In-Plant Corrosion Testing in Ozone Bleaching Environments

Pekka Pohjanne – VTT Industrial Systems, P.O.Box 1704, FIN-02044 VTT, Finland

Marko Siltala – UPM-Kymmene, Pulp Center, P.O.Box 42, FIN-68601 Pietarsaari, Finland

The corrosion behavior of different stainless steel grades was investigated with mill tests both in ozone bleaching and in ozone production environments. The corrosion resistance was evaluated both by immersion and electrochemical tests.

The mill tests showed that the AISI 316L and the other more alloyed stainless steels do have good corrosion resistance both in the reaction tube and in the ozone reactor ($T = 60–70°C$, $pH = 2.5–3.0$, $CI = 0.1–0.15$ g/l, O_3- dosage ca. 3.3 kg/t). The AISI 304L type stainless steel is not suitable for use in ozone bleaching due to poor localized corrosion resistance. The low corrosion rates of the highly alloyed UNS S31254 and UNS S32654 stainless steels were surprising.

The ozone gas feed line environment ($T = 20–30°C$, pressure 1000 kPa, $O3$-content = 9.5%) was very corrosive to all stainless steels examined.

Introduction

Ozone is currently used as a bleaching agent of pulp as a replacement for chlorine based bleaching chemicals. Ozone as bleaching chemical has a great potential for reducing and re-placing chlorine based chemicals in acidic bleaching stages. Ozone can be used both in elementary chlorine free (ECF) bleaching processes, where it replaces gaseous chlorine, and in totally chlorine free (TCF) bleaching where ozone replaces chlorine dioxide [1–3].

As a strong oxidizing agent ozone may also react with bleach-ing equipment and in some cases cause unexpected corrosion failures. According to the literature data [4,5] the corrosion resistance of traditional austenitic AISI 304L and 316L type stainless steels is good in ozone containing solutions (pH = 3) and ozone gas. Their resistance is superior compared to highly alloyed 6% Mo type austenitic and duplex stainless steels [4]. Due to the good corro-sion resistance AISI 304L and 316L type stainless steels are commonly used as a construction material for ozone generators [6].

However, there have been suspicions that the traditional AISI 304L and 316L type stainless steels may suffer from localized corrosion in ozone containing solutions if critical amounts of chlorides are present in the pulp [4,5]. And yet there are few articles, which are dealing with corrosion resistance of stainless steels in actual bleaching conditions.

Wisaforest Pulp Mill

The Wisaforest pulp mill is located in Pietarsaari, Finland. It is a part of UPM-Kymmene Corporation. It was one of the first mills to introduce a medium consistency (MC) ozone bleaching stage and has been producing TCF_Z-bleached kraft pulp since 1993. The total production capacity of the mill is 600 000 tp/a.

The pulp mill has two ozone stages on its first fiber line (950 tp/d). The main product of the fiber line is TCF bleached birch kraft pulp, which is bleached using sequence A-Z/Q-OP-Z/Q-P. In addition to TCF bleaching ozone is also used in ECF light bleaching together with a small dosage of chlorine dioxide (Z/D).

Ozone is produced from oxygen in four ozone generators (Fig. 1). After production the ozone gas is compressed and mixed into pulp in the two ozone bleaching stages. The consistency of the ozone gas after the ozone generators is approximately 9.5%. The remaining 90.5% consists of oxygen and minor amount of impurities (e.g. N_2, Ar, CO and CO_2). The compressors are of water ring type, hence during compression some humidity is introduced to the ozone gas.

The ozone stage itself is carried out at pH 3.0 and a temperature of 60–70° C. The pH is adjusted by adding sulfuric acid to the pulp prior to ozone dosing. The pulp consistency at the ozone stage is approximately 12%. Due to the fast reaction of ozone in medium consistency the recidense time in
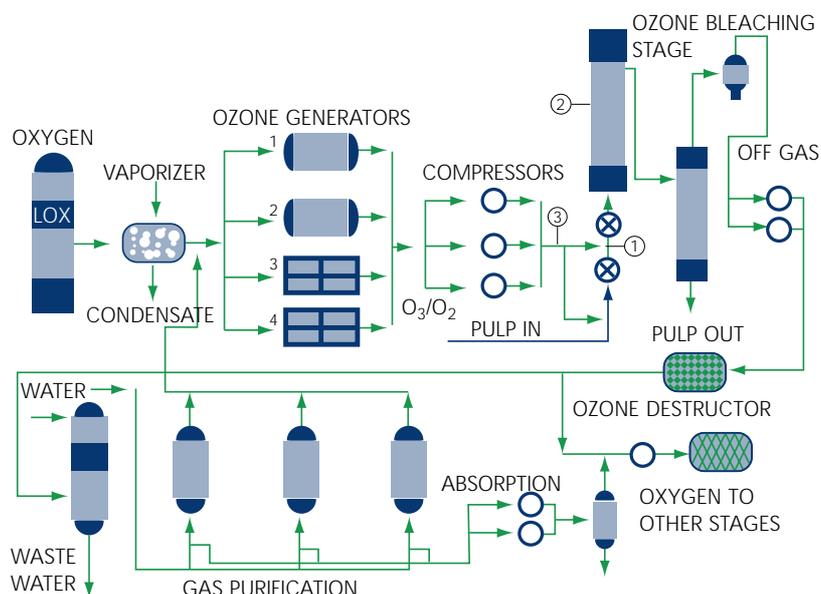
Fig 1. A schematic picture of the ozone bleaching processes and test locations (marked as 1, 2 and 3).

the ozone reactor is only about three minutes.

After the ozone stage the excess oxygen carrier gas is separated from the pulp in a blow tank. The

pulp is washed and fed to the subsequent bleaching stage. The off gas is purified using vacuum swing absorption molecular sieves and recirculated to the generators. Thus, the oxygen fed to the generators is a mixture of recirculated and fresh oxygen.

Table 1: Chemical compositions of the tested alloys (wt%). (PM = powder metallurgy product.)

Alloy	C	Cr	Ni	Mo	N	Cu	Mn	Si	Fe
Austenitic stainless steels									
AISI 304L	0.035	18.1	9.1	0.22	0.046	0.17	1.49	0.49	Bal.
AISI 316L	0.016	17.0	11.4	2.58	0.017	0.13	1.59	0.57	Bal.
UNS N08904	0.017	19.8	24.7	4.6	0.045	1.42	1.46	0.38	Bal.
UNS S31254	0.008	19.9	17.6	6.2	0.20	0.69	0.54	0.37	Bal.
Ralloy 26G PM[A]	0.039	17.9	11.2	2.2	0.20	<0.01	10.4	3.4	Bal.
UNS S32654 PM	0.012	24.3	20.4	7.2	0.36	0.42	3.2	0.37	Bal.
Duplex stainless steels									
UNS S32304	0.029	22.7	5.0	0.20	0.083	0.19	1.47	0.35	Bal.
Duplok 27 PM[A]	0.028	26.4	7.1	3.1	0.26	2.2	0.69	0.15	Bal.

[A]*Trademarks of Rauma Materials Technology*

Table 2: Welding techniques and filler metals, wt%.

Alloy	Method	Filler	C	Cr	Ni	Mo	Mn	Si	Fe
AISI 304L	SMAW	OK 61.30[B]	0.030	19.5	10	–	0.8	0.8	Bal.
AISI 316L	SMAW	OK 63.30[B]	0.030	18	12	2.8	0.8	0.7	Bal.
UNS S31254	GMAW	OK 19.82[B]	0.030	22	>60	9	0.2	0.2	<3

[B]*Trademarks of Esab Ab*

Test Materials

The aim in this study was to examine the corrosion behavior of different stainless steel grades in ozone bleaching conditions. Tests were performed both with base materials and their welds. Chemical compositions of the base materials are shown in Table 1. Table 2 presents the compositions of the filler metals and welding methods. The powder metallurgy alloys were polished with a 600 grit emery paper while the plate materials were tested in as received condition.

Experimental Methods

The corrosion tests were done as well in ozone bleaching as in ozone production environments. In ozone bleaching the tests were performed both in the reaction tube just after the first ozone mixer and in the ozone reactor. The third test location was the pressurized ozone gas feed line just before the first ozone stage mixers. A schematic picture of the process including test locations is shown in Figure 1.

Z1-STAGE REACTION TUBE

In the reaction tube the corrosion resistance evaluation was based on long term immersion tests and cyclic polarization measurements. In both cases a special specimen holder, placed directly in the reaction tube just after the chemical mixer, was used (Fig. 2). The specimen holder allowed both electrochemical corrosion or weight loss measurements and corrosion potential monitoring.
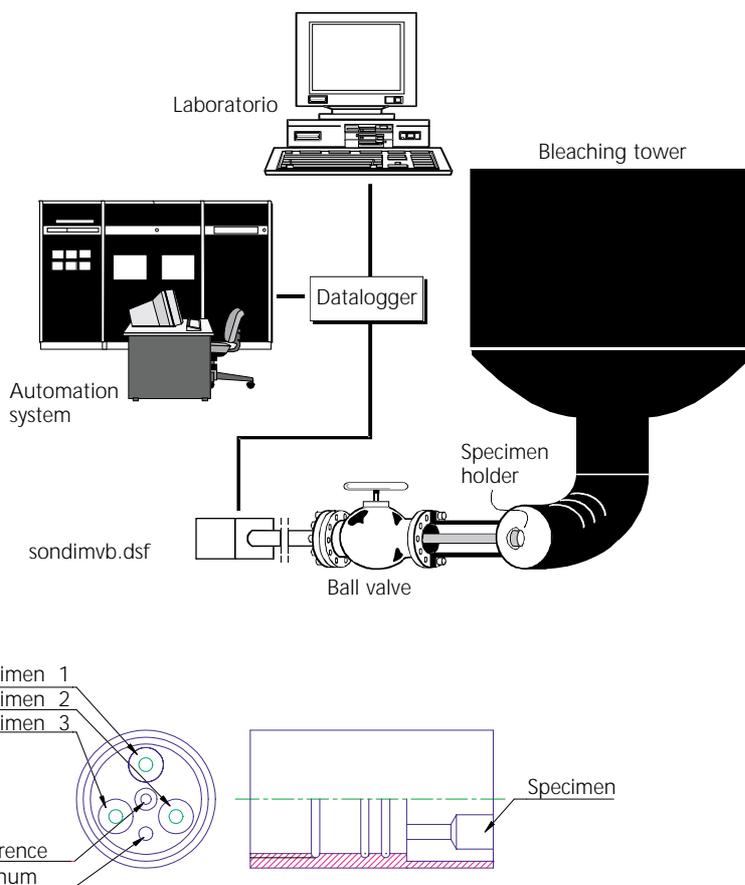
Fig 2. *Experimental set-up and figure of the specimen holder used in the reaction tube.*
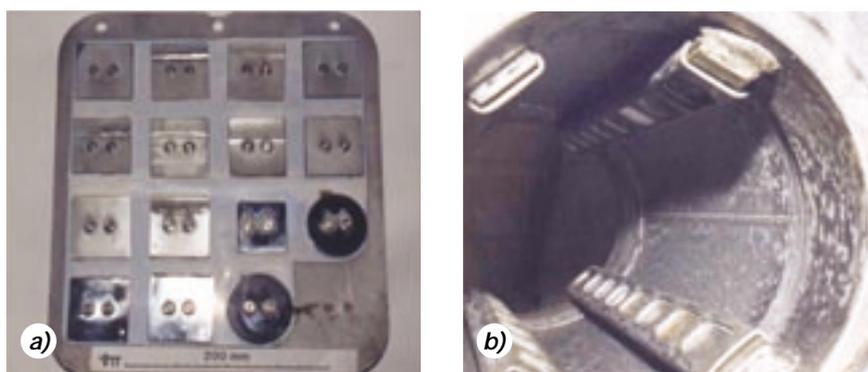
Fig 3. *Test racks used in coupon tests: a) the rack used in the ozone reactor manhole and b) test rack used in the ozone gas line.*

Both the redox and corrosion potentials were continuously recorded during the immersion tests.

The specimens used in the holder were rather small (ø=10 mm) and therefore only base materials were included in the tests in the reaction tube. Redox electrode was made of platinum wire The counter/redox electrode was

platinum wire. An external silver/silver chloride electrode or SCE was used as a reference electrode.

Z1-STAGE OZONE REACTOR

In the ozone reactor tests were performed using test coupons, measuring typically 80x80x2– 5mm. The coupons were attached to a test rack, which was bolted to the reactor manhole (Fig. 3a). The specimens were insulated from the test rack and from each other by PTFE plate and washers.

OZONE GAS LINE

In ozone gas line the test coupons (48x23x2–4mm) were mounted to tests racks welded inside of a stainless steel pipe ($\emptyset_{ID}$=150 mm), which was then placed to the ozone gas line (Fig. 3b). The specimens were insulated from the test rack and from each other by PTFE.

Results

GENERAL

All tests were performed in first ozone stage. This stage was selected because the ozone dosage is higher in the first than in the second stage. The trials were made during birch pulp production but also short eucalyptus and softwood campaigns were carried out at the fiberline during the immersion test period.

Z1-REACTION TUBE

In the reaction tube the tests were performed just after the first ozone mixer, where the ozone concentration is expected to be highest.

The tests in the reaction tube were performed in three periods because only four materials could be tested at time in the specimen holder. The duration of the three periods varied from 24 to 27 days. Average environmental conditions in the reaction tube during the tests are shown in table 3.

The reaction tubes and pumps in the first ozone stage are made from AISI 316L type stainless steel. Until now no corrosion has been reported.

During tests at Z1-stage the redox potential was typically in the range of +400–+550 mV$_{SCE}$. Only occasionally higher values around +800–850 mV$_{SCE}$ were measured. The high values were normally measured after the process startup. The corrosion potentials of the stainless steels were normally about 100–200 mV higher than the redox potential (Table 4).

The metallographic examinations and weight losses determined after the test showed that all examined stainless steels, except AISI 304L, had a good corrosion resistance in the Z1-stage reaction tube. The corrosion rates were very low, below 0.02 mm/a. The weight loss of the AISI 304L was low but the specimen had suffered from localized corrosion.

Table 3: Average environmental conditions in the reaction tube of Z1-stage.

Temperature, °C	60–70
pH	2.5–3.0
Ozone dosage, kg/t	3.3
Flow rate, m/s	0.3
Consistency, %	12
Delay time between the 1st mixer and test location, sec	2–4
Chlorides, g/l	0.1–0.15
Sulfates, g/l	1.5–1.9

Table 4: Test results in the Z1-stage reaction tube.

Material	E$_{corr}$ [mV$_{SCE}$]		Corrosion Rate [mm/a]
	Average	Maximum	
First test period			
AISI 304L	+710	+820	0.011*)
AISI 316L	+695	+825	0.024
Ralloy 26G PM	+670	+790	0.022
Redox potential	+510	+815	–
Second test period			
AISI 316L	+570	+655	0.006
UNS N08904	+550	+635	0.004
UNS S32654 PM	+540	+620	0.005
Duplok 27 PM	+580	+670	0.003
Redox potential	+440	+595	–

*) Localized corrosion

Table 5: Average process conditions in ozone reactor of Z1-stage.

Temperature, °C	60–70
pH	2.5–3.0
Ozone content , g/l	• 0
	Only occasional residuals
Delay time between the 2nd mixer and test location, sec	8–12
Flow rate, m/s	
Consistency, %	12
Chlorides, g/l	0.1–0.15
Sulfates, g/l	1.5–1.9

a)

b)

Fig 4. The AISI316L fixture pipe after the exposure tests in ozone feed gas line: a) Corrosion pits and wormeaten looking marks observed on the inner surface and b) SEM figure from a bottom of corrosion pit.

Z1-STAGE OZONE REACTOR

The test duration in the ozone reactor was 357 days. Average environmental conditions in the mixer to tower pipeline during the tests are shown in Table 5.

The ozone reactor is used as an equalizing tank to balance production. It also acts as degassing equipment. The reactor is made from AISI 316L type stainless steel and until now no corrosion has been reported.

After the tests all specimens were covered with dense white deposits, which in energy dispersive spectrometry analysis turned out to contain mainly barium. After removing the deposits the coupons were examined visually.

All base materials were in good condition, without any notable corrosion. The corrosion rates calculated from the weight losses were below 0.001 mm/a.

Also the welded AISI 316L and UNS S31254 were in good condition after the tests. The corrosion rates calculated from the weight losses were below 0.001 mm/a, and metallographic examination did not show any notable corrosion.

The SMAW weld of the AISI 304L was in good shape after the

Table 6: Average environmental conditions in ozone gas feed line to Z1-stage.

Temperature,°C	20–30
Pressure, kPa	1000
Ozone content, %	9.5
Flow rate, m/s	5

test, but the base material suffered from intense localized corrosion under the insulation washer.

OZONE GAS LINE

The third test location was the pressurized ozone gas feed line just before the first ozone mixer. The test duration in ozone gas was 357 days. Average environmental conditions in the gas line during the tests are shown in Table 6.

The ozone gas line is currently made from seamless AISI 316L type stainless steel pipe. Initially the pipeline was made from welded AISI 316L type stainless steel but it was replaced by seamless pipe few years ago because of the welding seam corrosion.

The tests showed that the ozone gas line environment is very aggressive. Corrosion was observed in all specimens, test racks and also in the stainless steel pipe used for fixture.
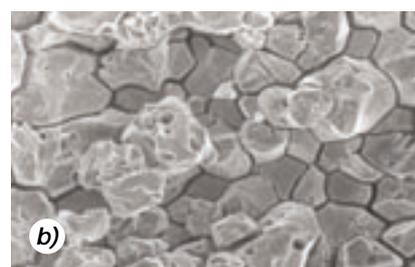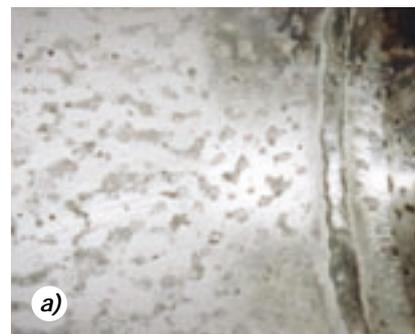
The AISI 316L type tests racks and the fixture pipe had suffered from intense localized corrosion. Corrosion was observed both in the base materials and in the welds. The size of the corrosion pits varied from 1 to 5 mm in diameter and from 0.4 to 0.7 mm in depth. In addition to pits the surfaces were covered with marks that looked like wormholes (Fig. 4a). The appearance of the pits was not typical of pitting corrosion. The bottoms of the pits were rather typical of intergranular corrosion (Fig. 4b).

All tested base materials were corroded, although the corrosion was less intense than expected based on corrosion observed on the tests racks and fixture pipe. The corrosion rates calculated from the weight losses were relatively
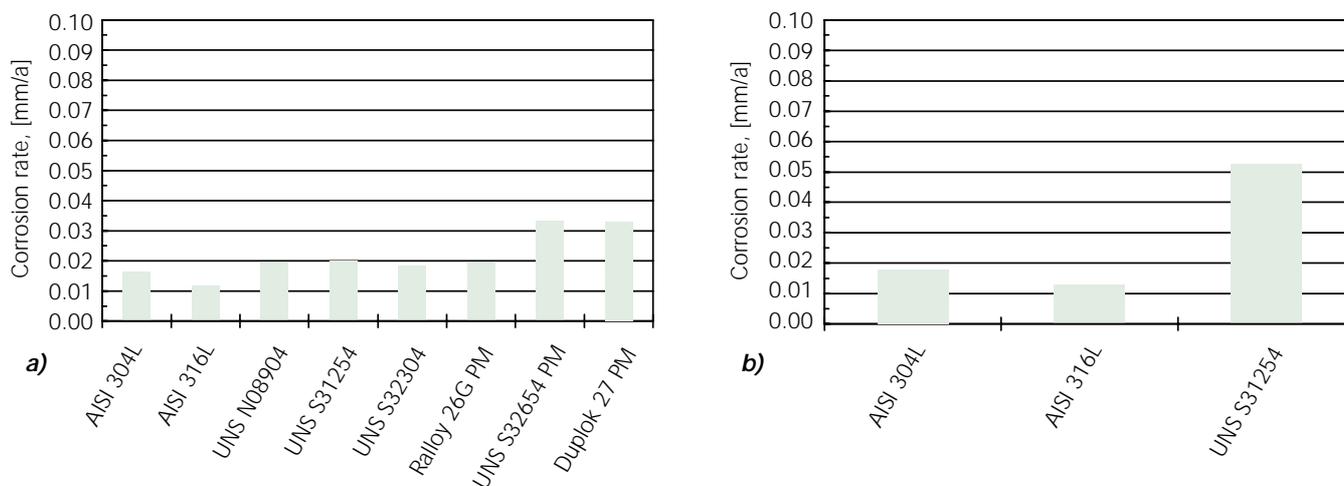
Fig 5. Corrosion rate of different stainless steel grades in ozone gas feed line environment: a) unwelded base materials and b) welded stainless steels.

small (Fig. 5a). Highest corrosion rates, around 0,035 mm/a, were determined for the highly alloyed UNS S32654 PM and Duplok 27 PM steels. All specimens were covered with similar intergranular corrosion pits as observed in the test racks. An exception was the UNS S32654 PM steel which surface was uniformly corroded with a mechanism of transpassive dissolution (Fig 6a).

The corrosion rates of welded AISI 304L and AISI 316L were at the same order with the unwelded base materials specimens (Fig. 5b). The corrosion rate of SMAW weld of UNS S31254 steel was two times higher than the un-welded specimen. Metallographic examination revealed that the welds and fusion lines had partially selectively corroded, revealing the dendrite structure. Selective corrosion was most intense in the nickel base weld of the UNS S31254 (Fig. 6b).

Discussion
REACTION TUBE
The AISI 316L and other more highly alloyed stainless steels performed well in the ozone bleaching. The corrosion rates of the AISI 316L type stainless steel in reaction tube were low as expected. Similar low corrosion rates in ozone containing environments have been reported earlier [4,5,7].

The AISI 304L type stainless steel is not suitable to chloride containing ozone environments due to poor localized corrosion resistance. A chloride content of 0.1–0,15 g/l at 60–70 oC was sufficient to cause crevice corrosion.

However, the low corrosion rates of the highly alloyed UNS S31254 and UNS S32654 stainless steels were surprising. Previous laboratory and field tests have shown that highly alloyed stainless steels are susceptible to transpassive dissolution in ozone containing solutions [4,5,7].

According to the electro-chemical tests the low corrosion rates are related to the fact that in real bleaching environments the corrosion potentials do not achieve so high values that marked transpassive dissolution is possible. In mill tests the
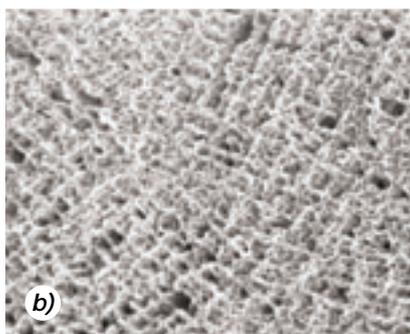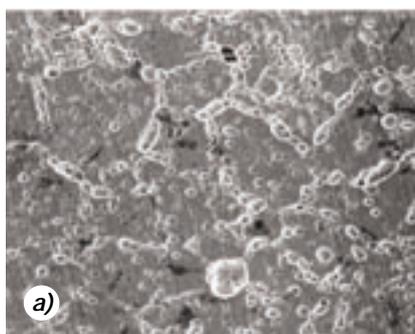
Fig 6. Examples of observed steel surfaces after the exposure tests in ozone feed gas line: a) transpassive dissolution in the UNS S32654 PM and b) selective corrosion in the weld of the UNS S31254.

measured corrosion potentials were systematically 100–200 mV below the potentials measured in the ozonated sulfate solutions [7–8]. The measured corrosion potentials were only occasionally so high that marked transpassive dissolution is possible.

The reason for these low potentials is still obscure. One reason could be that the reaction between the pulp and ozone is so fast that the ozone concentration and thus the oxidative capacity of the environments fall rapidly after the chemical mixing.

Another reason could be that there are some chemicals in the bleaching solutions that over-shadow the effect of ozone. This conclusion is supported by the fact that the high corrosion potentials were typically measured after the process startup. Generally the corrosion potentials dropped down within 2–3 days after the startup, when the bleaching process reached a stationary state. During the normal operation corrosion potentials were low and quite stable, although there were varia-tions within different monitoring periods. One chemical that might cause this is hydrogen peroxide, which is always present in bleaching solution due to counter current washing.

Preliminary tests have shown that hydrogen peroxide addition (0.05 g/l) to ozone containing solution cause immediate drop in redox and stainless steel potentials.

OZONE REACTOR
The AISI 316L and other more highly alloyed stainless steels, which are suitable to Z1-reaction tube environment, are also suitable to Z1-reactor.

The highly alloyed stainless steels are expected to have better corrosion resistance in the reactor than in the reaction tube because there are only occasional ozone residuals present in the reactor. Low ozone concentration is due to fast reaction between the pulp and ozone. Because of the low concentrations the corrosion potentials will remain so low that no marked transpassive dissolu-tion will occur.

The AISI 304L type stainless steel is not suitable to chloride Z1-reactor environments due to poor localized corrosion resistance. Chloride content of 0.1–0,15 g/l at 60–70°C was adequate to cause crevice corrosion although the ozone concentration was low.

OZONE GAS LINE
The ozone gas feed line environ-ment (T = 20–30°C, pressure 10 bar, O_3-content = 9.5%) was very corrosive to all stainless steels examined. All materials were subject to intensive general and intergranular corrosion. Highest corrosion rates were determined for the welded UNS S31254 stainless steel. The highly alloyed UNS S32654 stainless steel had second highest corro-sion rate.

The results are in contrast to previous investigations where no corrosion in stainless steels in

moist ozone gas has been observed [4,5]. Due to the good corrosion resistance AISI 304L and 316L type stainless steels are commonly used as a construction material for ozone generators [6]. However, it is mentioned that precautions must be taken to avoid the presence of humidity in the ozone generator, which leads to formation of nitric acid [6,9]. Nitric acid itself, although it is oxidizing acid, is not usually corrosive to stainless steels.

The most likely reason for the observed gas line corrosion is the interaction of nitrogen with ozone at the presence of moisture resulting in an extremely oxidizing acidic environment which is corrosive to all examined materials. In the mill the ozone is produced from liquid oxygen and recycled surplus oxygen containing gas coming from Z-stages. Before the excess oxygen is used it is cleaned with molecular sieves to remove impurities. Regardless of the molecular sieves there is a minor amount of nitrogen present in the cleaned gas. Moisture is always present in some amounts in the gas line. One possible place where moisture can originate is water ring compressors used for gas pressurization. Pressurization enables the decrease of the volume of the ozone gas and hence ensures efficient mixing of the gas to pulp. According to this information it is possible that in the gas line exist occasionally extremely aggressive conditions.

It should also be noted that if oxygen is manufactured on-site using PVSA equipment it would always contain some nitrogen. If such oxygen gas is used for ozone generation similar problems found in this paper will most likely arise.

The tests showed that the material selection, at least in the case of stainless steels, doesn't offer a solution to corrosion problems in the ozone gas line.

Conclusions

The mill tests showed that the AISI 316L and the other more alloyed stainless steels have good corrosion resistance both in the reaction tube and in the ozone reactor (T = 60–70°C, pH = 2.5–3.0, Cl^- = 0.1–0.15 g/l, O_3-dosage ca. 3.3 kg/t).

AISI 304L type stainless steel is not suitable for use in ozone bleaching due to poor localized corrosion resistance. Chloride content of 0.1–0,15 g/l at 60–70°C was sufficient to cause crevice corrosion.

The low corrosion rates of the super austenitic and super duplex stainless steels in ozone bleaching were surprising.

According to the electro-chemical tests this behavior is related to the fact that in real bleaching environments the corrosion potentials do not achieve so high values that marked trans-passive dissolution is possible.

The reason for this is still obscure. One possible reason could be that there are some chemicals in the bleaching solutions that inhibit the effect of ozone. One chemical that may do this is hydrogen peroxide, which is always present in bleaching solution due to counter current washing.

On the basis of these results it seems that if high amounts of chlorides are present in ozone containing solutions a compromise must be made between the localized and general corrosion resistance.

For the operational reliability slight uniform dissolution might be preferable compared to localized corrosion, because localized corrosion is difficult to detect and predict.

The ozone gas line environment (T = 20–30°C, pressure 10 bar, O_3-content = 9.5%) was very corrosive to all stainless steels examined. All materials were subject to intensive general and intergranular corrosion. In the gas line the highest corrosion rates were determined for the welded UNS S31254 stainless steel. The highly alloyed UNS S32654 stainless steel had second highest corrosion rate.

The possible reason for corrosion is the interaction of nitrogen with ozone in the presence of moisture resulting in an extremely oxidizing acidic environment which is corrosive to all examined materials. The tests showed that the material selection doesn't offer solution to corrosion problems in ozone gas line.

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