



Hydrogen Uptake of Duplex 2205 at H₂ Partial Pressures up to 100 bar

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Abstract: Microbiological methanation is investigated in an underground natural gas reservoir. Since H₂ is involved in the process, hydrogen embrittlement of steel must inevitably be considered. Therefore, a routine for testing has been developed and a unique autoclave test bench was designed to simulate field conditions. The 2205 duplex stainless steel (UNS S31803) was investigated. Constant load tests (CLTs) and immersion tests with subsequent hydrogen analyses were performed. The specimens were exposed to different partial pressures of H₂ under both dry and wet conditions (with brine). Additionally, the influence of CO₂ under wet conditions was covered. Tests were performed at two different temperatures (25 °C and 80 °C) and lasted for 30 days. In general, the duplex stainless steel shows a good resistance to hydrogen embrittlement, but a significantly higher hydrogen uptake was obtained compared to other steel grades.

Keywords: Hydrogen Embrittlement, Hydrogen Uptake, 2205 Duplex Stainless Steel, Methanation

Wasserstoffaufnahme von Duplex 2205 bei H₂-Partialdrücken von bis zu 100 bar

Zusammenfassung: In einem unterirdischen Erdgasspeicher wird die mikrobiologische Methanisierung untersucht. Da H₂ am Prozess beteiligt ist, muss zwangsläufig die mögliche Wasserstoffversprödung von Stahl berücksichtigt werden. Aus diesem Grund wurden eine Testroutine und ein spezieller Autoklavenprüfstand für Versuche unter Feldbedingungen entwickelt. Untersucht wurde der Duplexstahl 2205 (UNS S31803). Zugversuche unter konstanter Last

(CLTs) und Auslagerungstests mit anschließenden Wasserstoffanalysen wurden durchgeführt. Die Proben wurden sowohl unter trockenen als auch unter nassen Bedingungen (mit Salzlösung) unterschiedlichen Partialdrücken von H₂ ausgesetzt. Zusätzlich wurde der Einfluss von CO₂ unter nassen Bedingungen abgedeckt. Die Tests wurden bei zwei verschiedenen Temperaturen (25 °C und 80 °C) durchgeführt und dauerten 30 Tage. Im Allgemeinen zeigt der Duplexstahl eine gute Beständigkeit gegen Wasserstoffversprödung, jedoch wurde eine, im Vergleich zu anderen Stahlsorten, deutlich höhere Wasserstoffaufnahme beobachtet.

Schlüsselwörter: Wasserstoffversprödung, Wasserstoffaufnahme, Duplexstahl 2205, Methanisierung

1. Introduction

To achieve the climate goals, so-called green energy is becoming increasingly important. Changing weather conditions lead to fluctuating power outputs, which leads to the fact that the excess electricity needs to be stored. Transformation of electricity to hydrogen via electrolysis is an option, but the lack of adequate infrastructure for the storage and transport of the gas is a problem. This issue can be addressed by methanation of hydrogen and carbon dioxide to obtain natural gas:



A new approach is to use methanogenic archaea that perform the methanation process [1]. Such microorganisms can produce natural gas in an underground natural gas reservoir. With H₂ involved in the process, hydrogen embrittlement has to be considered. This phenomenon, although known since 1874 [2], is not yet fully understood. In presence of H₂ and CO₂ as well as a chloride-containing,

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TABLE 1
Chemical composition of the investigated material

C [wt%]	Si [wt%]	Mn [wt%]	P [wt%]	S [wt%]	Cr [wt%]	Ni [wt%]	Mo [wt%]	N [wt%]	Fe [wt%]
0.027	0.53	1.60	0.025	0.001	22.23	5.18	3.16	0.193	Bal

humid environment under anaerobic conditions, there are two main potential sources of absorbed hydrogen. The first one is the dissociation of gaseous H₂:



The hydrogen molecule H₂ dissociates into two adsorbed hydrogen atoms H_{ad}. According to Sieverts and Krumbhaar [3], the hydrogen solubility of metals increases with increasing temperatures. This is depicted in Sieverts's law:

$$S = S_0 \cdot \sqrt{p} \cdot e^{-\Delta H/RT} \quad (3)$$

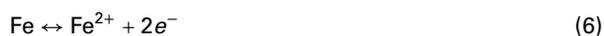
where S₀ is the solubility constant, p the partial pressure, ΔH the heat of solution, R the universal gas constant, and T the absolute temperature [4]. When CO₂ dissolves in water, carbonic acid H₂CO₃ is formed [5]:



The carbonic acid dissociates. The increasing concentration of H⁺ results in a lower pH, and the cathodic reaction



is promoted [6]. Simultaneously an anodic dissolution of iron takes place:



Not all of the reduced H⁺ ions recombine to H₂ as shown in Eq. 5, some of the adsorbed hydrogen atoms (H_{ad}) can get absorbed (H_{ab}):



Thus, the second potential source of absorbed hydrogen is the cathodic corrosion reaction. In general, this source can be neglected when using corrosion resistant alloys (CRAs).

Whiteman and Troiano [7] stated that the amount of absorbed hydrogen necessary to produce hydrogen embrittlement is one or two orders of magnitude greater for austenitic stainless steels compared to steels with a bcc lattice. Thus, a duplex stainless steel, which is a mixture of both microstructures, is of interest for being tested to identify application limits in terms of hydrogen embrittlement.

The diffusion of hydrogen is much faster in ferrite compared to austenite, while the solubility of hydrogen atoms shows a reverse behaviour [8, 9]. Olden et al. [8]. stated that austenite acts as a hydrogen sink in a duplex stainless steel, attracting and absorbing the hydrogen atoms that

diffuse in the nearby ferrite. Tohme et al. [10] recently confirmed this behaviour combining Scanning Kelvin Probe Force Microscopy (SKPFM) measurements with finite element (FE) modelling. The diffusion against the concentration gradient is a phenomenon known as "up-hill" diffusion, described by Darken [11] for carbon in steels as early as 1949.

Since it can be challenging to make suggestions for field service based on standard laboratory tests [12], simulating field conditions is very reasonable. To answer the question of whether steel grades are suitable for underground methanation, a routine for testing has been developed. An autoclave test bench was designed to simulate field conditions. In this paper, tests were conducted with the 2205 duplex stainless steel (UNS S31803).

2. Experimental Procedure

The tested steel grade presented in this paper was the duplex stainless steel UNS S31803, commonly known as 2205. Samples were taken from commercially available casing tube sections. The chemical composition of the investigated material is shown in Table 1.

The steel had a pitting resistance equivalent number (PREN) of 35.7. This value was calculated according to the following equation [13]:

$$\text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N}[\text{wt}\%] \quad (8)$$

The mechanical properties of the investigated steel grade are listed in Table 2. Tensile tests were performed on small, non-standard tensile specimens with an initial gauge length of 25 mm and a diameter of 3 mm. The specimens were drawn at room temperature with a crosshead speed of 0.1 mm/min.

The corrosion tests were conducted within autoclaves made of UNS N06625 (Alloy 625). Fig. 1 shows one of the used autoclaves.

Each autoclave contained three different specimens: an immersion specimen (Fig. 2a) i) for measuring the hydrogen uptake, a coupon (Fig. 2a) ii) for determining the presence of pitting or other corrosion phenomena, and a small tensile specimen (Fig. 2a) iii) for a constant load test (CLT).

TABLE 2
Specified Minimum Yield Strength (SMYS), Yield Strength (YS), Ultimate Tensile Stress (UTS) and fracture elongation (A) of the investigated material

SMYS		YS		UTS		A
[MPa]	[ksi]	[MPa]	[ksi]	[MPa]	[ksi]	[%]
758	110	822	119	885	128	16.5

Fig. 1: Autoclave made of Alloy 625



Fig. 2: Specimen assembly to be mounted in the autoclave. **a** Three specimens connected with PTFE parts: Immersion specimen (i), coupon (ii), and constant load specimen (iii). **b** Small tensile specimen with spring and ceramic nuts for constant load test



The load was applied to the CLT specimen with a spring made of a cobalt-base alloy and ceramic nuts (Fig. 2b), the latter ensuring electronic decoupling of the specimen from the more noble spring. The specimens were connected with PTFE parts.

The specimen assemblies were mounted in the autoclaves. The vessels were evacuated and purged with argon several times to get very low partial pressures of oxygen and other atmospheric gases. Further the autoclaves were filled with an aqueous test solution and test gases (Fig. 3a, b). The last step was to mount the autoclaves on rotating shafts within a heated chamber (Fig. 3c).

Tests were performed with two different partial pressures of H_2 gas: 20bar and 100bar. Also, the influence of 5 bar of CO_2 gas was investigated. In more than half of the tests, an aqueous NaCl solution (brine) with a chloride concentration of 15,000 mg/l was used. The tests were conducted at 25 °C as well as at 80 °C (near field conditions) and lasted for 30 days. Thus, the material was tested under 10 different conditions.

The load for the CLTs was 90% of the specified minimum yield strength (SMYS). The load was applied by compressing a spring with a defined load and connecting it with the respective specimen and two ceramic nuts. To simulate the

periodically changing conditions in the gas well, the autoclaves were rotated with a speed of 1 RPM. Consequently, the specimens were periodically wetted with the aqueous electrolyte.

Directly after the test, the immersion specimens were removed from the autoclaves and immediately cooled in liquid nitrogen. The cooled specimens were ground with silicon carbide paper (grit 120), rinsed with acetone and blow-dried quickly prior to hydrogen analysis. The hydrogen content was measured with a thermal conductivity cell after hot extraction at 950 °C. At the end of the tests, the constant load specimens were examined for possible fractures that occurred. Unbroken specimens were examined with a stereo microscope to see if any cracks or pits were visible. The coupons were examined for pits or other visible corrosion phenomena.

3. Results

None of the specimens loaded at 90% of the SMYS broke under the tested conditions. None of the unbroken specimens showed visible cracks or pits under the stereo mi-

Fig. 3: Filling and mounting of the autoclaves: **a** Filling of autoclaves with aqueous test solution. **b** Pressing the test gas into the autoclave. **c** Several autoclaves mounted on rotating shafts within a heated chamber



		temperature		
		25 °C	80 °C	
medium	dry gas	20 bar H ₂	✓	✓
		100 bar H ₂	✓	✓
	gas with electrolyte 15 000 mg/l Cl ⁻	20 bar H ₂	✓	✓
		5 bar CO ₂	✓	✓
		100 bar H ₂	✓	✓

✓ CLT specimen intact

Fig. 4: Results of the constant load tests

crosscope. Fig. 4 gives an overview for the results of the constant load tests.

Also, on the corrosion coupons, no pits or other visible corrosion phenomena were detected. The results of the hydrogen analyses of the 2205 tested in autoclave wheel tests at 25°C are illustrated in Fig. 5. Where two or more tests under same conditions were performed, the mean value and standard deviation are shown in the diagrams. For individual tests, a deviation of ±15% is shown.

In comparison to the uncharged condition, which is shown in each diagram as the leftmost bar, a hydrogen uptake by dry H₂ gas at 20 bar or 100 bar and 25°C was not clearly detectable. A similar result was found for 20 bar of H₂ and 5 bar of CO₂ gas under wet conditions (with brine). At 100 bar of H₂ in the presence of brine, a hydrogen content of 4.01 ppm was detected, which corresponds to an uptake of 1.76 ppm. Hydrogen contents for tests in the same media, but at 80°C are shown in Fig. 6.

At 80°C there was no detectable hydrogen uptake in 20 bar dry H₂ gas or in the wet, CO₂ containing atmosphere, while 100 bar dry H₂ led to a measurable hydrogen uptake. In the presence of brine, H₂ gas led to a hydrogen content of 6.00 ppm (3.75 ppm uptake) at 20 bar and 14.21 ppm (11.96 ppm uptake) at 100 bar.

Both at 25°C and 80°C, the presence of NaCl brine with a chloride concentration of 15,000 mg/l was found to promote the hydrogen uptake due to H₂ gas. The higher temperature (80°C compared to 25°C) led to significantly higher hydrogen contents in the specimens exposed to 20 bar or 100 bar H₂ gas and brine. Dry H₂ gas only led to hydrogen uptake at 100 bar and 80°C, although the measured amount was not significant.

Using stereomicroscopy, no signs of corrosion were found on any coupon. The presence of 6.00 and 14.21 ppm after testing with brine at 80°C compared to 2.77 and 3.08 ppm without brine is a strong argument for hydrogen uptake during a corrosive process. While the α-phase is less noble, the γ-phase is more noble [14]. In the brine, the α-phase serves as the anode, while the γ-phase represents the cathode at which adsorbed atomic hydrogen is formed. Only when there is a high hydrogen partial pressure, the adsorbed hydrogen cannot recombine against this “back pressure” and is absorbed resulting in the high described concentration (6.00 and 14.21 ppm). Lack of brine and/or hydrogen pressure in the autoclave does not result in a substantial hydrogen absorption. Without brine, corrosion may not occur. Corrosion may occur without the presence of hydrogen gas, but adsorbed atomic hydrogen then tends to recombine to its molecular form which is released to the gas.

Although hydrogen contents up to 14.21 ppm were measured, no substantial embrittlement at 90% of the SMYS was observed in the constant load tests. In previous tests on carbon steels, it was found that the API 5CT [15] P110, which has the same SMYS as the duplex, had a hydrogen content of 0.38 ppm after being tested under same conditions without a failure. The significant difference in hydrogen content can be explained with the different microstructure (tempered martensite vs. ferrite-austenite). Austenitic structures provide more hydrogen traps, where the small atoms can get stuck. Since the amount of absorbed hydrogen required to produce hydrogen embrittlement of these structures is one or two orders of magnitude greater than that of steels with bcc lattice alone, the mixture of both—present in the investigated material—survives the CLT despite a hydrogen content of 14.21 ppm.

In tests on the austenitic stainless steel Alloy 28 (UNS N08028), a maximum hydrogen uptake of 7 ppm was found, while in this work on 2205 duplex stainless steel a hydrogen uptake of 12 ppm was measured after

Fig. 5: Hydrogen content for 2205 duplex stainless steel (UNS S31803) tested in different media in autoclave wheel tests for 30 days at 25°C and 1 RPM. The chloride concentration of the brine was 15,000 mg/l

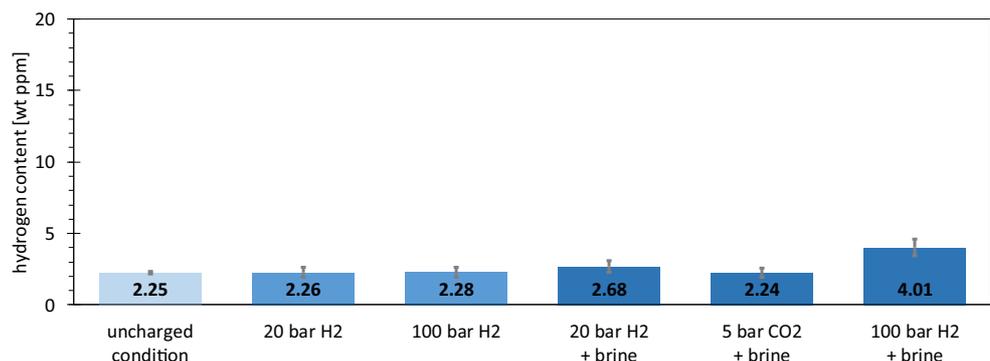
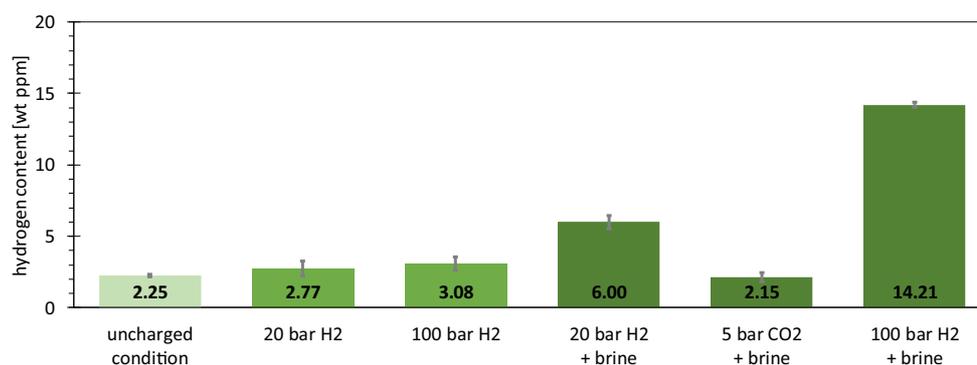


Fig. 6: Hydrogen content for 2205 duplex stainless steel (UNS S31803) tested in different media in autoclave wheel tests for 30 days at 80 °C and 1 RPM. The chloride concentration of the brine was 15,000 mg/l



charging under the same conditions. Despite the much lower austenite content with its high solubility for hydrogen atoms, the 2205 absorbs more hydrogen than the fully austenitic material. The unique behaviour of duplex stainless steel can be described with the up-hill diffusion phenomenon mentioned in the introduction: due to the rapid diffusion, the ferrite transports the hydrogen atoms very well to the austenite, where the solubility and thus the driving force for the diffusion into it is very high. The ferrite seems to permanently “pump” hydrogen atoms into the austenite, resulting in higher hydrogen uptake compared to a martensitic or fully austenitic material. This effect seems to be further enhanced by the galvanic corrosion of the α -phase of the duplex steel being coupled to the more noble γ -phase as described above.

4. Conclusions

- No cracks occurred under the constant load of 90% SMYS within 30 days of testing in rotated autoclaves containing up to 100 bar hydrogen gas with or without brine (15,000 mg/l chloride).
- The 2205 duplex stainless steel (UNS S31803) did not show a corrosive attack after the immersion in brine with CO₂ at 25 °C and 80 °C (evaluation with stereo microscope).
- The presence of brine was found to promote hydrogen uptake.
- A temperature of 80 °C led to significantly higher hydrogen contents in the specimens exposed to 20 or 100 bar H₂ gas and brine compared to 25 °C.
- A maximum hydrogen content of 14.21 ppm (uptake of 11.96 ppm) was found in the test with 100 bar H₂ and brine at 80 °C after 30 days.
- In the hydrogen uptake, significant differences to other steels were measured. The two-phase α - γ -microstructure and thus the individual solubility and diffusion behaviour as well as the different corrosion potential have a decisive influence on the hydrogen uptake during the 30 days of testing.
- The 2205 duplex stainless steel (UNS S31803) seems to be suitable for application in an underground microbiological methanation facility.

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