

Testing of OCTG Materials in Simulated CCS Environments: Comparing different Approaches for Impurity Concentrations Definition

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ABSTRACT

The underground injection of dense CO₂ containing impurities for carbon capture and storage (CCS) applications poses potential risks to the integrity of downhole materials, particularly under conditions that may allow the presence of liquid brine. Testing materials for these environments remain challenging due to their complexity and the lack of standardized methodologies. Typically, materials are exposed to simulated CCS environments in autoclaves containing brine in contact with dense-phase CO₂ being the incorporation of impurities one of the main challenges. This paper compares two approaches for the addition of impurities into the autoclave during experimental testing. In the first approach, impurities were added based on the nominal composition of the CO₂ stream to be simulated. In this case, dissolution into the brine and chemical reactions among impurities will alter the actual composition of the CO₂ phase. In the second approach, the amount of each impurity was adjusted to achieve target concentrations in the CO₂ phase after accounting for solubility and dissociating reactions into the brine. Materials such as Martensitic Stainless Steels—known to be susceptible under the low pH conditions that can develop during CO₂ injection with impurities—were evaluated under both scenarios. This paper describes the relative severity of each experimental approach and prompts further discussion on the need for standardized testing methodologies.

Key words: CCUS, CCS, CO₂ injection, impurities, corrosion, tubing, testing, Martensitic Stainless Steels, material selection, Super 13Cr.

INTRODUCTION

To address the global issue of greenhouse gas emissions, namely CO₂ emissions and climate change, Carbon Capture and Storage (CCS) is considered a crucial tool.^{1,2} Multiple countries are implementing policy incentives to advance CO₂ capture from industrial sources and its long-term storage, primarily through supercritical CO₂ injection into deep saline formations.^{3,4}

The geological storage of supercritical CO₂ can have a significant impact on the integrity of downhole materials, particularly under conditions where liquid water is present during well shut-in periods or

generated through condensation. The first-barrier tubulars, being in continuous exposure to the aggressive environment formed by the interaction between the injected CO₂ stream and in-situ formation brine, are especially vulnerable. This exposure may accelerate corrosion and environmentally assisted cracking, thereby posing a critical risk to long-term wellbore integrity.^{5,6}

The oil and gas industry has developed extensive expertise in materials selection and qualifications for wells exposed to CO₂, with this knowledge stated in various standards and guidelines.^{7,8} Despite these advances, the operating conditions of CCS injection wells may differ from those encountered in conventional oil and gas production. A key distinction is the elevated CO₂ pressures expected in CCS applications, which result in higher dissolved CO₂ concentrations and associated reduction in the pH of formation or condensed water. Such conditions render carbon and low-alloy steels unsuitable for water-wetted tubulars, given their pronounced susceptibility to CO₂-induced (sweet) corrosion.^{9–12}

Furthermore, the composition of the CO₂ stream will inherently include impurities, the type and concentration of which depend on both the emission source and the capture technology employed. While some contaminants are familiar from oil and gas operations such as H₂S in production or injection wells or O₂ in water injection systems, CCS introduces the likelihood of additional species which are not typically encountered in hydrocarbon production. In particular, NO_x and SO_x are expected in varying amounts and their interaction within the storage environment can promote the in-situ formation of strong mineral acids such as sulfuric and nitric acids.^{13–15} Such conditions may generate chemical environments that diverge significantly from those associated with conventional oil and gas wells, with implications for corrosion and long-term material integrity.

The evaluation of materials suitable for CCS injection wells is inherently complex due to the anticipated long-term exposure conditions, the absence of standardized testing protocols, and the variability of impurities within the injected CO₂ stream. These impurities can significantly alter the chemistry of the environment, broadening the range of corrosive species that must be considered relative to those typically encountered in oil and gas production systems. To address these challenges, the Association for Materials Protection and Performance (AMPP) has recently developed a dedicated guideline aimed at providing a framework for material selection and qualification in CCS applications.¹⁶

Corrosion resistant alloys (CRAs) are being considered as downhole materials for CCS wells due to the high corrosivity of CO₂ saturated brines at elevated pressures and temperatures, particularly in the presence of impurities such as O₂, H₂S, NO_x and SO_x.^{17–19} Although preliminary investigations have been conducted by several institutions and organizations, significant knowledge gaps remain, especially regarding the criteria for reliable material qualification under realistic CCS conditions. Recent studies have highlighted the complex influence of impurities and environmental conditions on the corrosion behavior of Super Martensitic Stainless Steels (S13Cr) alloys in CCS environments.²⁰ While S13Cr exhibits relatively low corrosion rates in CO₂ saturated water containing O₂, its performance further deteriorates in the presence of multiple impurities such as O₂ and SO₂ at high concentrations.²¹ Similarly, the presence of chloride ions can compromise the material's resistance to pitting and crevice corrosion, even under CO₂ rich conditions.²² Studies performed in the autoclaves simulating high-temperature and high-pressure environments further confirm that temperature, dissolved gases and ionic species collectively influence the corrosion behavior of 13Cr alloys.²³ These findings underscore the need for systematic evaluations of CRA corrosion behavior with and without impurity interactions and their concentrations.

The present study investigates the corrosion behavior of Super 13Cr in supercritical CO₂ environments by evaluating the effects of impurities under two injection scenarios: one based on the nominal composition of the CO₂ stream, and another representing elevated impurity concentrations due to interactions with the fluid phase, including solubility and corresponding dissociation reactions—referred to as the “as dissolved” condition. The impurities considered were O₂, H₂S, SO₂, and NO₂, each introduced at concentrations of 0, 20, 50, and 100 ppm-mol. Material performance under these conditions was assessed using Cyclic Potentiodynamic Polarization (CPP) curves and subsequent evaluation of the samples with SEM/EDS.

EXPERIMENTAL PROCEDURE

The material selected for testing was a martensitic stainless steel, Super 13Cr grade 95 PSL2 (S13Cr, 13-5-2 PSL2 API 5CRA, UNS S41426). Test samples were taken from seamless OCTG pipes. The chemical composition of the test material and its mechanical properties are listed in Table 1.

Table 1

(a) Chemical composition and (b) mechanical properties of test material of S13Cr (UNS S41426) 95 grade.

(a) Chemical Composition							
C	Si	Mn	Cr	Mo	Ni	N	Others
0.020	0.25	0.20	12.2	2.00	5.5	0.02	Ti

(b) Mechanical Properties				
YS (ksi)	YS (MPa)	UTS (ksi)	UTS (MPa)	EI (%)
100	689	119	819	26

Materials were machined into cylindrical specimens with 5 cm² exposed area (Figure 1a). Initially, the specimens were ground with #400 and #600 grit silicon carbide paper with water flow. They were rinsed with deionized (DI) water, sonicated in an isopropyl alcohol bath for 60 seconds, and dried with air. Prior to exposure, one side of each cylindrical specimen featuring a hole for electrical connection, was dip coated using a fluoropolymer coating for ~2 mm along the length (Figure 1b). The coated samples were let to cure at 70°C for 40 min and at 150°C for 1 hour. The specimens were preserved in a desiccator 24 hours prior to each test.

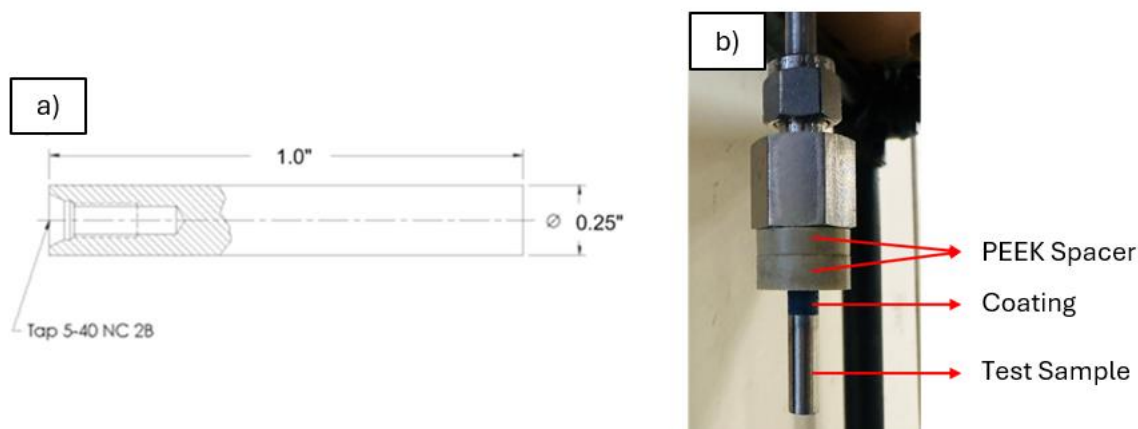


**Figure 1: (a) Geometrical design of the samples used for electrochemical test.
(b) Electrochemical test sample arrangement.**

Electrochemical corrosion tests were conducted in a high-pressure, high-temperature (HPHT) autoclave, following the test matrix outlined in Table 2. The experimental temperature was 125°C, the total pressure was 130 bar and the CO₂ partial pressure was 128 bar. The volumes of water and CO₂ phases were 5L and 2.5L, respectively. The composition of the brine was 5 wt.% NaCl. Corrosion tests consisted of cyclic potentiodynamic polarization (CPP) curves. A single test was performed for each condition. After the specimen reached a stable open circuit potential (OCP), approximately one hour, the CPP measurement was initiated. The polarization scan began at -100 mV versus OCP, progressing until a current density of 5 mA/cm² was reached, and then reversed at a scan rate of 0.166 mV/s. Electrochemical measurements were carried out using a three-electrode setup, consisting of a high-pressure high-temperature (HPHT) Ag/AgCl reference electrode, a platinum-coated niobium counter electrode, and a Super 13Cr working electrode, as shown in Figure 2.

Given that the autoclave is a closed system, the impurities injected into the CO₂ phase gradually dissolve into the brine, causing the impurity concentrations in the CO₂ phase to vary over time. To account for this dynamic behavior, corrosion tests in this study were designed using two distinct approaches for defining impurity concentrations:

a) The first approach, referred to as “**as-nominal**” in Table 2, where the concentration of each impurity to be injected into the autoclave was defined based on the specified nominal composition of the CO₂ stream, without considering potential chemical reactions among the contaminants or their dissolution into the aqueous phase following injection into the autoclave.

b) The second approach, referred to as “**as-dissolved**” in Table 2, where the impurity concentrations to be injected were calculated to reflect the target composition in the CO₂ dense phase after the interaction with the brine phase considering only the solubility reactions (including dissociation reactions for CO₂, H₂S, SO₂, NO₂) but not reactions between impurities. OLI Studio 12.0 (MSE-SRK model) was employed to calculate the total moles of each impurity to be additionally injected into the autoclave.

The injected impurities were H₂S, SO₂, O₂, and NO₂, each evaluated at three concentrations: 20, 50, and 100 ppm-mol. A reference condition without impurities was also included for comparison. Table 3 presents the calculated impurity concentrations to be injected into the autoclave for both approaches: as-nominal and as-dissolved.

Table 2
Test matrix for the electrochemical experiments (125°C, pCO₂ 128 bar, total pressure 130 bar).

Test ID.	Target Impurities Concentrations (ppm-mol)	Impurities Concentration Condition
A	20 ppm O ₂ + 20 ppm H ₂ S+ 20 ppm SO ₂ + 20 ppm NO ₂	As-dissolved
B		As-nominal
C	50 ppm O ₂ + 50 ppm H ₂ S+ 50 ppm SO ₂ + 50 ppm NO ₂	As-dissolved
D	100 ppm O ₂ + 100 ppm H ₂ S+ 100 ppm SO ₂ + 100 ppm NO ₂	As-dissolved
E		As-nominal
F	No impurities	Not Applicable

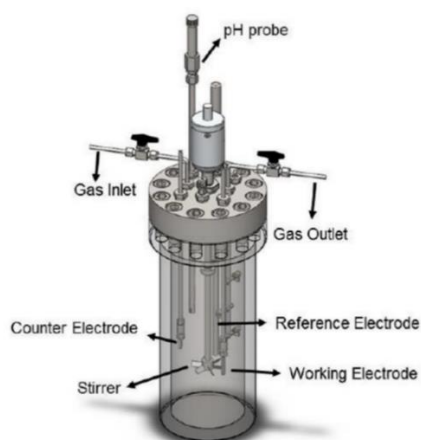


Figure 2: Schematic of the working autoclave for electrochemical test (125°C, pCO₂ 128 bar, total pressure 130 bar).

Table 3

Injected impurities' concentrations. As-nominal stream conditions and as-dissolved conditions in the CO₂ phase calculated by OLI Studio 12.0.

Test ID	Target Impurity Concentrations (ppm-mol) and Condition		SO ₂ (mol)	NO ₂ (mol)	H ₂ S (mol)	O ₂ (mol)
A	20	As-dissolved	0.00349	0.00153	0.00062	0.00027
B		As-nominal	0.00025	0.00025	0.00025	0.00025
C	50	As-dissolved	0.00630	0.00312	0.00139	0.00068
D	100	As-dissolved	0.01365	0.00765	0.00312	0.00136
E		As-nominal	0.00128	0.00128	0.00128	0.00128
F	0	N/A	0	0	0	0

The tests were conducted in a high-pressure system consisting of a 7.5 L Hastelloy autoclave, an impurity injection system and a high-pressure CO₂ booster pump as shown in Figure 3.

The injection methodology is as follows. Once the 5 L of test solution containing 52 g/l NaCl was prepared and poured into the autoclave, the solution was purged with ultra-high purity CO₂ for 1-3 hours in order to minimize dissolved oxygen content. Subsequently, the test sample was placed in the autoclave while purging with CO₂ to avoid air ingress. After closing the autoclave, additional CO₂ purging was performed for ~2 hours to ensure the saturation with CO₂ and further deaeration before the injection of impurities. The impurities were then added from technical grade (ultra-high purity) CO₂/SO₂, CO₂/NO₂, CO₂/H₂S or CO₂/O₂ cylinders with a custom-built gas injection system as shown in Figure 2b. Impurities were injected one by one into the autoclave in the following order: H₂S, SO₂, O₂ and NO₂. NO₂ was the last injected contaminant based on their reactivity.

The moles of gases required for each test as calculated in Table 3 were obtained by first injecting the gas into the syringe pump of known volume at ambient temperature and pressure. The moles of each impurity was then calculated from the Peng-Robinson equation of state. The gas was then pushed into the autoclave using CO₂. For effective injection, removal of remnant impurity gas in the syringe pump and the gas lines, the injection lines are flushed with additional CO₂ between each impurity injection.

After high pressure CO₂ sourced from ultra-high purity bottle was introduced into the autoclave using a gas booster pump to achieve half of the working pressure (~60 bar) at room temperature and then the temperature was increased to 125°C. Once the testing temperature was reached, additional CO₂ was added to achieve the total pressure of 130 bar. The pH of the test electrolyte was simulated using OLI Studio. When determined, pH was measured with a ZrO₂ pH electrode.

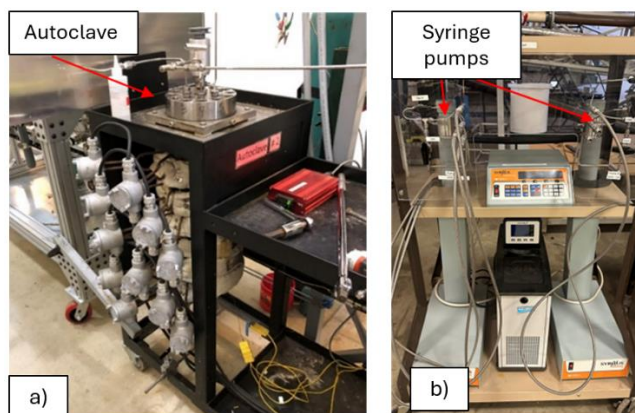


Figure 3: Photographs of the autoclave system used for corrosion testing: (a) autoclave, (b) impurity injection system.

After each experiment, the surface of the specimens was characterized using Scanning Electron Microscopy (SEM) to evaluate morphological changes, and Energy Dispersive X-ray Spectroscopy (EDS) to analyze the elemental composition of corrosion products. For selected conditions, pitting morphology and severity were further analyzed in accordance with ASTM G46.²⁴

RESULTS AND DISCUSSION

Effect of impurities in “as-dissolved” condition

The CPP curves of S13Cr for 0, 20, 50 and 100 ppm-mol in “as dissolved” condition for each impurity, are shown in Figure 4. The corresponding electrochemical parameters derived from the plots are summarized in Table 4, while Table 5 presents impurities concentrations in CO₂ phase and pH calculated using OLI Studio for these tests.

In a pure CO₂ environment, S13Cr exhibited spontaneous passivation, with a passive region extending approximately 200 mV above the open circuit potential (OCP). The passive current density was ~0.005 mA/cm², and the pitting potential was measured at -0.18 V_{Ag/AgCl}. A uniform corrosion rate of approximately 0.058 mm/year was estimated using Tafel extrapolation. Even under this impurity-free condition, S13Cr did not exhibit repassivation.

When impurities were added, the pitting potential was significantly reduced compared to the pure CO₂ condition. The cathodic branch shifted toward higher current density as impurities concentrations increased and consequently the passive region was diminished as can be seen for 20 and 50 ppm-mol in Figure 4. The passive region completely disappeared when 100 ppm-mol of each impurity was present.

In the presence of 20 ppm-mol impurities, the CPP curve showed a passive region extending ~100 mV above OCP, with a passive current density of ~0.005 mA/cm² and a pitting potential of -0.26 V_{Ag/AgCl}. The uniform corrosion rate, estimated using Tafel extrapolation, was ~0.058 mm/year, similar to the rate observed under pure CO₂ conditions. At 50 ppm-mol impurities concentration, S13Cr still exhibited passive behavior, although the passive current density increased to ~0.01 mA/cm² and the pitting potential shifted to -0.23 V_{Ag/AgCl}. Under these conditions, the uniform corrosion rate doubled to ~0.12 mm/year. In the presence of 100 ppm-mol impurities, S13Cr did not exhibit passive behavior and the current density rapidly increased from OCP, indicating localized corrosion attack initiated at OCP. Furthermore, the exposure to 100 ppm-mol impurities increased 10 times the corrosion rate (1.02 mm/year) when compared to 50 ppm-mol and 176 times when compared to the no impurity condition.

S13Cr did not exhibit repassivation in the as-dissolved conditions for 20, 50 and 100 ppm-mol H₂S/SO₂/NO₂/O₂ impurity concentrations. CPP curves indicate that higher impurity concentrations reduce the stability of the passive layer and increase the trans-passive current density at a given potential. This behavior makes the material more susceptible to localized corrosion and leads to the loss of passivity.

Table 4
Electrochemical responses of S13Cr in as-dissolved condition.

Test ID.	Impurity Concentrations (ppm-mol) and Condition		Passive current Density (mA/cm ²)	Corrosion rate (mm/y)	OCP (V _{Ag/AgCl})	Ep Pitting potential (V _{Ag/AgCl})	Ep-OCP (V _{Ag/AgCl})
A	20	As-dissolved	~0.005	~0.058	-0.33	-0.26	0.07
C	50		~0.01	~0.12	-0.35	-0.23	0.12
D	100		-	~1.02	-0.27	~OCP	0
F	0	N/A	~0.005	~0.058	-0.4	-0.18	0.22

Table 5
Calculated Impurities concentrations in CO₂ phase and pH for the as-dissolved condition.

Test ID.	Impurity Concentrations (ppm-mol)	Calculated fraction in CO ₂ dense phase* (ppm-mol)					Brine Phase
		Mean	SO ₂	NO ₂	H ₂ S	O ₂	pH*
A	20	32	28	31	12	55	3.01
C	50	68	55	62	31	124	2.93
D	100	158	138	152	62	279	2.81
F	0	-	-	-	-	-	3.10

*Calculated by OLI 12.0 MSE-SRK model considering only dissolution reactions in the CO₂ phase

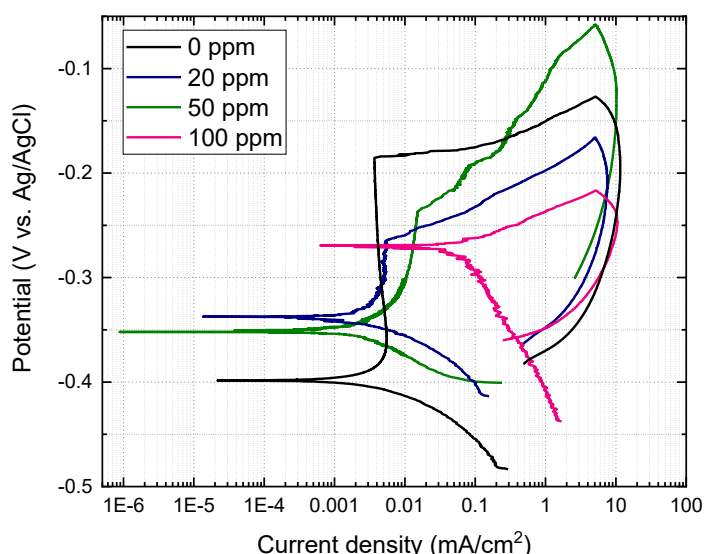
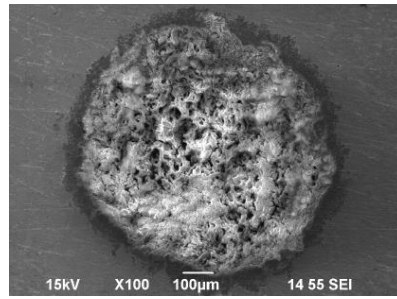
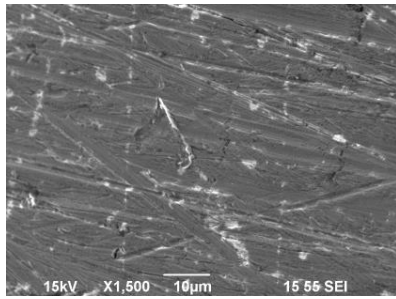


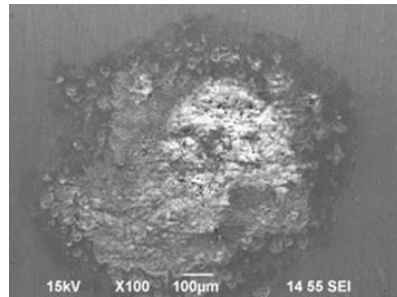
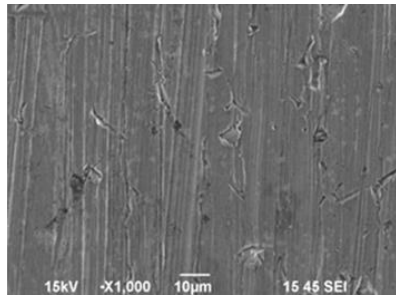
Figure 4: Cyclic potentiodynamic polarization curves for tests A, C, D with 20, 50, 100 ppm-mol impurity concentration in as dissolved condition and test F with 0 ppm-mol (pure CO₂).

After polarization in a pure CO₂, the surface morphology revealed a clean bulk surface, with the original polishing lines from sample preparation still visible. This indicates that no significant uniform corrosion occurred, and therefore, no noticeable corrosion products were formed (Figure 5a). The post-test surface of the sample tested at 20 ppm-mol impurity concentration exhibited a similar appearance to that observed under pure CO₂ conditions. As the impurity concentration increased, the general aspect of the surface changed: the polishing marks, which were clearly visible at 0 and 20 ppm-mol (Figure 5a and 5b respectively), began to fade, indicating the onset of more pronounced general corrosion (Figure 5c–e). For the samples tested at 50 and 100 ppm-mol, an increase in deposits rich in O and S were observed, consistent with the higher trans-passive currents recorded under these conditions.

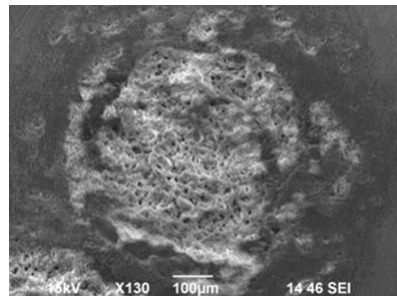
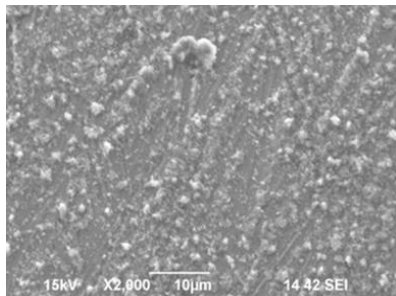
Specimens tested at 0, 20 and 50 ppm-mol exhibited isolated rounded pits as shown in Figure 5. The pit density was estimated to be 3×10^4 pits/m² for the 20 ppm-mol condition, which was not significantly different from the non-impurity condition. However, it increased to 4.2×10^4 pits/m² for the 50 ppm-mol condition and by an order of magnitude to 8.3×10^5 pits/m² for the 100 ppm-mol condition. The latter exhibited broader and asymmetrical morphologies and greater depths (up to 220 μ m), attributed to the coalescence of multiple smaller pits (Figure 5e). In all cases, corrosion products within pits were enriched in O, S, C, and Cr. Corrosion products formed under the 100 ppm-mol condition presented a significantly higher enrichment in S.



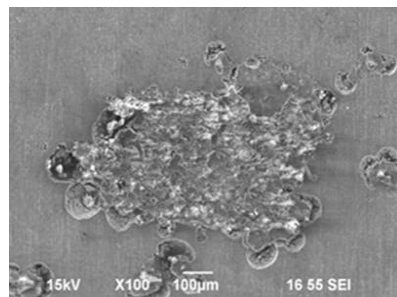
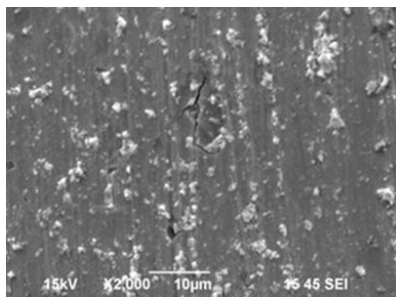
(a) Pure CO₂



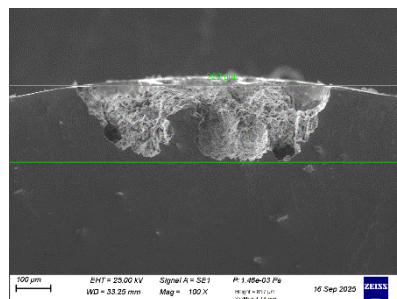
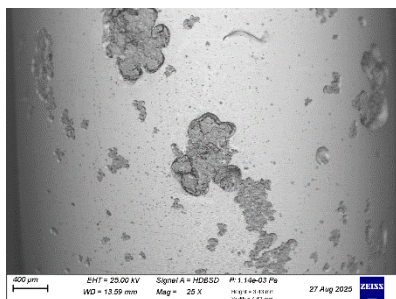
(b) 20 ppm-mol



(c) 50 ppm-mol



(d) 100 ppm-mol



(e) 100 ppm-mol

Figure 5: Surface characterization by SEM. General surface (left) and pit morphology (right). Specimens exposed to (a) 0, (b) 20, (c) 50 and (d) 100 ppm-mol in as-dissolved condition. Pit depth and density for 100 ppm as dissolved condition is included in (e).

Effect of impurities in “as-nominal” vs. “as-dissolved” condition

Figure 6 displays the CPP curves of S13Cr tested at an impurity concentration of 20 ppm-mol, comparing both the as-nominal and as-dissolved conditions. The corresponding electrochemical parameters determined from the plots are listed in Table 6.

S13Cr exhibited spontaneous passivation under both conditions, with comparable passive current densities and uniform corrosion rates. However, the passive region in the as-nominal condition extended over a wider potential range (in approximately 250 mV) relative to the as-dissolved condition, as shown in Table 6. This difference may be attributed to accelerated cathodic reactions under as-dissolved conditions, where increased impurity dissolution reduced the solution pH and generated more H^+ ions. Additionally, the pitting potential in the as-nominal condition was slightly higher than in the as-dissolved condition. Under both scenarios, S13Cr did not exhibit re-passivation.

As shown in Table 7, the calculated pH values after dissolution and dissociation are 3.10 and 3.01 for the 20 ppm-mol as-nominal and as-dissolved condition, respectively. The higher pH calculated for the latter was associated to the increased amount of SO_2 and NO_2 . The measured pH was 3.24 ± 0.10 (Table 6), showing no significant difference from the calculated value, which indicates the absence of strong acids formation such as H_2SO_4 or HNO_3 .

Table 6
Electrochemical responses of S13Cr for 20 and 100 ppm-mol in both conditions.

Test ID.	Impurities Concentrations (ppm-mol) and Condition		Passive current Density (mA/cm ²)	Corrosion rate (mm/y)	OCP (V _{Ag/AgCl})	Ep (V _{Ag/AgCl})	Ep-OCP (V _{Ag/AgCl})	pH*
A	20	As-dissolved	~0.005	~0.058	-0.33	-0.26	0.07	-
B		As-nominal	~0.006	~0.066	-0.45	-0.2	0.25	3.24
D	100	As-dissolved	-	~1.02	-0.27	~OCP	0	-
E		As-nominal	~0.007	~0.08	-0.38	-0.23	0.15	2.60

* pH measured with ZrO₂ probe. Standard deviation observed in pH measurement of ± 0.10 .

Table 7
Calculated Impurities concentrations in CO₂ and pH for 20 and 100 ppm in both conditions.

Test ID.	Impurity Concentrations (ppm-mol) and Condition		Calculated fraction in CO ₂ dense phase* (ppm-mol)					Brine Solution	
			Mean	SO ₂	NO ₂	H ₂ S	O ₂	pH*	pH**
B	20	As-nominal	10	2	5	11	22	3.10	-
A		As-dissolved	32	28	31	12	55	3.01	-
E	100	As-nominal	52	9	26	58	115	3.07	2.89
D		As-dissolved	158	138	152	62	279	2.81	2.31

*Calculated by OLI 12.0 MSE-SRK model considering only dissolution and dissociation reactions in the CO₂ phase
 ** Calculated by OLI 12.0 Aqueous frame considering REDOX reactions for S, O, N.

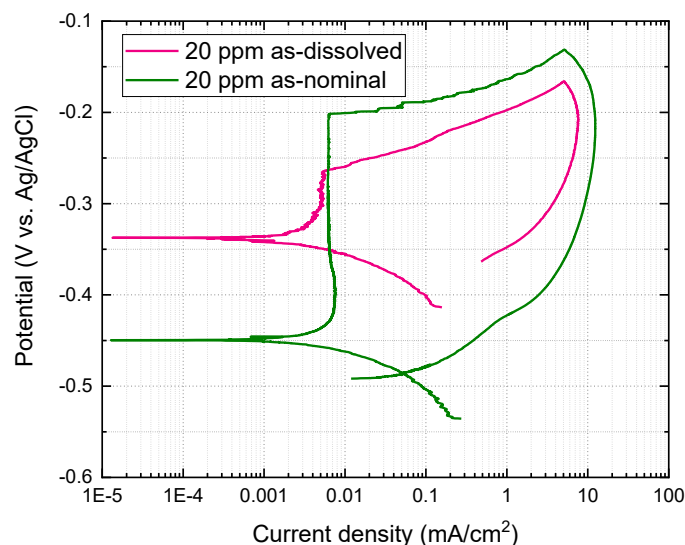


Figure 6: Cyclic potentiodynamic polarization curves for tests A, B: 20 ppm-mol impurities in as-nominal and as-dissolved condition.

Figure 7 shows the CPP curves of S13Cr tested at an impurity concentration of 100 ppm-mol under both as-nominal and as-dissolved conditions. As discussed in the previous section, under the as-dissolved condition, S13Cr did not exhibit passivity and the anodic current increased rapidly from the OCP, indicating an active corrosion behavior. In contrast, under the as-nominal condition, a passive region of approximately 150 mV was observed, with a passive current density of 0.007 mA/cm², a uniform corrosion rate of 0.08mm/y, and a pitting potential of -0.23 V_{Ag/AgCl} (see Table 6).

The pit density and depth of the 100 ppm-mol as-nominal condition was similar to that observed for the 0 and 20 ppm-mol as-dissolved and as-nominal conditions (Figure 8).

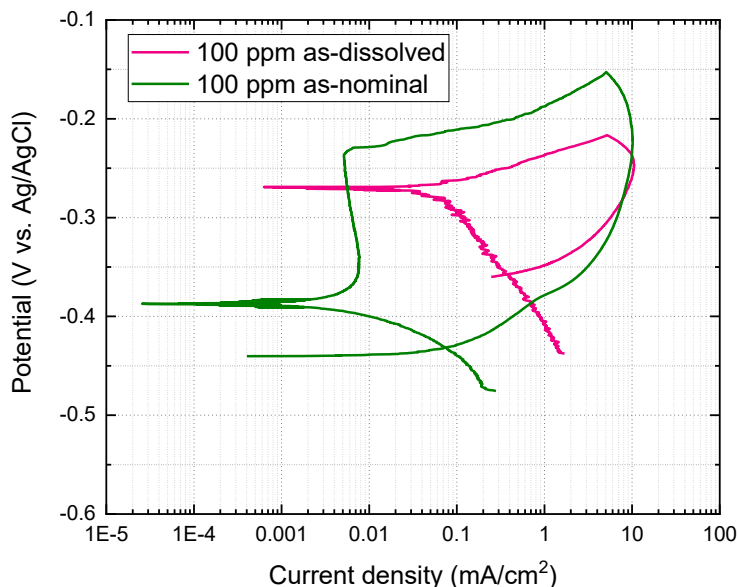


Figure 7: Cyclic potentiodynamic polarization curves for tests D, E: 100 ppm-mol impurities in as-nominal and as-dissolved stream concentrations.

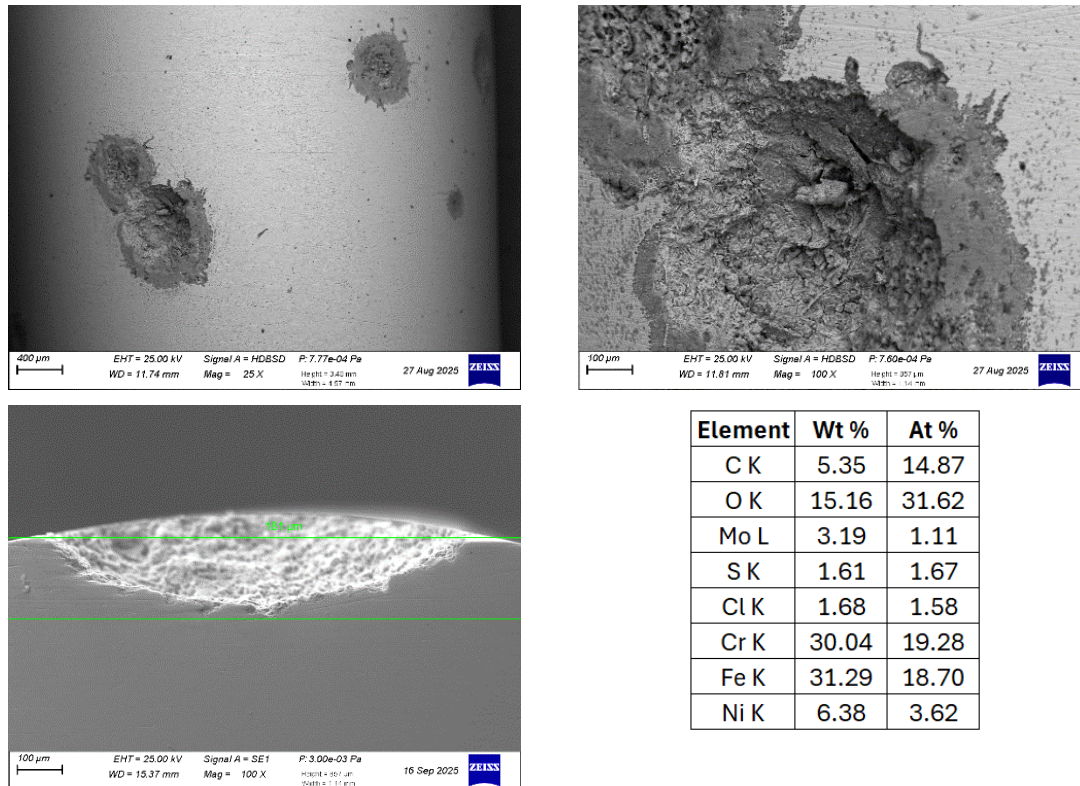


Figure 8: Pits analysis of S13Cr exposed to 100 ppm-mol in as-nominal condition.

Considering the trends in corrosion rate, passive current, pit density/depth and measured pH, the severity of the injection conditions upon introducing $\text{NO}_2/\text{SO}_2/\text{H}_2\text{S}/\text{O}_2$ increases with the mean calculated concentration in the CO_2 dense phase (Table 5 and 7) as indicated below:

No impurity~20 ppm as-nom~20 ppm as-diss. < 100 ppm as-nom. ~50 ppm as-diss.< 100 ppm as diss.

Transpassive corrosion behavior of S13Cr was observed when the $\text{pH} < 2.6$ and when the mean concentration of $\text{NO}_2/\text{SO}_2/\text{H}_2\text{S}/\text{O}_2$ was higher than 68 ppm-mol as-dissolved in the CO_2 phase at 125°C and 128 bar CO_2 .

The measured pH for the 100 ppm as-nominal condition (Table 6) was 2.60 ± 0.10 , which is considerably lower than the calculated value of pH 3.07 from dissolution and dissociation reactions. This discrepancy suggests the formation of strong acid, such as H_2SO_4 or HNO_x , in the supercritical phase (i.e., prior to dissolution in the water phase), which would be expected to cause a greater pH drop in the 100 ppm as dissolved condition. In order to explain the mismatch observed between the measured and calculated pH values for the 100 ppm-mol conditions, two explanatory approaches were considered:

a) Calculations were performed using OLI Studio 12.0 Aqueous Solution with REDOX reactions activated for S, N, and O. In these calculations, the formation of NaHCO_3 and Na_2SO_4 was identified in the brine solution. Meanwhile, NO_2 , SO_2 and O_2 were consumed in the supercritical CO_2 phase, whereas H_2S remained. The results are shown in Table 7.

b) Analytical calculations considered two reaction pathways leading to the formation H_2SO_4 or HNO_x ²⁵, under the assumption that O_2 and H_2S would be completely consumed in the supercritical phase. The formation of S_8 was not considered as it was not observed during the experiments. The results are shown in Table 8.

Although none of the chemical reactions considered in approaches a) and b) fully explained the pH drop observed for the 100 ppm-mol as nominal conditions, both are aligned with the experimental corrosion

active behavior of S13Cr below pH < 2.6 and in the presence of sulfate formation, and they can explain the transpassive transition observed in the CPP curve.

Table 8
Calculated pH based (analytical) for 100 ppm conditions.

Considered acidification reactions	pH for as-nominal	pH for as-dissolved
$H_2S + 3NO_2 \rightleftharpoons SO_2 + H_2O + 3NO$ $H_2S + \frac{3}{2}O_2 + H_2O \rightleftharpoons H_2SO_3$ $SO_2 + H_2O \rightleftharpoons H_2SO_3$ $NO_2 + H_2O \rightleftharpoons HNO_2$	2.95	2.62
$SO_2 + H_2O + 1/2O_2 \rightleftharpoons H_2SO_4$ $H_2S + 3NO_2 \rightleftharpoons SO_2 + H_2O + 3NO$ $SO_2 + H_2O + NO_2 \rightleftharpoons NO + H_2SO_4$ $SO_2 + H_2O \rightleftharpoons H_2SO_3$	3.10	2.28

CONCLUSIONS

Considering the trend in corrosion rate, passivity current, pit density/depth, and measured pH observed for S13Cr in the CO₂ phase at 125°C and 128 bar CO₂, the severity of the injection conditions upon introducing NO₂/SO₂/H₂S/O₂ increases with the mean calculated concentration in the supercritical CO₂ phase, according to:

No impurity~20 ppm-nom~20 ppm as-diss. <100 ppm-nom. ~50 ppm as-diss.<100 ppm as diss.

- Transpassive corrosion behavior of S13Cr was observed when the pH < 2.6 and when the mean concentration of NO₂/SO₂/H₂S/O₂ was higher than 68 ppm-mol “as-dissolved” in the supercritical phase.
- Under “as nominal” stream concentration, S13Cr exhibited typical passive behavior at 20 and 100 ppm-mol impurities. In contrast, under as-dissolved conditions at 100 ppm-mol impurities, S13Cr showed trans-passive behavior with severe pitting (up to 220-micron depth and pit density of 8.3 x10⁵/m²) and increment general corrosion rate (1 mm/yr) for which the expected pH would be 2.31.
- S13Cr showed no repassivation under either as-nominal or as-dissolved conditions for any level of impurity (0, 20, 50, 100 ppm-mol).
- Corrosion products identified in the pits were enriched in S and O, aligned with the formation of sulfate precipitates (result of H₂SO₄ formation) as calculated from possible chemical reactions.

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