr L80 and

API Specification 5CRA Group 1. The 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 1956 psi and 176°F for 96 hours and recorded corrosion rates as a function of impurity contents (5). 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 hours) to be considered valid for determining the effect of impurities on localized corrosion of CRAs and, therefore, may not be valid.

Hashizume et al. evaluated two 13Cr SS alloys in $scCO_2$. One was standard 13Cr and the other, referred to in the industry as Super 13Cr (S13Cr), which contains nominally 5% Ni and 2% Mo (6). In the absence of O_2, they evaluated 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 to 6.3 mpy at 4350 and 2175 psi, respectively. The S13Cr showed no localized corrosion in the same range of pressures except for localized corrosion of 0.4 mpy at 3625 psi. However, under the same conditions, both alloys displayed crevice attack in almost all environments.

Work by Hassani et al. demonstrated that 13Cr may work in $scCO_2$ in a 42,800-ppm chloride brine without oxygen or other impurities (7). The tests were only performed for 48 hours, 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 (4 mpy). Other work on 13Cr materials by Pfennig et al. (8) and Luo et al. (9) in $scCO_2$ conditions indicated that 13Cr may be prone to pitting in saline brine, both with and without oxygen. Hua et al. (10) showed that when the $scCO_2$ is undersaturated at 95°F and 1160 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.

These various results for corrosion of 13Cr in $scCO_2$ indicate that water saturation is a key 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 $scCO_2$. However, the presence of water, even at undersaturation, 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 $scCO_2$ 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 $scCO_2$ environments containing O_2.

Very limited work has been done on high CRAs in $scCO_2$. Zhang showed that 22Cr DSS exposed to $scCO_2$ 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 (11). Matsuo et al. assessed Super 13Cr and 25Cr SDSS in $scCO_2$ with impurities of SO_2 and O_2 (12). In the absence of any impurities, the S13Cr alloy was corrosion-resistant; however, for all amounts of O_2 and SO_2 assessed, S13Cr was not suitable, but 25Cr SDSS was corrosion-resistant.

Since there is little public information available, material testing may be required to determine which CRA material would be best-suited for the environment in the project of consideration. If material testing is performed, a range of grades of CRA material that include lower grades should be considered in the testing to determine if lower grades can be used or restricted from use for the project of consideration.

CONSIDERATION FOR SPECIFIC EQUIPMENT

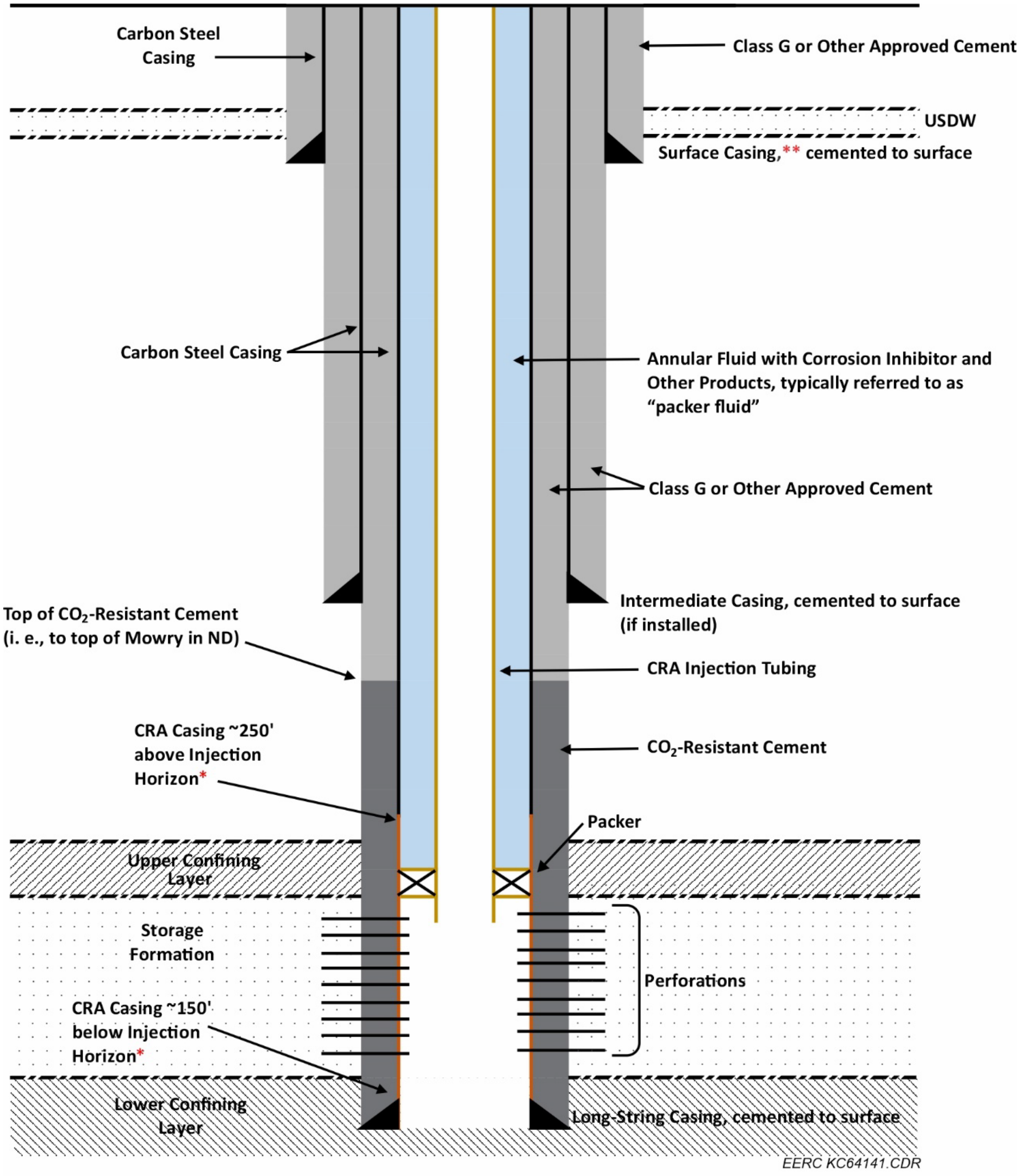
In injection and storage wells, the casing, tubing, packer, tubing hanger, and tree may each be exposed to the combination of liquid water and the CO_2 stream. A generic well schematic is shown in Figure 1 to illustrate the portions of the injection stream and storage formation that different equipment will see. The tree and tubing hanger at the surface would typically only see fresh condensed water that drops out of the $scCO_2$ 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.

At present, there is no a standardized 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 Intergovernmental Panel on Climate Change (IPCC) (4) 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, and exothermic CO_2 dissolution. According to some, CO_2 injectate may reach the formation at a lower temperature than the corresponding geothermal gradient (13). However, the conventional expectation is for injectate temperature to rise as it flows downhole.

When selecting metallurgy for injection well equipment, it is important to recognize the fundamental metallurgical fact that CRAs are not all processed the same way. For example, SS 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. 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.



NOTES:

1. Drawing is not to scale but to provide a representation for the construction of a CCS injection well.
2. CRA = corrosion-resistant alloy
3. Injection packer is to be installed within 50' of the top perforation.

*Indicated lengths are provided as a reference and would be defined on a project-by-project basis.
**Surface casing is required to be set 50' below lowermost source of drinking water.

Figure 1. Generic well schematic for CCS.

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 $scCO_2$ 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 SS have historically been used. For deeper, higher-pressure CO_2 injection wells, these materials are not capable of handling the pressures and hanging loads, so higher-alloy CRAs are required.

At present, 25Cr 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 Sleipner Field approximately 2600 ft below the seabed (4). The tubing alloy selected was 7″ 25Cr SDSS, and the portion of the 9⅝″ casing exposed to the combined formation fluids and CO_2 was also 25Cr SDSS. 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 (14).

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 DO, so the crossover should be made above the reservoir fluid contact. Furthermore, if the casing/tubing annulus has a packer fluid that 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.

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 $scCO_2$, 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 $scCO_2$ 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.

Wellheads, Trees, and Surface 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 $scCO_2$ 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 that 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).

For low pressure and temperatures of 140°F and less in the absence of oxygen, vessels, pumps, valves, and piping 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 15156-3 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 SS is not acceptable, then higher alloys such as Hastelloy C22 or Hastelloy C276 may be the only option. At this point, an SME should be consulted to aid in determining the best and most economical alloys.

SUMMARY AND CONCLUDING REMARKS

The most crucial step in selecting compatible alloys for $scCO_2$ 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 is intermittent, carbon steel with a corrosion allowance would be 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 exceptionally low, typically around 3, and the other factors discussed in this paper 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.

The 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 may be entirely different than for a stream without oxygen. Well conditions such as reservoir water chemistry, injection temperature, and bottomhole temperature also critically affect the choice of CRAs.

Summary guidelines for injection well metallurgy are presented in Table 4 (surface equipment), Table 5 (tree/wellhead equipment), and Table 6 (downhole equipment). These summary guidelines 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). 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 material 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 NACE MR0175/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.

Table 4. Guidelines for CRA Selection – Surface Equipment (ambient temperature to 200°F)

		CO_2 Sources					
		Power Generation					
Impurities	**Concentration**	**Coal-Fired**	**Gas-Fired**	**Chemical Plants**	**Natural Gas Plants and Other Industries**	**Ethanol Plants**	**Fertilizer Plants**
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%	TBC[5]	TBC[5]
H_2		≤2%	≤1%	–	–	–	–
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~0 ppm only condensed water from the $scCO_2$[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. 180°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

[1] Implicit in this table is the primary stream of $scCO_2$ at >95% CO_2.

[2] Numerous other CRAs 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 is expected to be higher, contact an SME.

[5] To be confirmed. CO_2 streams from ethanol plants and fertilizer plants may contain H_2S and, therefore, should be evaluated for H_2S.

Table 5. Guidelines for CRA Selection – Tree/Wellhead Equipment (ambient temperature to 200°F)

		CO$_2$ Sources					
		Power Generation					
Impurities	Concentration	Coal-Fired	Gas-Fired	Chemical Plants	Natural Gas Plants and Other Industries	Ethanol Plants	Fertilizer Plants
O_2		Present[3]	Present[3]	Present[3]	10 ppm	<2%	550 ppm
SO_2		≤0.5%	≤0.5%	≤0.1%	–	–	–
NO_x		0.01% NO	0.01% NO	0.01 % NO	–	–	–
H_2S		≤0.6%	≤0.6%	<0.01%	≤1%	TBC[4]	TBC[4]
H_2		≤2%	≤2%	≤1%	–	–	–
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~0 ppm only condensed water from the $scCO_2$	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

[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 SS 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.

[4] CO_2 streams from ethanol plants and fertilizer plants may contain H_2S and, therefore, should be evaluated for H_2S.

Table 6. Guidelines for CRA Selection – Downhole Equipment (ambient temperature to 300°F)

		CO_2 Sources					
		Power Generation					
Impurities	**Concentration**	**Coal-Fired**	**Gas-Fired**	**Chemical Plants**	**Natural Gas Plants and Other Industries**	**Ethanol Plants**	**Fertilizer Plants**
O_2		Present[4]	Present[4]	Present[4]	10 ppm	<2%	550 ppm
SO_2		≤0.5%	≤0.5%	≤0.1%	–	–	–
NO_x		0.01% NO	0.01% NO	0.01 % NO	–	–	–
H_2S		≤0.6%	≤0.6%	<0.01%	≤1%	TBC[6] –	TBC[6]
H_2		≤2%	≤1%	≤1%	–	–	–
N_2		Present	Present	Present	Present	Present	Present
Chlorides	~0 ppm only condensed water from the $scCO_2$	IPC/GRE[5] steel tubing T<230°F, 25 Cr SDSS	IPC/GRE steel tubing T<230°F, 25 Cr SDSS	IPC/GRE steel tubing T<230°F, 25 Cr SDSS	IPC/GRE steel tubing T<230°F, 25 Cr SDSS	IPC/GRE steel tubing T<230°F, 25 Cr SDSS	IPC/GRE steel tubing T<230°F, 25 Cr SDSS
	≤1000 ppm	25 Cr SDSS	25 Cr SDSS	25 Cr SDSS	25 Cr SDSS	25 Cr SDSS	25 Cr 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

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[1] Implicit in this table is the primary stream of $scCO_2$ at >95% CO_2. Maximum pressure is 3000 psi.

[2] For higher pressures and impurities outside these ranges, contact an SME.

[3] Numerous other CRAs 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 is expected to be higher, contact an SME.

[5] Internal plastic coating/glass-reinforced epoxy.

[6] CO_2 streams from ethanol plants and fertilizer plants may contain H_2S, and therefore should be evaluated for H_2S.

It cannot be overstated enough that there are insufficient test data and field experience to make complete materials choices without seeking the aid of an SME and, even more necessarily, performing laboratory tests to confirm the alloys selected are suitable for the specific well environment. In many of the more severe conditions where numerous impurities are present and contact with a saline formation is likely, laboratory corrosion and environmental cracking testing is strongly recommended.

Considerations of CRA materials are cost, manufacturing location, and delivery of materials. As a general statement, as the grade of a CRA material is increased, the cost is increased and the delivery can be extended. Because of the price and delivery of CRA materials, it is important to start the review of the material selection as early in the process as possible to determine the proper CRA material for the application as well as to provide time to perform any material testing required to verify that the material will withstand the environment that it will be exposed to.

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