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Transforming Black Liquor to Biofuel

Research and Innovation Action
H2020-LC-SC3-2019-NZE-RES-CC

D1.5 - Report on corrosion resistant alloys and recommendations (M30)

performance of the most relevant metal alloys
for HTL conditions.

WP1 - Task 1.5

Date [20220921]

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Abbreviations and acronyms

Acronym	Description
BL	Black Liquor
CRA	Corrosion Resistant Alloys
EDS	Energy Dispersive Spectroscopy
EFC	European Federation for Corrosion
HTL	Hydrothermal Liquefaction
ICC	Inter Crystalline Corrosion
ICC	Intercrystalline Corrosion
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IG	Inter-granular
NACE	National Association of Corrosion Engineers
SC	Super Critical
SCC	Stress Corrosion Cracking
SDSS	Super-Duplex Stainless Steel
SEM	Scanning Electron Microscopy
SINTEF-ER	SINTEF Energy Research
SS	Stainless Steel
WP	Work Package
XRF	X-Ray Fluorescence



Executive Summary

As of September 2022, the corrosion- and materials evaluation study in a) water-based simulated black liquor and b) water-based simulated black liquor at super-critical conditions was successful. The conclusion from the testing program was that the most resistant alloy for the defined conditions is the chrome-rich carbon steel candidate P91 (UNS K91560). This is a type of creep strength enhanced ferritic (CSEF) alloy, which are steels designed to retain strength at extremely high temperatures. The P91 abbreviation represents the material's chemical composition, i.e. 9wt% chromium (Cr) and 1wt% molybdenum (Mo). Further work is required to at conclude on corrosion resistance for the P91 quality at supercritical conditions in the welded condition and to better understand caustic corrosion mechanisms. The progression and the results were consecutively reported at the monthly meetings and stored at BL2F's Eduuni web-site.

Keywords

Black liquor, Fuel, Aviation, Shipping, Corrosion, Stress corrosion cracking, Caustic Corrosion, HTL, Super critical conditions

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1 Introduction

Black Liquor to Fuel (BL2F) is a Horizon 2020 project that will produce drop-in biofuels for aviation, transport and shipping, using black liquor, a side stream of the chemical pulping industry as raw material. By using cost-effective and low-emission refinery processes, BL2F will help provide solutions to the demand for more environmentally friendly fuels for aviation and shipping, see: <http://www.bl2f.eu/>. The project is EU funded, has 12 participants from 8 countries, and it will last for 3 years. Among the partners you find both Valmet and Neste who are "business significant" in the designing and manufacturing of the future full-scale HTL-process plants for converting black liquor to fuel.

In this project, suitability of different types of alloys as reaction vessel- and process component material was evaluated by testing in simulated- and in real process conditions with special focus on resistance to corrosion and/or cracking. The testing program was performed by SINTEF.

Task description for Task 1.5 Material selection and corrosion (SINTEF, SINTEF-ER, Valmet) [M1-M30].

To make HTL a viable industrial process, the corrosion resistance of the candidate construction materials must be known. In Task 1.5, industrially relevant construction alloys will be exposed to artificial and real HTL conditions. Different commercial alloys will be evaluated for application in a full-scale plant in cooperation with the project partner Valmet. SINTEF will produce small C-ring test specimens for each alloy that are stressed to their respective yield strength at the test temperature, i.e. compensated for high temperature de-rating. To obtain the specific stress levels equal to yield for the different alloys, tensile testing will be conducted at the actual test temperature for each alloy and then used as basis for correct deflection of the C-ring specimens. Correct deflection (stress) will then be obtained by strain control and use of strain gauges. Deflection will stop when the target strain, corresponding to the yield strength, is achieved. Prior to testing in real HTL conditions, screening testing of the different candidates will be carried out in simulated water-based black liquor and then examined for corrosion and cracking. Then, to mimic the real conditions as good as possible, the most promising alloy candidates will be exposed in the same electrolyte in SINTEF-ER's continuous HTL reactor at super critical conditions (both flowing and stagnant). Selection of candidates for this test at supercritical conditions will be based on the results from the initial screening test and expected lifetime, durability, formability, weldability, sourcing aspects like delivery time and redundancy, industrial experience and costs. Specific conditions for this final test in water based simulated black liquor at supercritical conditions will be adapted from other WPs to ensure realistic conditions for the BL2F project and further upscaling. After all testing, possible forms of corrosion and/or cracking will be evaluated by microscopic examination. Then the specimens will be sectioned for further detailed metallographic examination to conclude on extent of corrosion or cracking and plausible mechanism(s). When found necessary, SEM and other techniques will be used for further post-test analyses and characterization as basis for the final recommendations on suitable material qualities in a full-scale plant.

2 Experimental: Corrosion screening test of selected material candidates

A thorough selection of candidate materials and corrosion testing strategy has been carried out at SINTEF according to the workplan. Before a list of potential material candidates for application in a full-scale BL2F plant was established as basis for the corrosion testing program, several criteria were evaluated:

- Industrial experience and recommendations
- Expected lifetime
- Extent of maintenance and inspection
- Availability and redundancy
- Price
- Delivery time
- Weldability
- Formability/machinability
- Mechanical properties (durability), and
- IPR/sharing/publishing aspects

Since high pH environments at supercritical conditions with aggressive organic (radical) species are not typical conditions used as basis for development of large volume corrosion resistant alloys (CRAs), both literature research and discussions with contacts within chemical processing industry, as well as project partners, was required. It was also noted that some suppliers did not want to reveal their identity through post-test publishing of a test program like this.

Further, it was a go no-go criterion that high costs for development of brand-new alloys is not compatible with costly development of a new alternative process for drop-in fuel competing with established fossil fuel alternatives. The same applied for patented tailor-made alloys available at one supplier only. Hence, it was agreed that well known commercially available qualities provided by several suppliers should be selected.

Based on internal discussions within the project, it was also proposed to include a couple of Al-containing qualities widely used in e.g. syngas processes for production of hydrogen, ammonia and methanol, and reformers in the chemical and petrochemical industries. These are characterized by very good corrosion resistance in carburizing and oxidizing media as well as excellent resistance to metal dusting, high-temperature creep, and oxidation at high temperatures.

The well-known pressure vessel steel quality P91 (EN 10222-2) in the normalized and tempered condition, was also proposed by the project.

Summarized, it was decided to include the following qualities in the corrosion test program:

- Titanium grade 2
- Stainless steel alloy 316, SAF 2507 and 254 SMO
- Nickel-chromium-molybdenum based alloy Inconel 625 and Hastelloy C276
- Nickel-chromium-aluminium alloy 602 CA and 699 XA
- The chrome-rich carbon steel P91 (X10CrMoVNb9-1)

Un-alloyed carbon steel qualities were not selected as the corrosion rate will be unacceptable high and potentially cause problems with clogging etc. of critical process equipment in addition to extended need for maintenance, inspection and replacements.

A detailed presentation of the selected 9 material candidates for the corrosion testing are presented in Figure 1.

Pipe no.	Plate no.	Marked	Grade	UNS No.	C%	Si%	Mn%	P%	S%	Cr%	Ni%	Mo%	Co%	Cu%	Al%	N%	V%	Nb%	Nb +Ta%	W%	Zr%	Y%
1		None (paper tube)	Ti grade 2	R50400	0,006											0,005						
2		Sandvik 3R60	316	S31603	0,02	0,45	1,64	0,03	0,007	17,34	13,12	2,63	0,12	0,26	0,003	0,037						
3		Sandvik SAF2507	25Cr SDSS	S32750	0,013	0,28	0,44	0,02	0,0005	25,35	6,46	3,85	0,11	0,13	0,014	0,29						
4		2X22RK69	254 SMO	S31254	0,012	0,44	0,43	0,025	0,0005	19,97	17,78	6,12	0,091	0,65	0,02	0,2						
5		EN10216-2, ASTM A3350	X10CrMoVNb9-1	K94560 P91	0,095	0,31	0,5	0,014	0,001	8,23	0,27	0,85		0,07	0,01	0,045	0,2	0,066				
6		NiCr22Mo9Nb	Alloy625 (Inconel)	N06625	0,023	0,19	0,07	0,005	0,002	21,6	61,41	8,6	0,03	0,03	0,15			3,35				
7		2.4819-4578	Hastelloy C-276	N10276	0,003			0,005	0,003	16,07	57,01	16,14	0,46				0,19		3,44			
8		NiCroFer 6025 HT, NiCr25FeAlY	Alloy 602 CA	N06025	0,18	0,12	0,1	0,004	0,002	25,36	61,7			0,01	2,23						0,07	0,07
9		30402	Alloy 699 XA	N06699	0,2	0,05	0,01	0,002	0,002	29,6	67,8	0,01		0,01	2,2	0,017	0,14				0,03	



Figure 1. Upper: The short list of 9 potential material candidates to be tested with alloy composition. Lower: Photos of the received test materials.

The testing methodology was approved by the project including the use of a generic simulated water based black liquor. The simulated water based black liquor (see Table 1) was chosen as corrosion media instead of black liquor to prevent an oily protective film from forming on the sample surface originated from the lignin content. By inhibiting the formation of the protective layer, it is expected that the testing time for corrosion can be greatly reduced. Security Data Sheet for Water Based Simulated BL has been created by KIWA. The mixing of a total volume of 45L with the chosen composition (by means of weighing) was purged with N₂(g) while simultaneously cooling.

Table 1. Model simulated water based black liquor defined in the project. Source: David Baudouin and Darius Yeadon, PSI: Mixing while cooling in de-aerated H₂O by bubbling with N₂(g). NaHS is dissolved first because it is oxidized. The organics are added as bases and the NaOH content adjusted.

Salt	wt.% in	g/kg	mmol/kg
	pristine BL		
NaOH	1.2	11.8	295.1
NaHS	0.2	2.3	41.3
Na ₂ SO ₄	1.8	17.6	124.0
Na ₂ CO ₃	1.7	16.6	156.7
NaCl	0.1	1.4	24.2
K ₂ SO ₄	0.6	6.4	47.5
Total	5.62	56.18	688.79
Sodium formate	0.5	4.9	71.8
Sodium acetate	0.3	2.5	30.8
Sodium D-gluconate	0.7	6.6	30.0
Sodium DL-lactate	0.7	7.3	65.2
Guaiacol	2.5	24.5	197.4
Total organics	4.58	45.77	395.20

The test specimens have the form of C-rings to simulate the hoop-stress from the high inside pressure in the real process. Hoop stress is the stress that occurs along the pipe's circumference when pressure is applied. Hoop stress acts perpendicular to the axial direction. Hoop stresses are tensile and generated to resist the bursting effect that results from the application of pressure. Stress-strain curves were generated by tensile testing for the different materials at the desired test temperature to be able to stress (pre-load/deflect) the C-rings with bolts and nuts to achieve the desired yield strength on the inside of the rings. The C-ring test is NACE TM0177 method C /4/, and there is also guidance given in EFC 16 /5/ and EFC 17 /6/, see Figure 2.

To avoid galvanic corrosion problems, the threaded rods and nuts were machined from the same material quality as the C-rings.

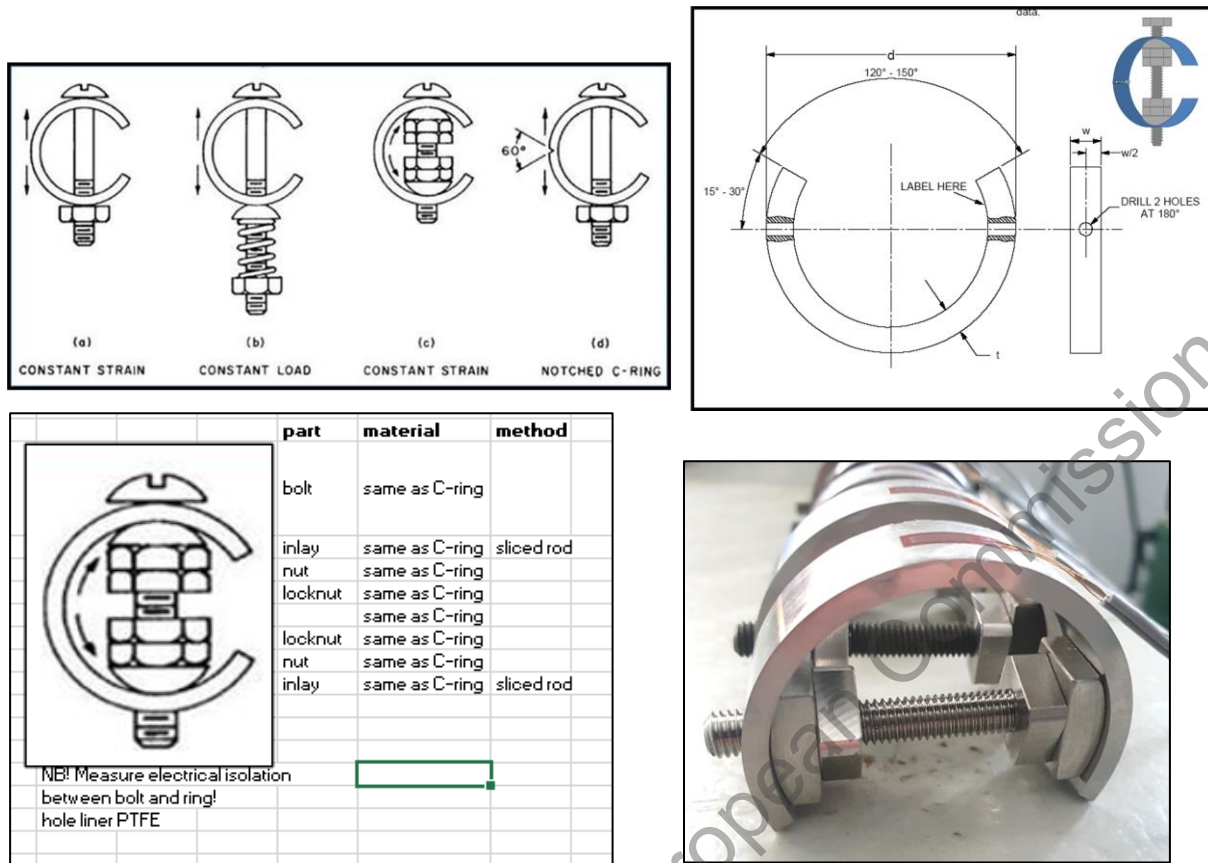
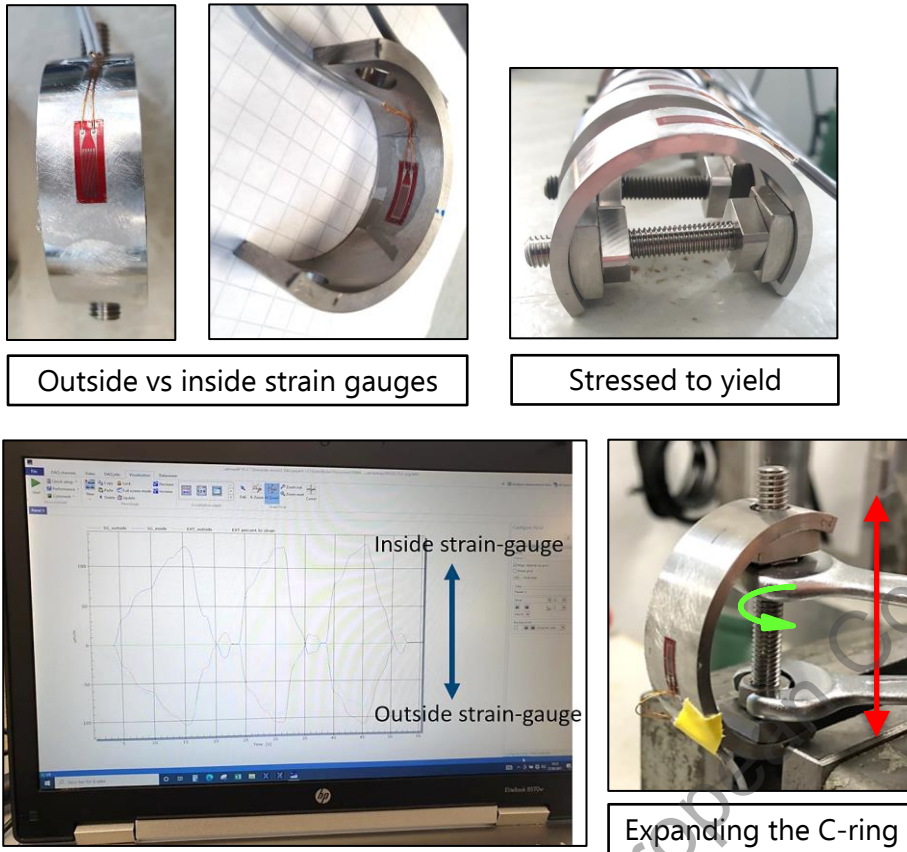


Figure 2. Schematic drawing of C-ring sample according to NACE TM0177 method C.

The C-ring test is effectively a bend/deflection test, suitable for relatively small tubulars. If the ring is compressed, a tensile stress is generated on the outside. However, as pipes usually carry the environment of concern on the inside, the ring must be expanded, producing stress in the hoop direction by opening the C-ring with the centered bolt as shown in Figure 2.

The samples were pre-loaded to achieve the desired inside yield stress by strain control and use of strain gauges. Ideally, in theory, the compression on the outside shall be the same as the strain on the inside. However, this is not the case in practice, and it was therefore produced compression- and corresponding strain data for all materials by use of glued strain gauges on spare specimens. Then, when a compression/strain ratio (correction factor) was found for all materials, the real specimens were deflected by placing the extensometer on the outside and the rings expanded till the target strain values (equal to yield) were achieved, see Figure 3 for this process.



	Candidate	Sample	Target Compression outer (µm/m)	Applied Compression (µm/m)	AYS (Mpa)	Strain at AYS (%) (inner)	Outer Strain Gage (µm/m)	Inner Strain Gauge (µm/m)	Deviation in (%) applied comp./target comp.
Ti grade 2	1	1	-3074	-3052	146	0,426	-3074	4260	1%
		2	-3074	-3074	146	0,426	-3074	4260	0%
		3	-3074	-3074	146	0,426	-3074	4260	0%
316	2	4	-2966	-2982	319	0,406	-2966	4060	-1%
		5	-2966	-3005	319	0,406	-2966	4060	-1%
		6	-2966	-2977	319	0,406	-2966	4060	0%
25Cr SDSS	3	7	-3336	-3339	468	0,411	-3336	4111	0%
		8	-3336	-3335	468	0,411	-3336	4111	0%
		9	-3336	-3319	468	0,411	-3336	4111	1%
254smo	4	10	-2532	-2549	241	0,339	-2532	3390	-1%
		11	-2532	-2529	241	0,339	-2532	3390	0%
		12	-2532	-2525	241	0,339	-2532	3390	0%
X10CrMoVNb9-1	5	13	-3143	-3175	501	0,477	-3143	4770	-1%
		14	-3143	-3172	501	0,477	-3143	4770	-1%
		15	-3143	-3149	501	0,477	-3143	4770	0%
Alloy625 inconel	6	16	-2712	-2689	369	0,374	-2712	3740	1%
		17	-2712	-2719	369	0,374	-2712	3740	0%
		18	-2712	-2762	369	0,374	-2712	3740	-2%
Hastelloy C-276	7	19	-2489	-2485	276	0,35	-2489	3500	0%
		20	-2489	-2477	276	0,35	-2489	3500	0%
		21	-2489	-2477	276	0,35	-2489	3500	0%
Alloy 602 CA	8	22	-2147	-2147	249	0,322	-2147	3220	0%
		23	-2147	-2136	249	0,322	-2147	3220	1%
		24	-2147	-2153	249	0,322	-2147	3220	0%
Alloy 699 XA	9	25	-2273	-2264	232	0,313	-2273	3130	0%
		26	-2273	-2278	232	0,313	-2273	3130	0%
		27	-2273	-2292	232	0,313	-2273	3130	-1%

Figure 3. Measurements of compression on the outside versus strain on the inside of C-rings by use of glued strain gauges on spare specimens to find a correlation factor for final deflection of the test rings. This was done for each material quality since they have different mechanical and de-rating properties.

For the initial screening testing the samples were inserted into an autoclave and exposed at 180°C, 200 bar for 31 days in simulated water based black liquor at stagnant conditions. The initial pH was measured to 12,47 and the oxygen level to 2 ppb, see

Figure 4.

Description	Value
Test method	C-ring (inside in tension = hoop stress) in Autoclave (Ti gr 2, 30L)
Electrolyte composition	Standardised model composition of BL
Temperature	180 °C
Pressure	200 bars
Specimens dimensions	D: 40-60mm WT: 2-5mm
Dissolved oxygen limit	< 10 ppb (actual 2ppb, pH 12,47)
Surface finish	Ground to SiC 500
Stress level (by strain control)	Ref. NACE (100 % AYS)
Test duration	4 weeks
3 winner material candidates to be exposed in SINTEF ENERGY reactor @ supercritical conditions	

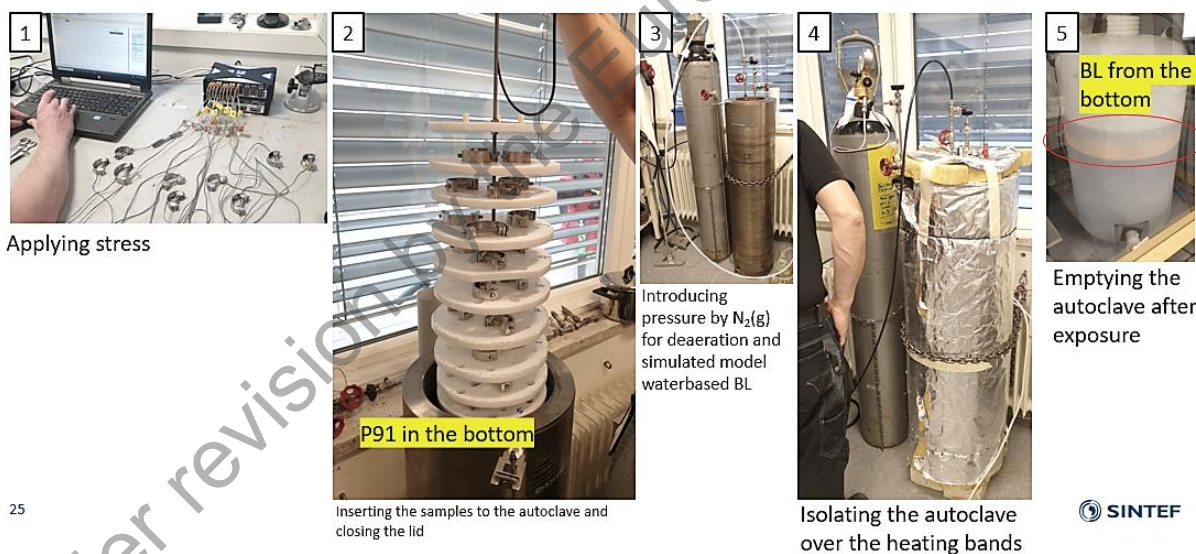


Figure 4. Screening test description and experimental setup with autoclave.

3 Experimental: Corrosion testing at super critical conditions in the SINTEF-ER HTL-reactor

The winner candidates were chosen based on corrosion performance in the screening tests (pitting, cracking, intergranular corrosion, general corrosion), material aspects (forming, weldability, machinability) and commercial aspects (availability, delivery-time, price, redundancy of suppliers, common practice). The material and commercial aspects were revealed through interviews with the manufacturers. This evaluation gave 4 "winner" candidates, 254SMO, P91, HastelloyC276 and 699XA, to undergo further testing in the SINTEF ER reactor at 390°C, 350 bar in the simulated model water based black liquor. was done

As for the screening testing reported above, it was machined rods and nuts from the same material quality as the C-rings to avoid galvanic corrosion. Thereafter, the C-rings were pre-loaded with strain-gauges to achieve the desired inside yield strength at 390°C.

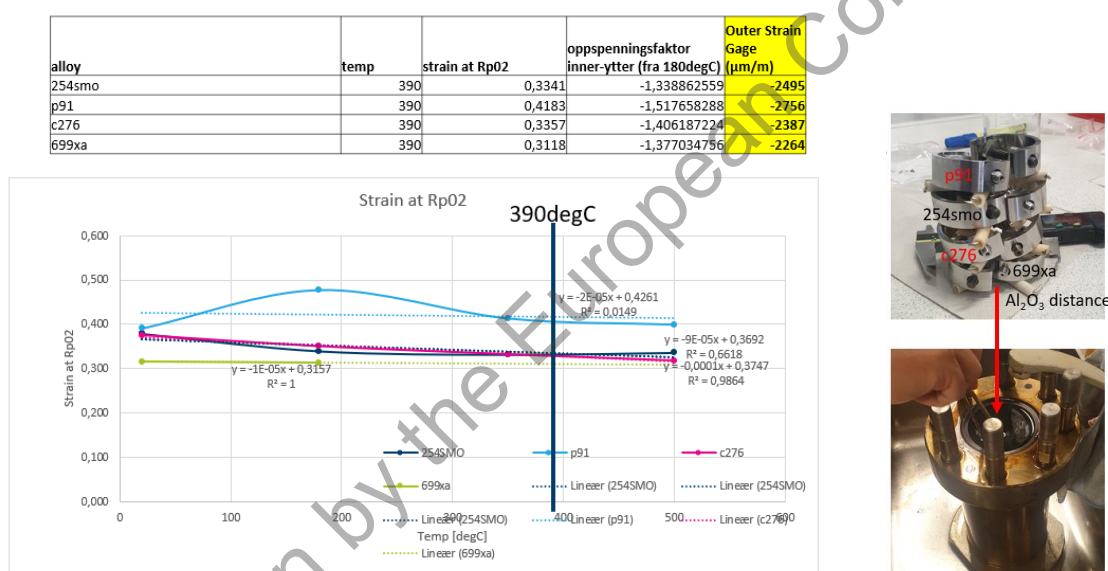


Figure 5. Left: Outside compression vs. inside stress at yield at 390°C (based on in-house data and some extrapolation). Right: C-rings insertion into the HTL-reactor.

SINTEF Energy Research has processed black liquor in continuous mode and produced a sample for the project partners for analyses and further use. An experimental campaign was carried out at two different temperatures and black liquor to water ratios to find the optimum processing conditions, which were 390°C and 300 bar. The SINTEF-ER reactor does not have a salt separation option, but the biocrude and aqueous phase samples are very useful to avoid further delays in the project and be able to proceed with work that requires that. At SINTEF-ER, the produced biocrude was analysed in TGA (thermogravimetric analyser) which revealed a rather high inorganic (salt) content as well as corrosive volatiles [3]. Further analyses were performed by TAU. The SINTEF-ER reactor was thereafter slightly modified to perform the long-term experiments with the metal alloys. The modifications consisted of de-risking of the experimental setup, where valves were mounted to be able to turn the reactor to batch mode in case of clogging. If that happens the reactor will be switched to batch mode and the experiments will be performed as planned. Long-term pressure tests both cold and hot were carried out to ensure that the reactor can keep the necessary conditions even in batch mode. Switching to batch mode is expected to have a no-

to-minor effect on the results, as the alloys will be exposed to the right conditions. In addition, a sampling point for measurement of the dissolved oxygen in the water was implemented and a test was carried out to establish knowledge on oxygen content in the liquid during experiments. Dissolved oxygen can compromise corrosion results, and the dissolved oxygen level was within an acceptable level $\sim 10\text{-}20\text{ppb}$. As mentioned before, the experiments were carried out in a water based liquid solution that resembles black liquor but where the lignin is removed. The reason was two-fold. Firstly, it is observed that the biocrude, mainly consisting of the product from lignin forms a protective layer (oil-film) on the surfaces which is expected to inhibit/reduce corrosion. Allowing that would require much longer tests to reveal the alloys' suitability to these conditions. Secondly, black liquor is not a standard resource, it varies severely among pulp mills. Hence, the corrosion results will be conservative by using a standardized solution developed in BL2F and will cover for formation of corrosive water pockets that often form inside tubing, tanks etc. in process plants.

The exposure in the SINTEF-ER HTL-reactor with the same simulated water-based BL as used in the screening test purged with $\text{N}_2(\text{g})$ for degassing of dissolved O_2 , see Figure 6. The O_2 -concentration was optically measured in the electrolyte by a Fibox 3 LCD stand-alone fiber optic oxygen meter based on use of a 2 mm optical in-situ fiber. The oxygen concentration was $< 10\text{ppb}$ O_2 , measured in the SINTEF-ER reactor before start-up.

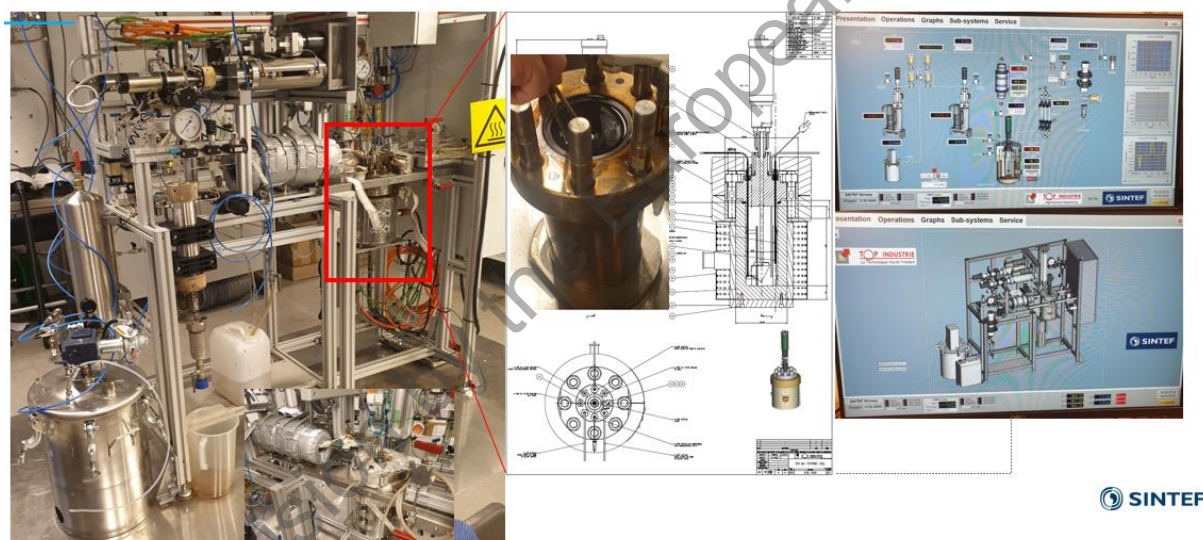


Figure 6. Pictures of the SINTEF ENERGY reactor operating at supercritical conditions in simulated model water based black liquor.

The long-term corrosion test was performed in a semi-continuous mode, by continuously operating during daytime at the first days and leaving the reactor at batch conditions during night-time. Due to clogging, the reactor was operated only in batch mode after the first week. Figure 7 shows the reactor conditions during the test, indicating the correct pressure and temperature conditions ($390\text{ }^\circ\text{C}$; 300 bar) during the entire test period. The figure indicates also that there were disturbances due to clogging also during the first week but at that time, continuous operation was still possible with increased pump pressure and reduced flow.

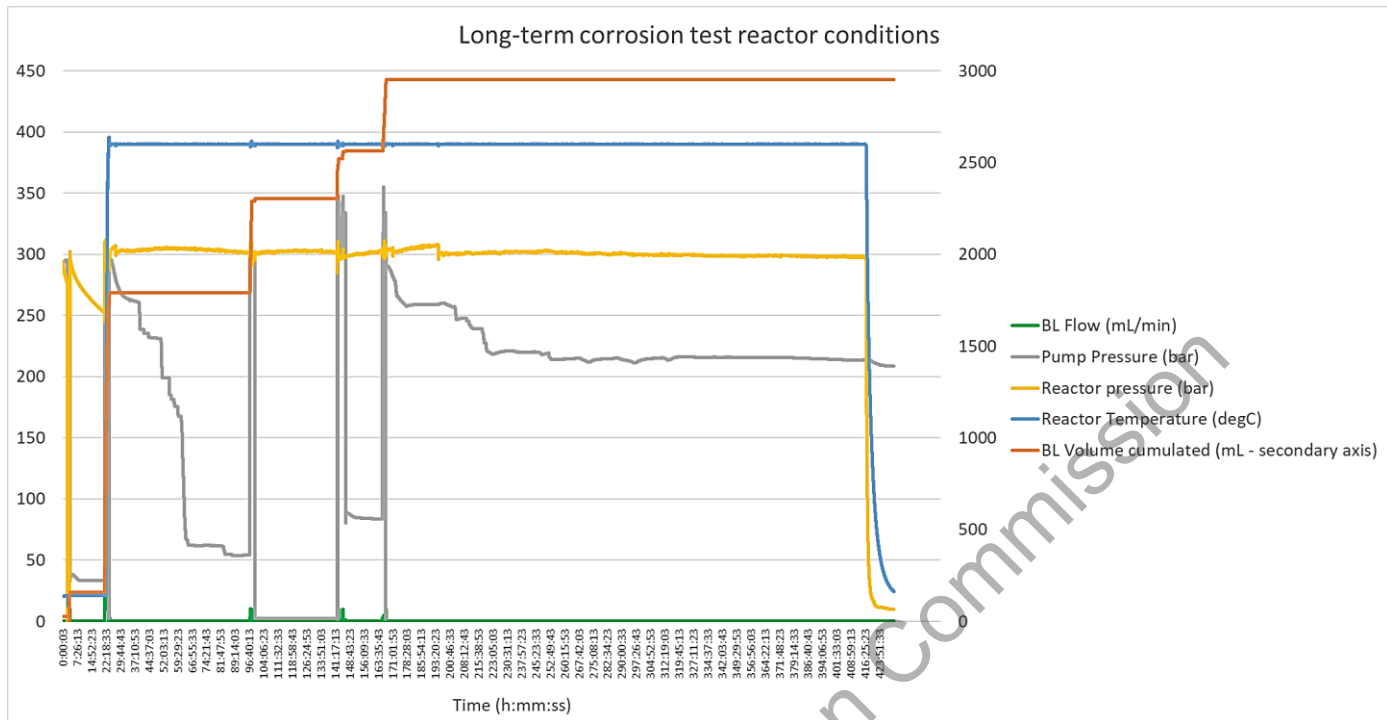


Figure 7. Reactor conditions during long-term corrosion tests. BL: simulated water based black liquor

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4 Results

Salt deposits were clogging the reactor and were found at the inlet to the reactor, in the reactor (both on the sample spacers and at the reactor bottom) and at the outlet as well. The clogging was seen to consist of salt crusts, see Figure 8.

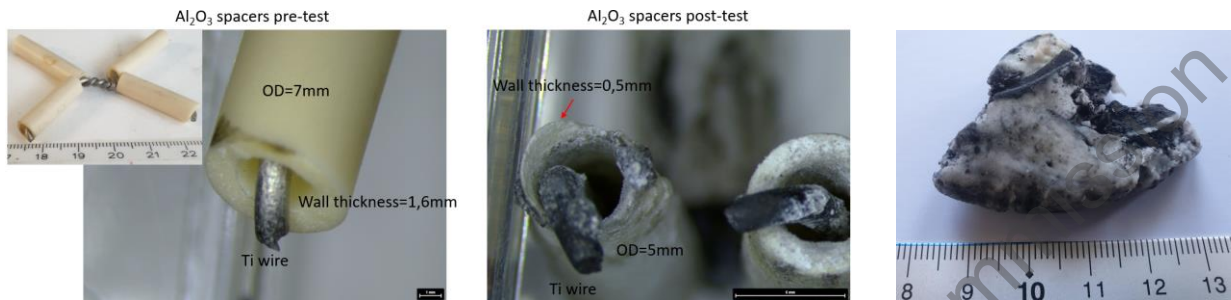


Figure 8. Left: Images of alumina spacers on Ti-wire suffering from dissolution in SC conditions. Right: salt crust found at the bottom of the reactor after the test.

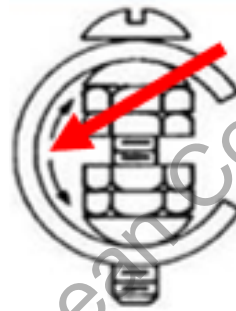
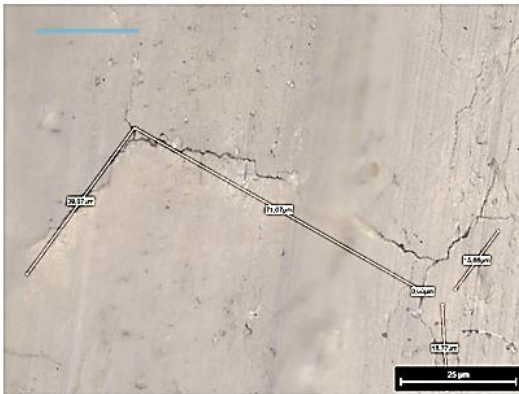
Analysing the salt crusts with ICPMS showed the presence of Na (from the BL), Cr, Mn, Fe, Ni, Mo, W and Al from the corroded samples and the alumina spacers, and N from the HNO₃ in which the salt crusts were dissolved.

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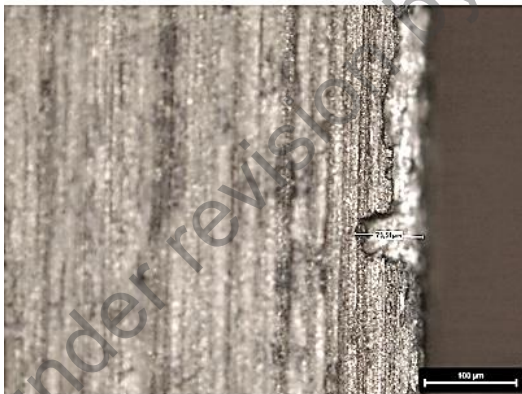
4.1 Ti Gr.2, AISI 316, SAF 2507, Inconel 625 and 602 CA

After the screening test, the post-test examination revealed an unacceptable corrosion performance of Ti grade 2, AISI316, SAF2507, Inconel 625 and 602 CA, see Figure 9. These alloys were hence not included in the final exposure to the supercritical conditions in the SINTEF ER reactor.

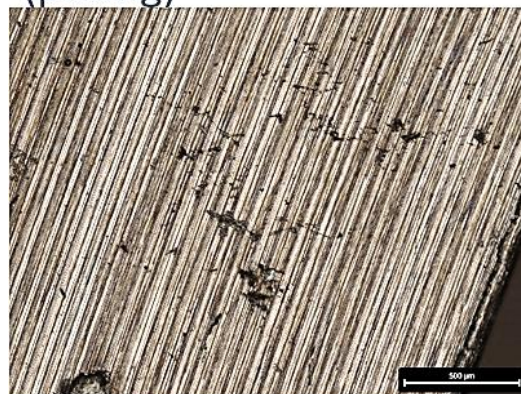
Sample 1, Ti grade 2
(pitting, cracking)



Sample 2, AISI 316
(pitting)



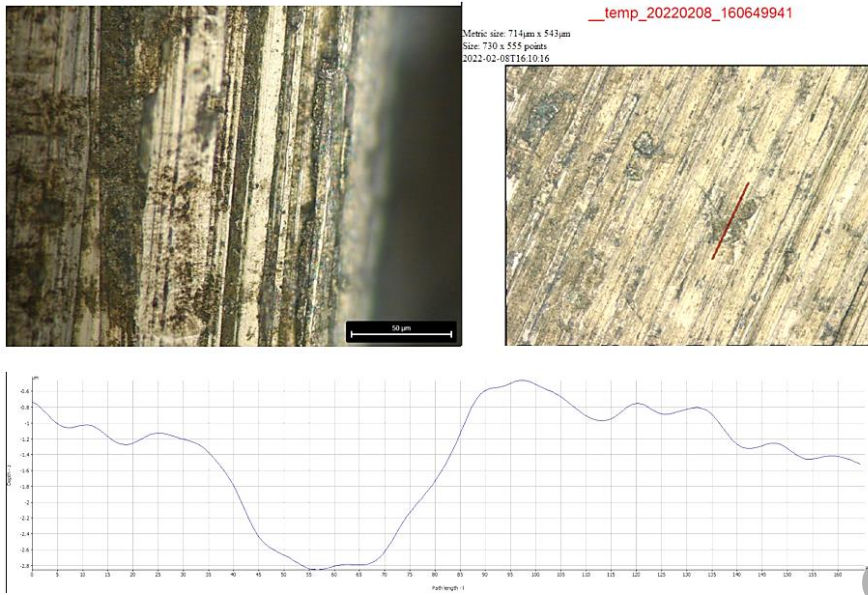
Sample 3, SAF
2507, SDSS
(pitting)



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Inconel 625 (some pitting)



602 CA (some pitting and inter-crystalline corrosion)



Figure 9. Optical microscopy images obtained from post-screening test examination of the inner, stressed edge of the C-rings as indicated by the red arrow (upper right on previous page). Candidates with insufficient corrosion resistance:

- Ti grade 2**
- AISI 316**
- SAF 2507**
- Inconel 625**
- 602 CA.**



4.2 254SMO

The optical microscopy images of 254SMO, SAF 2507(SDSS) as tested is seen in revealed burnt-in BL residue and salt crystals. Some cracking of the tension side indicating stress corrosion cracking (SCC) was also seen.



Figure 10. Post-test analysis of 254SMO by optical imaging of tension side

The SEM/EDS analysis revealed stress corrosion cracking on the tension side and a delaminated oxide layer of about 2-5µm. This layer was partly separated from the sample surface and was richer in O, Ni and Mo compared to the substrate but lower in Fe and Cr. The Ti is most probable coming from the dissolved spacer wires which has precipitated on the sample surface. Also, Si grains from the polishing SiC-paper is seen.

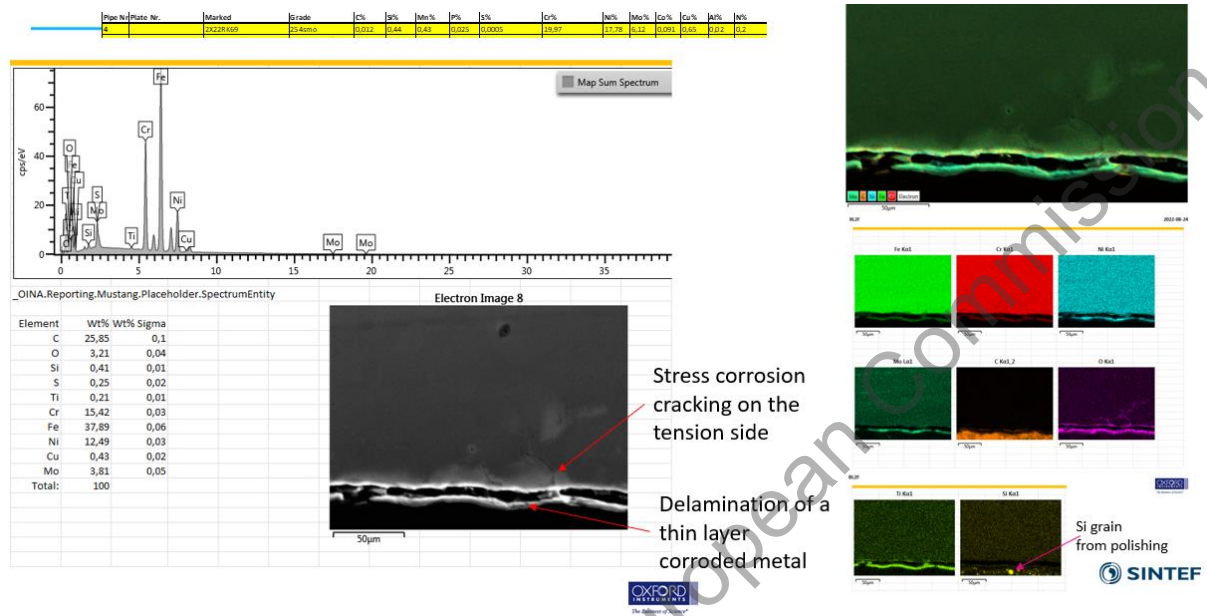


Figure 11. Post-test SEM/EDS element mapping of 254SMO revealing SCC and a thin delaminated oxide layer on the stressed surface.

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4.3 P91

For the P91 samples, some crevice- and edge corrosion were seen on the nuts and hemispheres (also made of P91) used for tensioning of the C-rings. Also, residues from the BL and salt crusts were seen. However, very little signs of corrosion were evident on the stressed inside of the P91 C-rings after the 18 days of exposure in SC environment in the SINTEF-ER reactor, see Figure 12. Some minor pitting corrosion was seen in the mid-section of the C-ring, see Figure 13.



Figure 12. Post-test analysis of P91 performed with optical microscopy of sections.

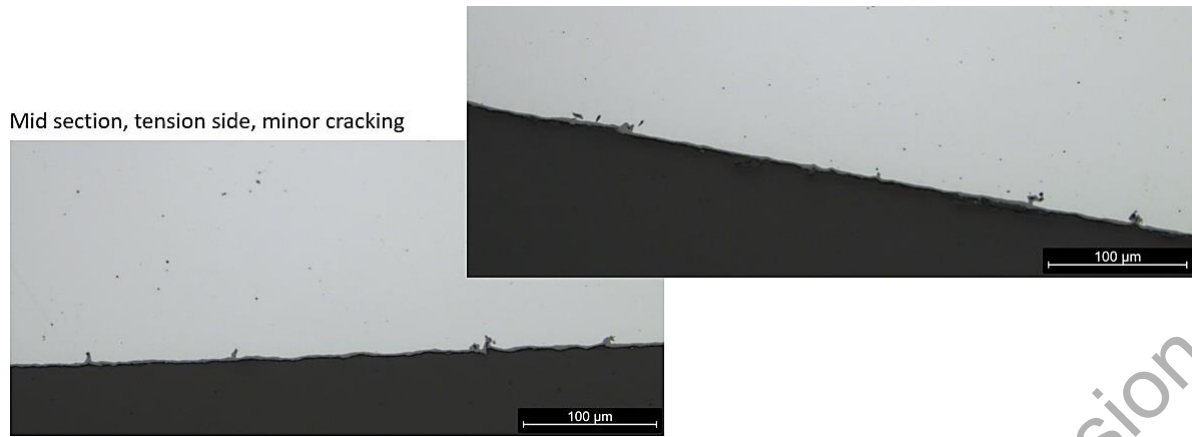


Figure 13. Optical microscopy images of P91 mid-section after exposure to SC conditions revealing only minor pitting.

Also, the SEM/EDS analysis revealed a Cr-rich oxide layer probably due to selective corrosion leaving Cr behind, evenly distributed on the sample surface, see Figure 14. The Si intense spot is suggested to come from the polishing of the section (SiC-paper).

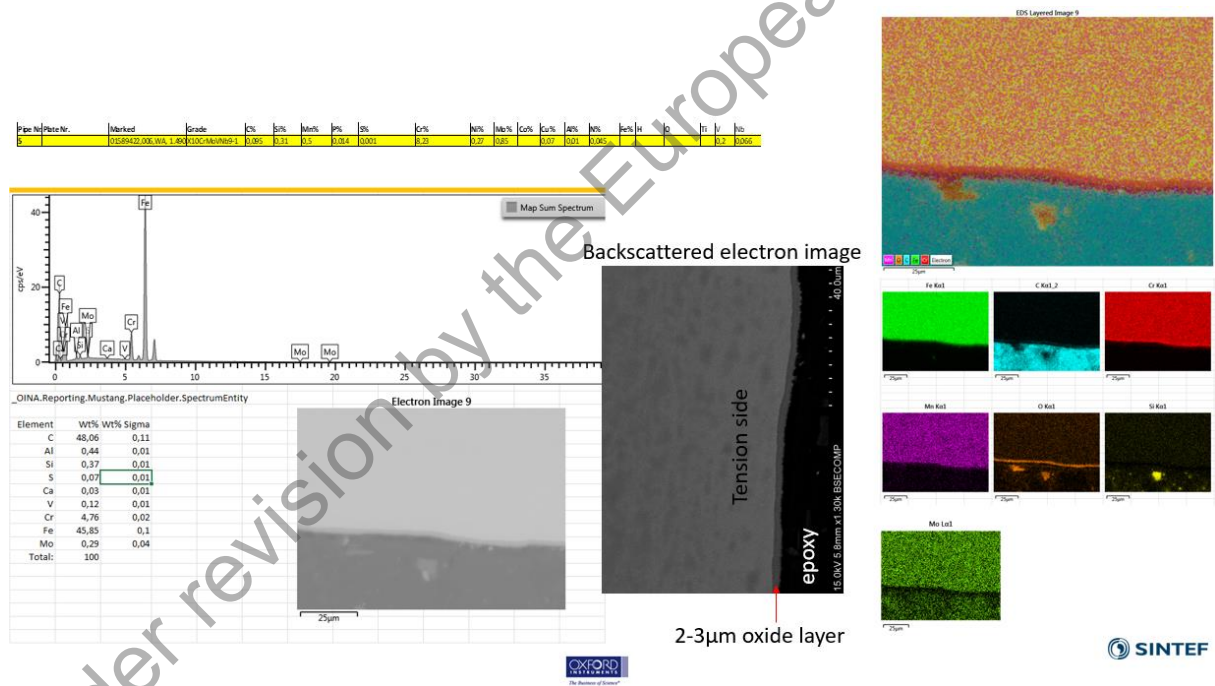


Figure 14. In the SEM/EDS mapping it is seen that the oxide layer is richer in Cr compared to the substrate on the exposed P91 samples.

4.4 Hastelloy C-276

For the austenitic Ni-base Hastelloy C-276 samples, BL residues and salt crystals on the exposed surface were found. Pitting corrosion was evident on the stressed inner edge of the C-rings and on the surface, see Figure 15.

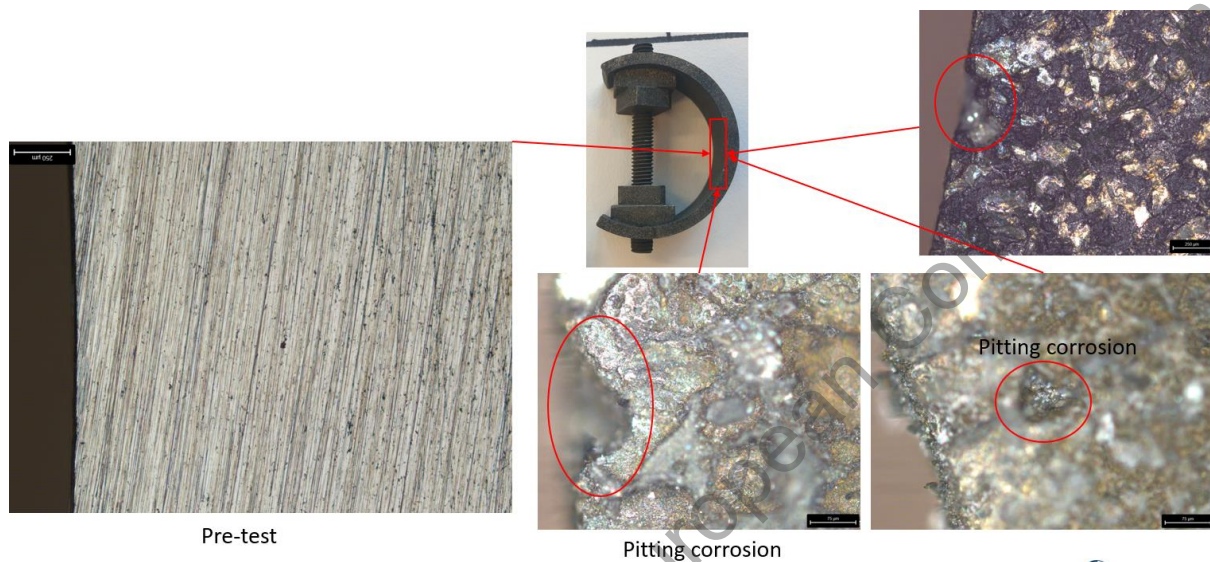


Figure 15. Optical microscopy images of C276, as tested. Burnt-in BL residue and salt crystals on samples are seen after cleaning with ethanol and acetone in ultrasonic bath.

A more detailed analysis showed that also intercrystalline corrosion had taken place with the loss of occasional grains because of the applied stress in combination with corrosion, see Figure 16.

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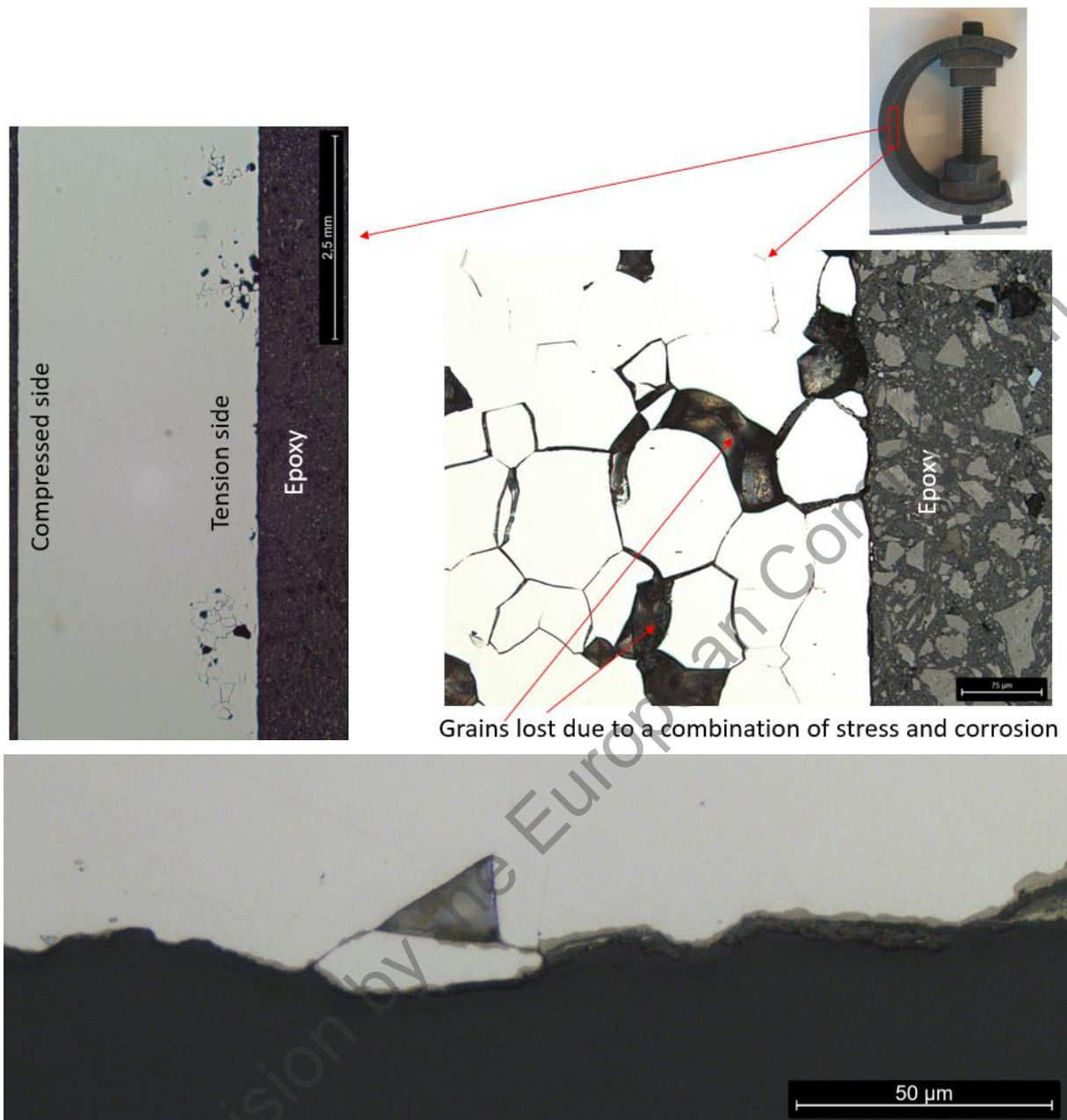


Figure 16. Optical microscopy images of as tested C-276 C-rings. The loss of some grains is seen because of the combination of applied stress and corrosion.

In the SEM/EDS mapping images below, the lost grains can be seen as black voids. The sharp sides and edges around the lost grains suggest that they have failed along the grain boundaries. Also, some stress corrosion cracking is seen. There is an additional layer which is rich in Cr, Mn, Fe and Al. The Al is believed to originate from the partly dissolved alumina spacers. Unfortunately, the oxygen signal here was not mapped. However, by mapping an adjacent area, the layer was seen to also contain oxygen indicating that this is a corrosion layer.

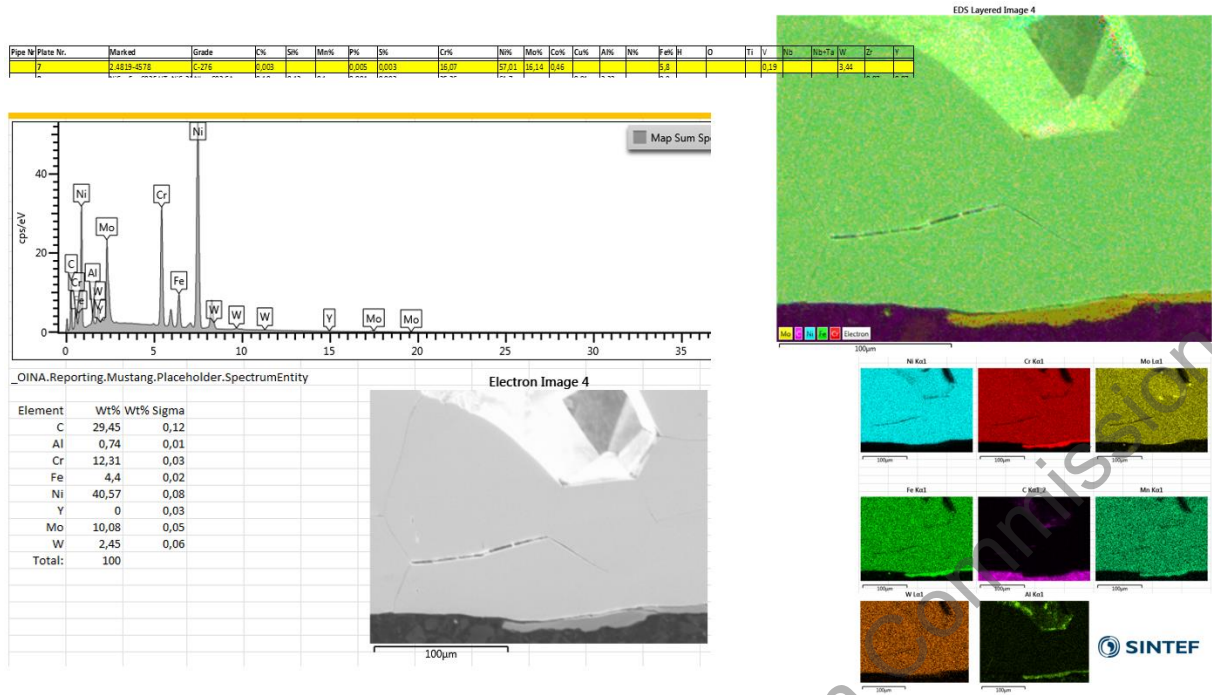


Figure 17. SEM/EDS mapping of Hastelloy C-276 showing SCC with dropped-out grains.

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4.5 699XA

The as-tested 699XA NiCr alloy is just like the other 3 candidates seen to have BL residues left on the surface after testing in the HTL-reactor at SC conditions. Also here, salt crystals are present. A general corrosion attack is evident on the edge of the tension side of the exposed C-rings, see Figure 18. Stress corrosion cracking and lost grains are seen on the tension side of the 699XA section after exposure to SC conditions.

Also, on the mid-section of the C-ring, general corrosion was seen.



Figure 18. Optical microscopy images of sections of the 699XA NiCr alloy with Al as tested revealing general corrosion.

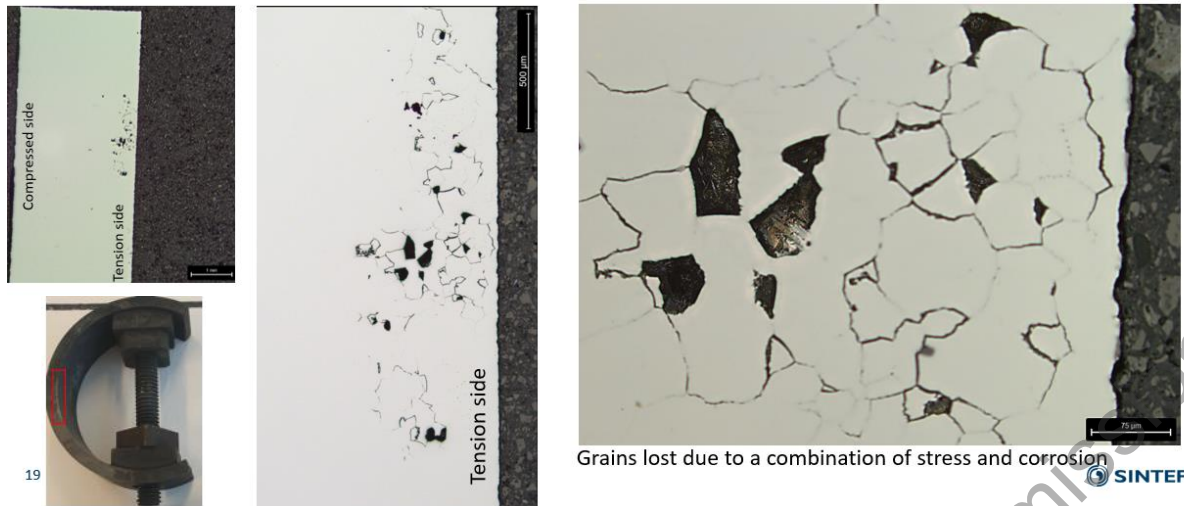


Figure 19. SCC and lost grains on the tension side of the 699XA imaged by optical microscopy.

In the SEM/EDS elements mapping, SCC along the grain boundaries with lost grains is seen. The Al intensity is somewhat higher in the grain boundaries, see Figure 20. This could come from the 2,2wt% Al-alloy itself, but also from precipitation of the partly dissolved alumina spacers.

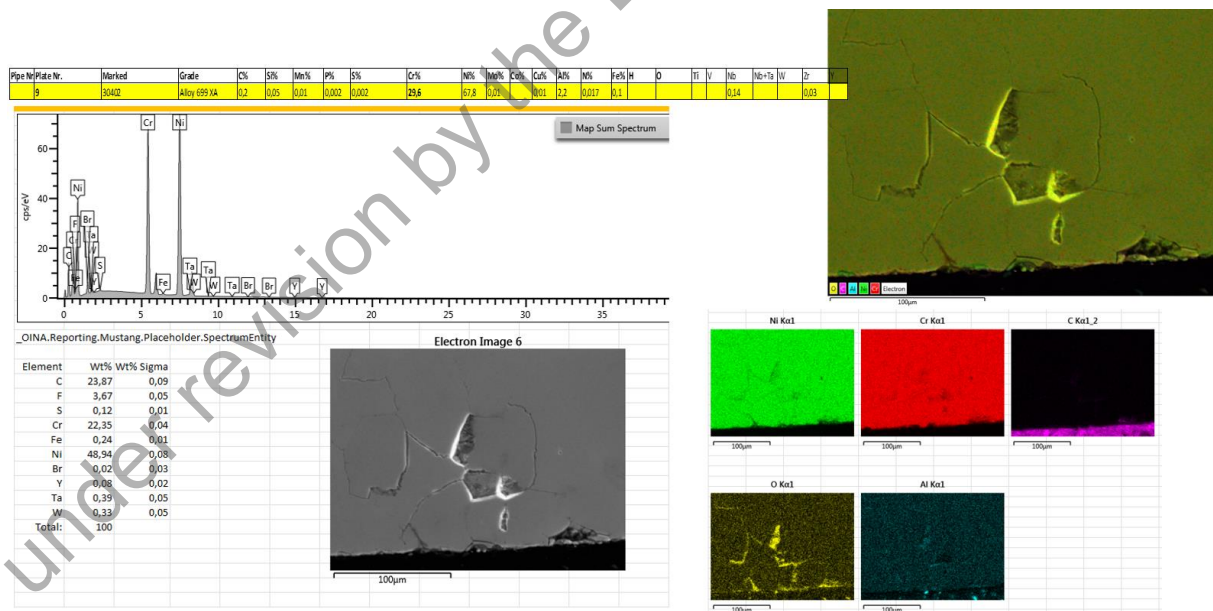


Figure 20. SEM/EDS element mapping of 699XA exposed to super critical conditions.

5 Discussion

There is not much literature, nor experience, available on corrosion in black liquor process systems operating at supercritical conditions. Most data apply for 100-200°C, i.e. not supercritical /1/. Hence, it has been aimed to investigate the behaviour of certain commercial steel qualities at supercritical conditions as basis for construction of a small-scale pilot system.

In general, it is known that presence of chlorides, hydroxide, sulphides and certain wood extractives increase the corrosivity of black liquor /2/. This can result in weakening of the protective passive film (i.e. corrosion) on carbon steels and cause cracking in stainless qualities. More information can be found in the literature /1/. However, these results apply for non-supercritical conditions and cannot uncritically be considered as applicable at supercritical conditions as well, a condition at which the properties of the vapour and the gas phase behaves quite different, affecting e.g. the solubility of protective passive films (e.g. carbonate).

It is also an important point that most non-supercritical laboratory tests reported in the literature have been conducted in real black liquor containing oil components forming a protective layer on the exposed steel surfaces. This can result in non-conservative results as it is quite normal that water and oil separate under laminar flow conditions resulting in steel surfaces not covered with an oil film. As a result, severe corrosion may take place at locations wetted with supercritical water containing chlorides, sulphides etc.

A selective dissolution (dealloying) of essential alloying elements (Ni, Mo, Fe) has been observed in the supercritical region for certain Ni-based super alloys. A subsequent transformation of metal into scale is accompanied by reduction in the wall thickness. IG attack precedes the dissolving of alloying elements and causes sub-surface damage /7/.

The results reported herein should be considered as indicative only until further tests have been carried out on the P91 "winner candidate" in the **welded** condition. This is important as it is a well-known fact that welds always reduce the resistivity to corrosion for most materials due to grain coarsening, chromium depletion, intercrystalline carbide formation, residual stresses, undercuts/defects, poor post-welding pickling etc.

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6 Summary and Conclusion

As of September 2022, the corrosion- and materials evaluation study in a) water-based simulated black liquor and b) water-based simulated black liquor at super-critical conditions was successful. The conclusion from the testing program was that the most corrosion resistant alloy for the defined conditions is the chrome-rich carbon steel candidate P91 (UNS K91560). This is a type of creep strength enhanced ferritic (CSEF) alloy, which are steels designed to retain strength at extremely high temperatures. The P91 abbreviation represents the material's chemical composition, i.e. 9% chromium (Cr) and 1% molybdenum (Mo). Further work is required to at conclude on corrosion resistance for the P91 quality at supercritical conditions in the **welded** conditions and to better understand caustic corrosion- and cracking mechanisms.

The progression and the results were consecutively reported at the monthly meetings and stored at BL2F's Eduuni web-site.

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