MATERIAL INTEGRITY ASPECTS OF CCS: AN OVERVIEW FOR CO_2 TRANSPORT AND STORAGE

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Introduction

Carbon capture and storage (CCS) are technologies aimed at capturing CO_2, followed by transportation to a storage site, injecting into one of several types of stable geological formations, trapping and preventing its subsequent emission [1]. Though CO_2 transport and injection for enhanced oil recovery (EOR) are known for over 40 years, new challenges arise when the CO_2 source is anthropogenic and not natural (as in EOR) [2]. EU Directive 2009/31/EC states that CO_2 streams from power stations or industrial plants "shall consist overwhelmingly of CO_2" but may contain associated incidental substances (e.g., SOx, NOx, O_2, H_2S) [3]. These anthropogenic impurities pose a bottleneck in extending the established corrosion prediction models used in oil and gas environments to CCS [2]. They add to the system's complexity by influencing CO_2's physical properties and the water solubility, segregating CO_2 into the aqueous phase, potentially lowering the solution pH and increasing corrosion risk [2], [4]. Figure 1 presents a schematic of the CCS process, along with the associated risks at each step.

The paper intends to briefly highlight the risks involved with the transport and storage of anthropogenic CO_2, the material selection criteria and concludes with highlighting the present challenges.

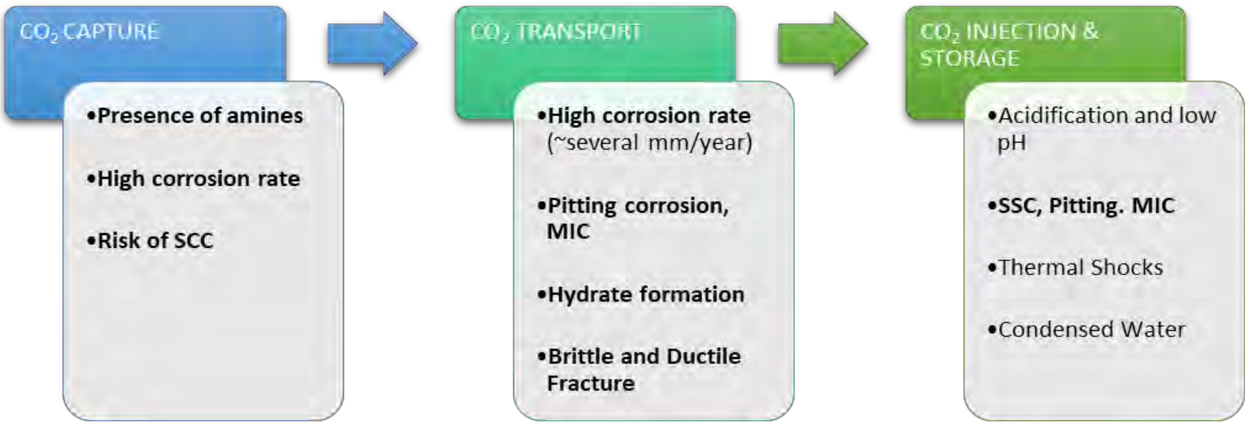

Figure 1: A schematic of the CCS process, threats and the material risks associated with each step (SSC: Sulfide Stress Cracking / MIC: microbiologically induced corrosion)

Risks involved during CO_2 transport

There is currently a lack of standards for CO_2 stream quality specifications, making it difficult to accurately define the safe operating conditions for CO_2 transport and storage. There could be a distinct difference in the contaminants present in the CO_2 stream, depending on the sources [2]. The CO_2 stream will contain SO_2, NO_2, O_2 or H_2S based on the source, the capture process, and the gas treatment level.

Most CCS projects in the planning phase intend to transport and store CO_2 in a supercritical state (Figure 2). When present within the solubility limit, water content in-stream poses no significant corrosion risk; however, it will separate as an aqueous phase and wet the pipeline walls if it exceeds the saturation level. Water is a potent cause of CO_2 pipeline corrosion, mainly if the water accumulates as a liquid at low or dead points within the pipes [5]. Water and acid gas impurities co-exist under such conditions, causing general corrosion at rates up to several mm/y, accompanied by pitting corrosion or a risk of sulphide stress cracking (SSC) in presence of H_2S. Impurities also lower the water solubility in the supercritical CO_2 stream, exacerbating the issue. A study reported among CO_2 related pipeline failures, 45% was due to corrosion, i.e. it was the single most significant cause of pipeline failures [2]. Water may also lead to hydrates formation at low temperature in the pipeline, blocking the pipeline. Additionally, O_2 might be present in the CO_2 stream (unlike CO_2 from natural sources), increasing corrosion issues by additional cathodic reduction, inhibiting protective scale formation and possible microbiologically induced corrosion (MIC).

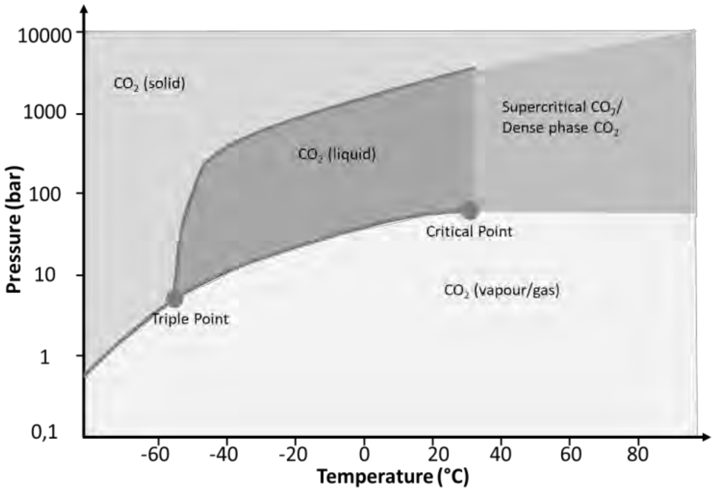

Figure 2: Pressure-temperature phase diagram for CO_2 [6]

Apart from stream composition, another difference in CCS and EOR transportation is that generally, EOR pipelines are confined to low population areas and operate well below the supercritical conditions [6]. In CCS pipelines, defects by mechanical damage, corrosion, or operational issues may result in leakage from the damaged sections, posing a threat to the population and the vicinity's local environment [7]. Given that CO_2 is an asphyxiant at high concentrations, the safety assessment of CO_2 pipelines in the unlikely event of rupture is paramount and central to public acceptance [6]. In the case of a rupture, the rapid depressurization will reduce the CO_2 temperature in the leakage point's proximity (Joule-Thomson effect) [8].

Risks involved during CO_2 storage

Figure 3 illustrates the process of CO_2 injection in geological reservoirs. CO_2 injection for storage requires tubing material to withstand the corrosive environment defined by the near-wellbore conditions (pressure, temperature, brine properties and injected CO_2 composition). The injection point temperature depends on the CO_2 injection rate and the reservoir conditions, ranging from 10- 120 °C. The pressure is typically 50-150 bar, for which the CO_2 will be in the liquid or supercritical state, depending on the temperature. Different brines have different salt contents, and pH is usually in the range of 3.5 – 4.5. Condensed water, which may form during shut-in, has no buffer capacity and can have pH as low as 3.0; resultantly, condensed water is much more aggressive than buffered formation water. Impurities in the CO_2 stream can reduce the pH (SO_x, NO_x and other acids) and increase corrosivity. During injection, at the bottom hole, formation water will dissolve CO_2 up to saturation. Impurities will partition to the water phase, with the acidic gases in CO_2 reacting with formation water producing strong acids. Thus, a significant corrosion risk is at the interface between formation water and CO_2. During the shut-in period, wellhead temperature decreases with CO_2 in gas and supercritical phase co-existing at the wellhead. If residual water is present, the wellhead is exposed to corrosion issues. If H_2S gas is present in the stream, there might be a risk of SSC. Oxygen will enormously increase the localized corrosion attack and promote MIC. Finally, during prolonged storage, the tubing may be removed or stay in place, ensuring against CO_2 leakage under both conditions.

If shut-in conditions are frequent, injection well suffers from thermal shocks due to pressure changes. Therefore, an essential aspect for the material selection would be a good material impact toughness property at low temperatures. Material impact toughness is also an important consideration for material selection in case of a blow out where rapid depressurization of supercritical CO_2 will result in a huge temperature drop. Vallourec is conducting experiments to measure the impact toughness of different CRA materials in sub-zero temperatures (down to -80°C) to help with a risk-based approach for material selection for CCS applications.

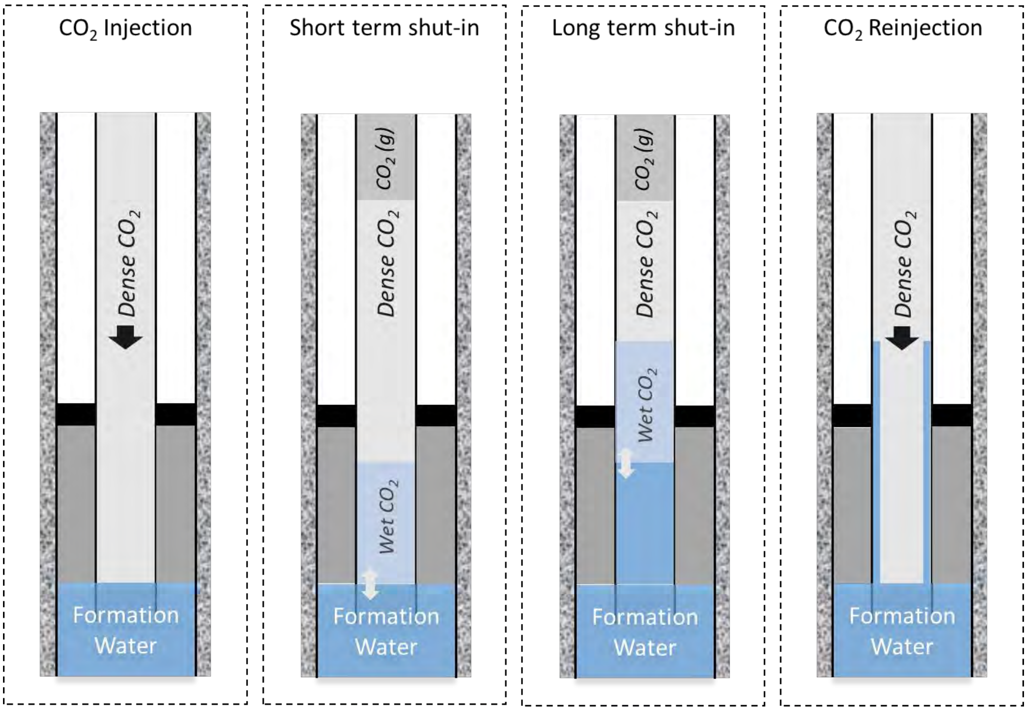

Figure 3: Sketch illustrating corrosion risks during injection and storage

Material Selection for CO_2 storage

Corrosion risks will depend on impurities

In the case of injection, recommendations and guidelines for materials selection are limited, particularly with impurities like O_2. It is common practice to assume the same material limits for CO_2 injection wells as oil and gas wells. However, the conditions can be significantly different in dense anthropogenic CO_2 depending on its composition and specific position in the well under consideration [9].

criteria based on the position within the well. Main corrosion risks to be considered for material selection occurs during shut-in and long storage.

Several corrosion resistant alloys (CRA) materials are used for well tubing in oil and gas production. 13Cr (martensitic and super martensitic) and duplex stainless steels are most common [10]. 13Cr has good resistance to CO_2 corrosion due to its high chromium content. Still, it may be susceptible to pitting and localized corrosion, particularly at high temperatures in the presence of high chloride contents. Supermartensitic 13Cr steels are generally more resistant to pitting corrosion than conventional 13Cr [11]. Duplex stainless steels have good corrosion resistance in CO_2 environments but may be susceptible to stress corrosion cracking (SCC) under certain aggressive conditions. The SCC susceptibility depends on parameters like temperature, chloride concentration and oxygen.

The practical challenge for using duplex stainless steels is, in many cases, to decide whether the operational conditions are inside or outside the safe window. In particular, the temperature, chloride content and oxygen content are essential factors for stress corrosion cracking. In short, several materials can be used for well tubing. Still, the use can be restricted by pitting corrosion and stress corrosion cracking when oxygen and high chloride levels are present.

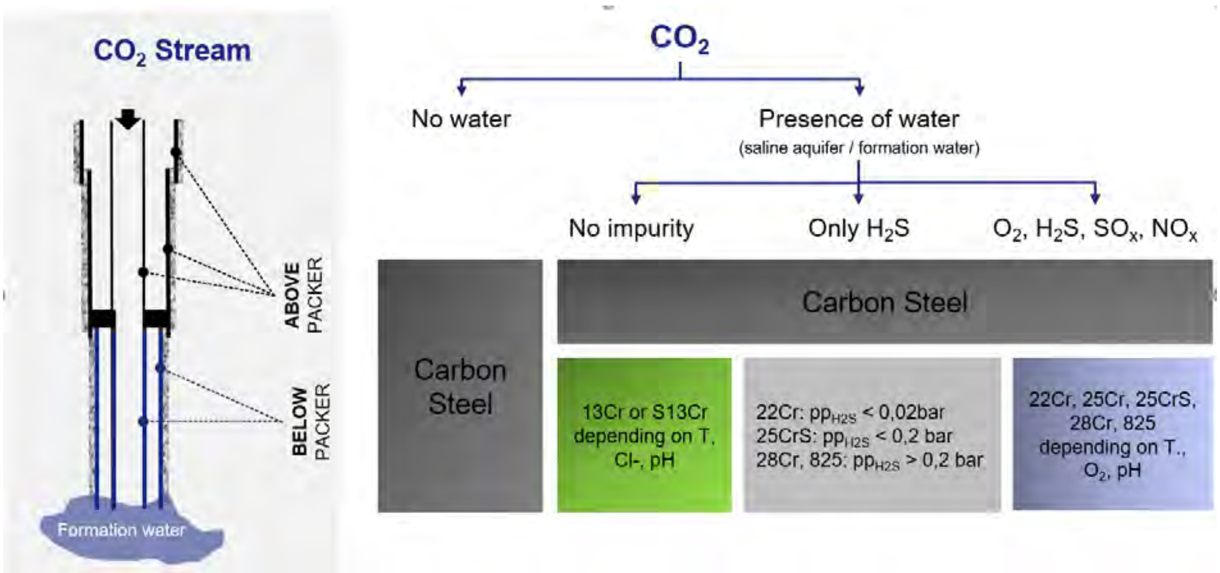

Figure 4: Material selection criteria for different sections of the CO_2 well.

Impact toughness at low temperature

The material impact toughness is the material's ability to absorb energy in the plastic region. Typically, as the temperature drops below 0˚C, the hardness, yield strength, ultimate tensile strength and modulus of elasticity of a metal increase but ductility decreases**.**

Impact toughness is driven by alloying elements, residual elements, micro-cleanliness, microstructure, and manufacturing process. At low temperatures, in general, austenitic steels exhibit higher impact toughness than the relatively brittle martensite. Duplex stainless steels, widely used in petrochemical industries (consists of discontinuous ferrite in an austenitic matrix), exhibit impact toughness values intermediate to those of austenitic and martensitic steels.

The impact toughness value of a material is measured using the Charpy V notch method as per ASTM E23. Initially developed as a quality control test, the Charpy V notch method is currently used for materials design based on the toughness requirement. In this study, 4 different duplex stainless steels were studied for their impact toughness values. As shown in Table 1, two duplex stainless steels (22-5-3) were studied, one in cold worked (CW) condition and the other in solution annealed (SA) condition. Similarly, four super suplex stainless steels (25-7-4) were studied in solution annealed condition (SA) and cold worked condition (CW). The specimens were machined using the largest possible size of the specimen considering wall thickness of the tubes. Since the wall thickness of the tubular specimens were non identical, different size specimens were used in the study as indicated in Table 1. The impact toughness of solution annealed and cold work 25-7-4 in both transversal and longitudinal direction is plotted in Figure 5. When SA and CW materials are compared, SA materials appear to have much better impact toughness resistance than the cold worked materials.

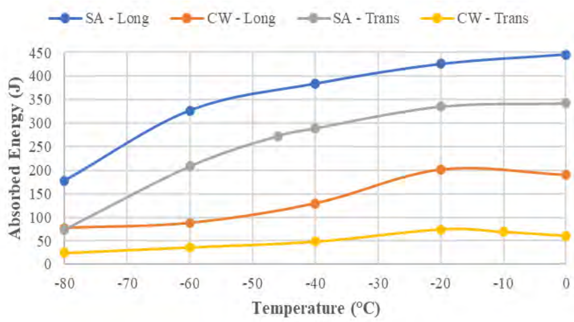

Figure 5 - Transition curves of 25-7-4 in SA and CW state with different testing orientations (converted to full size)

This is due to the highest residual stress induced by the cold hardening process which results in higher yield strength but a lower impact toughness values. Additionally, longitudinal values are always higher than transversal ones due to the grain orientation given by the extrusion process.

Table 1: Materials investigated in the study

Material	Tube OD x Wt [mm]	Specimen Size (KCV)[mm]	AYS [ksi]
22-5-3 SA	168,3 x 10	10 x **7.5**	70
22-5-3 CW	114 x 10,92	10 x **5**	131
25-7-4 SA	168,3 x 10,97	10 x **7.5**	90
25-7-4 CW	114 x 7,05	10 x **5**	142
25-7-4 SA	204 x 25,6	10 x **10**	87
25-7-4 CW	179 x 10,36	10 x **7.5**	137

As there is no available standards currently available for CCUS, material selection at present depends on the available standards used in oil and gas industry. According to the NORSOK M-601 specification, the minimum average impact toughness requirement for a material is 45J at -46°C. Applying the reduction factor for KCV 7.5 and KCV 5 specimens, according to

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NORSOK M-601, the minimum required average impact toughness values are 37.5J and 30J respectively. On Figure 6, we compare differences between 22-5-3 Duplex and 25-7-4 Super Duplex Stainless Steel. Results show that super duplex stainless steels exhibit better impact toughness properties than the duplex stainless steel in both cold worked and solution annealed conditions. It is evident that the investigated materials exhibit different level of toughness depending on process route. As per project requirements, product qualification would be required to confirm material suitability.

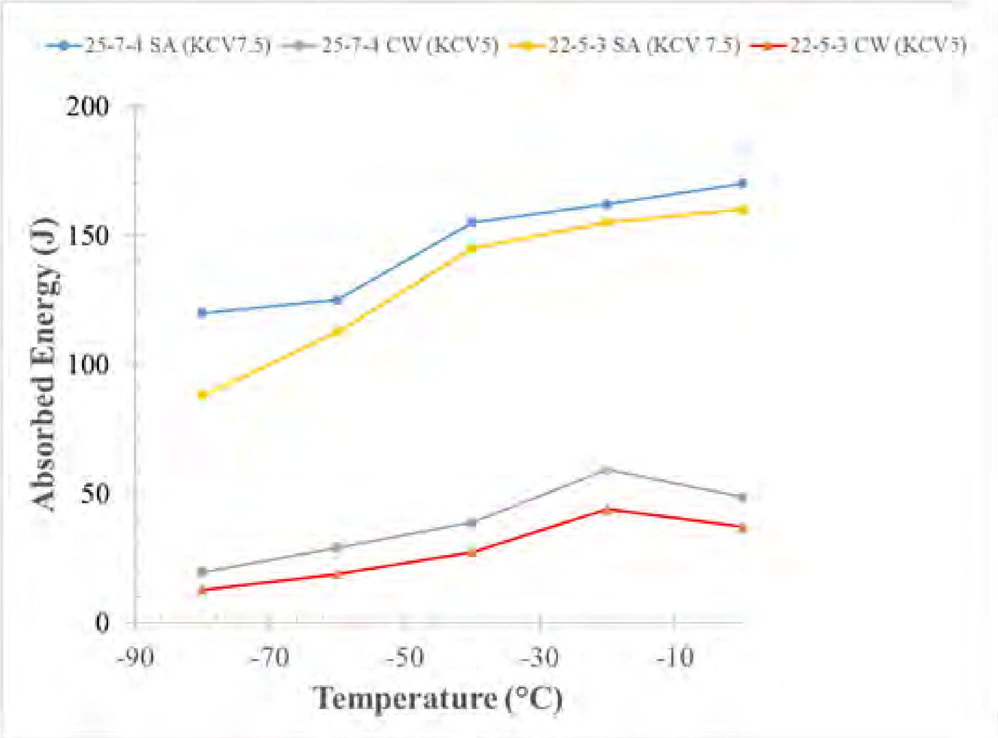

Figure 6 - Temperature dependent transversal impact toughness values of the investigated duplex and super duplex stainless steels.

Conclusion, Challenges and Research Opportunities

Conclusion

This paper aims to highlight the major challenges in the CCUS technology from a materials perspective. The key challenges identified for the material selection CO_2 storage is corrosion and material impact toughness properties. The impact toughness properties of 4 duplex and super duplex stainless steels were compared and the values were compared againsed the minimum requirement. It was seen that all the stainless steels show good impact toughness properties. Super duplex stainless steels show better impact impact toughness properties as compared to duplex stainless steels.

Challenges and Research opportunities

One of the significant experimental challenges is understanding the impurity behavior under dynamic flow conditions [12]. Another issue with non-dynamic testing is the depletion of impurity during the experiment. It could be imperative when considering tests of longer duration. In a study, IFE reported that a large part of the impurities became 'non-active' due to immobilization of the corrosive phases and reactions in the bulk phases [13].

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