

# Summary report on steels K55, L80 including H<sub>2</sub>S containing atmosphere and a quenched reference material

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#### TABLE OF CONTENT

1. Introduction	7
2. Investigation of the effect of $CO_2/O_2$ adsorption	8
3. Investigation of quenched carbon steel	9
3.1. Time to failure of Constant Load Tests (CLT) specimens	9
3.2. SEM investigation of fracture layer	9
4. Investigation of steel K55	12
4.1. Time to failure of Constant Load Tests (CLT) specimens	12
4.2. Hydrogen content	12
4.3. SEM investigation of surface layers	15
4.4. Permeation tests	24
5. Investigation of steel L80	26
5.1. Time to failure of Constant Load Tests (CLT) specimens	26
5.2. Hydrogen content	26
5.3. SEM investigation	29
5.4. Permeation tests	30





# **1.Introduction**

In the course of work package WP4 of the Hystories project, the materials K55 and L80 steels selected at an earlier stage and reported in D4.2 (List of the steel grades to be investigated) were carried out in autoclave tests by the Chair of General and Analytical Chemistry, Montanuniversitaet Leoben.

All materials, except the welded K55 have been handed over in full scope. As all materials were sent at a different time, the testing plan was changed. The two carbon steels K55 and L80 accounting for 50% of the whole test program have been investigated first, furthermore the quenched material was tested as well.

The full test program includes:

- Autoclave tests including
- time to failure,
- hydrogen content,
- SEM investigation of surface layer and
- permeation tests.

Experiments are described in detail in report D4.1\_Final protocol for material testing, here only results are described.

Further investigations that are planned are:

- Tensile tests in glycerine at 120°C and in air at room temperature for the welded K55,
- steel characterization of the microstructure including the average grain diameter and, if applicable, the average ferrite content for the welded K55,
- the full test program for the welded material in autoclaves for 720 hours,
- all other material in the autoclaves under the most severe conditions, and
- ripple load tests.



# 2. Investigation of the effect of $CO_2/O_2$ adsorption

Before starting the tests matrix, preliminary tests were carried out to investigate whether  $CO_2/O_2$  adsorption influences hydrogen uptake. As a matter of fact, it was suspected that  $O_2/CO_2$  contained in air could be absorbed on steel sample before the beginning of the tests and could have an influence on the final hydrogen uptake results.

In order to investigate this phenomenon, two experimental conditions were chosen and six samples per condition were selected to check the possibility of oxygen uptake in the evacuation station.

These tests were carried out in autoclaves. To do this, the first batch of samples were evacuated and flushed 3 times with argon which is the usual approach. Furthermore, to see if this standard approach was sufficient, the second batch of samples were not only submitted to the usual approach, but were also heated three times in a furnace at 120 °C for 24 hours. This additional heating should help to desorb any trace of  $CO_2$  or  $O_2$  before the beginning of the experiment.

For this second batch, Hydrogen content with thermally desorbed  $CO_2/O_2$  was 0.36 ± 0.06 ppm. For the first batch that was processed with the normal procedure, hydrogen content "with adsorbed  $CO_2/O_2$ " was 0.31 ± 0.06 ppm. The results show no significant effect on hydrogen uptake by eventually adsorbed oxygen and  $CO_2$  during the tests. Consequently this investigation shows that the usual approach is adequate and that adsorbed  $CO_2/O_2$  does not prevent hydrogen uptake during testing.



### 3. Investigation of quenched carbon steel

# 3.1. Time to failure of Constant Load Tests (CLT) specimens

Steel L80 has been austenitized and quenched in water. Due to its quenched properties, this material is very sensitive to hydrogen embrittlement and can easily crack if hydrogen is present under stress. The presence of cracks in this quenched material makes it possible to implement the reliability of testing a material with this method.

For Constant Load Tests, tensile specimens are stressed at 90 % of their yield strength. The test is static and last 720 h.

So far two tests under very different conditions (Figure 1) have been performed. Both tests resulted in a failure. The time to failure cannot be given since the autoclave are only opened after 720 h.

A fracture occurred in both conditions. This is shown in Figure 1.



Figure 1: Time to failure of quenched material after testing in a) gas A (120 bar H<sub>2</sub>), no electrolyte, 25 °C, b) gas D (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub> + 1 bar H<sub>2</sub>S), 200 g/l NaCl, immersion in gas + electrolyte, 120 °C.

#### 3.2.SEM investigation of fracture layer

Figure 2 shows a fracture image of a quenched steel. The test condition was the more aggressive one in gas D ( $H_2 + CO_2 + H_2S$ ) with an electrolyte of 200 g/l sodium chloride NaCl at 120°C. Under these severe conditions a fracture occurred. It did not make sense to make a SEM examination with this fracture surface, because the surface is covered by a thick layer of



corrosion products. The hydrogen content in the specimen was 0.86 ppm after the experiment.



Figure 2: Fracture surface of quenched steel tested in gas D (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub> + 1 bar H<sub>2</sub>S), 200 g/l NaCl, immersion in gas + electrolyte, 120 °C.

Figure 3 shows a fracture image of the quenched steel tested under more mild conditions. The test condition was dry gas A ( $H_2$ ) at room temperature. Under these conditions also a fracture occurred. On the upper site of the fracture the starting point of the fracture can be observed. A hydrogen amount of only 0.10 ppm was measured using the TDS.



Figure 3: Fracture surface of quenched steel tested in gas A (120 bar H<sub>2</sub>), no electrolyte, 25 °C, 30x.

Figure 4 shows the different fracture zones in detail of the quenched material in a SEM. The fractured surface of a hydrogen crack can be separated into several parts. In Figure 4 a), in the light blue frame from Figure 4, a clear hydrogen fracture can be observed. It is an area, in which a ductile and brittle area are present side to side. Figure 4 b) the same fracture area in



the light blue frame is shown with a higher magnification. There is a cleavage like fracture with river patterns and some fine pores typical for a hydrogen induced fracture. In Figure 4 c) the green area shows a brittle fracture as well. In the dark blue area from Figure 3 and magnified in Figure 4 d), the transition area between brittle hydrogen crack and ductile forced fracture is visible.



Figure 4: Details of fracture surface of quenched steel a) hydrogen fracture 300x, b) river patterns at hydrogen fracture 3000x, c) hydrogen fracture 300x d) transition zone between hydrogen fracture (left) and ductile forced fracture (right), 300x.



## 4.Investigation of steel K55

# 4.1. Time to failure of Constant Load Tests (CLT) specimens

Figure 5 shows the time to failure of ferritic perlitic steel K55 for all gas compositions. Gases without  $H_2S$  (non-sour gas) are gas A (120 bar  $H_2$ ) and gas B (120 bar  $H_2 + 15$  bar  $CO_2$ ). Gases with  $H_2S$  (sour gas) are gas C (120 bar  $H_2 + 1$  bar  $H_2S$ ) and gas D (120 bar  $H_2 + 15$  bar  $CO_2 + 1$  bar  $H_2S$ ). No fracture at all occurred under any condition. The Figure 5 below shows as an example time to failure in gas D. No cracks at all occurred for steel K55. The same happened for gases A, B and C.



Figure 5: Time to failure of ferritic perlitic steel K55 in gas D: 120 bar  $H_2$  + 15 bar  $CO_2$  + 1 bar  $H_2S$ .

#### 4.2.Hydrogen content

Figure 6 shows the hydrogen uptake of steel K55 in four test gases A to D at room temperature (25  $^{\circ}$ C).

In this autoclave tests with steel K55 at room temperature (20°C), the lowest hydrogen value is 0.07 ppm for gas A (see Figure 6 a)) and the highest value is 2.33 ppm for gas C (see Figure 6 c)). The hydrogen content was measured by thermal desorption spectroscopy (TDS).

Gases A and B show no increased hydrogen uptake. Gases C and D with  $H_2S$  show increased values whenever an electrolyte is present. If no electrolyte is present, the presence of  $H_2S$  has almost no effect on hydrogen uptake. In gases C and D higher hydrogen contents were generated with the presence of an electrolyte. However, no failure occurred.





Figure 6: Hydrogen uptake of steel K55 in autoclave tests at RT in, a) gas A (120 bar  $H_2$ ), b) gas B (120 bar  $H_2$  + 15 bar  $CO_2$ ), c) gas C (120 bar  $H_2$  + 1 bar  $H_2$ S) and d) gas D (120 bar  $H_2$  + 15 bar  $CO_2$  + 1 bar  $H_2$ S).

Figure 7 illustrates the hydrogen uptake of steel K55 in all conditions at 120 °C. In the autoclave tests with the steel K55 at 120 °C, the lowest value is 0.19 ppm in gas B (see Figure 7 b)) and the highest value is 0.49 ppm in gas D (see Figure 7 d)). The amount of hydrogen was also measured by TDS.





Figure 7: Hydrogen uptake of steel K55 in autoclave tests at 120 °C in, a) gas A (120 bar  $H_2$ ), b) gas B (120 bar  $H_2$  + 15 bar  $CO_2$ ), c) gas C (120 bar  $H_2$  + 1 bar  $H_2S$ ) and d) gas D (120 bar  $H_2$  + 15 bar  $CO_2$  + 1 bar  $H_2S$ ).

In all conditions no specimen failed.

The table 1 below compares the hydrogen uptake for different conditions at room and at high temperatures.



		Hydrogen content [ppm] after immersion in						
		dry gas	humid gas (1 g/l)	electrolyte (1 g/l)	gas + electrolyte (1 g/l)	humid gas (200 g/l)	electrolyte (200 g/l)	gas + electrolyte (200 g/l)
	gas A	0.07	0.13	0.12	0.18	0.26	0.21	0.21
room temperature	gas B	0.11	0.14	0.15	0.21	0.20	0.23	0.21
	gas C	0.17	0.78	1.00	2.33	0.36	0.38	0.24
	gas D	0.17	1.88	1.41	1.30	1.24	0.77	0.63
	gas A	0.37	0.30	0.26	0.30	0.26	0.35	0.28
120 °C	gas B	0.20	0.20	0.19	0.33	0.26	0.24	0.22
	gas C	0.28	0.23	0.32	0.27	0.24	0.21	0.30
	gas D	0.26	0.49	0.44	0.37	0.45	0.34	0.41

Table 1: Hydrogen uptake of steel K55 in autoclave tests at 25 °C and 120 °C in, a) gas A (120 bar H<sub>2</sub>), b) gas B (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub>), c) gas C (120 bar H<sub>2</sub> + 1 bar H<sub>2</sub>S) and d) gas D (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub> + 1 bar H<sub>2</sub>S).

g/l = g/l NaCl

Slightly more hydrogen was absorbed at higher temperatures in  $H_2S$  free conditions.

On the contrary, the addition of  $H_2S$  to the gas resulted in fast sulfide layer formation at 120°C and consequently in a reduction of the absorbed hydrogen content compared to the tests conducted at room temperature.

In the following the effect of different hydrogen uptake at different temperatures was investigated by characterizing the surface layers formed at specimens with a scanning electron microscope (SEM).

#### 4.3. SEM investigation of surface layers

Figure 8 a) shows a microstructure image of ferritic and perlitic steel K55 in the SEM at a magnification of 300. Figure 8 b) also shows the microstructure of the steel K55 but at a higher magnification of 1000.





Figure 8: Microstructure of steel K55 a) 300x b) 1000x.

In Figure 8, the pearlite grains are shown having different shades of grey, while the ferrite grains have a uniform, white or gray color.

Specimens with layers have been cut partially and the residual ligament was broken after cooling in liquid nitrogen to obtain a brittle fracture and to characterize the surface layers. Figure 9 a) shows a layer of steel K55 in a SEM at a magnification of 30x. Figure 9 b) also shows the layer on steel K55 but at a larger magnification (100x) and Figure 9 c) is a magnification of 300x. Specimen was tested in gas C with 1 g/l NaCl immersed in gas and electrolyte at 25 °C. There is no uniform layer but a porous and not dense one with many flakes and microcracks.





Figure 9: Surface of steel K55 after exposure to gas C, immersed in gas and electrolyte (1g/l NaCl) at room temperature, a) 30x, b) 100x and c) 300x.



In Figure 10 element mappings of the surface of the same specimen are shown to characterize the chemical composition of the layer. There is a mixed oxide-sulfide layer on the surface and a clear distinction (separation), whether the oxide or sulfide is the top layer cannot be given. Therefore, a cross section was prepared, shown in Figure 11.



Figure 10: Element mappings of the surface of steel K55 tested in gas C, 1 g/l NaCl, immersed in gas and electrolyte, room temperature.

In Figure 11 a metallographic section for better characterization of the layer is shown. The SEM images were taken at magnification 30x, 300x and 1000x. In the higher magnification images, it is clear that the layer is not uniform. It can also be seen, that the layer is porous and not dense and tends to spall off.









Figure 11: SEM images of cross section of steel K55 tested in gas C with 1g/l NaCl (immersed in gas and electrolyte) at room temperature, a) 30x, b) 300x and c) 1000x.



Element mappings of the layer are presented in Figure 12. The layer consists of two parts, an inner iron oxide and an outer sulfide layer. These two layers are not distributed uniformly on the surface. There is a high degree of spelling off.



Figure 12: Element mappings of layer on steel K55 tested in gas C, 1 g/l NaCl, immersed in gas and electrolyte, room temperature.

In Figure 13 SEM images of steel K55 tested in gas C, 1g/l NaCl, immersed in gas and electrolyte, 120 °C, are shown in three magnifications. There is a uniform layer of corrosion products.





Figure 13: Surface of steel K55 after exposure to gas C, immersed in gas and electrolyte (1g/l NaCl) at 120 °C, a) 30x, b) 100x and c) 300x.



In Figure 14 element mappings are shown to characterize chemical composition of the layer. In the individual element evaluations, it can be seen that there are two different layers. The oxide layer is the inner layer and the outer layer is the sulfide layer. The iron sulfide layer is more densely packed and this inhibits more the hydrogen uptake. For determination of layer thickness a metallographic cross section was prepared, shown in Figure 15.





Figure 14: Element mappings of the surface of steel K55 tested in gas C, 1 g/l NaCl, immersed in gas and electrolyte, 120 °C.

The SEM images of the section show that the layer is uniform (Figure 15). It is also observed, that the layer is more uniformly distributed on the surface, compared to tests at room temperature. This says for a better barrier to hydrogen absorption at higher temperatures, so that the absorbed hydrogen content is lower at 120 °C when compared to room temperature.





Figure 15: SEM images of cross section of steel K55 tested in gas C with 1g/l NaCl (immersed in gas and electrolyte) at 120 °C, a) 30x, b) 300x and c) 1000x.



Figure 16 shows the chemical analysis of the layers in element mappings. Two layers are clearly visible, an oxidic and a sulfidic one. Both layers are clearly separated from each other and obviously more dense when compared to the layers obtained at room temperature.



Figure 16: Element mappings of layer on steel K55 tested in gas C, 1 g/l NaCl, immersed in gas and electrolyte, 120 °C.

#### 4.4.Permeation tests

By performing the permeation tests, the effective hydrogen diffusion coefficient has been determined, which gives information about the trapping behaviour of the material. The permeation test was conducted according to standard ISO 17081 in a Devanathan-Stachursky-Cell. By multiple charging and decharging of the material it can be determined, whether deep or flat hydrogen traps are present in the material and which type predominates.

The oxidation current was measured over the time to determine the effective diffusion coefficient. Results from hydrogen permeation tests on steel K55 can be seen in Figure 17. In Figure 17 a) the permeation current as function of time for 2 consecutive loadings can be seen, in Figure 17 b) a detail of the permeation current as function of time for first loading with evaluation is shown, in Figure 17 c) a detail of the permeation current as function current as function of time for the second loading with evaluation is given.





Figure 17: a) Results from hydrogen permeation tests on steel Permeation current as function of time for 2 consecutive loadings, b) detail permeation current as function of time for 1<sup>st</sup> loading with evaluation, c) detail permeation current as function of time for 2<sup>nd</sup> loading with evaluation.

The first loading has an effective diffusion coefficient  $D_{eff}$  of  $6.22 \cdot 10^{-6} \frac{cm^2}{s}$ , seen in Table 1 and the second loading has an  $D_{eff}$  value of  $7.96 \cdot 10^{-6} \frac{cm^2}{s}$ , see Table 2. There is a small amount of deep traps and the second loading is slightly faster than the first one. The literature confirms, that the value is within the range for carbon steels. The results show diffusion coefficients for non-sour gas resistant steels as expected from the literature review as well.

Table 2: Effective diffusion co	coefficient of hydrogen in steel	K55 at room temperature
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# loading	$D_{eff}\left[\frac{cm^2}{s}\right]$			
1	6.22 · 10 <sup>-6</sup>			
2	7.96 · 10 <sup>-6</sup>			



## 5.Investigation of steel L80

# 5.1. Time to failure of Constant Load Tests (CLT) specimens

Figure 18 shows the time to failure of tempered martensite steel L80 for all gas compositions. No fracture occurred under any condition. The Figure 18 below shows as an example time to failure in gas D. No cracks at all occurred for the steel L80. The same happened for gases A, B and C.



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Figure 18: Time to failure of a tempered martensitic steel L80 in gas D: 120 bar H_2 + 15 bar CO_2 + 1 bar H_2S.
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#### 5.2.Hydrogen content

Figure 19 illustrates the hydrogen uptake at 25 °C in a) gas A and b) gas B, both gases do not contain hydrogen sulfide H<sub>2</sub>S. Figure 19 c) shows the uptake in gas C and Figure 19 d) shows the hydrogen content after exposure to gas D. In the autoclave tests with the steel L80 at room temperature, the lowest value is 0.09 ppm for gas A (see Figure 19 a)) and the highest value is 1.03 ppm for gas C (see Figure 19 c)), the amount of hydrogen was measured using TDS. There is a certain hydrogen uptake in gases C and D when an electrolyte is present. This is due to the lowering of the solution pH by H<sub>2</sub>S.





Figure 19: Hydrogen uptake of L80 in autoclave tests at RT in, a) gas A (120 bar  $H_2$ ), b) gas B (120 bar  $H_2 + 15$  bar  $CO_2$ ), c) gas C (120 bar  $H_2 + 1$  bar  $H_2S$ ) and d) gas D (120 bar  $H_2 + 15$  bar  $CO_2 + 1$  bar  $H_2S$ ).

Figure 20 shows the results after testing L80 in all conditions at 120 °C. In the autoclave tests with the steel L80 at 120 °C, the lowest value is 0.15 ppm for gas A (see Figure 20 a)) and the highest value is 0.32 ppm for gas D (see Figure 20 d)). There is almost no hydrogen uptake in the autoclaves. Even H<sub>2</sub>S containing conditions results in low H concentrations in the steel compared to tests at room temperature.





Figure 20: Hydrogen uptake of L80 in autoclave tests at 120 °C in, a) gas A (120 bar H<sub>2</sub>), b) gas B (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub>), c) gas C (120 bar H<sub>2</sub> + 1 bar H<sub>2</sub>S) and d) gas D (120 bar H<sub>2</sub> + 15 bar CO<sub>2</sub> + 1 bar H<sub>2</sub>S).

The table 3 below compares the hydrogen uptake for different conditions at room and at high temperatures.



		Hydrogen content [ppm] after immersion in						
		dry gas	humid gas (1 g/l)	electrolyte (1 g/l)	gas + electrolyte (1 g/l)	humid gas (200 g/l)	electrolyte (200 g/l)	gas + electrolyte (200 g/l)
	gas A	0.09	-	0.19	0.14	-	0.10	-
room temperature	gas B	0.11	0.20	0.18	0.17	0.19	0.12	0.16
	gas C	0.14	0.51	0.47	0.38	0.77	0.83	1.03
	gas D	0.17	0.82	0.96	0.34	0.82	0.46	0.67
	gas A	0.36	0.20	0.20	0.16	0.19	0.15	0.20
120 °C	gas B	0.16	0.23	0.21	0.16	0.18	0.25	0.25
	gas C	0.18	0.16	0.16	0.26	0.28	0.18	0.17
	gas D	0.17	0.17	0.30	0.19	0.17	0.32	0.21

Table 3: Hydrogen uptake of steel L80 in autoclave tests at 25 °C and 120 °C in, a) gas A (100 bar  $H_2$ ), b) gas B (120 bar  $H_2 + 15$  bar  $CO_2$ ), c) gas C (100 bar  $H_2 + 1$  bar  $H_2S$ ) and d) gas D (100 bar  $H_2 + 15$  bar  $CO_2 + 1$  bar  $H_2S$ ).

g/l = g/l NaCl

The tempered martensitic material L80 is more susceptible to hydrogen embrittlement than the ferritic perlitic steel K55 with lower strength. Nevertheless, the 22 HRC criterion for resistance to  $H_2S$  is met and this is confirmed by the fact that no cracking at all did occur.

#### 5.3.SEM investigation

Figure 21 shows the microstructure of tempered martensite steel L80 at a 300x and 1000x magnification. The grain size is between 20 and 40  $\mu$ m, which is fine. There are only very little non-metallic inclusions.





Figure 21: Microstructure of steel L80, a) 300x, b) 1000x.

#### 5.4.Permeation tests

The oxidation current was measured as function of time to determine the effective diffusion coefficient. Results from hydrogen permeation tests on the tempered martensite steel L80 can be seen in Figure 22. In Figure 22 a) the permeation current as function of time for two consecutive loadings can be seen, in Figure 22 b) a detail of the permeation current as function of time for the first loading including the evaluation is shown, in Figure 22 c) a detail of the permeation current as function is presented.





Figure 22: a) Results from hydrogen permeation tests on steel L80 a) Permeation current as function of time for 2 consecutive loadings, b) detail permeation current as function of time for 1<sup>st</sup> loading with evaluation, c) detail permeation current as function of time for 2<sup>nd</sup> loading with evaluation.

The first loading has an effective diffusion coefficient  $D_{eff}$  of  $2.68 \cdot 10^{-6} \frac{cm^2}{s}$  and the second loading  $D_{eff}$  has a value of  $3.98 \cdot 10^{-6} \frac{cm^2}{s}$  (Table 4). These values are comparable to those found in the literature. The steel L80 has more traps, as this steel is also more deformed than the ferritic-pearlitic steel. Consequently the diffusion coefficients are lower.

#### Table 4: Effective diffusion coefficient of hydrogen in steel L80 at room temperature

# loading	$D_{eff}\left[rac{cm^2}{\mathrm{s}} ight]$			
1	2.68 · 10 <sup>-6</sup>			
2	3.98 · 10 <sup>-6</sup>			





### Hystories project consortium





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