

Corrosion characteristics of different stainless steels, austenitic and duplex, in NaOH environment.

Daniel Leander Sandvik AB Sweden
Angela Philipp Sandvik Materials Technology Deutschland GmbH

Abstract:

Black liquor in production is maintained to be about 50% caustic, NaOH. General corrosion behaviour in 30% to 70% NaOH of the different alloys: UNS S32304, UNS S32205, UNS S32750, UNS S32906, a proprietary duplex alloy X and commercially pure nickel (UNS N02200) were investigated. The general corrosion resistances of the different alloys were in the above stated order, with UNS N02200 tolerating the highest pure caustic concentration.

Alloying element importance on the corrosion rate in pure caustic solutions was also performed by an analysis with the statistical software tool Simca P+10.0. The most important alloying elements were found to be chromium, nitrogen and nickel. Stress corrosion cracking tests were also performed in 50 % NaOH at 137°C for UNS S32906. UNS S32906 experienced no stress corrosion cracking at 50 % NaOH, 137°C.

1 INTRODUCTION

NaOH is a widespread and common chemical. It is used in the organic and inorganic chemical industries, pulp and paper industries, aluminium refining (from bauxite), etc.

The different applications utilise different mixtures of NaOH and experiences different degrees of corrosiveness. The manufacture of NaOH and the alumina industry are two of the most corrosive NaOH environments where stainless steels are used.

The main methods for the manufacture of NaOH are the mercury, diaphragm and the membrane processes. In the NaOH manufacturing processes NaOH is produced together with chlorine and hydrogen gas. Each ton of NaOH yields 0,9 ton chlorine gas and 25 kg hydrogen gas (1).

The first way of manufacturing caustic soda was to let a salt brine flow over a mercury electrode as cathode with an iron electrode as anode above it. The obvious disadvantage is the Hg-contamination risk of the environment. A less obvious danger with this process is the contamination risk of the mercury. If the mercury is contaminated with other heavy metal ions the difference between the hydrogen and the amalgamation potentials is decreased and hydrogen can form. Since hydrogen and chlorine gases then mix above the cell compartment, the explosion risk is obvious.

More recent developments are the membrane and the diaphragm processes, where the membrane process is the most energy efficient today, but also difficult to control. The membrane in the membrane process is a sensitive polymer film that divides the anode and cathode compartments. The use of such a sensitive membrane requires very pure brine and gives a large cost when replacing the membranes. The advantages are a highly concentrated, pure product and high total energy-efficiency. The diaphragm process is not as sensitive as the membrane process due to its more robust cell-dividing asbestos membrane. The disadvantages of this process are the ClO_3^- contamination of the anode compartment, which lowers the energy efficiency and contaminates the final product. The evaporation requirements are much higher than for the membrane process and the total energy consumption is higher.

In the future, the membrane process will be the predominant due to the high energy-efficiency and low contamination risk. The aggressiveness of pure NaOH increases with increasing temperature and concentration. The lower alloyed steel grades i.e. UNS S30403 to S31603 can handle caustic solutions up to 70°C and 50% (2). These alloys are also readily affected by impurities, such as NaCl in the diaphragm process, and the limits regarding temperature and NaOH concentration will decrease significantly as NaCl concentration increases. The austenitic stainless steels have in general a lower general corrosion resistance in caustic solutions compared to the ferritic stainless steels. The austenitic grades have a higher resistance against SCC (Stress Corrosion Cracking) than the ferritic on the other hand. Both phases are present in a duplex stainless steel, and high resistance to both general corrosion and SCC can be achieved by balancing the phases.

The duplex stainless steels are used at higher caustic concentrations than UNS S30403 and UNS S31603, especially for erosive applications and SCC risk applications. The oxygen content is a critical factor for the duplex stainless steels, since they must maintain the oxide layer. In a boiling solution the oxygen content becomes low and lower alloyed duplex stainless steels can have difficulties to repassivate.

Commercially pure nickel (UNS N02200) tolerates very highly concentrated NaOH solutions. In the presence of ClO_3^- and NaCl the corrosion rate of UNS N02200 will increase and the duplex stainless steels will manage better due to the contamination of the oxidising ClO_3^- ion.

Besides the general corrosion, SCC-stress corrosion cracking, is a known problem in NaOH applications. SCC is usual in NaCl and H_2S environments but is also seen in NaOH environment (3). Most duplex stainless steels and higher alloyed austenitic steels are immune to SCC at and below 30% NaOH concentration (4) without NaCl. Previous work has proved that stainless steels are prone to crack in 30% NaOH at higher temperatures (5). The lower alloyed duplex stainless steel,

UNS S32304, displays very good SCC properties, previously reported by Rondelli et.al. (5). The very good SCC behaviour was explained with the low Mo content. The Mo content of UNS 32906 is also low and its SCC properties constitute an interesting investigation.

The SCC behaviour at higher concentration and lower temperature is performed in this report. Tests at 50% NaOH concentration just below boiling temperature (137°C) was performed for UNS S32906 to evaluate its SCC performance at higher concentration. The SCC characteristics were investigated with the Slow Strain Rate Test (SSRT) at ambient pressure. A prerequisite for SCC to occur is that the general corrosion is below 0,1 mm/year. If the general corrosion is higher, no oxide can form in the small cracks in the deformation zone and a slow strain rate test will only show regular tensile characteristics. All steel grades showing general corrosion at boiling 50% NaOH in the general corrosion part was thus excluded due to protection from SCC with general corrosion.

2 OBJECTIVES

The main objective of this work is to study the corrosion characteristics of duplex stainless steels in NaOH environments. Alloying element importance on the corrosion rate was investigated between the different alloys and within alloy UNS S32906 (between different experimental heats).

3 MATERIAL

The materials used in this investigation are common in NaOH process equipment and were chosen to spread both in performance and cost.

Table 1 the different steel grades and the chemical compositions

Grade UNS no.	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
S32205	0,015	0,5	0,85	0,02	0,001	22,07	5,49	3,17	0,14	0,17
S32304	0,021	0,46	0,87	0,021	0,001	22,4	4,65	0,2	0,19	0,122
S32750	0,018	0,32	0,55	0,019	0,001	24,79	6,93	3,8	0,15	0,29
S32906**	<0.03	-	-	-	-	29	6	2	-	0,40
Duplex X*	x	x	x	x	x	x	x	x	x	x
N02200**	0,08	0,2	0,2	-	0,005	0	99,2	-	-	-

* Proprietary alloy

** Nominal chemical composition

An investigation of alloying element importance was also performed on a series of experimental heats.

Table 2 Chemical composition and corrosion rates (mm/year) for the experimental heats in boiling caustic solution.

Charge	Cr	Ni	Mo	W	Cu	N
605 088	29,7	7,62	0,97	1	2	0,31
654 089	27,5	7,18	0,98	3,8	2	0,31
654 793	30,1	7,4	1,04	1,29	1,98	0,3
654 796	30,2	6,5	1	1,2	0,55	0,405

4 EXPERIMENTAL PROCEDURE

4.1 General Corrosion

The general corrosion tests were performed on two sets of alloys. The commercial grades (table 1) and experimental alloys of (table 2).

All general corrosion experiments are carried out in boiling caustic solutions and it shall be noted that the corrosion rate for most stainless steels increase in boiling solutions compared to results from below the boiling point.

The weight loss was recorded and used for the calculation of the corrosion rate, according to equation 1.

$$\text{Equation 1: } \frac{V * 87600}{A * t * d} = \text{mm/year}$$

Where:

V = Weight loss of the sample (g)

A = Specimen area (cm²)

t = Test time (h)

d = Density of the steel grade (g/cm³)

Test specimens in dimensions 50 x 20 x 4 mm were mounted on a Teflon rig and immersed in the NaOH solution. The test period was divided in three parts, 1+3+3 days. The first period is an adjustment of the specimen surface to the solution and the

last two periods are used to calculate the corrosion rate. Due to the corrosiveness of the NaOH the tests were performed in Teflon beakers fitted with coolers. The corrosion attacks were analysed with light optical microscope in etched condition.

4.1.1 General corrosion in pure caustic

Pure NaOH concentrations from 30 to 70 weight percent, in 10 % intervals, were investigated for the different commercial steel grades.

4.1.2 General corrosion in membrane and diaphragm specific conditions

An investigation in 50% NaOH, including NaCl content of 20 ppm to 7% and ClO_3^- content of 20 ppm to 800 ppm was performed as a simulation of the different processes. The higher contamination levels of ClO_3^- and NaCl represent the diaphragm process and the lower levels represent the membrane process.

4.1.3 General corrosion vs. Cr-content in the austenite

The general corrosion rate as a function of Cr-content in the austenite in 60% NaOH was investigated for the experimental alloys.

4.2 Statistical Analysis of the Corrosion Rate vs. Alloying Elements.

The statistical analysis program Simca-P +10.0 was used for the element importance investigation. Simca-P +10.0 utilises the Partial Least Squares (PLS) method for the description of the data set. The goodness of fit, R^2 , and the predictive ability, Q^2 , is the measure of how well the results from the model corresponds with reality and these values (R^2 and Q^2) should be as close to 1 as possible.

The data set in this investigation was the alloying element concentration in weight percent for each alloy (table 1) as X and the concentration of boiling NaOH solution giving a corrosion rate of 0.2 mm/year as Y (Table 3).

In this investigation only the major alloyed elements (Cr, Ni, Mo, and N) are described since the fluctuation of the non-alloyed elements are of less significance in this investigation.

4.3 Stress Corrosion Cracking in NaOH.

Slow strain rate tests at a rate of $1 \times 10^{-6} \text{ s}^{-1}$ was utilised in this investigation.

The material was tested in 50% NaOH concentration at 137°C under air purging until failure.

The specimens were of cortest round tensile test type with gauge length 25.4 mm, diameter 3 mm and tested in a cortest slow strain rate test rig. The solution containers were refabricated in S32906 as a replacement of the original ones, made of UNS N10276.

Poly ethylene glycol was used as inert environment in all SSRT tests.

The maximum stress (UTS), percentage of elongation at fracture (EI) and time to failure (TTF) were obtained from the stress-elongation curves. The fracture surfaces were investigated with SEM-BSE.

5 RESULTS

5.1 General Corrosion

5.1.1 General corrosion in pure caustic

The general corrosion rates are displayed in figure 1.

In table 3 the concentration limits of boiling NaOH at 0,2 mm/year corrosion rate for each steel grade are stated.

Table 3 The different steel grades and their concentration limits in boiling caustic

Grade	0.2 mm/y
UNS no.	Conc. Limit
S32205	30,5
S32304	30,3
S32750	42
S32906	43
Duplex X*	57,5
N02200	100

* Proprietary alloy

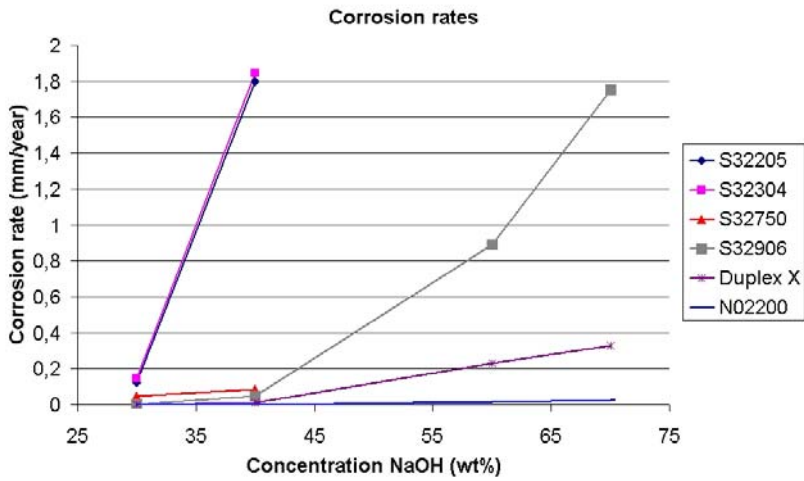


Figure 1 General corrosion rates of the different steel grades at boiling temperature in pure caustic. The values at 70% are only preliminary (2 out of three periods), for S32906 only the value from the first period (out of three) was available.

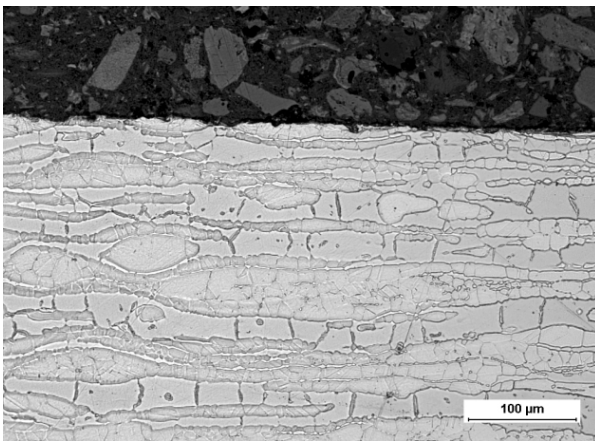


Figure 2 General corrosion of UNS S32906 in 70% NaOH.

5.1.2 General corrosion in membrane and diaphragm specific conditions

Table 4 Corrosion rates (mm/year) of UNS S32906 and UNS N02200 in boiling membrane and diaphragm specific caustic environments.

Steel grade (UNS)	30 ppm Cl ⁻ , 20 ppm ClO ₃ ⁻		7% NaCl, 800 ppm ClO ₃ ⁻
	32% NaOH	50% NaOH	50% NaOH
S32906	0,001	0,001	0,016
N02200	0,001	0,001	0,15

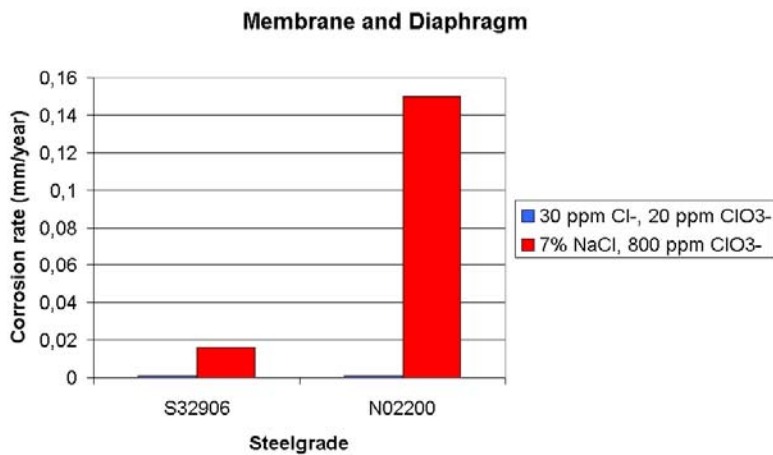


Figure 3 Corrosion rates in boiling 50% NaOH with different contamination levels, membrane (left) and diaphragm (right)

5.1.3 General corrosion vs. Cr-content in the austenite

Corrosion rates vs. the Cr-contents are found in table 5 and displayed in figure 4.

Table 5 The Cr-contents in the austenite and their corrosion rates in boiling 60% NaOH for the different experimental heats

Heat	Cr-austenite	60% NaOH
605 088	27,63	0,27
654 793	28,02	0,19
654 796	29,04	0,05
654 089	26,54	0,39

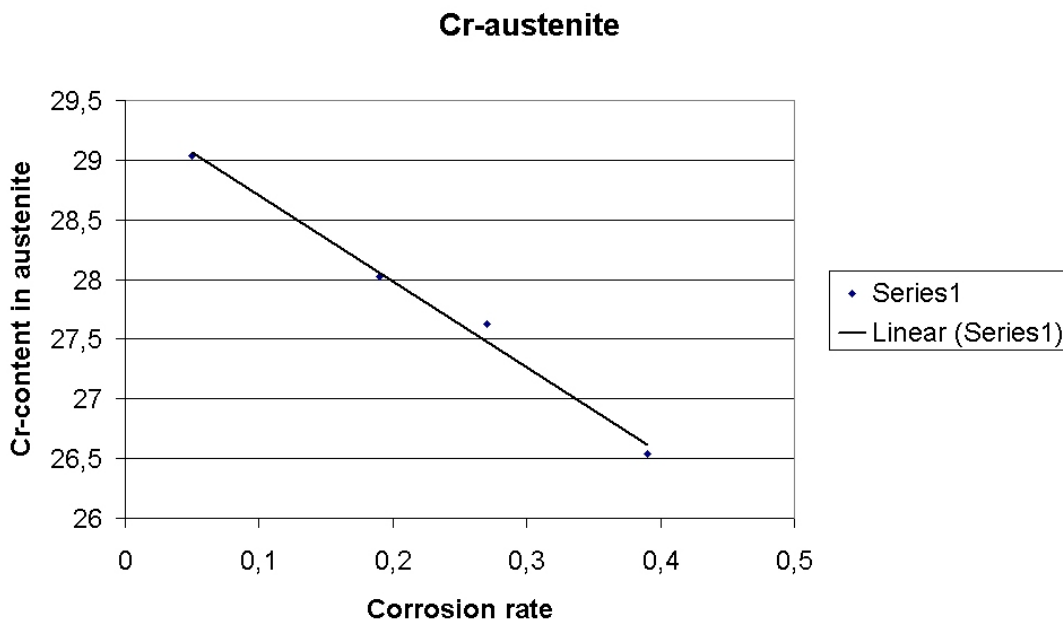


Figure 4 The corrosion rate in 60% NaOH vs. the Cr-content in the austenite phase for the experimental alloys in table 2.

5.2 Statistical Analysis of the Corrosion Rate vs. Alloying Elements

Model diagnosis (duplex stainless steels):

$$R^2 = 0.765$$

$$Q^2 = 0.858$$

The different contributions of the alloying elements are presented figure 4. A bar pointing upwards indicates an alloying element that will affect the concentration limit in a positive way. In order for the effect of an alloying element to be significant, the std. deviation lines must not cross zero. The steel grades in table 1, except UNS N02200, constitute the data set for this investigation.

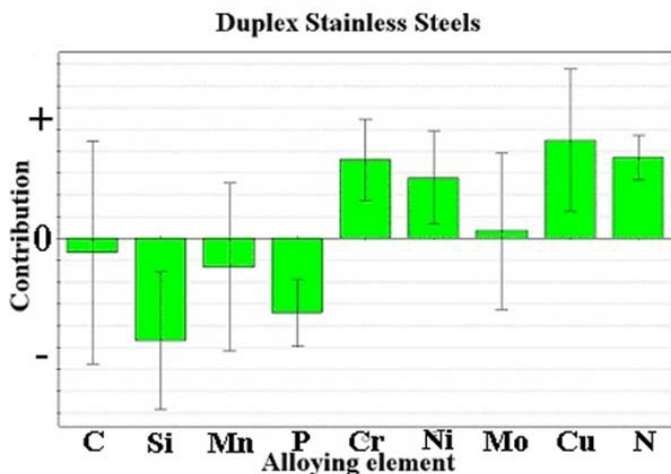


Figure 5 Statistical analysis of alloying element importance on the corrosion rate for the duplex stainless steels.

5.3 Stress Corrosion Cracking in Pure NaOH for UNS S32906.

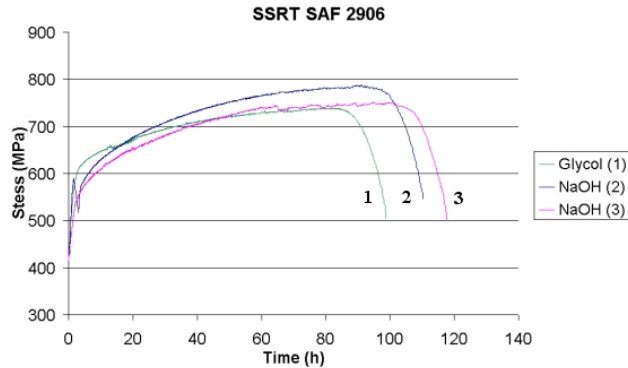


Figure 6 The SCC-behaviour of S32906 in 50% NaOH, 137°C.

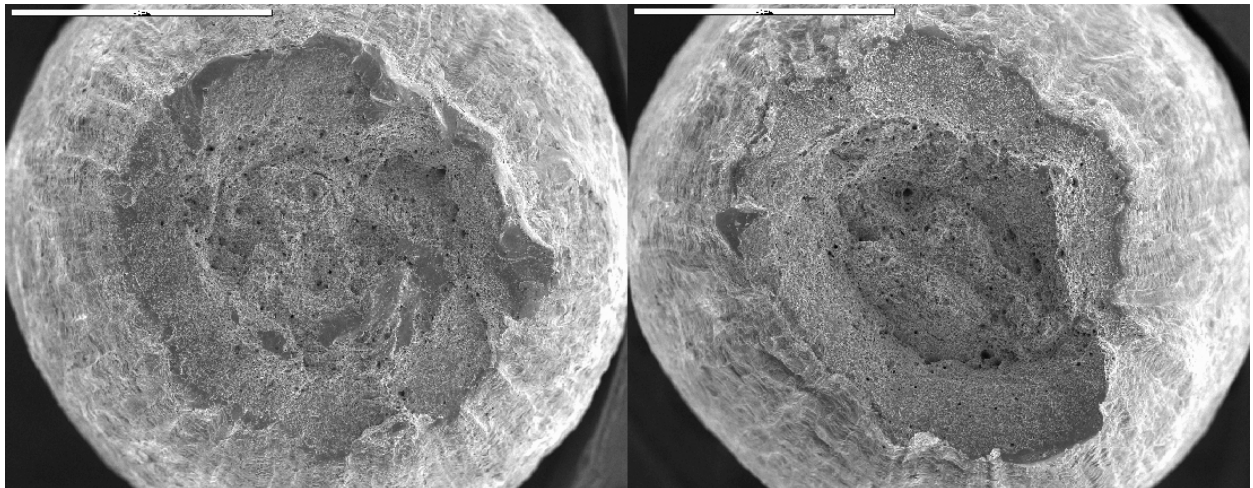


Figure 7 SEM-BSE Image (50x) of the fracture of S32906, inert (left) and active (right) environments. The length-bar in the upper left corner is 1 mm

Table 6 SSRT parameters normalised to the corresponding parameter in inert environment.

UNS Grade	EI	UTS	RTTF
S32906	0,98	1,04	1,16

6 DISCUSSION

6.1 General Corrosion

6.1.1 General corrosion in pure caustic solutions

The general corrosion behaviour for the stainless steels is showing a strong correlation to the chromium content and the more highly Cr-alloyed grades tolerates higher NaOH concentrations. In Figure 2 the surface of the duplex stainless steel UNS S32906 test coupon is displayed where the austenite phase is the predominant one facing the environment. The proprietary duplex alloy, Duplex X, reveals a surprisingly high resistance to caustic media since it tolerates higher concentrations than all the other duplexes.

The corrosion rate of UNS N02200 is low in this study and the material tolerates the highest pure caustic concentrations.

6.1.2 General corrosion in membrane and diaphragm specific conditions

Previous work and field studies have proven that UNS N02200 corrodes more quickly than UNS S32906 does in caustic solutions containing ClO_3^- ions (7) and in erosive environments.

This is also seen in this investigation of the corrosion rates in the membrane and diaphragm specific conditions (figure 3).

When increasing the ClO_3^- content, the corrosion rate of UNS 32906 decreases to the same extent as the corrosion rate of UNS N02200 increases. Applications where precipitates are present and erosive conditions thus arise are also more suitable for the duplex stainless steels since they withstand erosion well.

6.1.3 General corrosion vs. Cr-content in the austenite

The austenite phase is in NaOH environments the less resistant phase in a duplex stainless steel. This is proven in figure 4 where the corrosion rate follows the Cr-content of the austenite phase of the experimental alloys in table 5. It is important that the austenite phase is sufficiently resistant in order for the alloy to resist as high NaOH concentration as possible. Previous studies (6) have shown that the phases have varying corrosion behaviour in corrosive solutions giving corrosion rates exceeding 0.1 mm/year (i.e. active corrosion). For the experimental alloys in table 5 the corrosion rates are much lower than for the rate of UNS S32906 at the same concentration.

6.2 Statistical Analysis of the Corrosion Rate vs. Alloying Elements.

The model fit to the data very well, as can be seen in the Q^2 and R^2 values. In figure 5 the elements impact on the corrosion rate are displayed. The effect of an element can be both positive and negative in the case that the std. deviation line of a component crosses the zero-line. A bar reaching upwards indicate that an increase of that alloying element will increase the concentration limit in boiling solution for an alloy. The positive effect of Cr is obvious and well known. The effect of N for the duplex stainless steels is strongly correlated to the Cr-content, since the N content has to follow the Cr-content. In the investigation of alloying element importance, the real effects can be seen for the main alloying elements, i.e. Cr, Mo, Ni and N, for the different types of alloys incorporated in this investigation.

6.3 Stress Corrosion Cracking in NaOH for UNS S32906.

S32906 experiences no SCC at 137°C and 50% NaOH.

No stress corrosion cracking could be observed for this alloy. The SSRT behaviour in figure 6 shows no significant difference between the inert (glycol) and the active (NaOH) environments. The fractures in both environments had very similar appearance (Figure 7) with the characteristic ductile dimples. The values in table 6 for UNS S32906 confirms the absence of stress corrosion cracking as they are close to 1.

7 CONCLUSIONS

The usable range for the duplex stainless steels (commercial alloys) in boiling pure NaOH has been extended with UNS S32906 compared to the lower alloyed duplex grades, such as UNS S32304 and UNS S32205. A maximum in concentration of 43% (0,2 mm/year) was achieved for UNS S32906 as a comparison to 30% for the lower alloyed duplex stainless steels.

In boiling 50% caustic solutions containing NaCl and ClO_3^- UNS N02200 will experience higher corrosion rates than UNS 32906 even in stagnant solutions. The effect of erosion of UNS N02200 is added on top of the increased corrosion rate in flowing NaCl containing caustic solutions, which is seen in field tests.

The Cr-content of the austenite phase in a duplex stainless steel follows the corrosion rate. The Cr-content of the austenite phase should be kept as high as possible in order to keep the corrosion rate in caustic solutions as low as possible.

The SCC results show that UNS S32906 can be used in aerated 50% pure caustic solutions without any signs of caustic cracking.

8 REFERENCES

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5. G. Rondelli, B. Vicentini, Susceptibility of highly alloyed austenitic stainless steels to caustic stress corrosion cracking, Materials and corrosion 53, 813-819 (2002)
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Gateway to
the Future

Corrosion Characteristics of Different Stainless Steels, Austenitic and Duplex, in Sodium Hydroxide (NaOH) environment

Daniel Leander, Angela Philipp



AGENDA

- Target application
- Main objective of this work
- Experimental procedure and results
- Conclusions
- Tests in an existing evaporator in a pulp & paper mill

EVAPORATORS IN PULP & PAPER INDUSTRY

TYPICAL DESIGNS

- **Rising Film Evaporators**
 - Long Vertical Tubes (LTV)
- **Falling Film Evaporators (FF)**
 - Tubes or Plates



MAIN OBJECTIVE OF THIS WORK

- **Study of mainly duplex stainless steels in NaOH solutions**
- **Importance of alloying elements on the corrosion rate**
- Table 1: different material and the chemical composition

Grade UNS no.	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
S32205	0,015	0,5	0,85	0,02	0,001	22,07	5,49	3,17	0,14	0,17
S32304	0,021	0,46	0,87	0,021	0,001	22,4	4,65	0,2	0,19	0,122
S32750	0,018	0,32	0,55	0,019	0,001	24,79	6,93	3,8	0,15	0,29
S32906**	<0.03	-	-	-	-	29	6	2	-	0,40
Duplex X*	x	x	x	x	x	x	x	x	x	x
N02200**	0,08	0,2	0,2	-	0,005	0	99,2	-	-	-

* Proprietary alloy

4 ** Nominal chemical composition

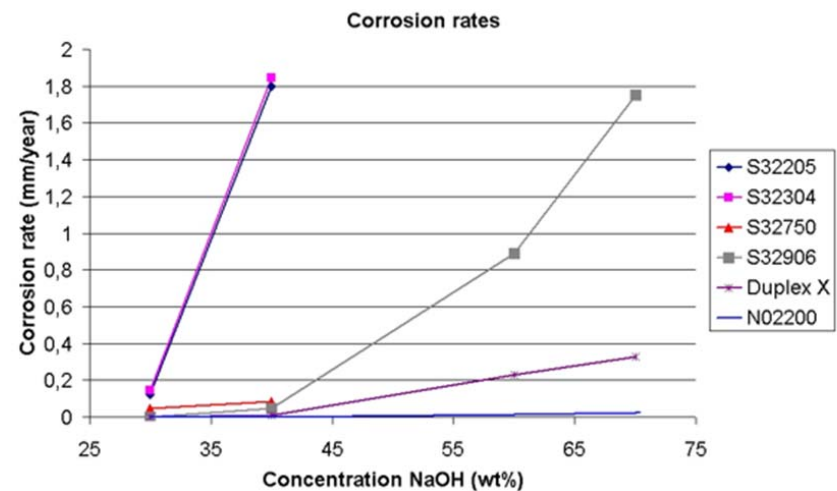
GENERAL CORROSION

CONCENTRATION LIMITS OF BOILING
NAOH AT 0,2 MM/YEAR CORROSION RATE

Grade	0.2 mm/y
UNS no.	Conc. Limit
S32205	30,5
S32304	30,3
S32750	42
S32906	43
Duplex X*	57,5
N02200	100

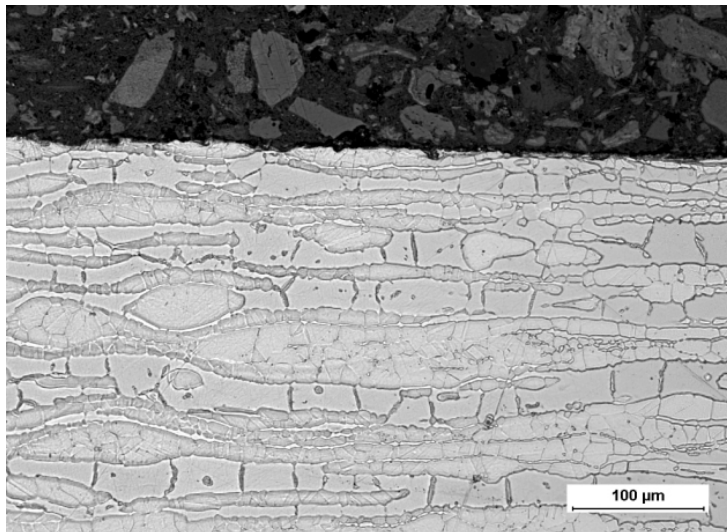
* Proprietary alloy

CORROSION RATES AT BOILING
TEMPERATURE IN PURE CAUSTIC



GENERAL CORROSION

UNS S32906 70% NaOH



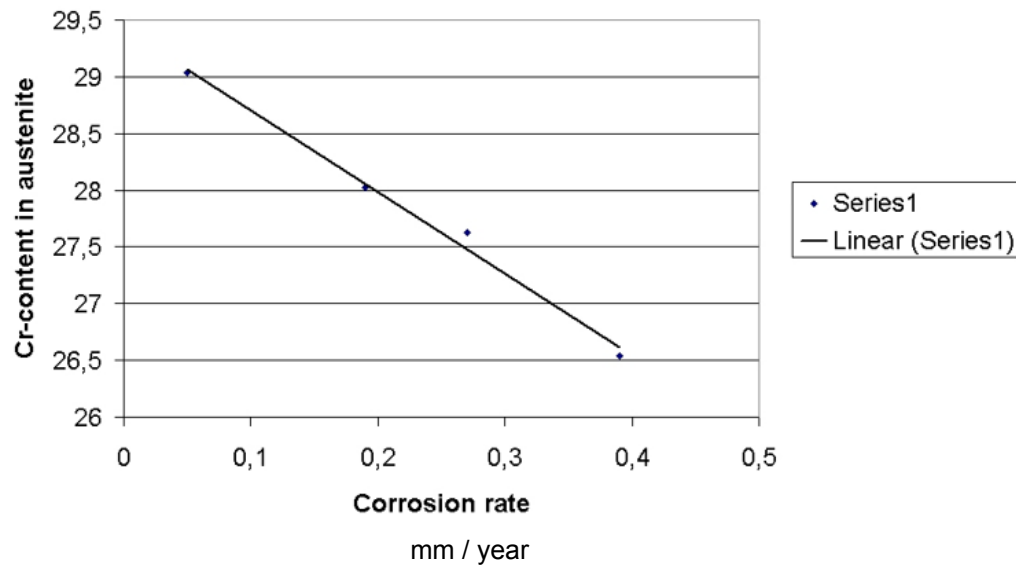
CORROSION RATES (MM/YEAR) IN BOILING MEMBRANE AND DIAPHRAGM SPECIFIC CAUSTIC ENVIRONMENTS

Steel grade (UNS)	30 ppm Cl ⁻ , 20 ppm ClO ₃ ⁻		7% NaCl, 800 ppm ClO ₃ ⁻
	32% NaOH	50% NaOH	50% NaOH
S32906	0,001	0,001	0,016
N02200	0,001	0,001	0,15

Membrane and Diaphragm

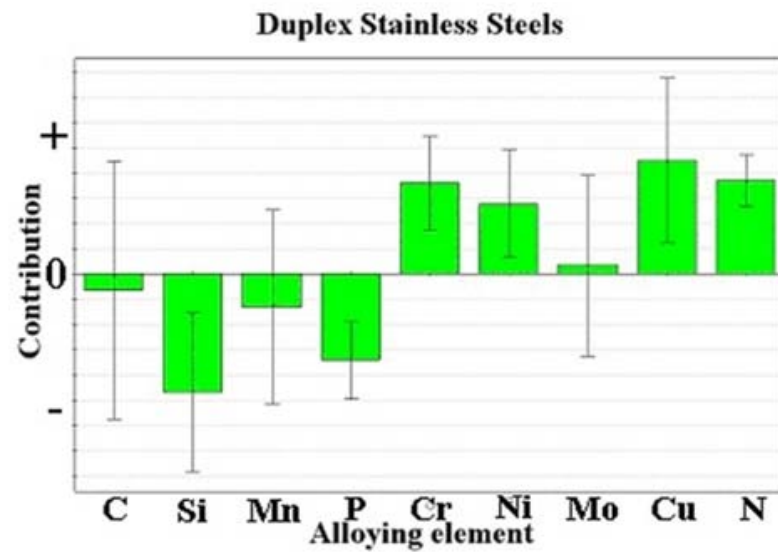
GENERAL CORROSION

IN 60% NaOH VS. CR-CONTENT (WEIGHT%) IN THE AUSTENITE PHASE FOR THE EXPERIMENTAL ALLOYS



Heat	Cr-austenite %	60% NaOH
605 088	27,63	0,27
654 793	28,02	0,19
654 796	29,04	0,05
654 089	26,54	0,39

STATISTICAL ANALYSIS OF ALLOYING ELEMENT IMPORTANCE ON THE CORROSION RATE FOR DUPLEX STAINLESS STEELS

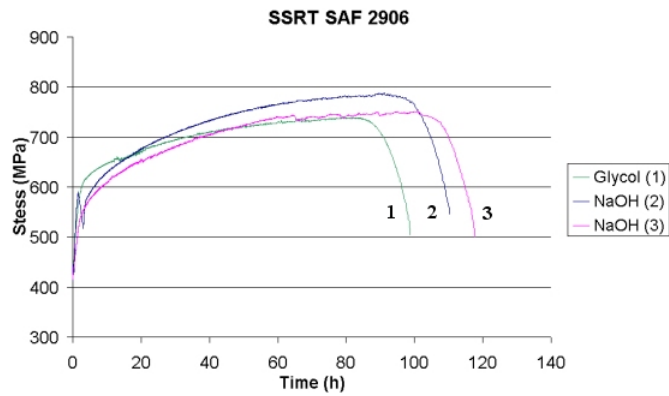


The effect of an alloying element is significant, if the standard deviation line doesn't cross the zero line.

STRESS CORROSION CRACKING

UNS S32906 IN 50% NaOH AT 137°C

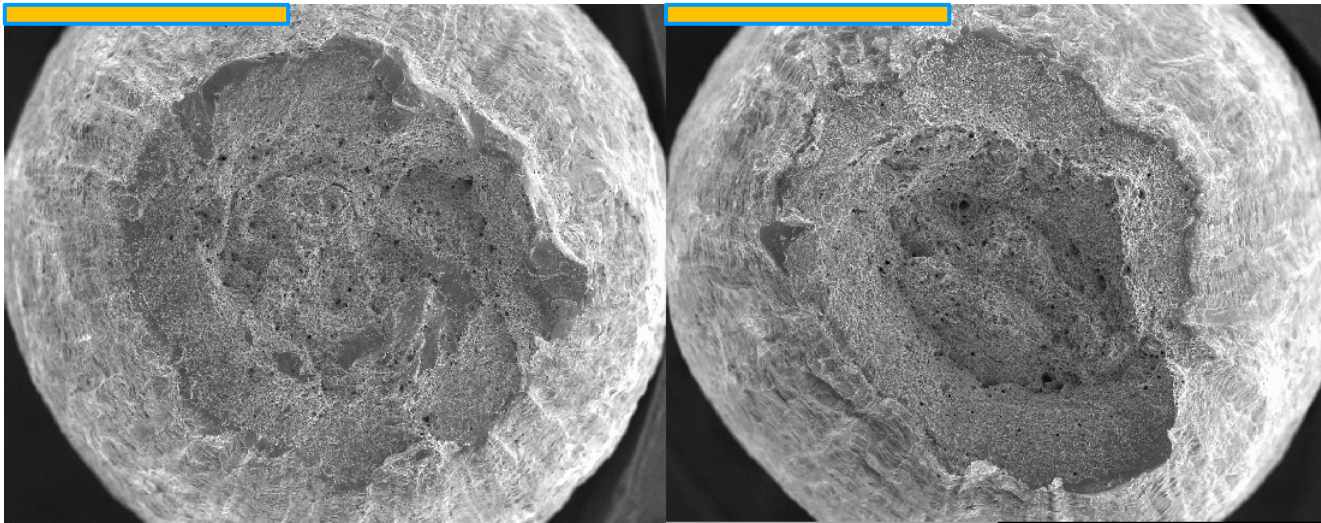
SSRT PARAMETERS NORMALIZED TO THE CORRESPONDING PARAMETER IN INERT ENVIRONMENT



UNS Grade	EI	UTS	RTTF
S32906	0,98	1,04	1,16

STRESS CORROSION CRACKING

SEM-BSE IMAGE (50X) OF THE FRACTURE OF S32906, INERT (LEFT) AND ACTIVE (RIGHT) ENVIRONMENTS. THE LENGTH-BAR IN THE UPPER LEFT CORNER IS 1 MM



CONCLUSION OF THE PRESENTED WORK

- The behavior of duplex steel UNS S32906 in caustic environments was investigated compared to lower alloyed duplex steels like UNS S32204 and UNS S32205 and commercially pure nickel UNS N02200
- A maximum in concentration of 43% (0,2 mm/year) was achieved for UNS S32906
- In boiling 50% caustic solutions containing NaCl and ClO_3^- UNS N02200 will experience higher corrosion rates than UNS S32906 even in stagnant solutions.
- Compared to nickel duplex steel UNS S32906 shows a better erosion resistance
- The Cr-content of the austenite phase follows the corrosion rate and should be kept as high as possible in order to keep the corrosion rate in caustic solutions as low as possible.
- The SCC results show that UNS S32906 can be used in aerated 50% pure caustic solutions without any signs of caustic cracking

CORROSION IN PULP MILL EVAPORATOR

LINE 1ST PHASE CONCENTRATOR – TEST APPLICATION MADE BY SAVCOR OY

- Background
 - Aggressive corrosion attack resulting in tube leaks and wall thinning
 - The production line had been in operation since 1995 and the first signs of corrosion were reported in 2007/2008
 - Remaining life time only 3 years
- Aims:
 - Extend the lifetime
 - Identify best cost beneficial material for new concentrator line

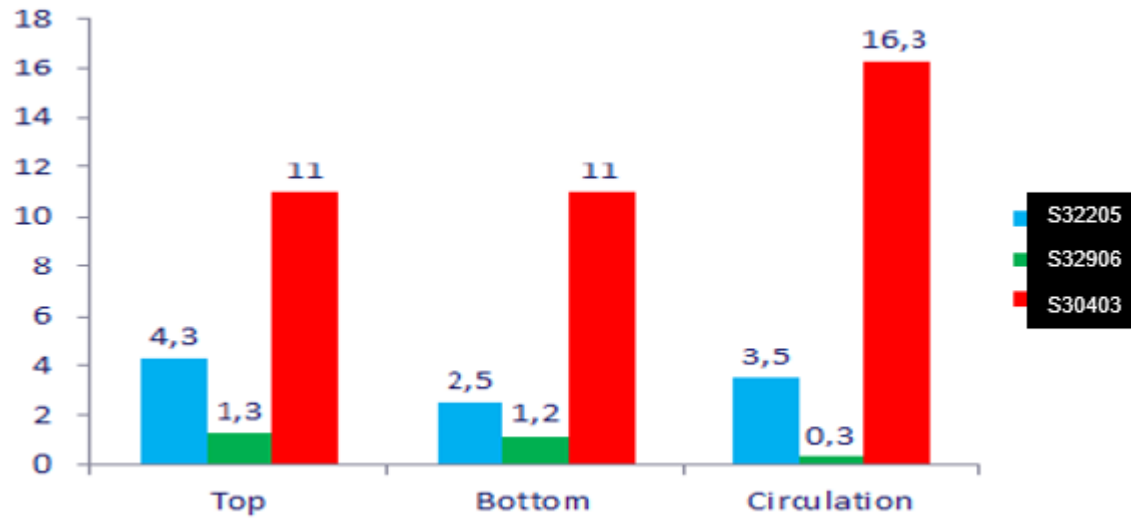
EXPERIMENT IN OPERATING EVAPORATOR

EXPERIMENTAL PROCEDURE

- Corrosion in pulp mill evaporator line 1st phase concentrator was studied
- Technique called Polarization Scan was used
 - This method reveals the passive area in which the metal is naturally protected against corrosion
- Open Circuit Potential (OCP) and Linear Polarization Resistance (LPR) were measured on-line
- Powerful data diagnostics tool was used for data analysis
- Material grades: UNS S30403; UNS S32205; UNS S32906

CORROSION TEST RESULTS

ANALYSIS RESULTS – AVERAGE CORROSION RATES, MILS



CONCLUSIONS

- Corrosion rate is at the highest level right after wash
- Less aggressive washing procedure and smooth start-up after the washing decreases the risk of corrosion and stress corrosion cracking
- Scaling decreases the corrosion rates but also the heat transfer efficiency
- Duplex stainless steel UNS S32906 is clearly the most corrosion resistant of the materials tested and austenitic stainless steel UNS 30403 was less resistant
- Remaining life time was doubled

ANGELA.PHILIPP@SANDVIK.COM