

GHGT-11

## Corrosion Studies on Casing Steel in CO<sub>2</sub> Storage Environments

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### Abstract

The corrosion behavior of casing steel N80 in brine plus CO<sub>2</sub> was studied in autoclave to simulate the CO<sub>2</sub> storage environment. The brine solution used in the study contained 130 g/l NaCl, 22.2 g/l CaCl<sub>2</sub> and 4 g/l MgCl<sub>2</sub>. The CO<sub>2</sub> was charged in the autoclave at different pressures (60, 80 and 100 bar) and at 45°C. The corrosion rate was measured using electrochemical and mass loss measurements. The surface of the samples after exposure to CO<sub>2</sub> and brine was analyzed using SEM, EDS and XRD. The polarization results show that the corrosion rate of N80 steel in the brine plus CO<sub>2</sub> is 6 mm/y in 1 hour and 0.3 mm/y after one week at 80 bar and 45°C. The corrosion of the steel at other pressures shows a similar behaviour. The mass loss measurements show the average corrosion rate 0.06 mm/y after immersion for 32 days. The decrease of the corrosion rate for N80 steel in this environment is attributed to the formation of dolomite layer on the sample surface.

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*Keywords: carbon dioxide; casing steel; corrosion; polarization; well integrity*

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### 1. Introduction

One of the measures to relieve the CO<sub>2</sub> emission impact on the environment is to inject carbon dioxide captured from emission plants into geological formations, either saline aquifers or depleted gas or oil reservoirs, for long-term storage [1, 2]. However, CO<sub>2</sub> in combination with water creates an acidic environment that causes corrosion of casing steel, and potentially affects the integrity of the CO<sub>2</sub> storage system. It has been reported that corrosion and operation problems happened in one CO<sub>2</sub> project in Sacro

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Unit [3]. One leak in the distribution system occurred once as a result of hydro-test water remaining in a low spot in line and opening the lateral to CO<sub>2</sub> pressure.

The corrosion rate of casing steel depends on the pressure, temperature, the presence and quality of well cement, salts and chemicals in the brine, pH etc. [4-7]. So far limited data are available for casing steel corrosion in CO<sub>2</sub> storage. Obtaining experimental data on the corrosion of casing steel in the CO<sub>2</sub> storage environment will support risk management of CO<sub>2</sub> storage.

Within the Dutch national research project on CCS, CATO-2, the corrosion of casing steel API N80 in CO<sub>2</sub>-saturated brine has been studied, using formation water composition typical for North Sea reservoirs. The aim of this study is to investigate the corrosion behaviour of the casing steel under realistic CO<sub>2</sub> storage conditions. Furthermore, this knowledge will help corrosion monitoring methodologies of the casing steel[8].

### Nomenclature

CCS	carbon dioxide capture and storage
API	American Petroleum Institute
SEM	scanning electronic microscopy
EDS	extensive expensive spectroscopy
XRD	X-ray diffraction

## 2. Experimental

### 2.1. Materials

The samples were cut from N80 steel tubes. The nominal composition of the N80 steel is presented in Table 1. To make an electrical connection it was necessary to weld a thread to the sample as the working electrode. The samples were embedded in epoxy coating and left one surface to be exposed to the electrolyte. After mechanical grinding (until 4000 grid SiC paper), samples were cleaned in ultrasonic ethanol before being transferred to an autoclave. The exposure area is about 2.8 cm<sup>2</sup>.

Table 1. Nominal composition of the steel (wt. %)

Element	C	Mn	Si	S	P	Cr	Mo	Ni	Al	Fe
N80	0.29	1.48	0.34	0.014	0.012	0.24	0.09	0.08	0.04	rest

### 2.2. Electrochemical measurements

The brine solution used in the study contained 130 g/l NaCl, 22.2 g/l CaCl<sub>2</sub> and 4 g/l MgCl<sub>2</sub>. The CO<sub>2</sub> was charged in the brine in the autoclave at different pressures (60, 80 and 100 bar) and at 45°C. The solution was stirred with a stirrer in a rotation speed of 600/min to make the solution homogeneous.

The electrochemical measurements were performed using three electrode cells, the steel as the working electrode, a KCl saturated Ag/AgCl electrode as the reference electrode and a platinum mesh as the counter electrode. The corrosion properties were studied using open circuit potential (OCP), linear or potentiodynamic polarization measurements. The linear polarization was performed by scanning the

potential from -20 mV vs. OCP to + 20 mV vs. OCP. The potentiodynamic measurements were performed by scanning the potential from -250 mV vs. OCP to +250 mV vs. OCP. The corrosion current density and the corrosion rate were calculated from the Tafel slopes on the polarization curves.

### 2.3. Mass loss measurements

The steel samples were cleaned and weighed before exposure to the brine and CO<sub>2</sub>. After immersion for 32 days, the samples were removed from the autoclave, rinsed immediately with running tap water to remove salts. Then the samples were chemically cleaned for 10 min. at 20°C in a fresh solution prepared as follows: mixing 1000 ml of hydrochloric acid (sp gr 1.19) with 1000 ml deionized water and adding 10 g of hexamethylenetetramine. After cleaning, the samples were rinsed in deionized water and dried in flow air. The mass loss was determined by reweighing and subtracting the sample mass after exposure from its original mass.

### 2.4. Surface analysis

After immersion test in the autoclave, the surface of the specimens and corrosion products deposited on the specimens were analysed using SEM and EDS. The components of corrosion products were analysed by XRD using Co  $\alpha$  radiation.

The methods and conditions are summarized in Table 2.

Table 2. Methods and conditions

Solution	Brine + CO <sub>2</sub> 60, 80, 100 bar; 45 °C	Brine + CO <sub>2</sub> 80 bar; 45 °C
Polarization	√	√
Mass loss test		√
SEM, XRD		√

## 3. Results

### 3.1. Polarization measurements

Fig. 1 shows a typical polarization curve for the N80 steel in brine plus CO<sub>2</sub> at 80 bar and 45°C after exposure for 2 hours. Corrosion current density  $i_{\text{corr}}$  is calculated from the curves using the Tafel slope method, using following equation[9, 10],

$$i_{\text{corr}} = b_a \times b_c / (2.3R_p(b_a + b_c)) = k/R_p \quad (1)$$

where  $b_a$  and  $b_c$  are anodic and cathodic slopes, respectively, on the curve;  $R_p$  is the polarization resistance and  $k$  is the proportional constant. In this case, the value of  $b_c$  is larger than  $b_a$ , indicating that the corrosion is a cathodic control process. The average  $k$  value is 25 mV.

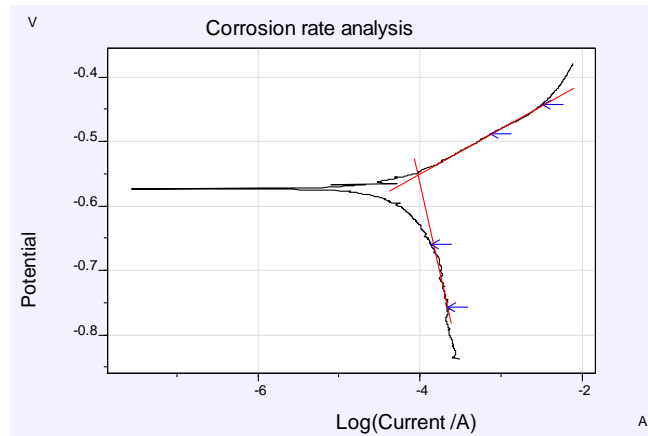


Fig. 1. Polarization curve for the N80 steel in brine plus  $\text{CO}_2$  at 80 bar and  $45^\circ\text{C}$  after exposure for 2 hours.

Fig. 2 shows the open circuit potential as a function of time for N80 steel in the brine plus  $\text{CO}_2$  at 80 bar and  $45^\circ\text{C}$ . The increase of potential with time (from  $-0.6 \text{ V}_{\text{Ag}/\text{AgCl}}$  at the beginning to  $-0.18 \text{ V}_{\text{Ag}/\text{AgCl}}$  at day 5) suggests that the surface is active at the beginning and then is polarized or covered with corrosion products.

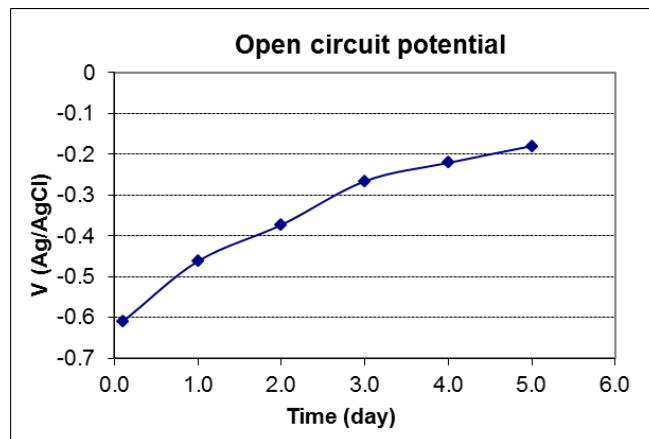


Fig. 2. OCP values as a function of time for N80 steel in the brine plus  $\text{CO}_2$  at 80 bar and  $45^\circ\text{C}$ .

Fig. 3 shows the corrosion rates calculated from the polarization curves. The corrosion rate is as high as 6 mm/y at the beginning and decreases to 0.3 mm/y after one week for N80 steel in the solution at 80 bar and  $45^\circ\text{C}$ . The corrosion rate at all three pressures decreases with time. The corrosion rate at 100 bar

decreases a little bit slowly that at 60 and 80 bar within 4 days. After 4 days the corrosion rate at 100 bar is lower than at 60 bar, which is in agreement with the reference [4].

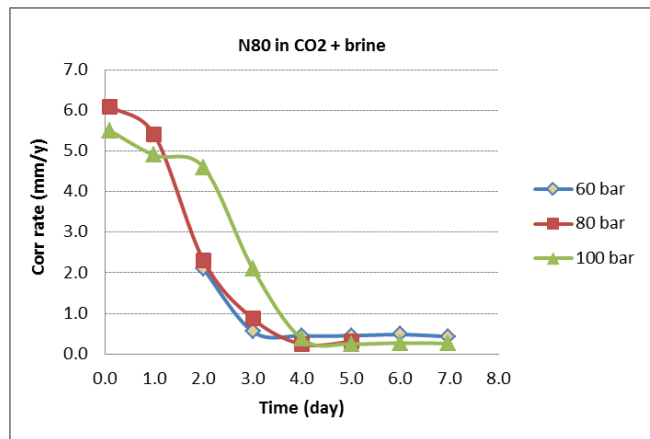


Fig. 3. Corrosion rate as a function of time for N80 steel in the brine plus CO<sub>2</sub> at 45°C and different pressure.

### 3.2. Mass loss measurements

The mass loss data are presented in Table 3. It shows an average corrosion rate of 0.06 mm/y measured in 32 days, which is lower than that measured by polarization measurements in stirred solution in a week.

Table 3. Mass loss rate measured for N80 steel exposed to the brine and CO<sub>2</sub> at 80 bars and 45°C for 32 days

Sample	Mass before (g)	Mass after (g)	Mass loss (g)	Surface area (cm <sup>2</sup> )	Mass loss/area (g/cm <sup>2</sup> )	Corrosion rate (mm/y)
1	122.836	121.728	1.108	246.67	4.49E-03	0.066
2	116.573	115.689	0.884	235.15	3.76E-03	0.056
3	120.240	119.390	0.850	243.48	3.49E-03	0.052

### 3.3. Surface analysis

The surface of the sample after the mass loss test has been analyzed by SEM and EDS. Fig. 4 shows (a) an SEM image and (b) the EDS spectrum measured in the square area 1 shown in (a) for an N80 sample after exposure in brine plus CO<sub>2</sub> at 80 bar and 45°C for 32 days. The corrosion products on the sample surface are crystalline, composed of C, O, Fe and Ca. Calcium signal present in the EDS spectrum means that partial calcium cations in the brine has precipitated and combined in the surface film.

Fig. 5 shows the XRD diagram and the fit phases for N80 steel after exposure to the brine plus CO<sub>2</sub> at 80 bar and 45°C for 32 days. The best fit of the patterns is dolomite CaMg<sub>0.77</sub>Fe<sub>0.23</sub>(CO<sub>3</sub>)<sub>2</sub>.

The layer formed on the surface of the casing steel in the condition investigated is compact, which hinders the corrosion process of the steel. That is why the corrosion rate decreases with time and is very low after immersion exposure for 32 days in the autoclave.

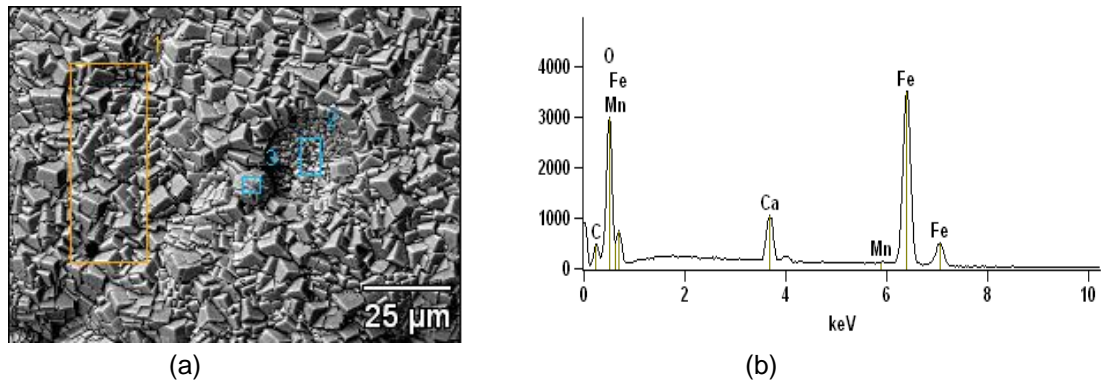


Fig. 4. SEM image (a) and EDS spectrum (b) for N80 after exposure to the brine plus CO<sub>2</sub> at 80 bar and 45°C for 32 days.

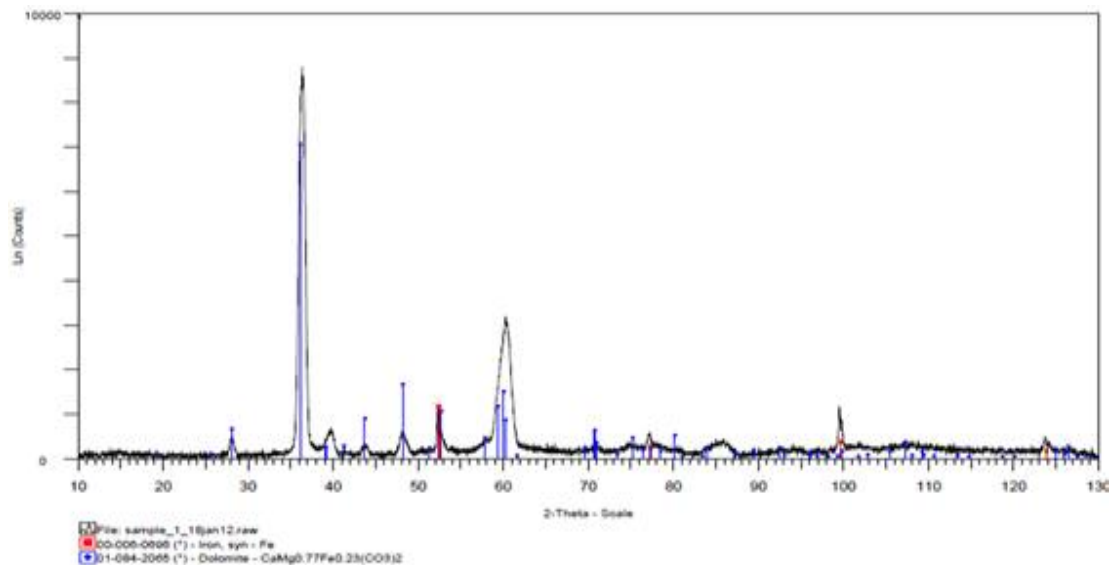


Fig. 5. XRD spectrum and fit phases for N80 after exposure to the brine plus CO<sub>2</sub> at 80 bar and 45°C for 32 days.

#### 4. Conclusions

The corrosion rate of N80 casing steel in a stirred brine plus supercritical CO<sub>2</sub> measured by polarization measurements is as high as 6 mm/y in 1 hour and is 0.3 mm/y after one week. The corrosion rate at other pressures shows also a decrease with exposure time.

The corrosion rate measured by mass loss test is 0.06 mm/y in the brine plus CO<sub>2</sub> at 80 bar and 45°C. The corrosion products deposited on the steel surface significantly reduce the general corrosion rate. The scale formed on the metal surface is dolomite CaMg<sub>0.77</sub>Fe<sub>0.23</sub>(CO<sub>3</sub>)<sub>2</sub> determined by XRD analysis.

## Acknowledgements

This research was conducted as part of the Dutch national project on CCS, CATO-2, which is supported by the Dutch government, and involves universities, private companies, and research institutes.

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