Technical Report

Nippon Steel's Corrosion Resistant Alloy for CCS Application

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Abstract

This report summarizes the properties required for tubing materials for CO_2 injection to store CO_2 underground, which is essential for the realization of a carbon-neutral society and NZE 2050. When water is present in the CO_2 injection environment, the pH is lower than in oil and gas wells where conventional OCTG materials have been used. In such an environment, based on our OCTG material lineup, we have anticipated the expected demand for high-alloy OCTG of 13%Cr steel or higher in terms of depassivation pH. In addition, we have summarized the issues to be considered from a corrosion resistance point of view according to various impurity concentrations in CO_2 and presented data on the corrosion behavior of our representative steel grades. We expect that our lineup of CRA materials and the selection of the Fit-For-Purpose material will expand the range of applications to meet users' requirements for CO_2 injection pipe characteristics and cost optimization.

1. Introduction

The impact of human activities on global warming has been described as "unequivocal" in the sixth assessment report of the Intergovernmental Panel on Climate Change (IPCC).[1)] While natural phenomena also contribute to global warming, the uncontrolled use of fossil fuels associated with human activities is a major factor. It is believed that by changing the way we use fossil fuels, we can halt global warming. Therefore, there is a growing call for CO_2 emission reduction in various fields. According to the report of the International Energy Agency (IEA),[2)] 7.6 billion tons of CO_2 will have to be captured and storaged (CCS) worldwide to achieve the net zero energy (NZE) scenario by 2050.

It is considered efficient to use a hub-cluster system whereby CO_2, which is the target for reduction, is collected from various emission sources and injected into underground reservoirs. The emitted CO_2 undergoes separation and capture processes, such as chemical absorption using amine solutions, membrane separation, and solid absorption, to enhance its purity. The collected CO_2 is injected deep underground through nested casing and tubing pipes in a wellbore structure similar to oil and natural gas drilling. Additionally, a method called direct air capture (DAC), which directly captures CO_2 from the air and injects the captured CO_2, is also being considered. The captured CO_2 is being investigated for utilization as injection gas in enhanced oil recovery (EOR) or for injection into aquifers below the sealing layer called caprock or porous sandstone layers, by mineralization through carbonate formation, as shown in **Fig. 1**. Suitable geological formations are identified through underground exploration and then used for injecting CO_2. It should be noted that the CO_2 to be injected is commonly transported and injected at high pressure for transportation efficiency.

This report specifically discusses corrosion resistant OCTG materials used during CO_2 injection.

2. Characteristics of CO_2

The CO_2 to be injected has a molecular weight of 44.01 g/mol, exists in the air as a gas at room temperature and pressure, and is heavier than air. According to its phase diagram (**Fig. 2**), it reaches a critical point at 31.1°C and 7.4 MPa (corresponding to a well depth of about 800 m or more). It becomes supercritical in higher temperature and higher pressure environments. This supercritical state is the basic environment for CO_2 injection. The supercritical CO_2 fluid has a density of 0.5 to 0.8 g/cm^3, is lighter than water, and has a viscosity of 0.03 to 0.08 cp, which is close to that of gas and has high fluidity. At normal temperature and pressure, its solubility in water is

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0.033 mol/L, which is about 10 times more soluble than that of oxygen. As shown in Eqs. (1) and (2), CO_2 generates H^+, acidifies the formation water, and is considered to create a severely corrosive environment.

$$H_2CO_{3(aq)} \rightleftarrows H^+ + HCO_3^- \quad (1)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad (2)$$

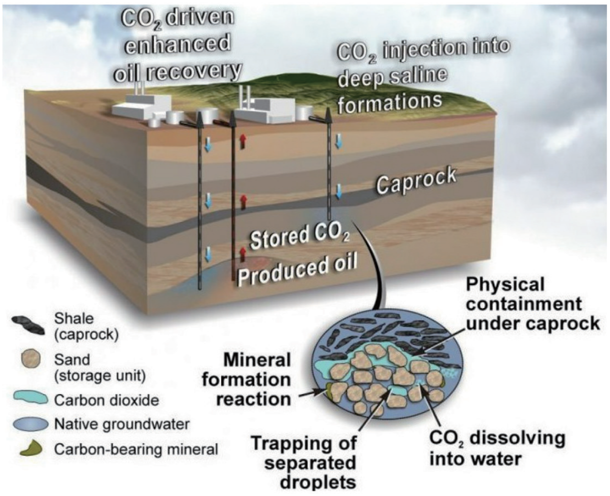

Fig. 1 Schematic image of CCS process

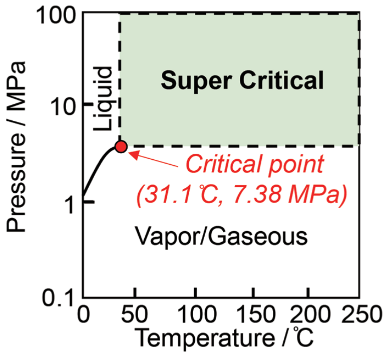

Fig. 2 Phase diagram of CO_2

3. Corrosion and Corrosion Resistant Materials in CO_2 Injection Environment

Currently, the materials used for CO_2 injection are expected to be used in wells with a depth of about 800 to 1 000 m and are required to have a mechanical strength of 80 ksi (560 MPa) and to withstand a severe environment. If there is no water in a completely dry CO_2 environment, there is no need to consider various corrosion phenomena, so carbon steel or low-alloy steel may be used. On the other hand, if we assume the case of wet gas or formation water flowback, corrosion phenomena such as CO_2 corrosion become an issue. Here, we will introduce materials for CO_2 injection in relation to the lineup of products that Nippon Steel Corporation has as OCTGs.

3.1 Lineup of high-alloy OCTGs suitable as CO_2 injection pipe materials

Nippon Steel manufactures seamless steel pipes made of a wide variety of materials, from carbon steel and low-alloy steel to martensitic stainless steel, duplex stainless steel, and Ni-based alloys. Until now, we have created a material selection chart according to CO_2 partial pressure, H_2S partial pressure, and well temperature (**Fig. 3**)[3)]. We have developed and provided optimal OCTG materials according to the chart. Carbon steel and low-alloy steel cannot avoid full-scale corrosion in environments with high CO_2 partial pressures. So, we have selected material grades that can be used in environments where the CO_2 partial pressure is 0.02 MPa or less.

However, the operating environment for CO_2 injection pipes is basically a high-pressure CO_2 environment where CO_2 becomes supercritical. Therefore, high-alloy OCTG materials such as 13%Cr martensitic stainless steel, duplex stainless steel, and Ni-based alloys are suitable materials.

3.2 Corrosion resistance of steels in supercritical CO_2 environment

The injected CO_2 is under high pressure, where it becomes a supercritical fluid. When the supercritical CO_2 comes into contact with water, it dissolves as carbonate ions (CO_3^{2-}) and forms a low-pH solution. When carbon steel or low alloy steel such as 5% Cr steel is used in such an environment, the corrosion rate (mm/year) becomes extremely high, and thinning corrosion is unavoidable (48-h immer-

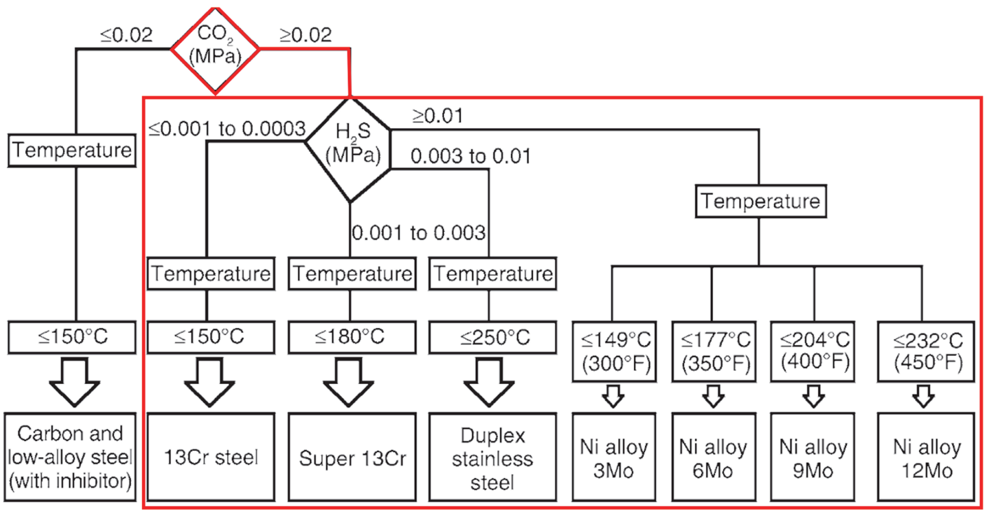

Fig. 3 A flow chart for the selection of OCTG Materials for H_2S and/or CO_2 service

sion test in a 43 kppm Cl^-, 8 MPa CO_2, 60°C environment[4]). In other words, stainless steel, such as 13% Cr steel, should be used in such an environment.

Stainless steel maintains its corrosion resistance by forming a passive film rich in chromium (Cr) on its surface, typically measuring 2 to 3 nm in thickness. An important factor in evaluating the integrity of the passive film is the depassivation pH (pH_d). If the pH of the environment is lower than the depassivation pH of a material, it indicates that the passivation film on that material may not be adequately formed. To enhance the CO_2 injection efficiency, CO_2 will predominantly be injected into an environment with a higher CO_2 pressure ranging from 10 to 30 MPa compared to the test environment mentioned earlier. With increasing CO_2 pressure, the amount of dissolved CO_2 in the environment is expected to rise, resulting in a lower pH. Consequently, materials with a lower depassivation pH are preferred to mitigate general corrosion risks. **Table 1** provides information on depassivation pH values for various stainless steels. Mo-alloyed Super13Cr steel (S41426), which is believed to have a more robust passive film compared to the API-13CR steel, duplex stainless steel with high Cr content, and Ni-based alloys are considered suitable as OCTG materials for injecting high-pressure CO_2.

Table 1 Depassivation pH of stainless steels

Grade	UNS No.	Tested environment	pH_d Value	Ref
SUS420J1 (API-13CR)	S42000	3%NaCl, 25°C 0.1 MPa CO_2	3.0–3.1	5)
SM13CRS	S41426	10%NaCl, 50°C 0.1 MPa N_2	2.81	6)
SUS316L (Austenite)	S31603	20%NaCl, 25°C 0.1 MPa Ar	2.0–2.1	7)
22CR (Duplex)	S31803	20%NaCl, 25°C 0.1 MPa CO_2	1.5–1.6	7)
SM25CR (Duplex)	S39274	5%NaCl, 200°C 0.1 MPa N_2	<2.0	8)
Alloy 625 (Ni alloy)	N06625	20%NaCl, 25°C 0.1 MPa Ar	<1.0	9)

In addition, the pH range that maintains the passive film is organized by the pitting resistance equivalent number (PREN) (%Cr+3.3 (%Mo+0.5%W)+16%N) (5%NaCl, 30°C, in Ar).[10]

Nippon Steel's lineup of high-alloy OCTG materials (**Table 2**) has a wide range of PREN values. It is necessary to select a material grade with an appropriate PREN depending on the pH of the CO_2 injection environment.

3.3 Corrosion phenomena under CO_2 containing impurities

The injected gas in CCS originates from exhaust gas from various industries and, in most cases, contains impurity gases. For example, when fossil fuels are used, such as in coal-fired power plants, the CO_2 emitted from power plants contains oxygen (O_2), carbon monoxide (CO), sulfur oxides (SOx), and nitrogen oxides (NOx). The CO_2 emitted from cement plants contains large amounts of O_2 and SOx, and the CO_2 emitted from steel plants contains large amounts of CO. Additionally, the gas from which hydrocarbons are removed during natural gas refining contains H_2S. The concentration of various impurity gases is reduced to a certain level during the purification stage, but the concentration of impurities in the injected CO_2 varies depending on the emission source concentrations and operating conditions (**Table 3**).[11–17]

Table 4 summarizes the main gas types that affect corrosion phenomena due to the inclusion of these impurity gases.

In the following sections, we mainly discuss corrosion from the mixture of various gases in the CO_2 injection environment.

3.3.1 Effect of O_2

O_2 is well known to induce local corrosion. For example, in the

Table 2 Chemical composition range and PREN value of Nippon Steel's CRA OCTG materials

Category	Grade	UNS No.	Chemical composition range (mass%, Fe balance)									PREN
			C	Si	Mn	Cu	Ni	Cr	Mo	W	N	
MSS	API 13Cr	S42000	0.15–0.30	≤1.00	0.25–1.00	≤0.25	≤0.50	12.0–14.0	–	–	–	12–15
SMSS	SM13CRS	S41426	≤0.03	≤0.50	≤0.50	–	5.0–6.5	11.5–13.5	1.5–3.0	–	–	16–22
DSS	SM25CRU	S82551	≤0.03	≤0.80	≤7.50	2.0–3.0	4.5–6.5	24.5–26.5	0.75–2.0	–	0.1–0.35	31–35
DSS	SM22CR	S31803	≤0.03	≤1.00	≤2.00	–	4.5–6.5	21.0–23.0	2.5–3.5	–	0.08–0.20	31–38
SDSS	SM25CRW	S39274	≤0.03	≤0.80	≤1.00	0.2–0.8	6.0–8.0	24.0–26.0	2.5–3.5	1.5–2.5	0.24–0.32	40–45
Ni alloy	SM2535	N08535	≤0.03	≤0.50	≤1.00	≤1.50	29.5–36.5	24.0–27.0	2.5–4.0	–	–	36–42
Ni alloy	SM2550	N06255	≤0.03	≤1.00	≤1.00	≤1.20	47.0–54.0	23.0–26.0	6.0–9.0	≤3.0	–	43–49

Table 3 CO_2 specifications recommended by each project[11)]

Project Name	Northern Lights[12)]	Sleipner[13)]	Dynamis[14)]	Porthos[15)]	Weyburn[14, 16)]	Carbon Net[17)]
Location	Norway	Norway	Europe	Netherlands	USA & Canada	Australia
H_2O, ppm	≤30	Saturated	500	≤70	20	≤100
H_2S, ppm	≤9	–150	200	≤5	9000	≤200
CO, ppm	≤10	Nil	2000	≤750	1000	900–5000
O_2, ppm	≤10	Nil	≤40000	≤40	70	20000–50000
NOx, ppm	≤10	Nil	100	≤5	Not specified	250–2500
SOx, ppm	≤10	Nil	100	≤20	Not specified	200–2000

Table 4 Main gas species contained in injected CO_2 and corrosion effects

Component	Corrosion effects
CO_2	• Balance Gas pH drop out
O_2	• Oxidant: risk of localized corrosion • Elemental Sulfur (S_0) produced by reaction with H_2S → risk of localized corrosion
SO_2	• Sulfuric acid (H_2SO_4) produced → pH drop out
NO_2	• Possibility of producing Nitric acid (HNO_3) → pH drop out • Oxidant: risk of localized corrosion
H_2S	• Risk of Hydrogen Embrittlement because H_2S acts as a poison in Hydrogen penetration

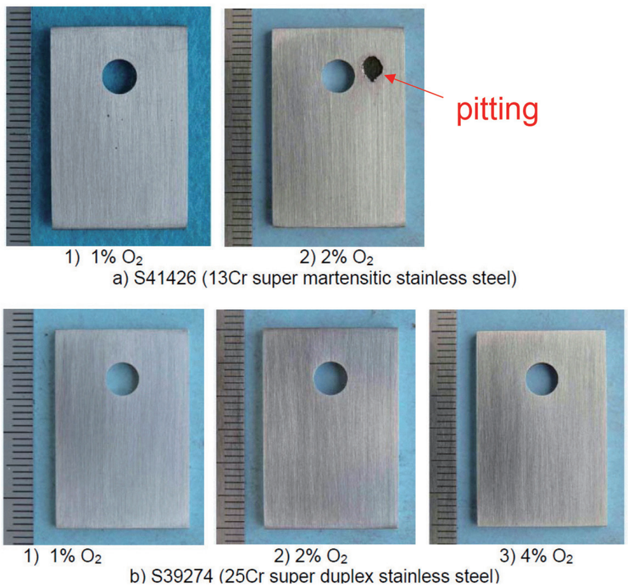

Fig. 4 The appearances of descaled specimens after the testing in the conditions with O_2 (Total 13 MPa-CO_2 balanced, 100°C, 5 wt% NaCl, 96 hours)

actual use of OCTGs, pitting corrosion and crevice corrosion occurred in the 13%Cr martensitic stainless steel used to inject seawater for EOR in the Gulfaks oil field in the North Sea. The cause was reported to be the insufficient deaeration of the injected seawater.[18)]

In a 5% NaCl environment in equilibrium with supercritical CO_2, the super martensitic stainless steel SM13CRS (S41426) was pitted in a 2% O_2 environment. On the other hand, the super duplex stainless steel SM25CRW (S39274) was not pitted even in a 4% O_2 environment. These results demonstrated the stability of a material with high PREN (**Fig. 4**).[19)]

For these reasons, a steel with higher corrosion resistance than that of the Super 13Cr steel is recommended for use in a CO_2 injection environment containing a certain amount of oxygen.

3.3.2 Effect of SO_2

SO_2 dissolves in water, forms sulfuric acid, and lowers the pH of the environment through the following reactions:[20)]

$$SO_{2(aq)} + H_2O_{(l)} \rightleftarrows H_2SO_{3(aq)} \quad (3)$$
$$H_2SO_{3(aq)} \rightleftarrows H^+ + HSO_3^- \quad (4)$$
$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \quad (5)$$

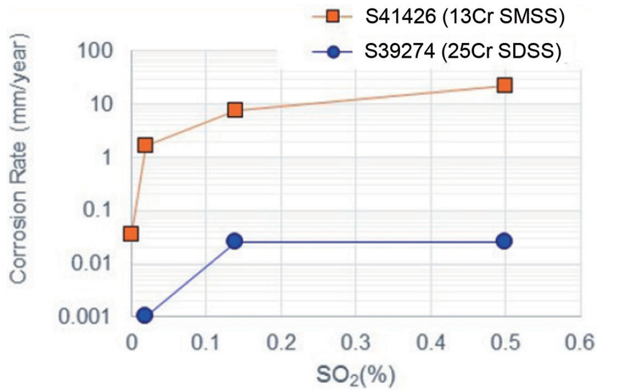

Fig. 5 Corrosion rate and SO_2 ratio (Total 13 MPa-CO_2 balanced, 100 °C, 5 wt% NaCl, 96 hours)

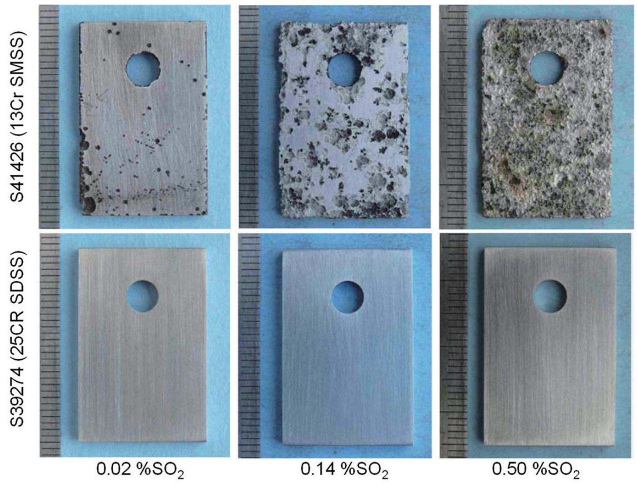

Fig. 6 The appearances of descaled specimens after the testing in the conditions with SO_2

The pH of the CO_2 injection environment is reduced to pH2.6 when SO_2 is contained in a mere 0.02% (200 ppm = 0.0026 MPa at 13 MPa total pressure). In such an environment, SM13CRS is severely corroded (**Figs. 5** and **6**).[19)] In the case of 0.5% (5 000 ppm), the pH is about 1.9 and approaches the depassivation pH of steels such as 316L. Even in this environment, the duplex stainless steel S39274 (SM25CRW) with PREN≥40 exhibits excellent corrosion resistance. High-alloy steels are recommended for use in the CO_2 injection environment.

3.3.3 Effect of NO_2

When NO_2 dissolves in water, it is considered to produce HNO_3 and lower the pH of the environment, but it is hardly soluble in water. However, it is a strong oxidizing acid and may increase the susceptibility to local corrosion. Furthermore, when it coexists with SO_2, it acts as a catalyst to oxidize SO_2 and promote the formation of H_2SO_4, as shown in Eqs. (6) and (7).[21)]

$$NO_2 + SO_2 \rightleftarrows NO + SO_3 \quad (6)$$
$$SO_3 + H_2O \rightleftarrows H_2SO_4 \quad (7)$$

Since such strong oxidizing agents promote many reactions, the removal of as much NO_2 as possible is thought to increase the allowable concentrations of other impurities.[22)]

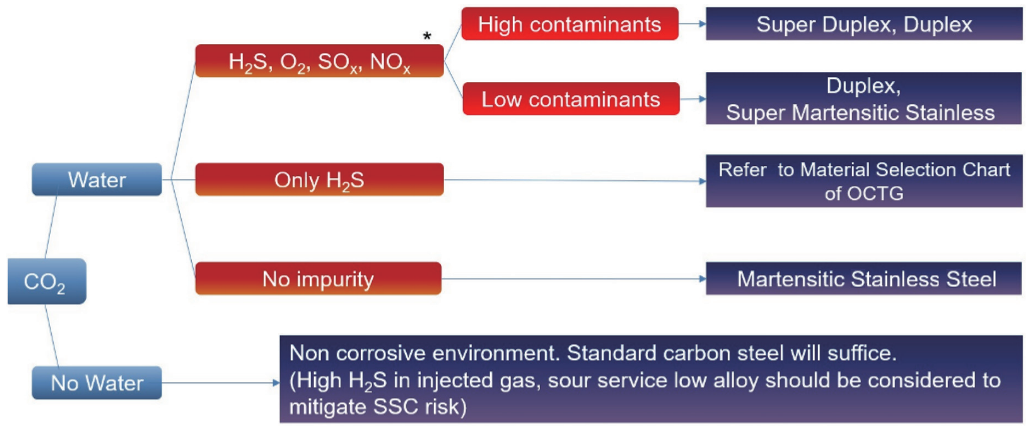

Fig. 7 Material selection concept for CO_2 injection materals

3.3.4 Effect of H_2S

The effect of hydrogen sulfide (H_2S) are well known in the oil and gas industry, the materials to be used in H_2S environments must be selected by considering sulfide stress cracking (SSC) at normal temperatures and stress corrosion cracking (SCC) at elevated temperatures. These environments require the selection of materials according to the databases and flowcharts that Nippon Steel has accumulated over the years. However, the CO_2 injection environment is characterized by a lower pH than the conventionally evaluated environments for the reasons mentioned in the previous section. More evaluation data on the CO_2 injection environment is required. Future data accumulation is essential.

3.3.5 Effect of H_2O

The previous sections have assumed the presence of condensed water or flowback water. It is also possible to assume completely dry environmental conditions where no water exists in a depleted well or above a safety valve. In such cases, carbon steel and low alloy steel may be used. In a high-pressure CO_2 environment, a certain amount of water is observed to dissolve into supercritical CO_2.[23] It is necessary to consider the possibility that this dissolved water may cause corrosion phenomena. The solubility of water in the CO_2 gas phase or supercritical phase depends on pressure and temperature.[24] Depending on the changes in operating conditions, an amount of water below the solubility level may condense, especially when the pressure and temperature decrease. The dissolution of the injected CO_2 gas promotes corrosion.

The corrosion phenomena in such an environment observed through a window installed in a small pressure vessel are reported.[24] In-situ observation found the gradual progress of carbon steel corrosion in the presence of a certain amount of moisture in a 10 MPa CO_2 and 25°C environment containing 75 ppmv of NO_2. Duplex stainless steel exhibited no signs of corrosion in the same environment.

4. Issues with CO_2 Injection OCTGs

It is reported that full-scale CCS projects will start in respective countries around 2030. Procurement of the various materials and equipment needed has already begun. On the other hand, since the CCS business depends on tax incentives such as carbon pricing, stainless steel pipes are required to be as inexpensive as possible.

From these points of view, it is preferable to use stainless steel pipes, which are economically rational, have a low alloying content and are easy to manufacture. However, as mentioned in the previous section, steels with a higher alloy content than the 13% Cr steel are required. Specifically, steels that take the following corrosion factors into account are required:

- Passivates in low pH ($<$3.0) environments
- Local corrosion resistance in oxidizing environments such as O_2 and NO_2
- Environmental embrittlement cracking resistance in environments containing H_2S

In other words, it is necessary to find the right materials with the right corrosion resistance to suit the environment of each project. Nippon Steel recommends materials according to the flowchart shown in **Fig. 7**. The flowchart has been developed based on the vast amount of data accumulated on the applicability of materials to oil and gas well environments. In the CCS environment, as in the case of oil and gas wells, it is essential to expand and accumulate more detailed corrosion test data. Nippon Steel's high-alloy OCTGs are adopted in the Northern Lights project, which is starting up as a large-scale CCS project.[25] While closely monitoring these operating conditions, we will promote our research and development to improve the accuracy of the flowchart (Fig. 7)[26] for selecting the right material in the right place in a CO_2 injection environment.

5. Conclusions

We have summarized the corrosion resistance requirements for steel pipes used in CO_2 injection, which is essential for storing CO_2 underground to achieve a carbon neutral society and NZE2050.

When water is present in the CO_2 injection environment, the pH becomes lower than that of oil and gas wells that have used conventional OCTGs. Based on Nippon Steel's OCTG lineup, it is shown that the demand for OCTGs with higher alloy contents than the 13%Cr steel is expected.

In addition, we have organized the considerations from a corrosion resistance perspective based on various impurity concentrations in CO_2. We have also discussed the corrosion resistance in high-pressure CO_2 environments. The lineup of Nippon Steel's CRA OCTGs and appropriate selection of material grade are expected to lead to expand the adaptability of CO_2 injection pipes to user requirements and cost optimization. Moving forward, we will continue to promote research and development towards creating OCTG materials that contribute to achieving a carbon-neutral society through systematic research and development.[27–29]

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