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Corrosion of Pipeline and Compressor Materials due to Impurities in separated CO_2 from fossil-fuelled Power Plants

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Abstract

It is well known that transporting CO_2 via pipelines even in the supercritical state is not a problem from the corrosion point of view, as long as CO_2 is almost pure and dry. Depending on the CO_2 separation technology, however, the untreated CO_2 stream contains also various impurities such as oxygen, sulphur oxides, nitrogen oxides, carbon monoxide and water. These impurities can cause severe corrosion to pipeline and compressor materials. To avoid corrosion in existing pipeline systems the transported CO_2 is usually purified and dried, which causes high energetic and financial expenditures. The aim of this investigation is to identify the corrosion potential of impure CO_2 on pipeline and compressor materials as well as to determine the required purity minimum of the CO_2 stream from the power plant, from the corrosion point of view. This is done by performing experiments with different materials exposed to impure CO_2. It is shown that some impurities enhance the corrosion and with a combination of oxygen, water and nitrogen oxide significant corrosion rates occur.

Keywords: CCS, Pipeline Corrosion, CO_2 Transport, CO_2 Purity, Wet CO_2, Oxyfuel

1. Introduction

When CO_2 is captured from power plant flue gases and is transported to a distant storage site, pipelines are economically and ecologically the most advantageous option. It is well known that transporting CO_2 via pipelines, even in the supercritical state, is not a problem from the corrosion point of view, as long as the gas stream is almost pure and dry. However, depending on the CO_2 separation technology used in the

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power plant the untreated CO_2 stream contains various impurities such as oxygen, nitrogen, argon, sulphur oxides, nitrogen oxides, carbon monoxide and water. These contaminants in the CO_2 stream can cause severe corrosion problems in pipeline and compressor parts. To avoid corrosion in existing pipelines the transported CO_2 is usually purified and dried until it reaches very low water concentrations of 50 ppmv or lower (e.g. <20 ppmv for the Weyburn pipeline [1]). There are some pipelines transporting CO_2 with higher water content. But in these cases the CO_2 only contains very little or no oxygen (e.g. 10 ppmv O_2 for the Kinder Morgan pipeline [2]). Additional purification leads to high energetic losses, however, depending on the treatment technology as well as on the required CO_2 purity, and increases the capital and operational expenditure of the power plant.

Hence the aim of the investigations described in this article and performed within the COORAL research project is to identify the corrosion potential of impure CO_2 on pipeline and compressor materials as well as to determine the required minimum purity for the CO_2 stream emanating from the power plant. The CO_2 purity specification is a prerequisite before designing the detailed power plant process. A significant reduction of the effort invested in the gas treatment could be possible if the critical concentrations of the impurities that keep the corrosion within acceptable limits were known.

In literature there are hardly any experimental data available about the corrosion potential of impure and wet CO_2 at high pressures which is typical in CCS. Earlier studies often investigated the corrosion potential of either CO_2-saturated water phase or water-saturated CO_2 phase [3][4][5]. But the water content in the separated CO_2 stream from power plant flue gas will probably be much lower than in water-saturated CO_2. Furthermore, the influence of other impurities such as SO_x, NO, CO and O_2 is not considered in most of the earlier studies and so no guidelines are available on the maximum tolerable concentrations of SO_x and NO_x [6].

To identify the critical concentrations of the impurities contained in the CO_2 a test rig for corrosion experiments under realistic boundary conditions was developed. The rig consists of two temperature controlled autoclaves made of Hastelloy and one stainless steel autoclave with inspection windows and a syringe pump to achieve supercritical pressure levels (up to 150 bar). Any desired gas composition can be obtained by mixing CO_2, SO_2, NO, CO, O_2 and H_2O. The metal specimens were hung from glass holders inside the autoclaves.

The first corrosion tests were performed in gas mixtures occurring in oxyfuel fired power plants. By changing parameters such as the concentration of water, oxygen and acid gas components in the gas mixture the influences of these parameters on the corrosion of different pipeline materials were determined. The corrosion rate was measured by weight loss. Additionally, the morphology and structure of the oxide scales were analysed by scanning electron microscopy.

2. Experimental Approach

In the Institute of Energy Systems static corrosion experiments were run in 1 l autoclaves made of Hastelloy. The specimens with the dimensions of 50 x 27 x 6 mm are mounted on glass holders in the autoclaves. The number of specimens was limited to two per experiment, to ensure a sufficient ratio of moles of corrosive medium to specimen surface. Two carbon steels L360NB (1.0582) and L485MB (1.8977), typical for the use as pipeline materials, and two high-alloy steels 1.4006 and 1.4542, typical for the use as compressor materials, were investigated. The chemical composition of these materials is listed in Table 1.

Table 1: Chemical composition of the materials investigated, in wt.-%.

Mater.-Nr.	Name	C	Si	Mn	P	S	Al	Cr	Cu	Mo	N	Nb	Ni
Compressor													
1.4006	X12Cr13	0.08-0.15	1.0	1.5	0.04	0.15	-	11.5-13.5	-	-	-	-	0.75
1.4542	X5CrNiCuNb16-4	0.07	1.0	1.0	0.05	0.03	-	15.0-17.0	3.0-5.0	-	-	0.15-0.45	3.0-5.0
Pipeline													
1.0582	L360NB	0.2	0.45	1.6	0.03	0.02	0.015-0.06	0.3	0.25	0.1	0.12	0.05	0.3
1.8977	L485MB	0.16	0.45	1.7	0.03	0.02	0.015-0.06	0.3	0.25	0.1	0.01	0.06	0.3

The experiments were performed with pressures of 110 bar and temperatures of 60 °C for pipeline materials and 150 °C for compressor materials. Hence, the CO_2 mixtures in the autoclaves were in the supercritical phase. 60 °C is assumed to be the inlet temperature in the pipeline. For compressor materials 150 °C were chosen instead, because CO_2 heats up during compression. The specimens were exposed to the different gas mixtures for one week. Afterwards, the mass gain as well as the mass loss was measured, after removing first corrosion products by etching with 9,7% HCl solution added with Urotropine to inhibit further corrosion of the bulk material. Further experiments were performed in an 290 ml autoclave with two inspection windows enabling a visual control of the corrosion. In this smaller autoclave only one specimen was mounted per experiment.

3. Impurities in the CO_2 stream

The amount of impurities in the CO_2 stream is strongly dependent upon the separation technology. The first investigations in this research project were focused on the oxyfuel process, because it is assumed that oxyfuel processes can have the highest amount of impurities compared to post-combustion and pre-combustion capture technologies. The CO_2 concentration in oxyfuel flue gases varies between 80 to 90 vol.% (dry). Depending on the flue gas purification system CO_2 concentrations up to 99.9 vol.%. in the separated CO_2 can be achieved. N_2, Ar, O_2 and H_2O are dominating the proportion of impurities. But there will always also be traces of SO_x, NO_x and CO. To ensure realistic gas compositions three different scenarios for oxyfuel processes (Zero Emission, Purification and Rectification) were defined prior to the experiments. These scenarios describe three flue gas purification systems leading to different contents of inert gases, oxygen and water in the separated CO_2 stream. Because inert gases like argon and nitrogen have no corrosive potential they were substituted by CO_2 in these experiments. However, argon and nitrogen do influence some properties of the gas mixture like density, viscosity, phase behaviour etc. The gas compositions used in the experiments are shown in Table 2. The components in these gas mixtures will react with each other, so that the gas compositions refer to the pipeline inlet. The concentrations of SO_x and NO_x in the separated CO_2 are expected to be somewhat lower than given in these three scenarios because of the lead-chamber effect. SO_x and NO_x form acids with the condensate occurring in the intercoolers of the CO_2 compressor and thus their concentrations in the CO_2 stream drop. It is not known yet to what extent the lead chamber effect reduces the acid gas concentrations in a large-scale power plant. Hence in these scenarios the worst case is assumed and the lead chamber effect was not taken into account.

Table 2: Gas compositions used in the corrosion experiments. Ar and N_2 are substituted by CO_2 in the experiments

Component	**Zero Emission**	**Purification**	**Rectification**
CO_2	Rest	Rest	Rest
O_2	4.7 vol.%	0.67 vol.%	100 ppmv
H_2O	0-1000 ppmv	100 ppmv	100 ppmv
NO	100 ppmv	100 ppmv	100 ppmv
SO_2	70 ppmv	70 ppmv	70 ppmv
CO	50 ppmv	50 ppmv	50 ppmv
(Ar + N_2)	(10.37 vol.%)	(1.3 vol.%)	(200 ppmv)

3.1. Zero Emission scenario

The Zero Emission scenario represents the compression and storage of the complete flue gas stream. Hence no vent gas is emitted to the atmosphere. With a CO_2 purity of ca. 85 vol.% the flue gas contains the highest amount of impurities out of the three scenarios. In this scenario an additional flue gas drying unit (e.g., with silica gel) is not obligatory, because the water content is already reduced significantly by condensation after the intercooler stages of the compression. To determine its influence, water content was therefore varied between 0 and 1000 ppmv in the experiments.

3.2. Purification scenario

In this scenario the CO_2 purity is raised to ca. 98 vol.% by partial condensation of CO_2. This lowers the content of Ar, N_2 and O_2 in the CO_2-stream. The partial condensation requires very low temperatures around -50 °C. To prevent ice formation the flue gas has to be dried to very low water contents of 100 ppmv or lower. Hence the water content is limited to 100 ppmv in the experiments.

3.3. Rectification scenario

This scenario is similar to the Purification scenario but includes a rectification of the condensed CO_2. The CO_2 purity is increased up to 99.9 vol.%. Therefore the Rectification scenario shows the least amount of impurities of all three scenarios. The water content is limited to 100 ppmv because of the same reason as in the Purification scenario.

4. Experimental Results

The corrosion rates showed in this paper are calculated by linear extrapolation of the mass loss after one week assuming that the mass loss is only due to the loss of iron using the following equation established in ASTM G31:

$$\text{Corrosion rate} = \frac{K \cdot W}{A \cdot T \cdot D} \tag{1}$$

where: K is a constant = $8.76 \cdot 10^7$
W is the weight loss in grams
A is the specimen surface in cm^2
T is the time of exposure in hours
D is the density in g/cm^3.

Experiments over several weeks indicated that the corrosion follows a logarithmic or exponential trend. These trends would result in lower corrosion rates than calculated with linear extrapolation. Hence the calculated rates in this paper are expected to be somewhat higher than in reality. The experiments revealed that all investigated impurities (H_2O, O_2, SO_2 and NO) except for CO are influencing the corrosivity of the CO_2 stream. The influence of each of these impurities is described below.

4.1. Influence of the water concentration

Figure 1 shows the annual corrosion rates of the two pipeline materials in five Zero Emission gas mixtures only differing in the water concentration. As expected, the corrosion rates decrease with decreasing water content. Only the water-free experiment with L360NB was not following that trend as shows slightly higher corrosion rates. A possible explanation is residual humidity in the autoclave from previous experiments. For both materials a reduction of the water concentration from 1000 to 600 ppmv leads to significantly lower corrosion rates.

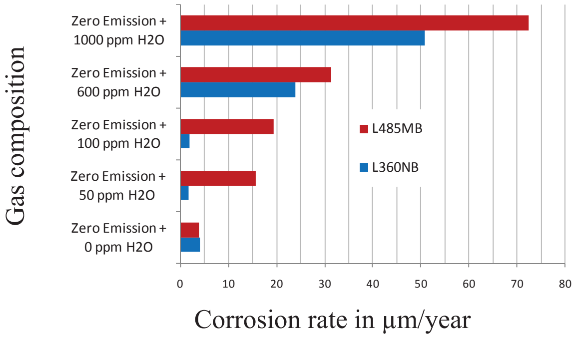

Figure 1: Annual corrosion rates in µm of L485MB and L360NB specimens in five gas compositions differing only in the water content.

A further reduction down to 100 ppmv or lower leads to negligible corrosion rates for the L360NB, whereas for L485MB the effect is less spectacular. Even in the gas mixture carrying 1000 ppmv water, however, corrosion rates below 100 µm/year for both materials were measured. The corrosion resistance of a material/medium combination is usually called acceptable if the corrosion rate does not exceed 100 µm/year [7]. Although both materials show only little corrosion rates, the L360NB seems to outperform the L485MB in these experiments. Photographs of L360NB specimens after the exposure to these gas mixtures are shown in Figure 2.

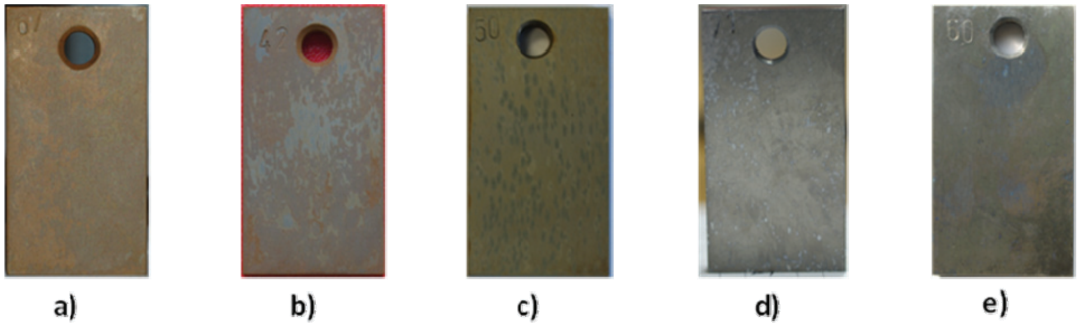

Figure 2: Photographs of L360NB specimens after one week exposure to a Zero Emission gas mixture with varying water contents: a) 1000 ppmv H_2O b) 600 ppmv H_2O c) 100 ppmv H_2O d) 50 ppmv H_2O e) 0 ppmv H_2O

4.2. Influence of the oxygen concentration

Figure 3 (a) shows the annual corrosion rate of the two pipeline materials in three gas mixtures only differing in the oxygen concentration. With decreasing oxygen concentration in the gas mixture the corrosion rate decreases for L485MB. For L360NB the corrosion rates are already so low, that a variation in oxygen concentration shows no effect. Figure 3 (b) shows the corrosion rate of L485MB in a Zero Emission mixture with 1000 ppmv water with (4.7 vol.%) and without oxygen. Without O_2 the corrosion rate is reduced by 88%.

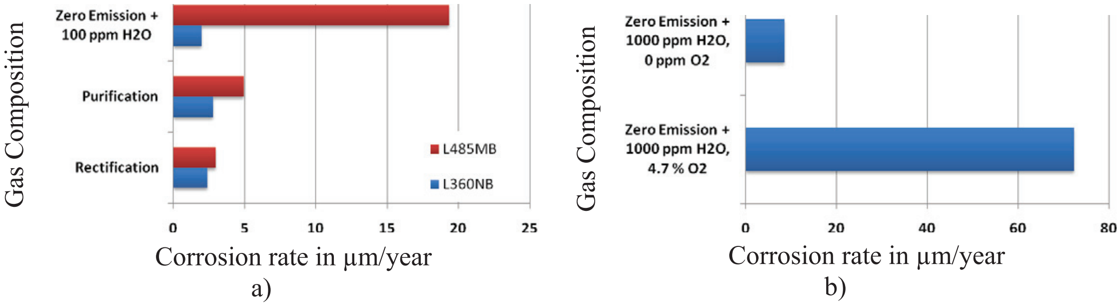

Figure 3: (a) Annual corrosion rates in µm of L485MB and L360NB specimens in three gas compositions only differing in oxygen content. (b) Annual corrosion rates of L485MB specimens in a Zero Emission gas mixture without oxygen and with 4.7 vol.% oxygen.

4.3. Influence of the trace impurities

In addition to oxygen and water there are traces of CO, NO_x and SO_x in the separated CO_2 stream. In an autoclave with inspection windows the influence of these trace impurities on the corrosion was studied visually. For the first experiment one specimen was mounted inside the autoclave and was exposed to a gas mixture consisting of CO_2, 1000 ppmv H_2O and 4.7 vol.% O_2. In further experiments one of the trace impurities (CO, NO_x and SO_x) was added to that gas mixture.

The specimens exposed to CO_2, H_2O and O_2 did not show any sign of corrosion even after several days. Also no corrosion was detectable when 50 ppmv CO or 70 ppmv SO_2 were added to the gas mixture. However, studies with considerably higher SO_2 concentrations (about 500 ppmw) report signs of localised corrosion, presumably due to the formation of $FeSO_4$ [8],[9]. In these experiments significant corrosion occurred only when NO was added. Adding 100 ppmv NO led to the formation of yellow corrosion layers which turned brownish after a few days (Figure 4). The reactions with NO were fast. Only a few minutes after the NO injection a uniform yellowish colouring was observed on the specimen surface. The longer the specimens were exposed to the gas mixture the browner the specimen became and a uniform corrosion layer was formed. This is corroborated by the literature as high corrosion rates in gas mixtures of CO_2, H_2O and NO_2 are also reported in [9].

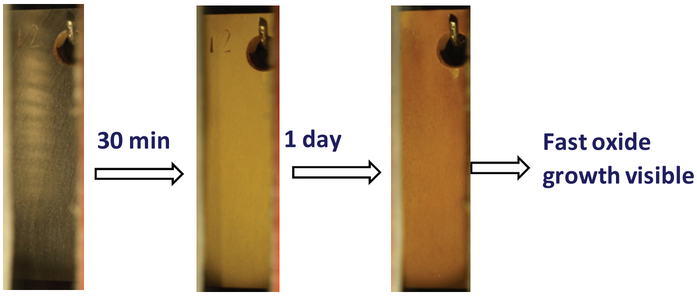

Figure 4: Pictures of a L360NB specimen exposed to a gas mixture of CO_2, 1000 ppmv H_2O, 4.7 vol.% O_2 and 100 ppmv NO

4.4. Analysis of the oxide layer

The oxide layers were analysed by X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Pictures in the electron microscope revealed that the oxide layer has a partly crystalline but mainly amorphous structure. Amorphous compounds cannot be identified by XRD. Hence the XRD-analysis could only identify α-FeO(OH) in the oxide layer, which is a typical component of rust. The SEM-EDS analysis shown in Figure 5 demonstrates that the oxide layer mainly consists of oxygen, iron and sulphur. There are only traces of carbon and nitrogen in the oxide layer. Hence no iron carbonates or iron nitrates were formed whereas sulphur reacts with the specimen. A possible reaction with sulphur oxide is the formation of $FeSO_4$ as mentioned in [8],[9]. The specimen was gold-sputtered prior to the analysis to increase the quality of the SEM pictures; this explains the gold peak.

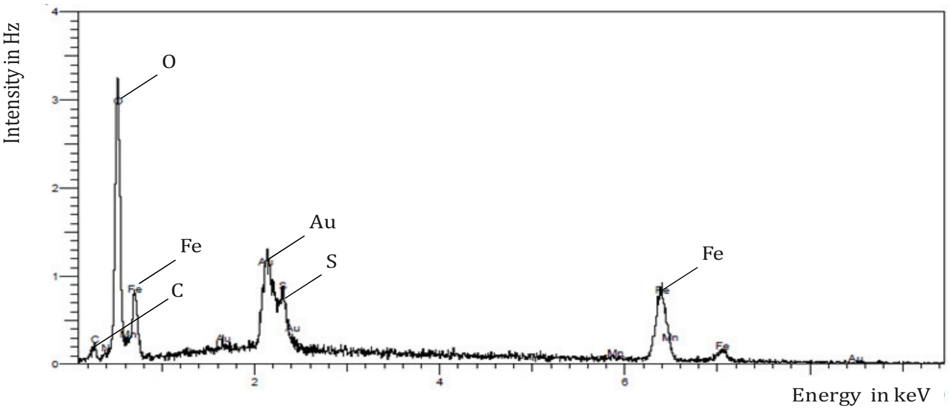

Figure 5: SEM-EDS analysis of an oxide layer of a L360NB specimen exposed to a Zero Emission gas mixture with 1000 ppmv water

4.5. Performance of the compressor materials

Both compressor materials did not show any signs of corrosion even in the gas mixture with the highest concentration of impurities (Zero Emission + 1000 ppmv H_2O). Hence both materials seem to be suitable for the compression of impure CO_2 from the corrosion point of view and under the experimental conditions used here. This may not be valid for parts where a free water phase may be present, as for example in interstage coolers.

5. Conclusions and Discussion of Results

The experiments revealed that impurities in separated CO_2 can cause corrosion on pipeline steel even without a free water phase. In contrast both investigated compressor materials did not show any signs of corrosion under the experimental conditions even in the most corrosive gas mixtures. The measured corrosion rates of the pipeline materials depend on the gas composition. The maximum measured values were about 80 µm/year. Only uniform corrosion was observed in the experiments. Therefore, both pipeline materials seem to be suitable for the use in CO_2 pipelines, assuming a maximum permissible corrosion rate of 100 µm/year. Nevertheless it is suggested to lower the corrosion potential of the gas mixtures by reducing the concentration of certain impurities. The impurities affecting the corrosion the most are water, oxygen and acid gas components (like nitrogen oxide and sulphur oxide). Significant corrosion occurred only when H_2O, O_2 and NO were present in the CO_2 stream.

The corrosion rates of the pipeline materials could be reduced significantly by drying the CO_2 stream. Most important is to avoid free water in the CO_2 stream, which would lead to extremely high corrosion rates. Furthermore it is suggested to dry the CO_2 stream to water concentrations below 600 ppmv at least, considering the other boundary conditions in these experiments. In addition to drying the CO_2, a reduction of the concentration of oxygen and acid gas components (SO_x and NO_x) would also lower the corrosion risk.

The metal specimens did corrode when NO was added. But this did not happen when SO_2 was added instead. An explanation for that behaviour would be the different kinetics in the formation of the respective acids. NO seemed to be oxidised to NO_2 rather fast. NO_2 together with water formed nitric acid which is a strong acid and initiates the corrosion. In contrast to the formation of nitric acid no sulphuric acid seemed to be formed when SO_2 was added. That is possibly so, because the oxidisation of SO_2 to SO_3 with oxygen is kinetically hindered at such low temperatures. Since sulphuric acid is only formed when SO_3 is present to react with water, the formation of sulphuric acid is hindered indirectly too. However, when adding both SO_2 and NO sulphur was nonetheless found in the oxide layer indicating that sulphuric acid did exist and reacted with the specimen. This can be explained with the catalytic behaviour of nitrogen oxides on the sulphuric acid formation. This behaviour is commonly referred as the lead chamber effect [10] and is described in the following equation:

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4 \tag{2}$$

At higher pressures than atmosphere NO_2 is catalysing the formation of sulphuric acid when SO_2 and water are present. H_2SO_4 is a strong acid and reacts with the metal specimen. This is a possible explanation why sulphuric acids were formed when NO and SO_2 were added and why sulphur was found in the oxide with SEM-EDS. Since water as well as oxygen and acid gas components are required to get significant corrosion of pipeline materials, any reduction of one of these components in the CO_2 stream would lower the corrosion risk of the pipeline. So far only experiments with oxyfuel gas mixtures were performed. However these findings should also apply to CO_2 streams from post-combustion capture units, because these can also include water, oxygen and acid gas components.

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